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Journal of physical chemistry

Tome 39

Volume 49

Washington **1935**

Source gallica.bnf.fr / Bibliothèque nationale de France

ANNULÉ

C Pg 4

The Journal of PHYSICAL CHEMISTRY

(Founded by Wilder D. Bancroft)

SOCIÉTÉ DE CHIMIE INDUSTRIELLE 28 rue St-Dominique PARIS (7e)
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Volume XXXIX

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS ORSAY

BALTIMORE
1935

ANNULÉ

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

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THE ADSORPTION OF CAUSTIC SODA BY CELLULOSE

7 a, C-250

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Received June 14, 1934

We have shown (1) that purified cotton will take up about 27 per cent of water from saturated water vapor at 25°C. when equilibrium is approached from both sides. Other investigators have approached the equilibrium only from the lower side and have obtained values of from 21 to 24 per cent. Leighton (11) tried to reach equilibrium from the upper end by using a slow-running centrifuge, and calculated that about 400 per cent of water was retained by the cotton. Coward and Spencer (5) used a more effective centrifuge, and reported that about 50 per cent of water was retained. We used a modified Foerst centrifuge and got the water content down to about 10 per cent, with no certainty that we could not have gone lower with a more effective centrifuge. Consequently, it is possible to remove some of the adsorbed water or adsorbed solution by sufficiently effective centrifuging. One must therefore obtain in each case some method of recognizing at exactly what point all of the unadsorbed solution or mother liquor has been removed.

When studying the adsorption of caustic soda from aqueous solution by cellulose, Vieweg (15) used a method depending on the change in concentration of the solution before and after the cellulose was added. This change-in-titer method has been used by practically everyone else, except Leighton, Coward, and Spencer, and ourselves (2). A known amount of a known concentration of caustic soda is shaken with cellulose. When equilibrium is reached, a measured quantity of the supernatant liquid is pipetted off and titrated for caustic soda. From the change in titer it is possible to calculate the amount of caustic soda adsorbed, provided no water is taken up, but not otherwise. Calkin has shown that the true equation for the adsorption is

$$\frac{G(X_0-X)}{S} + \frac{XB}{S} = \frac{A}{S}$$

Here G = grams of solvent (water) in caustic soda solution at the start.
X_0 = moles of caustic soda per gram of solvent at the start.
X = moles of caustic soda per gram of solvent in the supernatant liquid when equilibrium is reached.

[1] Fellow, The Textile Foundation.

A = moles of caustic soda taken up by the sample of cellulose.
B = grams of solvent (water) taken up by sample of cellulose when equilibrium is reached.
S = grams of cellulose in sample.

Analytically, the material adsorbed in cases of positive adsorption may be considered as adsorbed solution plus excess of adsorbed solute. In Calkin's equation $G(X_0 - X)/S$ represents the excess solute and XB/S represents adsorbed solution. If no water is taken up, $B = 0$ and the first term of the equation gives the true adsorption. This is the value given by the change-in-titer method. If the solution is adsorbed without change, $G(X_0 - X)/S = 0$. These are the two limiting cases, and this was pointed out in words, though not algebraically, by Leighton nineteen years ago. It is understood by colloid chemists, but is still a closed book to most cellulose chemists, especially the German ones.

Whenever water is adsorbed, as is the case with cellulose, the problem is to determine the term XB/S. If we could pipette off and weigh the whole of the mother liquor, an analysis of that or of the residue would give us the answer. We cannot do this directly and must therefore devise an indirect method.

The situation and the remedy are shown graphically in figure 1, which is not to scale. The abscissas represent at will grams of water per gram of cotton in the system or grams of water per gram of cotton in the adsorbing phase. The ordinates are the corresponding values for grams of caustic soda per gram of cotton. Suppose we start with 100 g. of such a caustic soda solution plus such an amount of cotton that the amounts of water and caustic soda are represented by F in figure 1. After equilibrium is reached a measured amount of solution is pipetted off and titrated. This gives a ratio of caustic soda to water represented by some point on the line OH, but we do not know where on that line because we only determine the ratio of caustic soda to water and we do not know how much caustic soda or how much water there is in the total mother liquor. If we make the assumption involved in the change-of-titer method, that no water is taken up by the cotton, then the point is at H where the line OH meets the perpendicular from F. The amount of caustic soda adsorbed is given by the distance FH.

If the true position of the point is at D, for instance, the amount of caustic soda adsorbed is FE and of water adsorbed is DE. Our problem is to locate D. The simplest way theoretically would be to centrifuge the system and to analyze the centrifuged solution from time to time. As long as only mother liquor is coming off, the composition will remain constant and will be represented by an unknown point on OH. As soon as the composition changes, we know that some adsorbed solution is coming off.

Analysis of the residual mass in the centrifuge at this moment will give the true adsorption, provided no cotton has been lost.

This was not practical with our centrifuge because the centrifuged liquid spattered a good deal and because the final amount to be driven off might be so small as to make the errors of analysis large. Another method was therefore tried. Going back to figure 1, we draw $F'D'$ and $E'D'$ such that $OF' = DE$ and $OE' = FE$. D' is then the composition of the cellulose phase in equilibrium with a cellulose-free, caustic soda solution whose

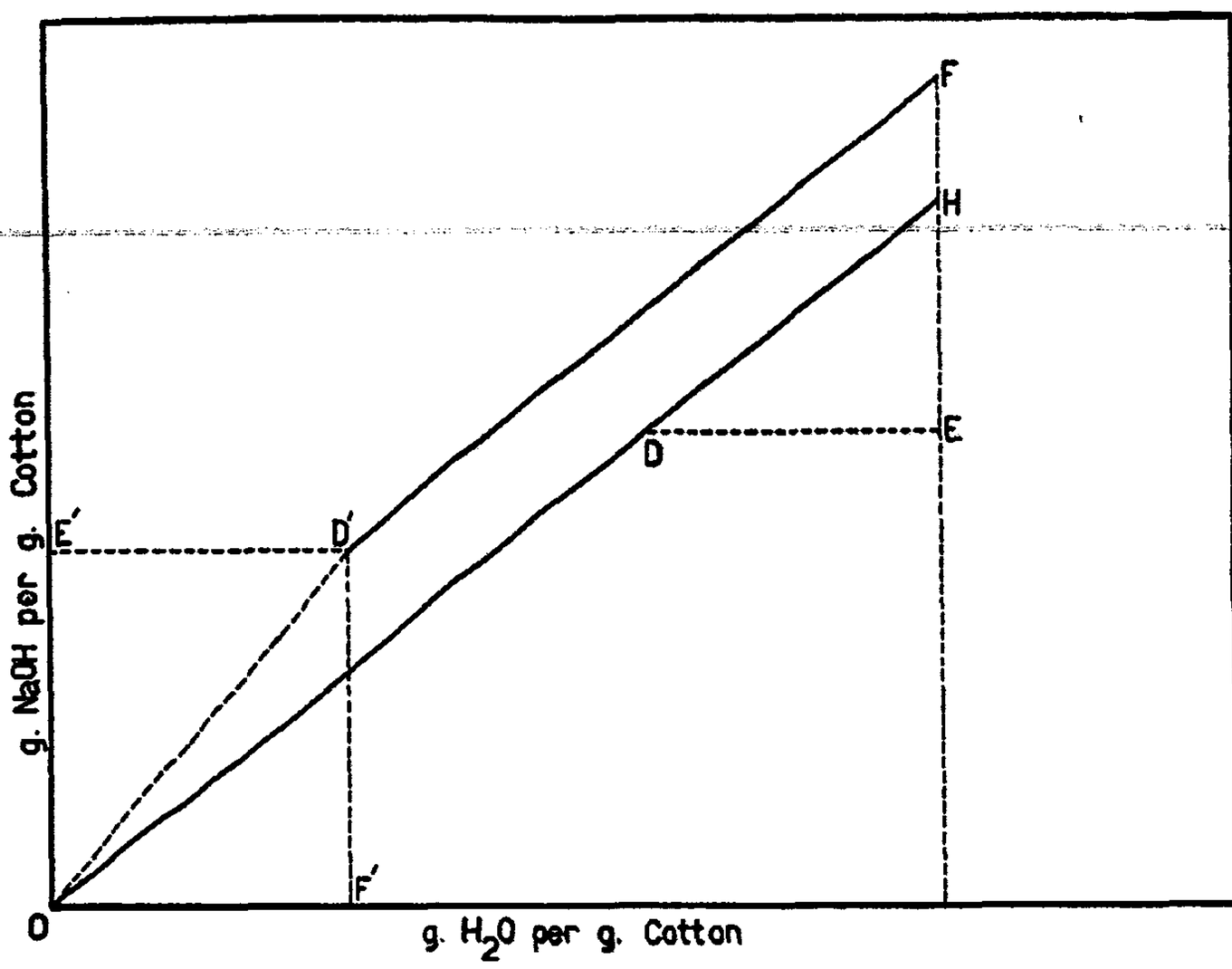

FIG. 1. DETERMINATION OF TRUE AND APPARENT ADSORPTION

composition is given by the line OH. If we centrifuge the original system for different lengths of time and analyze the residual masses, we shall get points on FD' so long as we are removing mother liquor only. After we pass D', the resulting points will lie somewhere in the rectangle $D'E'OF'$. If the adsorbed solution goes off without change we shall pass along $D'O$. If only water goes off, we shall get the line $D'E'$. If only caustic soda we shall get the line $D'F'$. Those are the three limiting cases. The point D' comes where the straight line FD' breaks. From the observed points on FD' and beyond, we can calculate the composition of the coëxisting

solution. So long as the calculated composition remains constant and corresponds to a point on OH, only mother liquor is coming off. The change from the constant value indicates that the system is passing through D'. This is the method that we have found most successful. The data for one run are given in table 1.

The cotton used in these experiments (4) was "standard cotton cellulose." The data shown in figure 5 were obtained with Johnson and Johnson absorbent cotton purified somewhat less rigorously. One hundred grams of cotton was placed in the A.C.S. apparatus and the cotton was

TABLE 1

Determination of true adsorption by cotton

TIME OF CENTRIFUGING	CENTRIFUGED COTTON		CENTRIFUGED LIQUID BY DIFFERENCE		CENTRIFUGED LIQUID
	NaOH per gram of cotton	H_2O per gram of cotton	NaOH	H_2O	NaOH PER GRAM OF H_2O
Initial concentration: 3.5971 g. of NaOH per gram of cotton, 18.379 g. of H_2O per gram of cotton					
minutes	*grams*	*grams*	*grams*	*grams*	*grams*
0	Solution in equilibrium with cotton				0.18832
¼	0.5435	2.169	3.0536	16.210	0.18838
½	0.5315	2.099	3.0656	16.280	0.1883
1	0.5172	2.013	3.0799	16.366	0.18819
3	0.5108	1.983	3.0863	16.416	0.1880
Assumed initial concentration: 0.7008 g. of NaOH per gram of cotton, 3.000 g. of H_2O per gram of cotton					
minutes	*grams*	*grams*	*grams*	*grams*	*grams*
0	Solution in equilibrium with cotton				0.18832
¼	0.5435	2.169	0.1573	0.831	0.1893
½	0.5315	2.099	0.1693	0.901	0.1879
1	0.5172	2.013	0.1836	0.987	0.1860
3	0.5108	1.963	0.1900	1.037	0.1833

steeped in a boiling solution of 1 per cent sodium hydroxide for 1¾ hours, after which it was washed by the A.C.S. method. The amount of cotton in the centrifuge was about 0.5 g.

The values entitled "Centrifuged liquid by difference" in the fourth and fifth columns are obtained by subtracting the values entitled "Centrifuged cotton" in the second and third columns from the corresponding concentrations given under "Initial concentration" and "Assumed initial concentration." The value given under "Solution in equilibrium with cotton" is a direct determination.

The break comes at about the half-minute observation. It can be made

more sharp by starting with a system containing much less supernatant liquid. One could pour off as much of the supernatant liquid as possible, weigh and analyze it, and calculate the filtered residue. We have taken arbitrarily a point on FD', figure 1, which we knew to be short of D'. The calculations in the lower half of table 1 are based on these values.

Another way of emphasizing the break is to calculate the apparent or change-in-titer adsorption, which is the amount of caustic soda adsorbed in excess of that due to adsorbed solution. For this particular case, we find 136, 135, 136, 138, and 141 mg. of sodium hydroxide per gram of cotton for 0, $\frac{1}{4}$, $\frac{1}{2}$, 1, and 3 minutes centrifuging, respectively. For an entirely different initial solution the values were 27.9, 27.4, 27.9, and 29.2 for $\frac{1}{2}$, 1, 3, and 5 minutes centrifuging, respectively. Here the break comes after the three minutes centrifuging.

TABLE 2

True adsorptions of sodium hydroxide and water by cotton

MOLALITY OF END SOLUTION	ADSORPTION PER GRAM OF COTTON	
	NaOH	H_2O
M	*grams*	*grams*
1.741	0.0767	0.701
3.421	0.3573	1.914
4.040	0.4938*	2.290*
4.708	0.5315	2.099
5.923	0.5923	1.894

* The quarter-minute centrifuging was too long, so these points have been obtained by extrapolation.

For this work it would be better to have a variable-speed motor to drive the centrifuge, as Coward and Spencer did. On a half-minute run there might easily be errors due to inadequate time for diffusion.

Similar runs have been made for other initial concentrations. The calculated values for the true adsorptions are given in table 2 and figure 2.

The abscissas in figure 2 are molalities of caustic soda in the solution in equilibrium with cotton. The bottom curve represents the apparent adsorption for caustic as given by the change-in-titer method. For 6 molal caustic soda the apparent adsorption is about 0.6 mole of caustic soda per mole (162 g.) of cotton, while the real adsorption is about 2.4 moles of caustic soda per mole of cellulose, an increase of approximately 300 per cent. As had been found by Leighton and by Coward and Spencer, the amount of water taken up by the cotton first increases with increasing caustic soda and then passes through a maximum. The curve for adsorbed caustic soda is smooth and shows no signs of the occurrence in mass of any

definite chemical compound in stoichiometric proportions between caustic soda and cellulose.

The general relations are shown in figure 3, where the ends of the dotted lines show the compositions of the caustic soda solutions in equilibrium with the cotton. The solid curve gives the true adsorptions expressed in grams of cotton, water and caustic soda equalling 100. The apparent or change-in-titer adsorption curve would be at the real bottom of the diagram, on the line connecting 100 g. of cotton with 100 g. of caustic soda. Our value of 27 per cent water taken up by cotton becomes 21.2 when plotted in the triangular diagram.

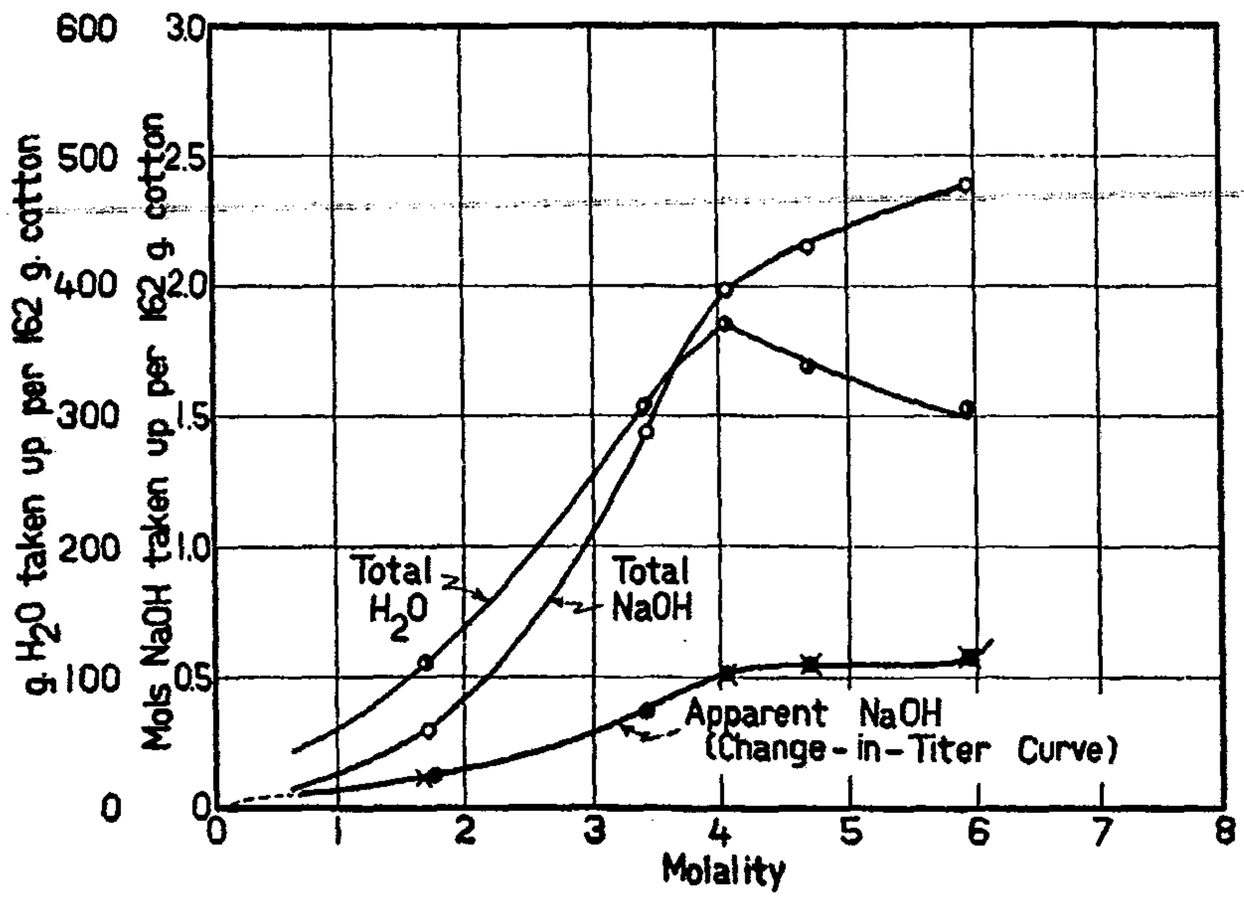

FIG. 2. SODIUM HYDROXIDE AND WATER TAKEN UP BY COTTON

Even if the change-in-titer method gave true adsorptions instead of containing errors of 300 per cent or so, the data would not justify the conclusions that the German chemists draw from them. In figure 4 is given a compilation made by D'Ans and Jaeger (6) of results obtained by Vieweg (15), Karrer and Nishida (10), Rassow and Wadewitz (13), Heuser and Niethammer (8), Heuser and Bartunek (9), Dehnert and König (7), and Liepatoff (12). With the concentration plotted along the abscissas, the presence of two solid phases would show itself by a vertical portion of the curve. There is no evidence of any such thing on any curve except that by Liepatoff, and the vertical portion of his curve ends at nearly 200 mg. of sodium hydroxide taken up per gram of cellulose instead of about 116 mg. of sodium hydroxide, which would correspond to $(C_6H_{10}O_5)_2 \cdot NaOH$.

That these data should be so divergent is quite natural in view of the results recorded in figure 5, showing the effect of the previous history of the cotton.

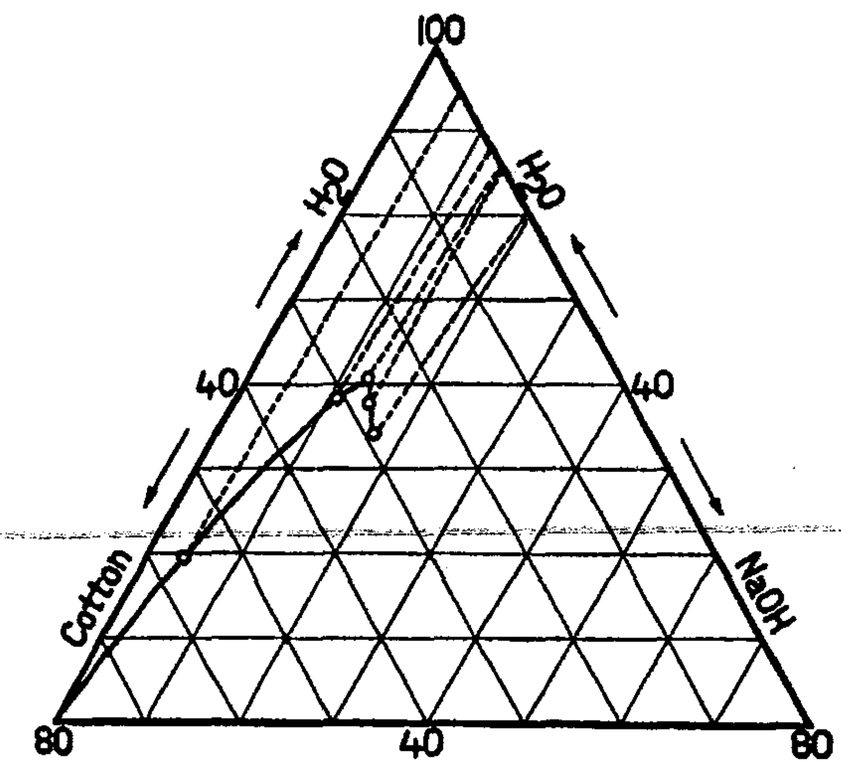

FIG. 3. SODIUM HYDROXIDE AND WATER TAKEN UP BY COTTON

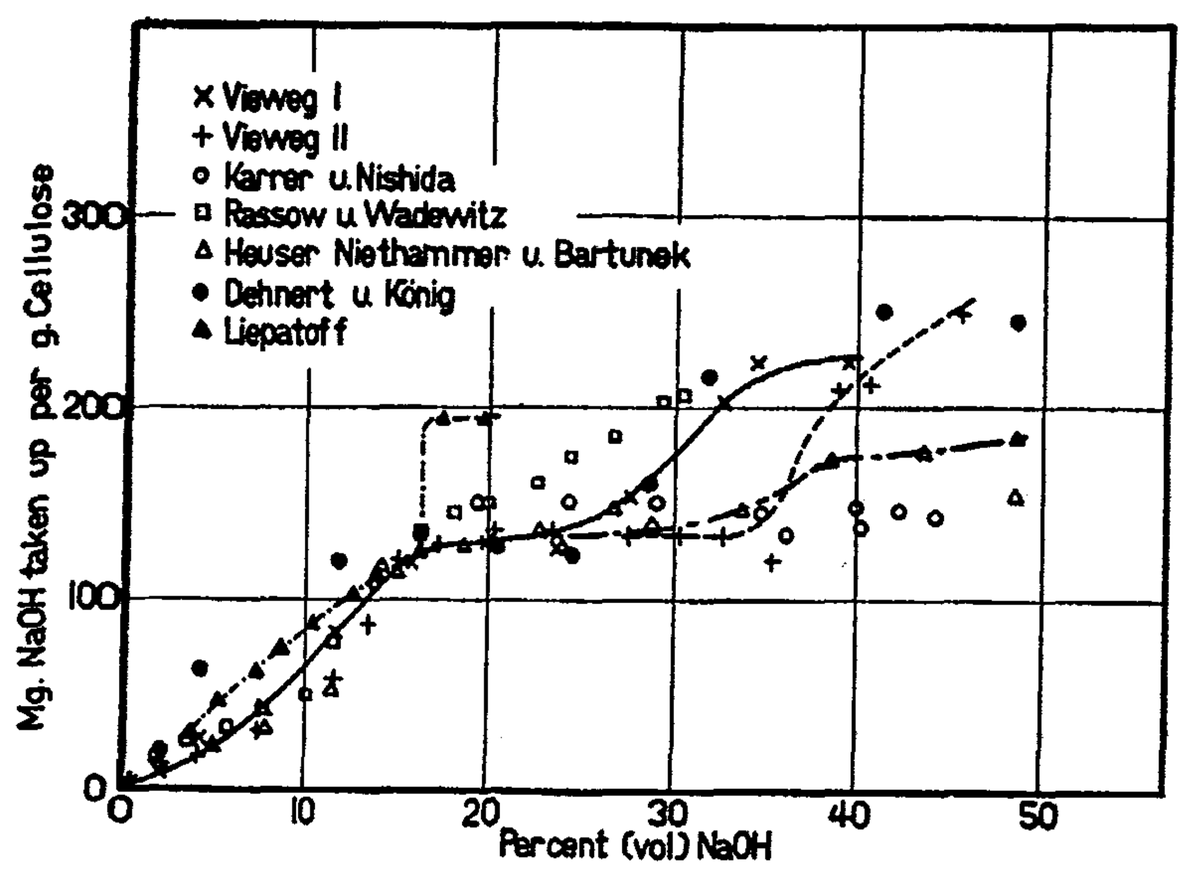

FIG. 4. SODIUM HYDROXIDE TAKEN UP BY CHANGE-IN-TITER METHOD

The table references are to the paper of Bancroft and Calkin (2). By working judiciously one can get almost any value of the adsorption that one wishes; if one works injudiciously, as most people have done, the sky

is the limit. The interesting thing for the moment is that the arrows show that one does not pass back along the same curve if one washes out the caustic soda, except for very low initial concentrations. The cotton behaves toward caustic soda as silicic acid does toward water. In our experiments the different up-curves came together at about 4 molal caustic soda or at about 14 per cent caustic soda; this is about the concentration at which the x-ray analysis for ramie (14) shows that the change from one space lattice to another is complete. Change from one space lattice to another would be expected to change the degree of adsorption, and appar-

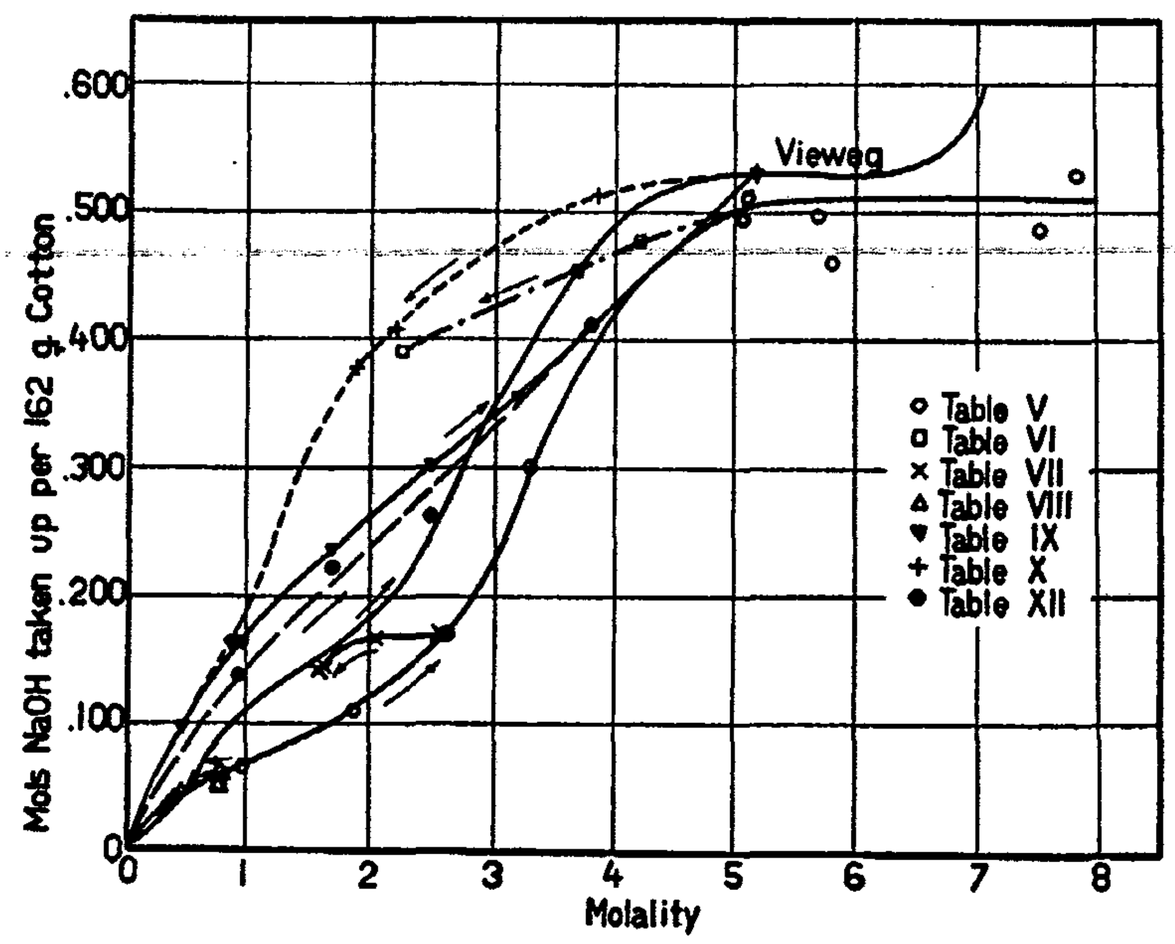

FIG. 5. SODIUM HYDROXIDE TAKEN UP BY CHANGE-IN-TITER METHOD

ently it does. This is not the whole thing however. If cotton, which has been treated with caustic soda of 14 per cent or more, is washed free of caustic soda and dried at about 105°C., the amount of adsorption decreases below that of washed cotton which has been dried at room temperature, but it does not go back to the value given by the raw cotton. We hoped that this meant that a suitable washing and drying reversed the change in the space lattice. X-ray tests (3) showed that this was not the case, and that the change in the x-ray space lattice is irreversible so far. The reversible part of the adsorption is therefore due chiefly to what one may call a sintering effect.

The general results of this paper are as follows:

1. The true amounts of adsorption of sodium hydroxide and water by

cotton can be ascertained by centrifuging the wet cotton and determining the point at which all the mother liquor has been driven off.

2. The Vieweg change-in-titer method measures only the caustic soda taken up in excess of the adsorbed solution and is consequently grossly inaccurate for this system.

3. The curve for the true adsorption of caustic soda by cellulose is a smooth curve, indicating that caustic soda is adsorbed by cellulose. There is no evidence of the existence in mass of any stoichiometric compound between sodium hydroxide and cellulose over the range up to 20 per cent caustic soda.

4. The curves for the apparent adsorption of caustic soda by cellulose (change-in-titer method) obtained by the German chemists would not justify the assumption of stoichiometric compounds, even if the data were true adsorption values, which they are not.

5. The apparent adsorption of caustic soda by cotton is a partially irreversible process except perhaps for dilute solutions of caustic soda.

6. The partial irreversibility is due to a change in space lattice, which is irreversible so far as the present facts go, and to a swelling which can be reversed more or less completely by heating at about 105°C.

7. The method herein developed for determining the true adsorptions of sodium hydroxide and water by cotton is a general method and can be applied to many other systems.

8. No experiments have yet been made on precipitated cellulose to determine the effect, if any, of the fibrous form of the cotton.

Our thanks are given to the Textile Foundation for a Research Fellowship and for other support, thus making this work possible.

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THE WETTING CHARACTERISTICS OF GALENA

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Received June 14, 1934

Recent work has shown that the free surface energy of a solid, hence its wetting characteristics, may be altered much more easily than had previously been supposed. In view of this fact, it is apparent that the pretreatment of a solid surface must be carefully controlled if significant values of its wetting properties are to be obtained. It seems probable that failure to consider carefully the exact surface condition of the solid accounts for the fact that existing data on wetting properties of solids show such an outstanding lack of agreement.

In recent years much work has been done in an effort to determine the wetting characteristics of galena, such information being highly desirable in connection with the ore flotation industry. The angle of contact of water on galena has been used as a measure of its wetting characteristics and there has been a surprising lack of agreement in the data which have been obtained. Sulman (11) found the advancing water–air angle for one sample of galena to be 73°, and for another 70°, the respective receding angles being 35° and 41.6°. Langmuir (9) obtained an angle of 86°, while Coghill and Anderson (5) found angles from 45° to 60°. These angles were apparently advancing angles. In none of these cases are we certain as to the exact condition of the surfaces. Wark and Cox (12) found an "equilibrium" angle of zero degrees for water upon a galena plate cleaved under water, the angle they measured being in reality a receding angle. They found that a finite angle was formed if the galena was cleaved in air and assumed that the difference was caused by contamination. Rehbinder, Lipetz, Remskaja, and Taubman (10) obtained a 47° advancing and a zero receding angle for water upon freshly cleaved galena.

In view of the lack of agreement in the literature concerning galena, we felt that a study of this solid should yield information of value. Our primary object was to determine the wetting characteristics of the galena surface by measurement of contact angles and to study the factors which might influence such measurements. This objective led to the investigation of the following factors:

1. Different methods for measuring contact angles.
2. The phenomenon of "hysteresis" of the angle of contact, i.e., the relation of the advancing to the receding angles.

3. The effect of the pretreatment of the solid surface upon the angle of contact.

SIGNIFICANCE OF CONTACT ANGLES

The degree of wetting or adhesion tension of a liquid against a solid has been defined as that change in free surface energy which occurs when a solid–air surface is replaced by a solid–liquid interface. The adhesion tension is related to the contact angle as follows:

$A_{13} = S_3 \cos \theta_{13}$ (8), where A_{13} represents the adhesion tension, liquid against solid, S_3 the surface tension of the liquid, and $\cos \theta_{13}$ the cosine of the contact angle between liquid and solid in air.

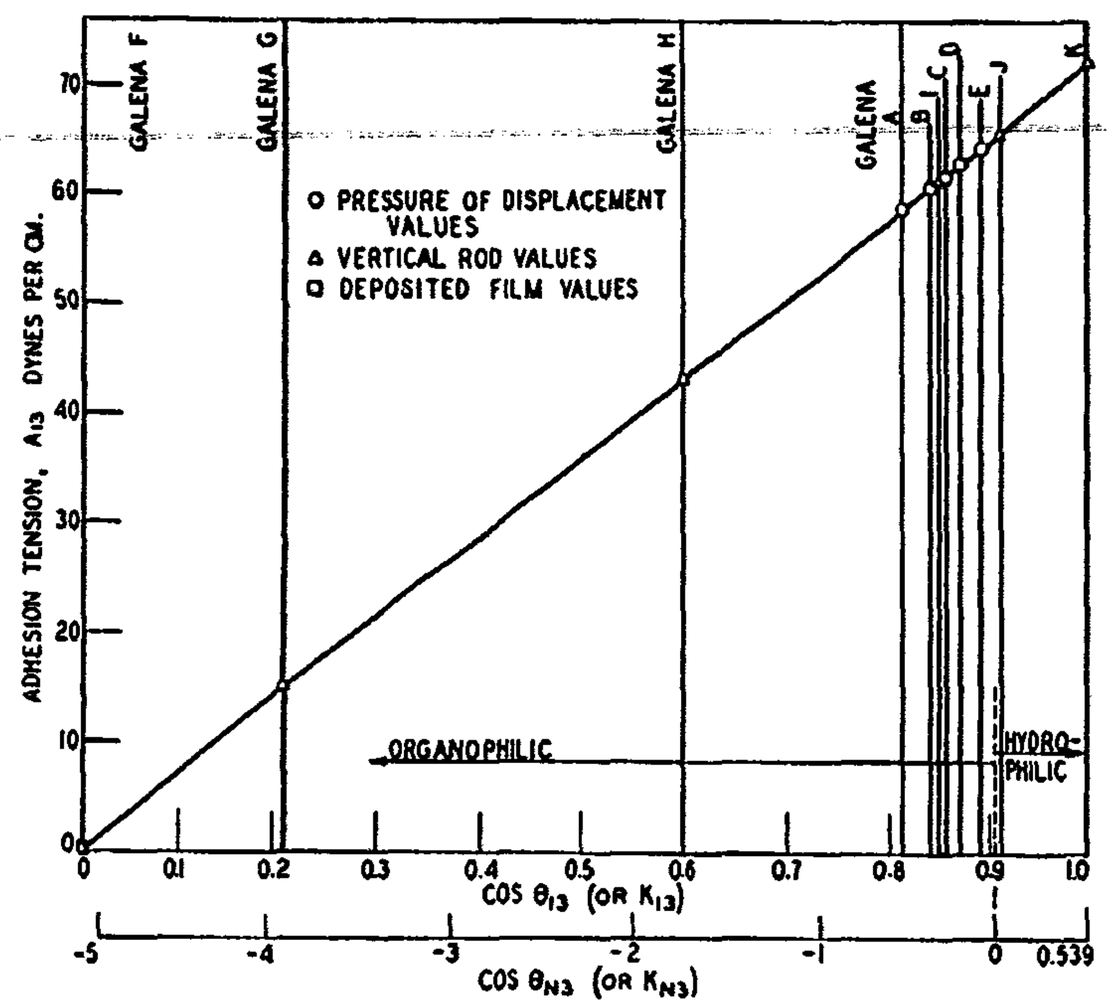

FIG. 1

It has been found from numerous studies in our laboratory that solids on which water gives a contact angle greater than approximately 25° ($\cos \theta_{13} = 0.90$) are organophilic in nature, i.e., they are preferentially wetted by organic liquids, while those giving an angle less than 25° are hydrophilic (1) and are preferentially wetted by water. The change in wetting properties progresses with change in contact angle (or $\cos \theta_{13}$).

In the present paper we shall express the wetting characteristics of the different solids in terms of the cosine of the solid–water–air contact angle, $\cos \theta_{13}$ (or K_{13})—and shall consider that the solids are organophilic when

$\cos \theta_{13} < 0.90$ and that they are hydrophilic when $\cos \theta_{13} > 0.90$. Straight line graphs, of slope S_3, may be made by plotting A_{13} against $\cos \theta_{13}$ (see figure 1). The position of a solid on the horizontal, $\cos \theta_{13}$, axis will show the relative degree of organophilic or hydrophilic nature of the solid.

QUALITATIVE WETTING TESTS

Preliminary studies on the wetting characteristics of galena powder yielded some rather surprising results. It was found that if the powdered material was first wetted with water, an organic liquid could not readily be stirred into the resulting paste, while if it was first wetted with an organic liquid, water could not readily be stirred into it. When the powder was packed into a U-tube, or a displacement pressure cell, half of the powder being wetted with the organic liquid and the remainder with water, no displacement of one liquid by the other occurred. To cause movement of the interface in either direction it was necessary to apply an external force. Once this force was removed, the line of contact of the interface with the solid appeared to remain fixed.

When these qualitative tests were repeated, using carbon or silica, entirely different results were obtained; the organic liquid would completely displace water from the carbon, and water would completely displace the organic liquid from the silica. In contrast to the behavior of these two solids, galena appeared to be preferentially wetted by either liquid, depending upon which was first present. Thus, if the galena was first wetted with water it behaved similarly to the hydrophilic silica, whereas if it was first wetted with the organic liquid it behaved as the organophilic carbon. It should be stressed that this wetting produced no permanent change of the surface. If the powder was dried after being wetted with water or with a volatile organic liquid, it behaved exactly as the freshly prepared material.

MATERIALS

Liquids

Liquids used in this investigation were water, benzene, *n*-butyl acetate, and α-bromonaphthalene. All were carefully purified, and their densities, surface tensions, and interfacial tensions (against water) agreed, within the limits of experimental error, with the generally accepted values. The following surface tension and interfacial tension values respectively (for 25°C.) were used in our calculations: water, 72.08; benzene, 28.22 and 34.00; *n*-butyl acetate, 24.06 and 13.17; α-bromonaphthalene, 44.00 and 41.57.

Solids

Galena in the form of powder, plates, rods, and films was used. In the measurement of contact angles by the pressure of displacement method,

TABLE 1

Contact angle data for galena by the displacement pressure method (advancing air-water-solid contact angles)

t = 25°C. ± 0.10°; r (pore radius) = 8.18 × 10^{-4} cm.

SOLID	DISPLACEMENT PRESSURE	θ_{13} (ADVANCING)	$\cos\theta_{13}$	A_{13}
	grams per sq. cm.			
Galena A	146	35.4°	0.815	58.7
Galena B	151	32.5°	0.843	60.7
Galena C	154	31.1°	0.856	61.7
Galena D	156	29.5°	0.870	62.7
Galena E	160	27.1°	0.891	64.2

The receding contact angles for the different samples of galena were all zero angles.

TABLE 2

Interfacial contact angle data for untreated galena by the pressure of displacement method

t = 25°C. ± 0.10°; galena A (r = 8.18 × 10^{-4} cm.)

LIQUID	DISPLACEMENT PRESSURE	$S_{n2}\cos\theta_{n3}$	θ_{n3}	$\cos\theta_{n3}$ (K_{n3})	A_{1n}
Water advancing					
					dynes per cm.
n-Butyl acetate	−16.2	−6.52	119.7°	−0.495	65.2
Benzene	−41.9	−16.8	119.6°	−0.494	75.5
α-Bromonaphthalene	−51.0	−20.6	119.5°	−0.493	79.3
Average			119.6°	−0.494	
Water receding					
n-Butyl acetate	30.1	12.1	23.5°	0.917	
Benzene	75.5	30.3	27.0°	0.891	
Average			25.3°	0.904	

finely ground galena was used, which had been graded through sieves between 250 and 300 mesh. The graded galena was first shaken with acetone to remove possible traces of oils, etc., dried, then thoroughly mixed in a rotating cylinder.

The following table shows the treatments to which the various samples of the graded galena powders were subjected:

Sample	*Treatment*
Galena A	No further treatment
Galena B	Heated in air for 2 hours at 180–190°C.
Galena C	Heated in air for 4 hours at 180–190°C.
Galena D	Heated in air for 8 hours at 180–190°C.
Galena E	Heated in air for 24 hours at 180–190°C.

TABLE 3

Interfacial contact angle data for galena A heated in air at 180–190°C. for different lengths of time; pressure of displacement method (water advancing)

$t = 25°C. \pm 0.10°$; $r = 8.18 \times 10^{-4}$ cm.

LIQUID	DISPLACEMENT PRESSURE	θ_{1n}	$S_{n3}\cos\theta_{n3}$	θ_{n3}	$\cos\theta_{n3}$ (K_{n3})	A_{1n}
Heated 2 hours = galena B						
						dynes per cm.
Benzene	−33.0	0°	−13.3	113.0°	−0.390	74.0
α-Bromonaphthalene	−42.2	0°	−16.9	114.0°	−0.407	77.6
Average				113.5°	−0.398	
Heated 4 hours = galena C						
Benzene	−24.2	0°	−9.71	106.6°	−0.286	71.4
α-Bromonaphthalene	−30.4	0°	−12.2	107.0°	−0.290	73.9
Average				106.8°	−0.288	
Heated 8 hours = galena D						
Benzene	−17.1	0°	−6.87	101.7°	−0.202	69.6
Heated 24 hours = galena E						
Benzene	−10.9	0°	−4.38	97.4°	−0.129	68.6

EXPERIMENTAL

In the course of this investigation four different methods for measuring the angle of contact were used, namely: (a) a pressure of displacement method; (b) a horizontal plate method; (c) a vertical rod method; and (d) a deposited film method. In the following section these four methods, together with the apparatus and its manipulation, will be discussed.

(a) *Pressure of displacement method for the measurement of contact angles*

The pressure of displacement method used was that described by Bartell and Walton (4). Both the advancing and receding contact angles

were determined for the different galena–water–air systems and the different galena–water–organic liquid systems. The results obtained for the former systems are given in table 1, and for the latter systems in tables 2 and 3. The cosines of the different contact angle values galena–water–air (i.e., cos θ_{13} values) are plotted against adhesion tension values (A_{13}) in the wetting characteristics graph in figure 1, and the cosine of the interfacial contact angle values (i.e., cos θ_{n3} or K_{n3} values) are plotted against adhesion tension values in figure 2.[1]

The adhesion tension values, A_{1n}, for the organic liquids against the different galenas were calculated from the advancing galena–water–air

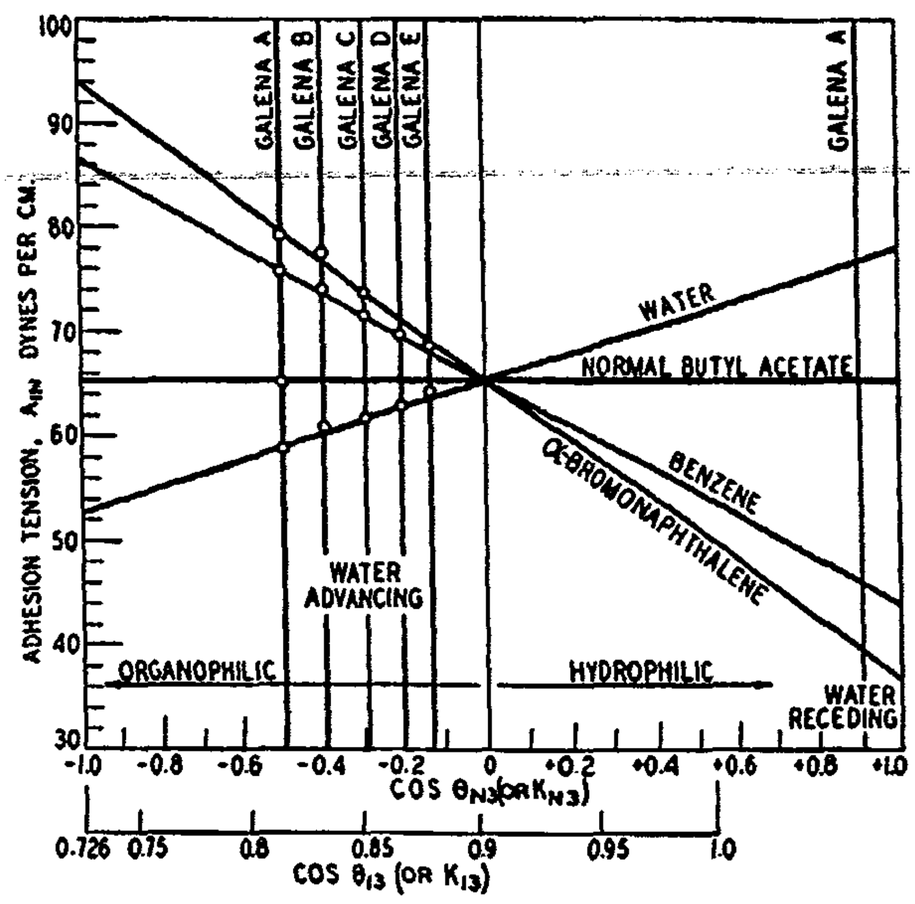

FIG. 2

and galena–water–organic liquid contact angle values from the equation $A_{13} - A_{1n} = S_{n3} \cos \theta_{n3}$ (3). The results were found to be in agreement with the linear relationship noted for similar systems by Bartell and Bartell (1). The effect of the heat treatment was similar in nature to that observed by Bartell and Walton (4) for stibnite, the powder becoming less organophilic the longer the period of heating.

[1] The adhesion tension versus cos θ_{n3} or K_{n3} values shown in figure 2 were plotted according to the relationship observed by Bartell and Bartell (1) and were determined by their empirical equations: $m_n = 12.8 - S_{n3}$ (where m_n is the slope of the organic liquid line and S_{n3} the interfacial tension water–organic liquid), and equation $A_{1n} = m_n K_{n3} + 65.2$ (where A_{1n} = adhesion tension of the organic liquid against the solid of corresponding K_{n3} value). The position of each solid on the horizontal axis (i.e., the wetting characteristics value) was determined from the galena–water–organic liquid systems, being the average of the cosines of the interfacial contact angles.

It will be noted that according to the advancing angles all the samples are organophilic in nature, while according to their receding angles they are all hydrophilic. It will be noted also that all the advancing interfacial angles for a given sample of galena give the same value. Likewise all the receding values are practically the same.

From the above discussion it is evident that galena, from the standpoint of its wetting characteristics, acts as two different solids depending upon whether or not it is wetted with water. Thus the pressure of displacement method quantitatively confirms the qualitative tests, previously cited, regarding the wetting characteristics of galena.

The values obtained for galena by the pressure of displacement method were duplicable to within ±2 per cent. .This deviation was slightly greater than that which has previously been found for the method (±1 per cent), the cause lying in the nature of the solid.

If we have a water–organic liquid interface in a membrane composed of galena powder, neither liquid will displace the other until a definite pressure is applied, the pressure necessary to cause the water to displace the organic liquid corresponding to the advancing contact angle value, and that necessary to cause the organic liquid to displace the water corresponding to the receding contact angle value. The system is apparently stable anywhere between these two limits. If, at any time in the course of the determination, the pressure falls to a value between those corresponding to the advancing and the receding contact angles, the pressure will remain at this value, there being no tendency for the interface to move and build up the pressure.

Since there was reason to believe that the surface of the original finely divided particles of powder might have been altered during their preparation (i.e., oxidized during the processes of grinding, sieving, and mixing), it was decided to attempt to obtain a fresh non-worked and non-oxidized surface. Crystals of galena were therefore cleaved, and measurements were made of angles formed by drops of water upon the cleaved surface. This method will be referred to as the horizontal plate method.

(b) *Horizontal plate method for the measurement of angles of contact*

This method consisted essentially in measuring the dimensions of small drops of a liquid resting upon a plane solid surface. Since small drops are approximately segments of spheres, the angle of contact may be calculated from their height and diameter, using the following equation:

$$\tan\frac{\theta}{2} = \frac{h}{r}$$

where h is the height of the drop, and r is the radius of the drop.

A freshly cleaved surface of the solid was placed in a small covered absorption cell having plane glass sides, the atmosphere within the cell having previously been saturated with the liquid the contact angle of which was to be measured. A small drop of the liquid was then introduced upon the surface of the solid. The height and diameter of this drop were measured by means of a cathetometer. The direction of motion of the liquid (i.e., advancing or receding) was controlled by adding or withdrawing liquid from the drop. One set of representative results is given in table 4.

Each of the determinations gave a zero receding water–air angle, but the finite advancing values were very erratic and varied by as much as 30°. The cause for this variation, we believe, lies in the methods used for introducing the liquid drop onto the solid surface. Several different methods were tried, the drop being added by means of a glass rod, a small glass pipet, and from a paraffin-coated rod, but none proved entirely satisfactory. It is almost impossible to place a liquid drop upon the solid

TABLE 4

Contact angle data for water upon freshly cleaved galena surfaces by the horizontal plate method

$t = 25°C. \pm 1.0°$

EXPERIMENT	θ_{12} (ADVANCING)	θ_{12} (RECEDING)
1	76°	0°
2	80°	0°
3	90°	0°
4	57°	0°
5	67°	0°

by means of a pipet or rod, and remove the pipet or rod without causing some vibration during the process. This vibration will cause the drop momentarily to flatten, the result being that the angle will exceed the advancing value and spreading will occur. Since this system is apparently stable with contact angles anywhere between the characteristic advancing and receding values, it will remain at an intermediate value. Some of the liquid is very apt to adhere to the rod or pipet upon its removal, and this also may cause the angle to be lower than the true advancing value. In spite of the common usage of this method, the importance of these sources of error has not been sufficiently stressed and different investigators have failed to take them into consideration, the result being that their advancing contact angle values have been too low.

The results of these measurements led us to believe that were it possible to cause the line of contact to advance slowly or recede slowly, one might obtain definite and characteristic values. Accordingly, the vertical rod method (2) was next tried.

(c) *Vertical rod method for the measurement of angles of contact*

A small freshly cleaved rod of the solid (approximately 3.0 × 3.0 × 12.0 mm.) was held in a vertical position in such a manner that it could be slowly raised or lowered. The rod was carefully adjusted to such a position that two of its sides were parallel to the plane of light entering the camera. The rod was then slowly lowered until it extended through the liquid surface, the liquid being contained in a small glass absorption cell having parallel plane sides, and the line of contact of the liquid surface with that of the rod was photographed. The advancing liquid–air contact angle was measured from the resulting photographic plate. The rod was then slowly raised until the liquid gradually receded from its surface, and the receding liquid–air contact angle thus formed was photographed.

TABLE 5

Contact angle data for galena by the vertical rod method; alteration of surfaces by heating in air

t = 25°C. ± 1.0°; time of heating = 1 hour

SAMPLE	TEMPERATURE OF HEATING	θ_{13}	$\cos\theta_{13}$	K_{n3} (CALCULATED)	A_{13}
	degrees C.				*dynes per cm.*
Galena F (untreated)	25	90°	0.0	−5.09	0
Galena G	100	78°	0.21	−3.9	15.1
Galena H	200	53°	0.60	−1.7	43.4
Galena I	300	32°	0.85	−0.33	61.3
Galena J	400	24°	0.91	0.03	65.6
Galena K	500	0°	1.0	>0.54	>72.1

The value of the advancing water–air contact angle obtained with this method was 90° ($\cos\theta_{13} = 0$), and the value of the receding angle was zero ($\cos\theta_{13} = 1$). Since the advancing water–air angle obtained by this method was much larger than that obtained by the displacement pressure method, tests were carried out on cleaved rods which had been heated at given temperatures for definite periods of time. The results obtained with such rods are given in table 5.

The data obtained have been placed upon the graph in figure 1 (according to Bartell and Bartell (1)). It will be noted that the wetting characteristics were greatly altered by the heat treatment, passing from the strongly organophilic condition ($\cos\theta_{13} = 0$) to progressively lesser organophilic conditions and finally to what appears to be a definitely hydrophilic condition.

The contact angles measured upon freshly cleaved galena surfaces by the vertical rod method were duplicable to within ±3°. The advancing

water–air angles of contact upon the heat-treated galena rods were considerably less duplicable, the cause apparently lying in the uneven alteration of the surface of the rods.

The results with the vertical rod confirmed our earlier views that failure to obtain definite and reproducible values with the horizontal plate method was caused by our inability to alter gradually the solid–liquid–air point of contact. Better control of the drop on the plate could be obtained by bringing the liquid through a hole in the plate, causing the drop to expand or contract. Since the drilling of galena plates offered some difficulty, and inasmuch as it is rather difficult to obtain perfectly smooth and plane surfaces by the cleavage of crystals, a method was devised which enabled us to accomplish the objectives mentioned above. This method will be referred to as the deposited film method.

(*d*) *Deposited film method for the measurement of angles of contact*

Numerous investigators have obtained mirror surfaces of various substances by slowly distilling the material in a high vacuum and condensing it upon the object it is desired to coat. We have employed this method in the preparation of surfaces for contact angle measurements.

In recent years considerable work has been carried out on the structure of deposited films. Finch and Quarrell (7) found that very thin films showed a distortion of crystal units, these tending to fit the lattice of the material of the base upon which they were deposited. They found the crystal structure of thicker films to be normal, the surface having a random orientation unless heated. In such a case orientation occurred. Dixit (6) found the orientation to be independent of the nature of the base, provided its surface was smooth and amorphous. This work appears to show that freshly deposited surfaces should be ideal for our purpose, provided the film is deposited upon a smooth and amorphous base.

The substance to be studied was deposited upon a polished glass surface having a small hole through the center (i.e., a tip, see figure 3). A drop of the liquid, the contact angle of which was to be measured against this solid, was introduced onto the surface by forcing the liquid up through the hole, and the angle of contact formed was then photographed. By proper manipulation of the apparatus both advancing and receding angles could be measured.

The method used in measuring the angles formed upon these deposited surfaces was a modified horizontal plate method. The arrangement for running the liquid out onto the plate permitted accurate control of the movement of the drop. Moreover, the system was comparatively free from vibration. In order to insure true advancing and receding values, the angle was photographed while the liquid was moving very slowly. The surface of the solid must not be in an inverted position if materials

giving an angle greater than 90° are used, as in such a case the drop advances to approximately 90°, elongates, and then falls off.

Data for advancing and receding water–air angles upon these different deposited films are given in table 6. It will be observed that the water–

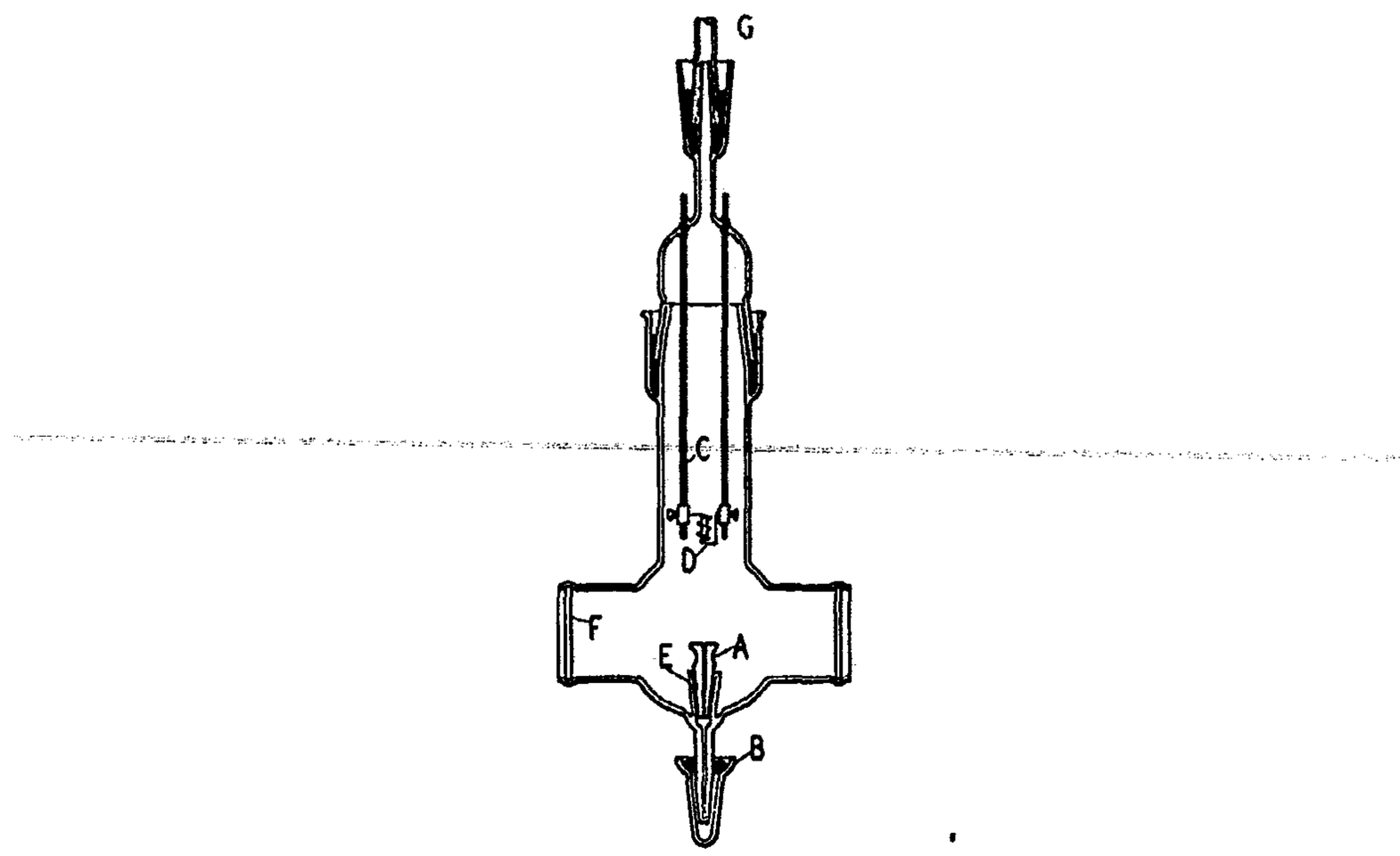

FIG. 3. APPARATUS FOR THE MEASUREMENT OF ANGLES OF CONTACT IN AN INERT ATMOSPHERE BY THE DEPOSITED FILM METHOD

A, tip; B, cap and seal; C, tungsten leads; D, heating coil; E, tip support; F, plane glass windows; G, vacuum outlet.

TABLE 6

Contact angle values of water upon deposited films

t = 25°C. ± 1.0°

MATERIAL	θ_{ls} (ADVANCING)	θ_{ls} (RECEDING)
Lead sulfide	90°	0°
Arsenious sulfide	97°	0°
Bismuth	110°	0°
Sulfur	98°	66°
Biphenyl	107°	35°
Naphthalene	103°	35°

air contact angles formed upon galena surfaces were the same as those which were found by the rod method, using freshly cleaved, unheated galena.

The angles of contact measured by this method were duplicable to within ±3°. The method has a very wide range of applicability. Other investigators have used the vacuum sublimation process for the preparation of mirror surfaces of practically all of the metals, a large number of salts, and several oxides. Our own work has indicated that many sulfides and organic materials would give good mirror films. Results obtained for some of these systems are given in table 6. The method should also be applicable to materials which are very readily oxidized by exposure to the atmosphere, as slight modifications in the design of the apparatus would allow the determination of contact angles upon these deposited films to be carried out in an inert atmosphere, or even *in vacuo* (see figure 3). Work is being extended along this line.

We believe that the process for preparing fresh mirror surfaces of various solids by sublimation of the material *in vacuo* could be advantageously used in the preparation of surfaces for the measurement of contact angles by other methods.

DISCUSSION OF METHODS AND RESULTS

A study of the methods used in this investigation for the measurement of contact angles reveals that each of the methods may be satisfactory for certain systems.

The pressure of displacement method gives duplicable and apparently significant results. It is the only method suitable for use with powdered materials. In case the surface properties of a solid become altered in the process of pulverization (which may sometimes be the case), this method obviously would not give values characteristic of an uncontaminated surface of the pure substance.

The horizontal plate method as generally employed is suitable for use with certain substances, but not for substances which give dual contact angles (advancing and receding angles), each of which is apparently stable, unless some means is employed to control very accurately the spreading of the drop.

The vertical rod method appears to give reliable results with those substances which will give clean smooth surfaces of proper shape.

The deposited film method is primarily suited for the determination of angles of contact upon pure materials, films of which can be formed by sublimation. This method offers greatest possibilities in fundamental studies of pure and uncontaminated surfaces.

Results obtained with the vertical rod method and with the deposited film method indicated that with a strictly clean galena surface the galena-water-air advancing contact angle is one of 90°, and that the receding angle is zero.

Results obtained using powdered galena and the pressure of displace-

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ment method indicated that the surface of the powdered galena used was less organophilic than was that of the freshly cleaved or freshly sublimed galena used in the vertical rod method and in the deposited film method. By heat treatment the galena used in the vertical rod method could be caused to approach in surface properties the powdered galena. In these cases it is believed the change in surface properties was caused by oxidation.

A study of all the results obtained with galena indicates that this solid has surface properties quite different from other solids previously studied by us (as carbon and silica), in that it gives widely different and apparently stable advancing and receding contact angles and in so doing appears to function either as an organophilic or as a hydrophilic solid depending upon whether it is first wetted by an organic liquid or by water. From data given in table 6, obtained with the film method, it appears probable that other substances will be found to possess properties similar to those exhibited by galena.

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X-RAY STUDIES ON THE HYDROUS OXIDES. VII

Ferric Oxide

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Received June 14, 1934

THE BROWN GEL

The interaction of solutions of ferric salts and soluble bases gives a highly gelatinous precipitate of hydrous ferric oxide, frequently misnamed ferric hydroxide. The composition and other properties of this brown gel depend upon the conditions of formation and the age of the sample. Heating under water (1, 4, 5, 8, 12) or dilute salt solutions (2) for a long time, or aging at room temperature (14) for a much longer time, gives an almost anhydrous, more or less brick-red product. X-ray analysis by Böhm (2) showed that boiling in the presence of water, potassium chloride, or ammonium chloride solutions gives α-Fe_2O_3, whereas aging at 150°C. in the presence of 2 *M* potassium hydroxide gives α-$Fe_2O_3 \cdot H_2O$. Katsuria and Watanabe (9) obtained the α-Fe_2O_3 x-ray pattern from a gel heated to 150°C. in an autoclave. Nichols, Kraemer, and Bailey (11) obtained the α-Fe_2O_3 pattern for the coagula from aged sols.

Although all the evidence points to the aged gel being α-Fe_2O_3, it is generally agreed that the x-ray diffraction pattern of the freshly precipitated oxide shows no lines or bands (2, 3, 6, 7, 15). The results of a systematic study of the transformation from the brown gel to α-Fe_2O_3 are given in the following section.

Aging under water and ferric chloride solutions

The brown gel was precipitated at about 20°C. by the addition of 300 cc. of 15 *M* ammonium hydroxide to 1 liter of 0.2 *M* ferric chloride solution. The precipitate was washed with dilute ammonia by the use of the centrifuge until free of chloride, and finally with water until only a trace of ammonia remained. Samples of the washed brown gel were aged as indicated in table 1. X-ray analysis of the products shows that, although no lines or bands can be detected in the original gel, the lattice of α-Fe_2O_3 appears gradually upon aging in the cold, and more rapidly at 100°C. In figure 1 are given densitometer curves (10) of the x-ray negatives for the products aged at 100°C. These show clearly the progress of the transformation from the brown gel to α-Fe_2O_3.

Aging in the presence of electrolytes

Since the results in table 1 show that the presence of ferric chloride delays the transformation from the brown gel to α-Fe_2O_3, a systematic study of the effect of added electrolytes was undertaken. The brown gel was precipitated at 32°C., as described above, and all washings were carried out by decantation without using the centrifuge. The washing was facilitated by this procedure, since the matting of the precipitate was avoided. Samples were aged in the presence of ammonium hydroxide, ammonium chloride, ferric chloride, and hydrochloric acid. Ten additional samples were aged under pure water as a control experiment. The results are

TABLE 1

Aging of $Fe_2O_3 \cdot xH_2O$ *in the presence of water and ferric chloride solutions*

AGING MEDIUM	TEMPERATURE	TIME OF AGING	RESULTS OBTAINED BY X-RAY ANALYSIS	COLOR
Water	Room temperature	0	No lines or bands visible	Brown
		8 days	No lines or bands visible	Brown
		3 months	No lines or bands visible	Brown
		5 months	One or two weak broad bands	Brown
		6 months	Weak α-Fe_2O_3 pattern	Brown
		1 year	Good α-Fe_2O_3 pattern	Brick-red
		2 years	Good α-Fe_2O_3 pattern	Brick-red
Water	100°C.	0	No lines or bands visible	Brown
		1 hour	α-Fe_2O_3 pattern, broad bands	Brown
		2–16 hours	α-Fe_2O_3 pattern, broad lines	Brick-red
		19 hours	α-Fe_2O_3 pattern, sharp lines	Brick-red
Ferric chloride solution	100°C.	0	No lines or bands visible	Brown
		1 hour	α-Fe_2O_3 pattern, few broad bands	Brown
		6 hours	α-Fe_2O_3 pattern, few broad bands	Brown
		24–36 hours	α-Fe_2O_3 pattern, broad lines	Some brick-red

summarized in table 2. It is apparent that added electrolytes retard or prevent the transformation from the brown gel to α-Fe_2O_3. The higher temperature of precipitation of 32°C., as compared with 20°C. in the preceding experiments, allowed the transformation to proceed more rapidly. This conclusion is further substantiated by the observation that a separate sample, precipitated at 100°C. and cooled rapidly to room temperature, gave a good pattern of α-Fe_2O_3 without further aging.

THIESSEN AND KÖPPEN'S "HYDRATES"

Thiessen and Köppen (17) have recently reported the preparation of a series of ferric oxide hydrates by the slow hydrolysis of ferric ethylate.

From breaks in dehydration isotherms they deduce the formation of $Fe_2O_3 \cdot nH_2O$ where $n = 4, 7/2, 3, 5/2, 2, 3/2, 1, 1/2$, and probably 5 and 9/2.

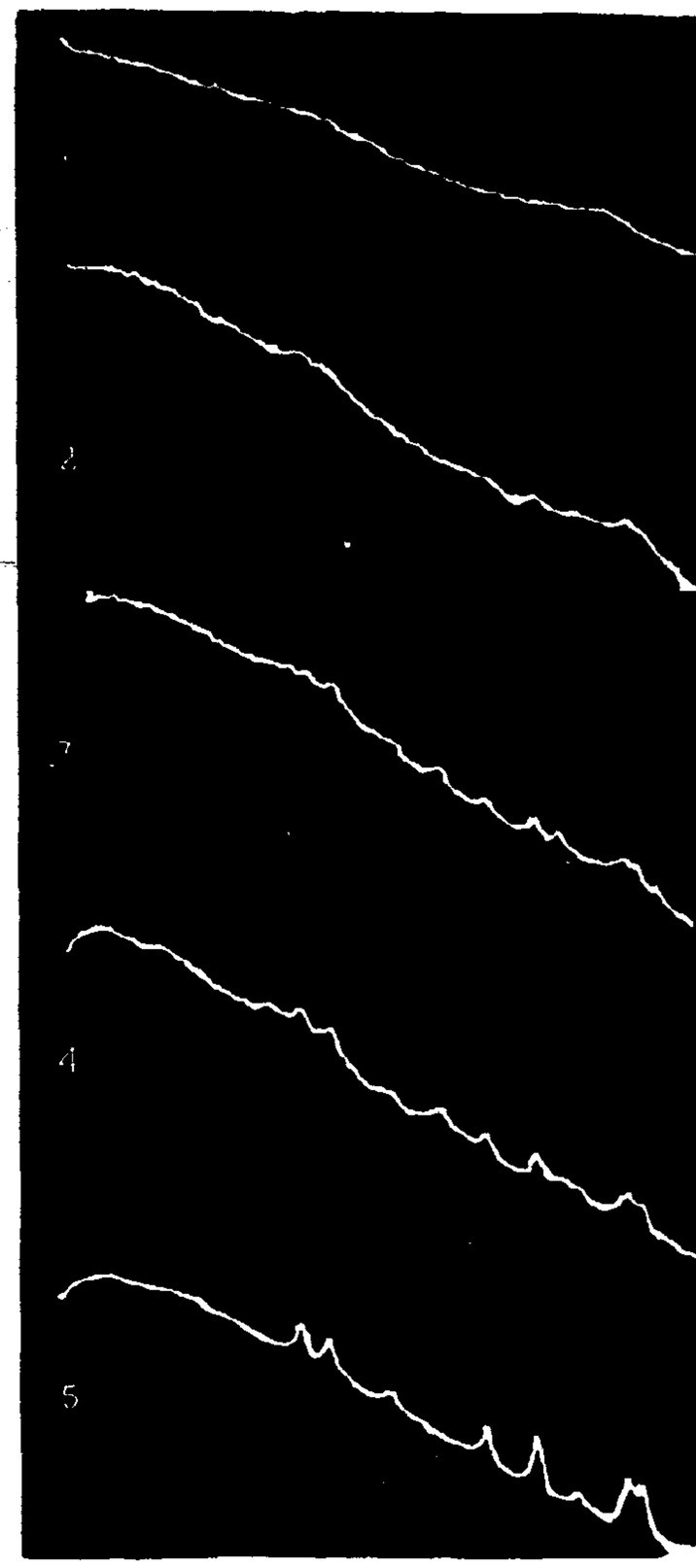

FIG. 1. DENSITOMETER CURVES FOR $Fe_2O_3 \cdot xH_2O$ AGED UNDER WATER AT 100°C.
Time of aging in hours: (1) 0; (2) 1; (3) 2; (4) 4; (5) 19

The existence of such a series of oxide hydrates is so unusual that it seemed advisable to confirm or disprove Thiessen and Köppen's experiments.

TABLE 2

Aging of $Fe_2O_3 \cdot xH_2O$ *at room temperature*

ELECTROLYTE ADDED	CONCENTRATION	COLOR OF PRECIPITATE AFTER				
		10 minutes	6 hours	40 days	125 days	10 months
	N					
NH_4OH	15	Brown	Brown	Brown	Brown	Brown
	11.3	Brown	Brown	Brown	Brown	Trace brick-red
	7.5	Brown	Brown	Brown	Brown	Trace brick-red
	3.8	Brown	Brown	Brown	Trace brick-red	Trace brick-red
	1.5	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.75	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.50	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.25	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
	0.05	Brown	Trace brick-red	Trace brick-red	Brick-red	Brick-red
NH_4Cl	5.0	Brown	Brown	Brown	Brown	Brown
	3.75	Brown	Brown	Brown	Brown	Brown
	2.5	Brown	Brown	Brown	Brown	Brown
	1.25	Brown	Brown	Brown	Brown	Brown
	0.5	Brown	Brown	Brown	Brown	Brown
	0.25	Brown	Brown	Brown	Brown	Brown
	0.03	Brown	Brown	Brown	Brown	Trace brick-red
$FeCl_3$	0.5	Brown	Brown	Brown*	Brown*	Brown*
	0.25	Brown	Brown	Brown*	Brown*	Brown*
	0.10	Brown	Brown	Brown*	Brown*	Brown*
	0.01	Brown	Brown	Brown*	Brown*	Brown*
HCl	0.10	Brown	Brown	Brown	Red sol	Red sol
	0.01	Brown	Brown	Brown	Brown	Red sol
H_2O only		Brown	Brown	Brick-red	Brick-red	Brick-red

* Deposits a yellow sediment (probably β-$Fe_2O_3 \cdot H_2O$).

Preparation of ferric ethylate

Samples of ferric ethylate were prepared by the interaction of solutions of anhydrous ferric chloride and sodium ethylate in absolute alcohol. In the first experiments the alcohol was dehydrated with metallic calcium, as was done by Thiessen and Köppen. At all times the apparatus and solutions were protected from the action of moisture in the air by the use of large drying towers containing calcium chloride and phosphorus pentoxide. A solution 15 millimolar with respect to ferric oxide in absolute alcohol was prepared from the ferric ethylate. Moisture from the air was allowed to diffuse into the solution, causing a slow hydrolysis which was complete at the end of three or four weeks, the exact time depending upon the atmospheric conditions prevailing during the hydrolysis period. Several samples prepared in this way were separated from the supernatant liquid and washed thoroughly, using the centrifuge, with alcohol alone or first with alcohol and then with water. The samples washed with alcohol alone contained considerable adsorbed alcohol, which was largely removed by washing with water. The following analytical results are typical: Sample washed with alcohol alone: Fe_2O_3 = 68.03 per cent; H_2O = 24.53 per cent; C_2H_5OH = 7.54 per cent. Sample washed with alcohol and with water: Fe_2O_3 = 64.14 per cent; H_2O = 34.85 per cent; C_2H_5OH = 1.01 per cent. The amount of adsorbed alcohol was determined by a combustion method. The samples actually used in dehydration experiments were always washed with water to remove excess alcohol. Since only 1 per cent or less of alcohol remained in the samples washed in this way, its presence may be neglected in the dehydration experiments described in the next section.

In a second series of experiments an improved method of drying the alcohol was adopted (16). "Absolute alcohol" was further dried with excess metallic calcium and distilled directly into a carefully dried flask containing metallic sodium and ethyl oxalate. Traces of water in the alcohol react with the sodium ethylate to give alcohol and sodium hydroxide. The reaction is shifted in the desired direction by allowing the sodium hydroxide to hydrolyze the ethyl oxalate, giving alcohol and sodium oxalate. The resulting highly anhydrous alcohol was distilled directly into the reaction vessels containing anhydrous ferric chloride and metallic sodium. The solutions of ferric chloride and sodium ethylate were mixed, giving ferric ethylate. The entire apparatus and solutions were protected from the action of moisture in the air by calcium chloride and phosphorus pentoxide towers. The slow hydrolysis of this sample of ferric ethylate was carried out in warmer weather than the first; hence the resulting ferric oxide gel contained less adsorbed water than the first preparation.

Dehydration isotherms

The samples of hydrous ferric oxide prepared as described above were dehydrated isothermally in an apparatus shown in figure 2, which needs no further description. The general method of procedure consists in pumping off a definite amount of water and measuring the vapor pressure of the resulting product at constant temperature by means of a manometer filled with "vacuum pump oil" of known density. In the case of the sample made from the alcohol dried with metallic calcium only, the weighed sample was sealed into the weighed tube, A, and changes in composition

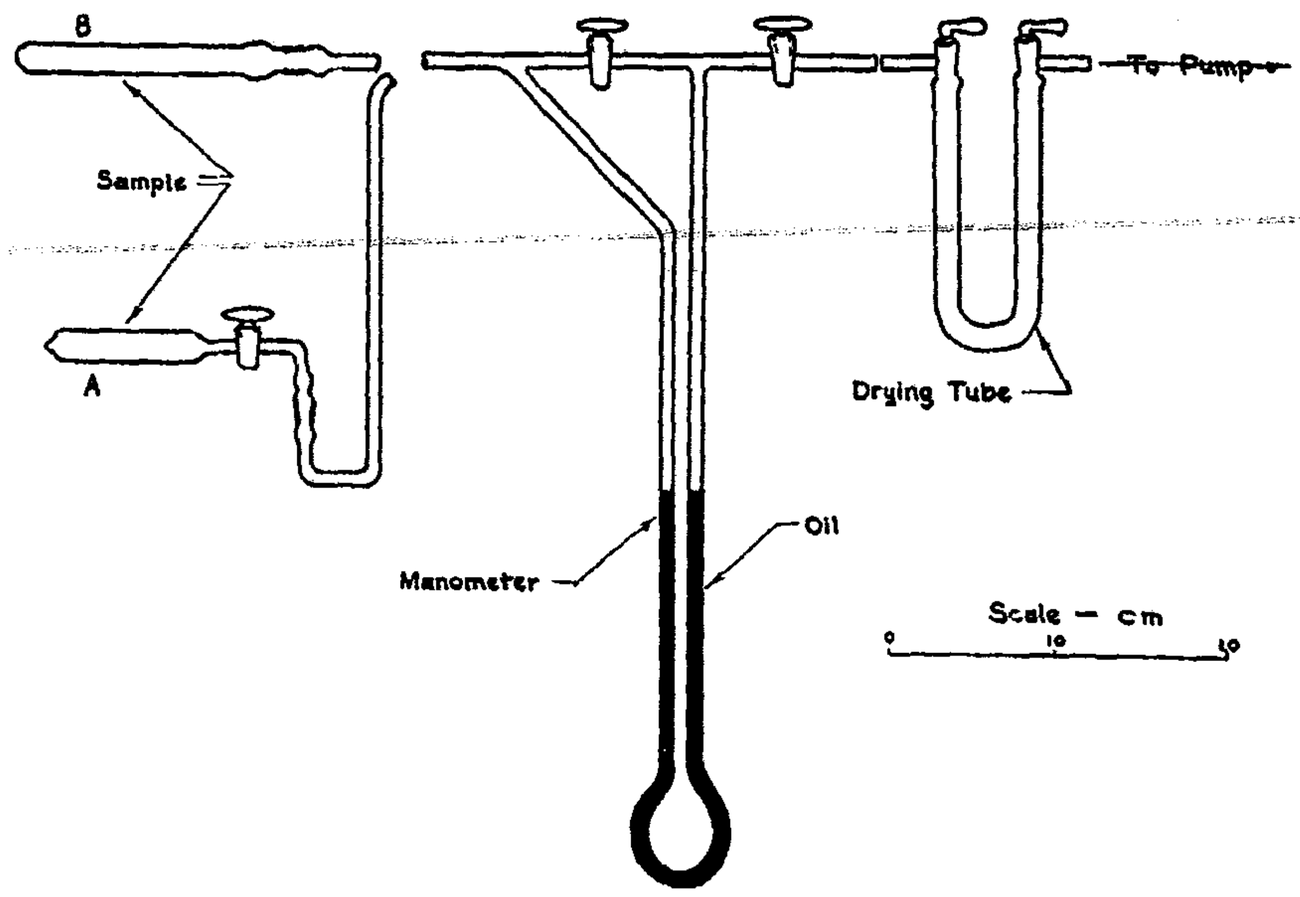

FIG. 2. APPARATUS FOR ISOTHERMAL DEHYDRATION

were followed by closing the stopcock and reweighing the tube with contents. Typical isotherms are given in figure 3.

An improvement was made in the apparatus used in the isothermal dehydration of the samples made from the drier alcohol. Tube B was substituted for tube A, and changes in composition were followed by collecting the water vapor in a drying tube filled with magnesium perchlorate trihydrate. Otherwise the apparatus was unchanged. Typical isotherms for this sample are given in figure 4. The equilibrium pressure at a given temperature and composition is established in half an hour or less. The pressure was read only after it had remained constant for half an hour. It is obvious that the isotherms contain no breaks which would suggest the existence of hydrates in the gel. We have no explanation to offer for

the series of breaks at just the right place in the isotherms of Thiessen and Köppen. Since these observers made no statement to the contrary, it is probable that they neglected to remove the alcohol from their samples before dehydration. This might account for one point of inflection in the

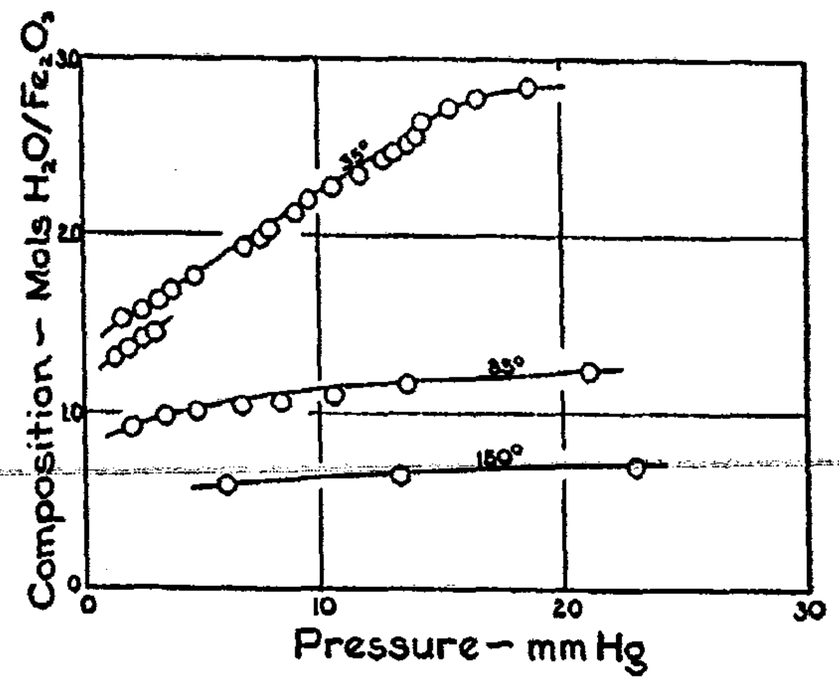

FIG. 3. DEHYDRATION ISOTHERM FOR $Fe_2O_3 \cdot xH_2O$

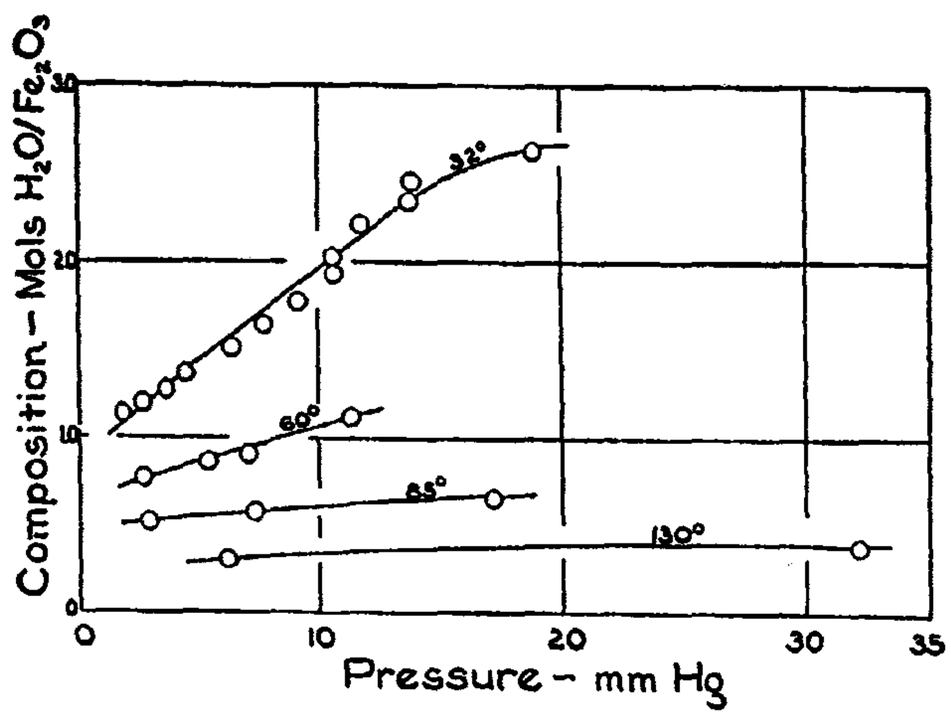

FIG. 4. DEHYDRATION ISOTHERM FOR $Fe_2O_3 \cdot xH_2O$

curve, but it would come at a point corresponding to a hydrate only by accident.

X-ray analysis

The freshly precipitated samples, either unwashed, washed with alcohol, or washed with both alcohol and water, gave x-ray patterns showing no

lines or bands. A sample washed with water and heated to about 185°C. gave a weak pattern corresponding to α-Fe_2O_3. The broad bands indicated extremely small particle size.

HYDROLYSIS OF FERRIC SALTS

A. Ferric sulfate

The system Fe_2O_3–SO_3–H_2O has been examined in detail by Posnjak and Merwin (13, 18), using phase rule methods. These investigators have proven that α-$Fe_2O_3 \cdot H_2O$ may be prepared by the hydrolysis of ferric sulfate at low concentrations and at temperatures below 130°C. More concentrated solutions give a basic salt of composition $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. The following experiments are in agreement with these observations. Solutions of ferric sulfate were prepared as indicated in table 3. The solutions were heated to the boiling point on a hot plate, using reflux condensers to prevent loss of water vapor. The more dilute solutions gave α-$Fe_2O_3 \cdot H_2O$, while the yellow precipitate obtained in the more concentrated solutions gave the same x-radiogram as the basic salt reported by Posnjak and Merwin.

TABLE 3

Hydrolysis of ferric sulfate solutions

CONCENTRATION	COLOR OF PRECIPITATE	SOLID PHASE IDENTIFIED BY X-RAY ANALYSIS
M		
1.00	Yellow	Mostly basic sulfate
0.50	Yellow	Mostly basic sulfate
0.25	Yellow	Mostly basic sulfate
0.10	Yellow	Mostly basic sulfate
0.05	Yellow	Mostly basic sulfate
0.01	Yellow	Mostly α-$Fe_2O_3 \cdot H_2O$

B. Ferric nitrate

A solution containing 25 g. of ferric nitrate hexahydrate per liter was heated slowly to 100°C. on a hot plate; a yellow precipitate was obtained which gave the x-ray pattern for α-$Fe_2O_3 \cdot H_2O$. A 0.1 *N* solution was allowed to stand at room temperature for about seven months. This was likewise identified as α-$Fe_2O_3 \cdot H_2O$. More concentrated solutions were not examined. Simon and Schmidt (15) dialyzed a ferric nitrate solution and examined the precipitate from the resulting sol by x-ray diffraction methods. The pattern was reported as being different from α-Fe_2O_3; it was probably that for the α-monohydrate.

C. Ferric bromide and oxalate

Hydrolysis of ferric bromide and ferric oxalate gives a yellow precipitate which was proven by x-ray analysis to be α-$Fe_2O_3 \cdot H_2O$.

D. Ferric chloride

Slow hydrolysis of ferric chloride solutions, either dilute or concentrated, always gives a third polymorph of ferric oxide monohydrate, which has been designated elsewhere (20) as β-$Fe_2O_3 \cdot H_2O$.

E. Ferric acetate

Fifteen years ago one of us (19) found that boiling freshly prepared ferric acetate solutions gave a brick-red colloid or precipitate, whereas solutions aged for ten days or more before boiling gave a definitely yellow colloid or precipitate. At that time the available evidence pointed to the conclusion that this yellow product consisted of hydrous ferric oxide, differing from the red-brown and brick-red varieties only in particle size. These experiments have been repeated, and the yellow product has been identified as α-$Fe_2O_3 \cdot H_2O$ and the brick-red powder as α-Fe_2O_3.

TABLE 4

Slow hydrolysis of ferric salts

SALT USED	PRODUCT IDENTIFIED BY X-RAY ANALYSIS
Sulfate	α-$Fe_2O_3 \cdot H_2O$ or $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
Nitrate	α-$Fe_2O_3 \cdot H_2O$
Nitrate inoculated with a trace of β-$Fe_2O_3 \cdot H_2O$	α-$Fe_2O_3 \cdot H_2O$
Bromide	α-$Fe_2O_3 \cdot H_2O$
Oxalate	α-$Fe_2O_3 \cdot H_2O$
Chloride	β-$Fe_2O_3 \cdot H_2O$
Acetate	α-$Fe_2O_3 \cdot H_2O$

Rapid hydrolysis of ferric salts always yields α-Fe_2O_3, and slow hydrolysis, except in the case of the chloride, yields the α-monohydrate. Slow hydrolysis of the aged ferric acetate solutions in the cold gives nuclei of α-$Fe_2O_3 \cdot H_2O$, which determine the course of the reaction at higher temperatures.

Table 4 summarizes the results obtained by the slow hydrolysis of various ferric salts.

SUMMARY

The brown gel formed by the interaction of solutions of ferric salts and bases in the cold gives an x-radiogram showing no lines or bands. Aging under water of the oxide freshly precipitated in the cold for a few weeks or

months at room temperature or a few hours near the boiling point brings about a transformation from the brown gel to brick-red α-Fe_2O_3. Excess electrolytes retard or prevent the transformation. X-ray examination of the products formed by systematic aging of the original gel indicates that the transformation consists in the growth of particles too finely divided to give a characteristic x-radiogram, to crystals of α-Fe_2O_3 large enough to give sharp diffraction lines. Gels thrown down near 100°C. give at once a weak x-radiogram of α-Fe_2O_3.

Dehydration isotherms of the ferric oxide gel formed by the slow hydrolysis of ferric ethylate show no breaks indicative of the existence of definite hydrates. This is contrary to the results of Thiessen and Köppen.

Rapid hydrolysis of ferric salts gives a brick-red precipitate identified by x-ray analysis as α-Fe_2O_3. Slow hydrolysis of ferric salts gives a yellow precipitate of hydrous α-$Fe_2O_3 \cdot H_2O$, except in the case of ferric chloride where β-$Fe_2O_3 \cdot H_2O$ is formed; ferric sulfate gives either α-$Fe_2O_3 \cdot H_2O$ or a definite basic sulfate, depending on the conditions.

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INTERFACIAL ENERGY AND THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS. III

THE EFFECT OF ORGANIC STRUCTURE ON ADSORBABILITY[1]

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Received June 14, 1934

I. INTRODUCTION

Freundlich's observations (5) indicated a general relationship between adsorption and solubility and an apparent parallelism between surface tension lowering and extent of adsorption. Langmuir (20, 21) and Harkins (14 to 17) developed independently the idea of molecular orientation, first suggested by Hardy (11 to 13), and gave a definite picture of the arrangement of solute molecules at interfaces. Still later, in investigating the mechanism of bacterial action, Quastel and his coworkers came to the conclusion that there are certain active centers "characterized by the possession of particular groupings which are able to adsorb a particular type of structure. A relatively large number of substances can be adsorbed in this specific manner, but out of this number only a few can be activated to act as hydrogen donators" (36). This work demonstrates the importance of molecular structure in specific adsorption.

The literature, although it shows the importance of chemical configuration in adsorption phenomena, reveals no adequate study of several structurally related compounds on a single interface over any concentration range or any reasonable basis for comparison. This study was accordingly undertaken to compare the influence of certain groupings in typical organic acids on the adsorption of these compounds from aqueous solution within definite concentration ranges, using a single and comparable interface.

[1] Paper No. 1291, Journal Series, Minnesota Agricultural Experiment Station. Greatly condensed from a thesis presented by E. R. Linner to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934. The detailed tabular experimental data are all included in a manuscript copy on file in the Library of the University of Minnesota. Photostatic copies of the detailed tables may be obtained approximately at cost from the University of Minnesota.

II. HISTORICAL

Surface tension lowering by solute and its relation to adsorbability

Following the establishment of the Freundlich (5) equation for adsorption, most studies dealt either with the relationships between solubility and adsorption or with the dependence of the phenomenon on surface tension lowering by the solute molecule. Freundlich has cited examples of a few substances which are strongly adsorbed from aqueous solution but which depress the surface tension of water only slightly, e.g., succinic acid and benzoic acid, together with some of the derivatives of the latter. Glucose, lactose, and cane sugar, although they raise the surface tension of water markedly, are all comparatively well adsorbed. Michaelis and Lachs (24) noted other exceptions, among them citric acid. King and Wampler (19) have shown that tartaric acid is negatively adsorbed at an aqueous interface, and that while fumaric acid has little effect on the surface tension of water, its isomer, maleic acid, lowers it slightly. Although the first three members of the series of dicarboxylic acids are positively adsorbed at an air–water interface, the effect is relatively small. However, all these compounds are adsorbed by charcoal and there is positive evidence that, to the limits of its solubility, fumaric acid is adsorbed to a greater extent than is maleic. Accordingly there can be no direct parallelism between surface tension lowering and adsorption.

Solubility and adsorption

Freundlich (5) pointed out that while there is a general relation between the solubility and the adsorbability of a solute there are still notable exceptions, e.g., benzenesulfonic acid and sulfanilic acid. The latter, though it is less soluble than the former, is less strongly adsorbed. The very soluble mellitic acid is strongly adsorbed. According to de Izaguirre (Freundlich (6) addenda, p. 817) in the case of maleic and fumaric acids and of citraconic and mesaconic acids, adsorption decreases with increasing solubility. Alekseevskii (1) confirmed this for fumaric and maleic acids, but found the opposite to be true for isobutyric and *n*-butyric acids. For six organic compounds, some of which are structurally related, Santa (40) showed that adsorption is greater the lower the solubility. Platonov, Borgman, and Salman (32, 33) and Roychoudhury (38) conclude that solubility is of only secondary importance.

With only few exceptions the conclusions summarized above are based on adsorption data obtained from series of experiments involving two or three different initial concentrations. However, some of these conclusions depend on ratios between "adsorbability" or the per cent adsorbed of two related compounds. It will be shown later that the numerical values for the $\frac{C_0 - C}{C_0} \times 100$ relationship can vary widely when calculated over a

range of concentrations. In spite of this objection it is evident that there is no strict antibasis between adsorption and solubility.

Relation of polarity to adsorption

Aside from surface tension lowering of the solvent by the solute molecules and adsorbability, and the antibatic solubility–adsorbability relationship, many studies have dealt with the rôle played by the polarity of the molecule. Bartell and Miller (2) showed that the introduction of the hydroxyl group in an organic acid decreased adsorption on carbon to an extent depending on the nature of the acid. The introduction of the amino group produced a greater effect. Miller (25) states that charcoal plays the same rôle at a charcoal–solution interface that an organic liquid plays in an organic liquid–aqueous interface, and that the Langmuir-Harkins theory of polar groups applies to adsorption from solution by charcoal. Alekseevskii (1) ascribes the difference in adsorbability between *n*-butyric acid and isobutyric acid to the branched chain. Shilov and Nekrassov (41) conclude that normal compounds are more strongly adsorbed than are iso compounds and that the *trans* forms are more strongly adsorbed than are *cis* forms. Platonov, Borgman, and Salman (32, 33) conclude that structure is a most important factor in predicting the degree of adsorbability. Langmuir (21) pointed out that a stoichiometrical equation cannot be written for adsorption, because the configuration of the molecules adsorbed makes a difference in the areas taken up by them on the adsorbent.

In view of the demonstrated influence of molecular structure on adsorbability, it seems most unusual that this field of investigation has received such scant attention.

III. EXPERIMENTAL

The adsorbate

A series of thirty-one organic acids, differing in most cases regularly in chemical configuration, was employed throughout this study. All were of satisfactory purity. The list of the acids used is given in the first paragraph of the summary, and the individual acids are also indicated on the various graphs and tables.

The adsorbent

A large sample of decolorizing carbon, Norite, was secured, thoroughly sampled, and used throughout all studies. Thus variations of the interface were only those existing through the mass of adsorbent. The Norite contained 1.25 per cent ash (chiefly silica with traces of iron), which was found to have an equivalent of 1.5 cc. of 0.01 *N* acid. This percentage of extraneous material should invalidate in no way comparisons between structurally similar compounds. Miller (25) has pointed out

that organic acids are strongly adsorbed on impure carbons and on such interfaces show the same selectivity as on ash-free carbon.

One gram of the adsorbent was used, except in those experiments involving caprylic acid. Caprylic acid is so slightly soluble that a weight of adsorbent greater than 0.1 g. tends to make the titre of the equilibrium concentration so low as to be of doubtful value. Fodor and Schönfeld (4) and Pavlov (31) have already shown variations in the amounts adsorbed with greatly diluted solutions and smaller amounts of carbon. The former authors point out that in the application of the Freundlich equation to their data, n varies notably with the amount of charcoal used, becoming less as the charcoal is increased. They report, however, that in the less dilute solutions n is independent of the amount of charcoal used. In the present study 1 g. of Norite and concentrations of reagents varying from 0.01 to 0.25 molar have been employed.

Experimental procedure

Where solubility permitted, stock solutions of the acids to be studied were made up to approximately 0.25 molar. With acids of limited solubility, saturated stock solutions were used. Aliquots of the stock solution were measured into Erlenmeyer flasks from a calibrated buret. Water was added to make the final volume 75 cc. One gram of Norite was then added. The flasks were closed with rubber stoppers and shaken with the adsorbent for a period of thirty minutes. They were then allowed to stand at room temperature for the same length of time. After this period they were filtered through #615 E. and D. filter paper into Erlenmeyer flasks. The filters were allowed to drain for fifteen minutes, after which the Erlenmeyers were removed and stoppered until titrations were made. To avoid errors due to adsorption by the filter paper, approximately the first 15 cc. of filtrate was discarded. A blank of 75 cc. of the stock solution without Norite was given the same treatment as each sample of the run.

In a few early experiments samples were allowed to stand in contact with the adsorbent overnight, but no essential differences were noted as a result of this longer period of contact. This is in accord with the observations of Freundlich (5), Dubinin (3), Lipatov (23), and Ruff (39).

The experiments were conducted at room temperature, which varied from 22°C. to 30°C. Freundlich (reference 6, pp. 174, 223–4) and Yajnik and Rana (42) found little change in adsorption over this temperature range.

Equilibrium concentrations were determined by titrating with standard solutions of sodium hydroxide, using phenolphthalein or thymol blue indicators. Equilibrium concentrations were calculated to moles per liter. The "adsorption in millimoles per gram" refers to the amount adsorbed by 1 g. of Norite from a volume of 75 cc. of solution.

Adsorption equations

From a consideration of the mosaic-like character of the solid surface, Langmuir (22) has made it clear that probably no single equation will express, in all cases, the relation between the equilibrium concentration and the quantity of adsorbed molecules. Many workers have stressed the complexity of the phenomena and the forces existing at surfaces. It is not the purpose of this paper to delve into any of these phases of the problem. The project at hand is one of showing the effect of molecular configuration of the adsorbate on adsorption. The difficulty of using isolated concentrations for comparison has been suggested above, and it will later be shown that in some cases the conclusions which authors have drawn can apply only at some particular concentration. It seems advantageous to make comparisons over a concentration range, and so to choose the range that the simpler mathematical relationships will hold. For this purpose Freundlich's adsorption isotherm and the equation of Langmuir for simple adsorption have been employed.

The Freundlich equation

The empirical equation proposed by Freundlich for the adsorption isotherm has been commonly used. Though it is undoubtedly only approximately correct, it fits much of the published data fairly well. Freundlich (5) himself has pointed out that for solutions the equation is not a complete formula covering all concentrations, for it is based on the apparent adsorption of the solute molecule, and adsorption of the solvent is not taken into consideration. Fodor and Schönfeld (4) and Pavlov (31) find that n varies with dilution and amount of carbon used. Garner (10) likewise demonstrated the limited range of application of the isotherm. In some preliminary experiments we tested adsorption from fairly dilute solutions. Over the range from 0.001 to 0.01 molar equilibrium concentrations, the values for the amount adsorbed were low as compared with equilibrium concentrations above 0.01 molar. For this reason initial concentrations were so chosen that the concentration at equilibrium would generally be between 0.01 and 0.25 molar. The logarithmic values for C and the corresponding values of a between these limits approximate a straight line.

Values for $1/n$ and α of the equations were calculated by the method of least squares applied to the logarithmic equation. Table 1 lists these constants, the number of points considered, and the average error between observed values and those calculated from the equation. The "average error" is the percentage difference between the various observed values and the values at comparable concentrations as given by the fitted equation. The agreement between the observed values of the adsorbed and the calculated is excellent, as evidenced by the average per cent error. The logarithmic curves in the graphs also show how nearly the values fall on the calculated straight lines.

The constants $1/n$ and α have no simple physical meaning. The equation, at best, can serve only to calculate the millimoles adsorbed for any

TABLE 1

Showing values of "$1/n$" and "α" of the Freundlich equation, $a = \alpha C^{1/n}$ for the various systems of Norite and organic acid at equilibrium, as well as the average per cent error and the number of points used for the calculations

ACID	α	$1/n$	AVERAGE PER CENT ERROR BETWEEN OBSD. AND CALCD. a	NUMBER OF POINTS
Formic	2.47	0.435	2.6	15
Acetic	2.46	0.351	2.6	18
Propionic	2.46	0.236	1.8	15
n-Butyric	2.46	0.177	2.3	15
n-Valeric	2.84	0.182	2.8	12
Caproic	3.03	0.175	1.8	11
Isobutyric	2.36	0.273	12.3	10
Isovaleric	2.51	0.227	2.6	9
Glycolic	1.54	0.390	4.1	13
Lactic	1.66	0.335	3.6	18
Glyceric	1.29	0.267	6.7	13
Glyoxylic	3.89	0.455	2.3	12
Pyruvic	2.44	0.273	3.5	15
Levulinic	1.83	0.183	2.9	8
Oxalic	3.62	0.551	4.9	29
Malonic	3.88	0.410	3.3	11
Succinic	2.83	0.303	4.3	16
Glutaric	1.96	0.201	5.1	13
Adipic	1.79	0.163	4.5	22
Malic	1.28	0.252	2.2	15
Tartaric	0.94	0.275	3.3	15
Maleic	1.90	0.203	2.9	14
Fumaric	2.81	0.248	4.6	9
Mesaconic	1.80	0.133	2.4	14
Citraconic	1.69	0.167	1.8	15
Itaconic	1.54	0.148	1.9	15
Methylsuccinic	1.30	0.172	1.6	14
Citric	0.73	0.203	3.3	8
Monobromosuccinic	1.82	0.195	2.0	9
Dibromosuccinic	2.58	0.320	2.2	8

equilibrium concentration within the range over which the relationship holds. Only the fatty acids display any regularities. From formic

through butyric acids the value of α is constant and from butyric through caproic acids the slope of the logarithmic curves is also constant (see figure 1). Any other attempt to interpret the α and $1/n$ of table 1 in terms of structural relationships is unfruitful.

The Langmuir equation (22)

By the usual rearrangement of this equation

$$\frac{C}{a} = \frac{1}{\alpha\beta} + \frac{C}{\beta} \tag{1}$$

the values of the constants α and β are determinable by plotting C/a against C. These constants were calculated from our data by the method

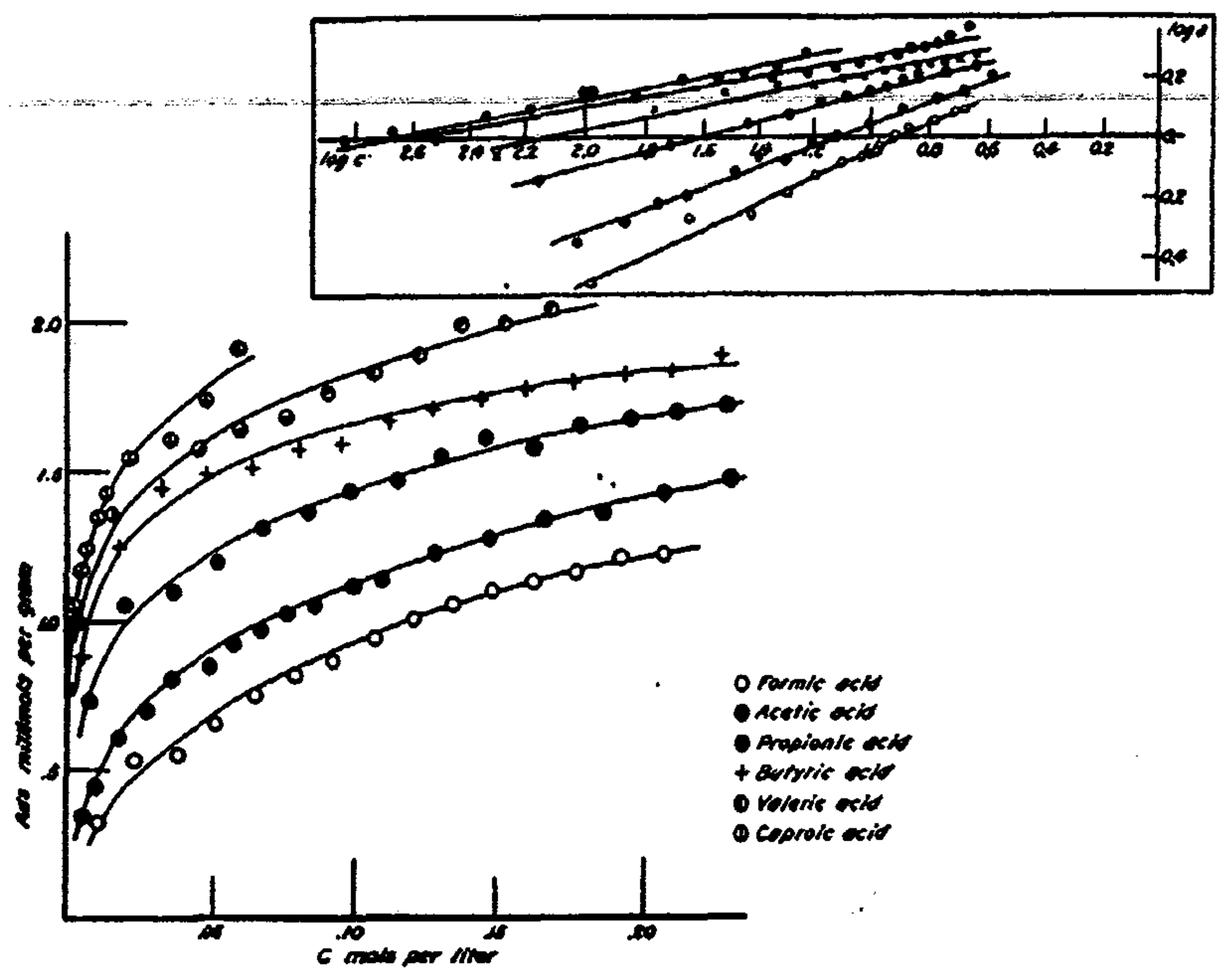


FIG. 1. ADSORPTION ISOTHERMALS FOR THE HOMOLOGOUS SERIES OF THE FATTY ACIDS

In the graph on the lower left the values are plotted arithmetically; in the one on the upper right, logarithmically.

of least squares. When plotted straight lines resulted in all cases. As with the Freundlich equation, the Langmuir relationship was not found to hold in very low concentrations; in fact the range over which the equation was applicable was slightly narrower than for the Freundlich equation. The Langmuir equation is applicable over the range corresponding to equilibrium concentrations of 0.02 to 0.22 molar. The average per cent error (table 2) is the error within this range.

TABLE 2

Showing values of α and β of the Langmuir equation, $a = \frac{\alpha\beta C}{1 + \alpha C}$ for various systems of Norite and organic acid at equilibrium

Columns 5 and 6 give the average per cent error over the range for which the Langmuir equation holds, together with the number of points considered

ACID	$\alpha\beta$	α	β	AVERAGE PER CENT ERROR BETWEEN OBSD. AND CALCD. a	NUMBER OF POINTS
Formic	0.273	0.159	1.710	1.0	13
Acetic	0.462	0.266	1.736	7.0	16
Propionic	0.925	0.491	1.885	2.0	13
Butyric	1.689	0.863	1.957	2.0	13
Valeric	1.878	0.872	2.154	5.8	11
Caproic	8.772	4.636	1.892	5.4	7
Isobutyric	0.883	0.497	1.776	5.5	7
Isovaleric	1.630	0.902	1.807	5.1	7
Glycolic	0.239	0.249	0.958	5.1	12
Lactic	0.437	0.415	1.054	4.0	18
Glyceric	0.668	0.812	0.823	8.5	13
Glyoxylic	0.508	0.223	2.275	3.0	11
Pyruvic	0.979	0.585	1.674	2.8	14
Levulinic	2.990	2.289	1.307	3.4	6
Oxalic	0.440	0.332	1.325	3.7	29
Malonic	1.897	1.540	1.232	5.6	11
Succinic	0.865	0.467	1.854	6.0	16
Glutaric	3.697	3.104	1.192	4.8	13
Adipic	2.347	1.886	1.245	4.5	19
Malic	0.531	0.574	0.927	2.3	14
Tartaric	0.322	0.468	0.687	2.5	14
Fumaric	7.097	5.798	1.224	4.1	9
Maleic	1.233	0.884	1.395	3.6	14
Mesaconic	2.706	1.886	1.435	2.9	14
Citraconic	1.356	1.014	1.337	4.7	14
Itaconic	1.167	0.904	1.291	4.0	14
Methylsuccinic	0.664	0.608	1.092	4.2	14
Citric	1.444	2.757	0.524	11.7	8
Monobromosuccinic	0.934	0.643	1.451	3.0	8
Dibromosuccinic	1.397	1.119	1.248	3.6	8

Langmuir's equation is more useful than the Freundlich adsorption isothermal for the latter is the analytical expression for the general parabola, while the former is that of a rectangular hyperbola passing through the origin. Hence, Langmuir's equation tends to a definite limit for the adsorption of the solute on the surface, while with Freundlich's equation the adsorption theoretically increases indefinitely with increasing concentration. It should accordingly be possible to use either the constants α or β of the Langmuir equation for comparison of the acids, especially since these constants have some physical significance. For comparisons of structural relationships we have used the constant β, which is equal to a (the amount adsorbed) when C (equilibrium concentration) is a maximum.

Interpretation of Traube's rule

Freundlich (reference 6, pp. 195–6) stated Traube's rule as applied to adsorption in the following manner: "The adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series." He applied this rule to the first four members of the fatty acid series, calculating the ratio $\frac{a_{n+1}}{a_n}$ at a given C (0.1 mole per liter). The value of the ratio was found to be approximately 1.5. For the ratio $\frac{C_n}{C_{n+1}}$, where $a = 1.26$ millimoles per gram of charcoal an approximate constancy of 2 to 3 was obtained. Many workers have since confirmed Freundlich's generalities. However, the comparison of ratios at any one concentration or any one value for the amount adsorbed should not of necessity give a constant value. It has already been pointed out that logarithmic isotherms (cf. figure 1) for formic, acetic, propionic, and butyric acids tend to meet at a common point, and that those for butyric, valeric, and caproic acids have a constant slope and are, therefore, parallel over the range studied. Further, it is evident from a study of the β of the Langmuir relationship that this homologous series of organic acids tends to approach a constant value of about 1.9 millimoles per gram of adsorbent. Calculations were made for the value of C at various concentrations by means of the Freundlich adsorption isothermal. The ratios $\frac{C_n}{C_{n+1}}$ were then calculated. They are shown in table 3. The values here fluctuate as one might expect from a knowledge of the constants. It is clear, too, that at higher values of a the ratio tends to become more nearly constant, and that the constant is somewhat lower than the ratio obtained by Freundlich. He reports an approximate constancy of about 2 to 3 at a single value of a of 1.26 millimoles per gram. In a similar manner values of C were chosen, and ratios between the corresponding values of a

were calculated for the Freundlich adsorption isotherm. The calculations are shown in table 4. The agreement is better for such a ratio than it is in the case of the $\frac{C_n}{C_{n+1}}$ ratio. The value of q tends to be more nearly constant as the equilibrium concentration approaches 0.25 molar.

TABLE 3

Showing the ratios of $\frac{C_n}{C_{n+1}}$ for various fatty acids at various values of a on the ordinate of their respective Freundlich adsorption isotherms

ADSORBED SUBSTANCE	C IN MOLES PER LITER WHEN							
	$a = 1.00$	q*	$a = 1.179$	q*	$a = 1.500$	q*	$a = 1.978$	q*
Formic	0.125		0.182		0.317			
Acetic	0.077	1.63	0.122	1.49	0.243	1.31		
Propionic	0.022	3.48	0.044	2.78	0.123	1.98	0.398	
Butyric	0.006	3.58	0.015	2.85	0.061	2.02	0.297	1.34
Valeric	0.004	1.88	0.008	1.93	0.030	2.01	0.126	2.35
Caproic	0.002	1.84	0.005	1.77	0.018	1.67	0.088	1.43

* $q = \frac{C_n}{C_{n+1}}$.

TABLE 4

Showing the ratios of $\frac{a_{n+1}}{a_n}$ for various fatty acids at various values of C (the equilibrium concentration) on the abscissa of their respective Freundlich adsorption isotherms

ADSORBED SUBSTANCE	a IN MILLIMOLES PER GRAM WHEN									
	$C = 0.01$	q*	$C = 0.025$	q*	$C = 0.088$	q*	$C = 0.10$	q*	$C = 0.25$	q*
Formic	0.33		0.50		0.86		0.91		1.35	
Acetic	0.49	1.47	0.68	1.36	1.05	1.22	1.09	1.21	1.52	1.12
Propionic	0.83	1.70	1.03	1.53	1.39	1.32	1.43	1.31	1.77	1.17
Butyric	1.09	1.31	1.28	1.24	1.60	1.15	1.64	1.15	1.92	1.09
Valeric	1.23	1.12	1.44	1.13	1.82	1.14	1.87	1.12	2.20	1.14
Caproic	1.35	1.10	1.59	1.10	1.98	1.09				

* $q = \frac{a_{n+1}}{a_n}$.

Relationships over a range of concentration should be more significant than at isolated concentrations. Such relationships may be secured by using the areas under the curves, i.e., for $\frac{C_n}{C_{n+1}}$ we have $\frac{\text{Area } (C)_{n+1}}{\text{Area } (C)_n}$ for the

curves a plotted against C; for $\frac{a_{n+1}}{a_n}$ we have $\frac{\text{Area (a)}_n}{\text{Area (a)}_{n+1}}$ for the curves C plotted against a. The relationships

$$\text{Area } (C) = \int_a^b \alpha C^{1/n} \, dC \tag{2}$$

and

$$\text{Area } (a) = \int_a^b (a/\alpha)^n \, da \tag{3}$$

were used. Employing equation 2 between the limits 0.01 and 0.06 (approximate solubility limit of caproic acid) and between 0.01 and 0.25, the values in table 5 and table 6 were obtained.

TABLE 5

The values for Area $(C) = \int_{0.01}^{0.06} \alpha C^{1/n} dC$ *for adsorption isotherms of the various fatty acids*

SUBSTANCE ADSORBED	AREA (C)	RATIO: $\frac{\text{AREA } (C)_{n+1}}{\text{AREA } (C)_n}$
Formic	0.0281	
Acetic	0.0371	1.32
Propionic	0.0549	1.48
Butyric	0.0671	1.22
Valeric	0.0760	1.13
Caproic	0.0831	1.09
Average		1.25

These calculations show more definite constancy. The constant is approximately 1.2 and as an average ratio is lower than Freundlich's value of 2 to 3.

Using equation 3 between the limits 1.06 and 1.9, we obtain the data shown in table 7. Except for the first ratio these average values are approximately constant and equal approximately 1.8, which is in general agreement with Freundlich's value for a single point of 1.5.

The constants of Langmuir's equation

In a discussion of the liquid-gas interface Freundlich (reference 7, pp. 76–9) combines the Szyszkowski equation and the Gibbs equation and shows that

$$a = \frac{b\sigma}{RT} \frac{C}{C + k} \tag{4}$$

where a = amount adsorbed, σ = the surface tension of the solvent, C = equilibrium concentration, and b and k are constants. Now Langmuir's equation may be written

$$a = \frac{\beta C}{1/\alpha + C} \tag{5}$$

TABLE 6

The value of Area $(C) = \int_{0.01}^{0.25} aC^{1/n}dC$ *for adsorption isotherms of various fatty acids excluding caproic acid*

SUBSTANCE ADSORBED	AREA (C)	RATIO: $\frac{\text{AREA } (C)_{n+1}}{\text{AREA } (C)_n}$
Formic	0.233	
Acetic	0.276	1.19
Propionic	0.352	1.28
Butyric	0.400	1.13
Valeric	0.456	1.14
Average		1.19

TABLE 7

The value Area $(a) = \int_{1.06}^{1.90} \left(\frac{a}{\alpha}\right)^n da$ *for adsorption isotherms of various fatty acids*

ADSORBED SUBSTANCE	AREA (a)	RATIO: $\frac{\text{AREA } (a)_n}{\text{AREA } (a)_{n+1}}$
Formic	0.269	
Acetic	0.211	1.28
Propionic	0.116	1.82
Butyric	0.065	1.79
Valeric	0.032	2.05
Caproic	0.019	1.63

Hence, it is apparent that

$$\beta = \frac{b\sigma}{RT} \tag{6}$$

and

$$\frac{1}{\alpha} = k \tag{7}$$

But $k = \frac{1}{q}$ where q is the capillarity. Therefore we see that $\alpha = q$ (the capillarity). The dimensions of the constant β are of interest. σ is de-

fined as force $\left(\frac{M}{T^2}\right)$, RT has the dimensions of energy $\left(\frac{ML}{T^2} \times L\right)$, and b can be proved to be a pure number. Therefore,

$$\beta = \frac{1}{L^2} \tag{8}$$

Accordingly β has the dimensions of the reciprocal of surface. It follows from the development above, that β will serve as a more logical basis for comparisons to be made than will α.

TABLE 8

Showing agreement between the experimentally determined values of β and the calculated values of a (at maximum adsorption) when C_e (equilibrium concentration) is that of a saturated solution

ACID	C_e IN MILLIMOLES PER 75 CC.	β	a (MAXIMUM) IN MILLIMOLES PER GRAM	PER CENT ERROR
Valeric	27.19	2.154	2.068	4.1
Caproic	6.60	1.892	1.862	1.6
Isobutyric	170.33	1.776	1.755	1.2
Isovaleric	31.13	1.807	1.745	3.5
Oxalic	97.92	1.325	1.286	3.2
Malonic	542.18	1.231	1.232	−0.1
Succinic	52.22	1.854	1.781	4.0
Glutaric	391.87	1.192	1.191	0.1
Adipic	8.11	1.245	1.169	6.0
Tartaric	696.23	0.687	0.685	0.7
Fumaric	4.52	1.224	1.179	3.7
Maleic	509.33	1.395	1.392	0.2
Mesaconic	20.55	1.435	1.399	2.5
Itaconic	53.11	1.291	1.265	2.0

Determination of values for maximum adsorption and the corresponding equilibrium concentration

If the a of Langmuir's equation is differentiated with respect to C, it becomes obvious that a will equal β when $\frac{da}{dC}$ equals zero, and this will be true when the slope of the isotherm approximates 0°. However, the determination of C for maximum a presents difficulties. From a purely theoretical standpoint it would seem that a should approach a maximum when C equals the concentration of a saturated solution of the acid. Such concentrations were substituted in our calculated Langmuir equations and were compared with β for the corresponding acid. Taking only compounds which have a limited solubility the values shown in table 8 were secured. This table shows remarkable agreement between the de-

termined and calculated values, indicating that the theory discussed above has a sound basis.

Another possible method of demonstrating the validity of the assumption of maximum adsorption when the equilibrium concentration is that of a saturated solution, is by a graphical device adapted from theoretical considerations of Polanyi and Goldman (34). In dealing with adsorption of vapors Polanyi and Goldman calculated "affinities" from the general relationship

$$A_x = RT \ln \frac{P_s}{P_x} \tag{9}$$

where P_s is vapor pressure of the pure substance at the temperature T, P_x is the equilibrium pressure obtained in adsorption studies. They plotted the values of A_x for a given P_x against the values for adsorption obtained at this equilibrium pressure. Curves were obtained which were all similar in character and were displaced slightly by changes in temperature. In a later paper Polanyi and Heyne (35) considered isothermals for "substances in solution." Here the affinity is represented by

$$A_x = RT \ln \frac{C_s}{C_x} \tag{10}$$

where C_s is the solution saturation value for the compound and C_x is any other lower concentration. When Polanyi and Heyne calculated A_x from equilibrium concentrations and plotted the resulting values against the a in millimoles per gram corresponding to that C, the same types of curves were obtained in the case of solutions as in the case of vapors. It is obvious from equation 10 that when $C_s = C_x$, $A_x = 0$. Hence, by extrapolation of the curves (see figures 2, 3, 4, 5, 6), one obtains values for a when A_x is zero. This should represent the "saturation value." It should be said at this point that Polanyi obtained similar curves regardless of the solvent used and that in all cases the substances to which he applied his treatment had a limited solubility. Increased temperature displaced the curves slightly in the direction of higher A_x.

In the present study affinities were calculated in calories for all acids used excluding only those which are infinitely soluble (miscible in all proportions). In the case of n-valeric, caproic, isovaleric, succinic, adipic, fumaric, mesaconic, and itaconic acids when the values were plotted and the curves extrapolated, values for a when $A_x = 0$ were within good agreement with β. Curves of all other acids for the most part tended to become practically asymptotic to the a-axis and no extrapolation was possible. In some cases (oxalic acid, figure 2) *straight lines* were obtained which could be extrapolated, but the values for the amount adsorbed were some 25

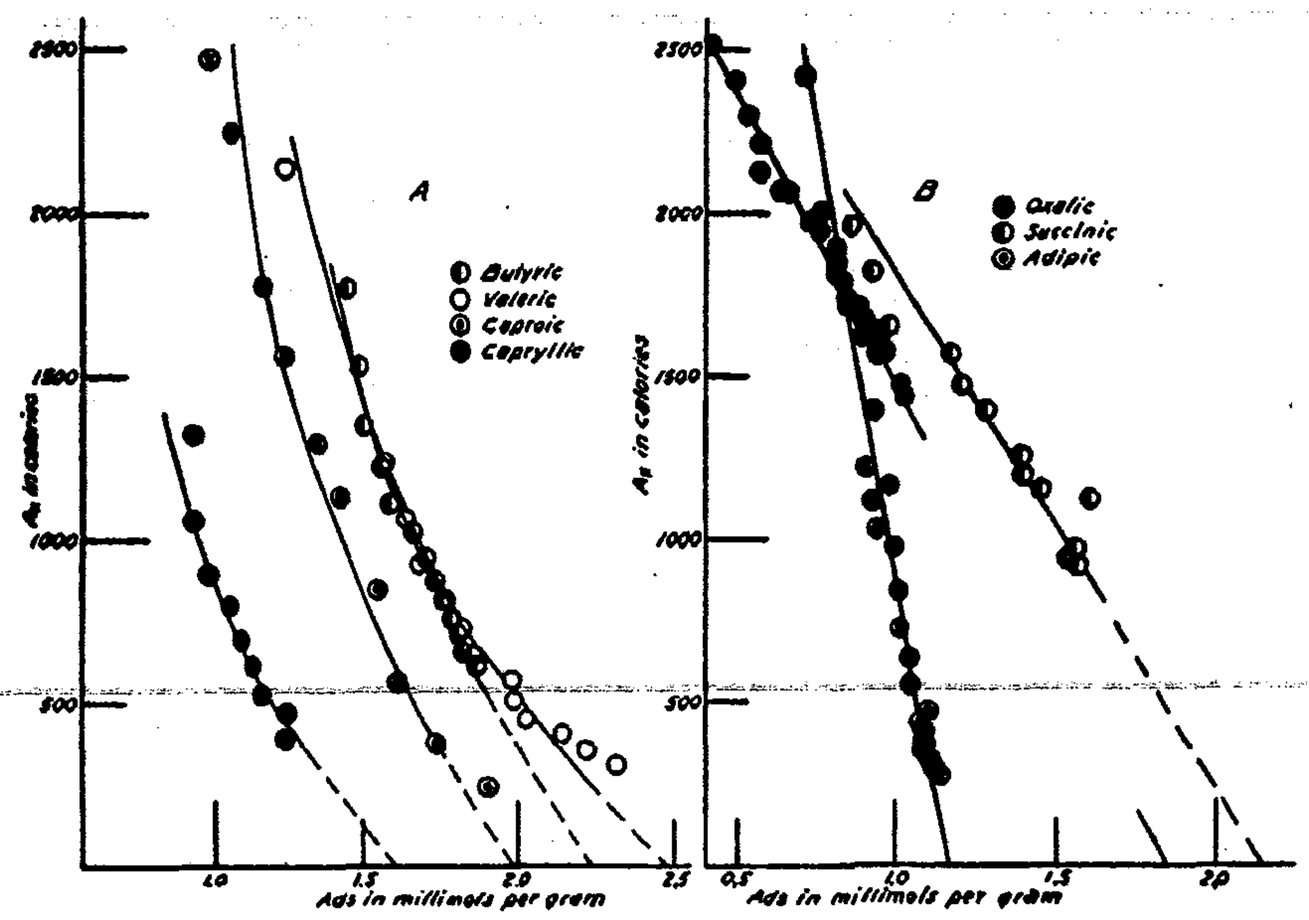


FIG. 2. THE AFFINITY CURVES OF THE MONO- AND DI-CARBOXYLIC ACIDS

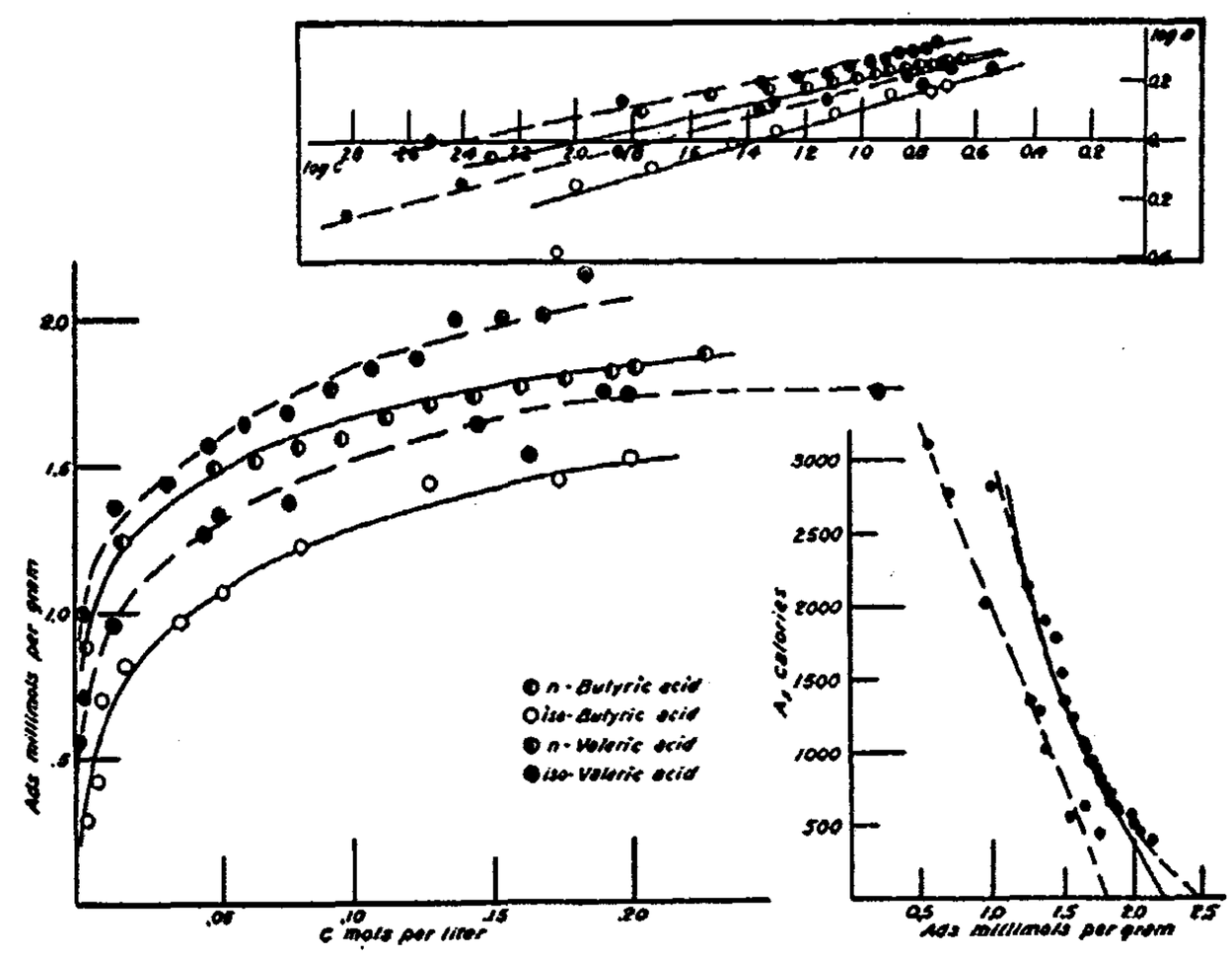


FIG. 3. ADSORPTION ISOTHERMS COMPARING NORMAL AND ISO ACIDS

The graph in the lower left corner represents the plot arithmetically; the one in the upper right, logarithmically. In the lower right are the affinity curves of these acids.

to 30 per cent higher than the experimentally determined values. In the case of butyric acid, however, activity coefficients (Parks and Huffman (30) were applied so that equation 10 becomes

$$A_x = RT \ln \frac{C_s \gamma_s}{C_x \gamma_x} \tag{11}$$

On plotting the values for butyric acid obtained through equation 11 extrapolation was possible and a value in approximate agreement with β

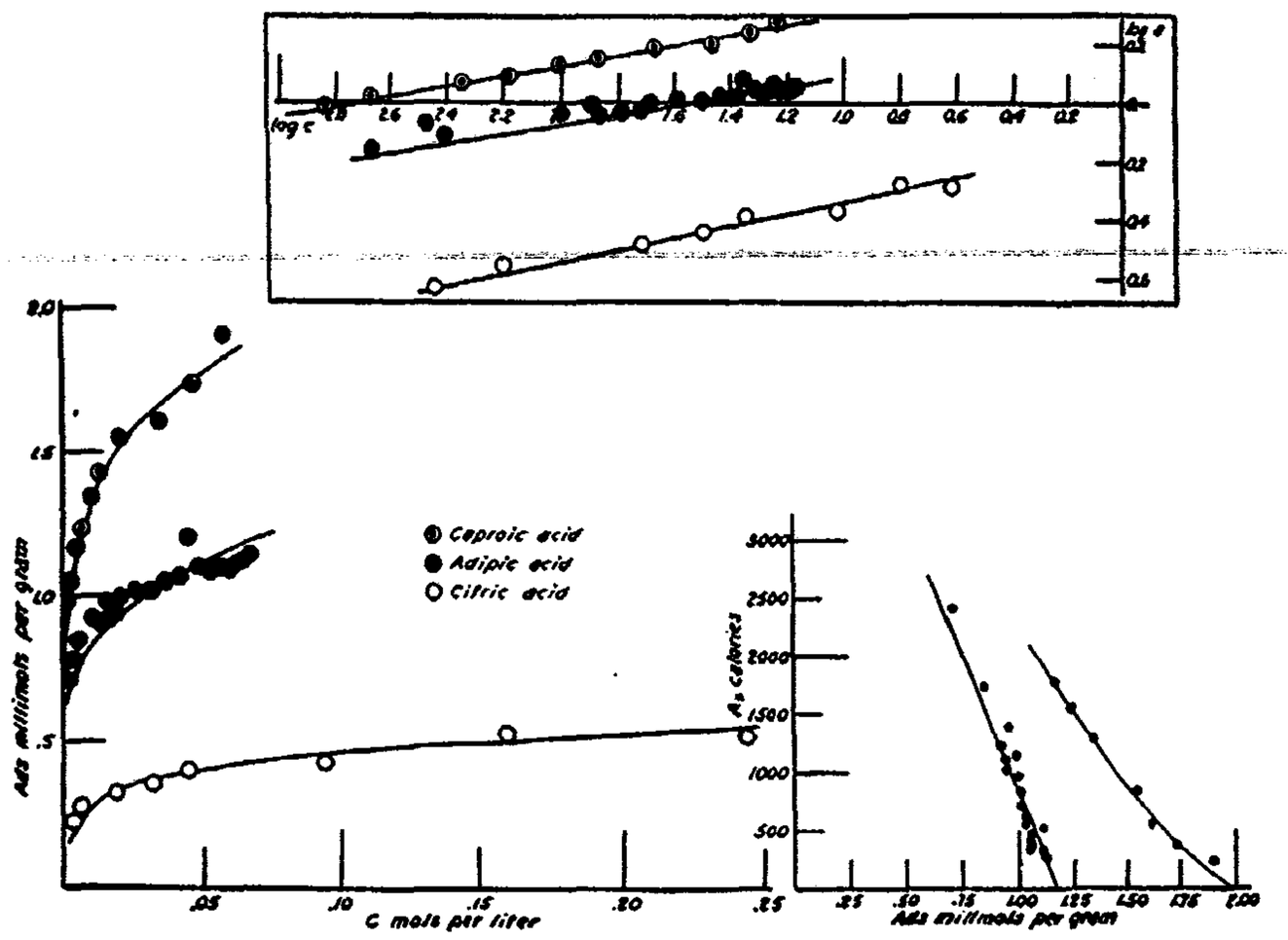


FIG. 4. ADSORPTION ISOTHERMALS FOR THE ACIDS HAVING THE SAME NUMBER OF CARBON ATOMS BUT DIFFERING IN THE NUMBER OF CARBOXYL GROUPS

In the graph in the lower left of the figure values are plotted arithmetically; in the upper right, logarithmically. The graph in the lower right represents the affinity curves for caproic and adipic acids.

and a maximum was obtained. The extrapolated values from the curves are listed in table 9 together with β and a maximum as calculated when the equilibrium concentration is that of a saturated solution (cf. table 8).

Calculation of cross-sectional areas of adsorbed molecules

The data in table 2 show that the values of the β of the Langmuir equation follow, relatively, the same general trends when comparisons are made between structurally related homologous series. It has already been

shown that β has the dimensions of surface. The value represents the maximum adsorption. If one makes certain assumptions it should be possible to calculate the approximate area possessed by 1 g. of Norite and from this area, in turn, to approximate the area occupied by the molecules of the various acids when adsorbed on the Norite. Ockrent (27, 28), following a slightly different method, has utilized Langmuir's equation for determining areas of molecules adsorbed on carbon.

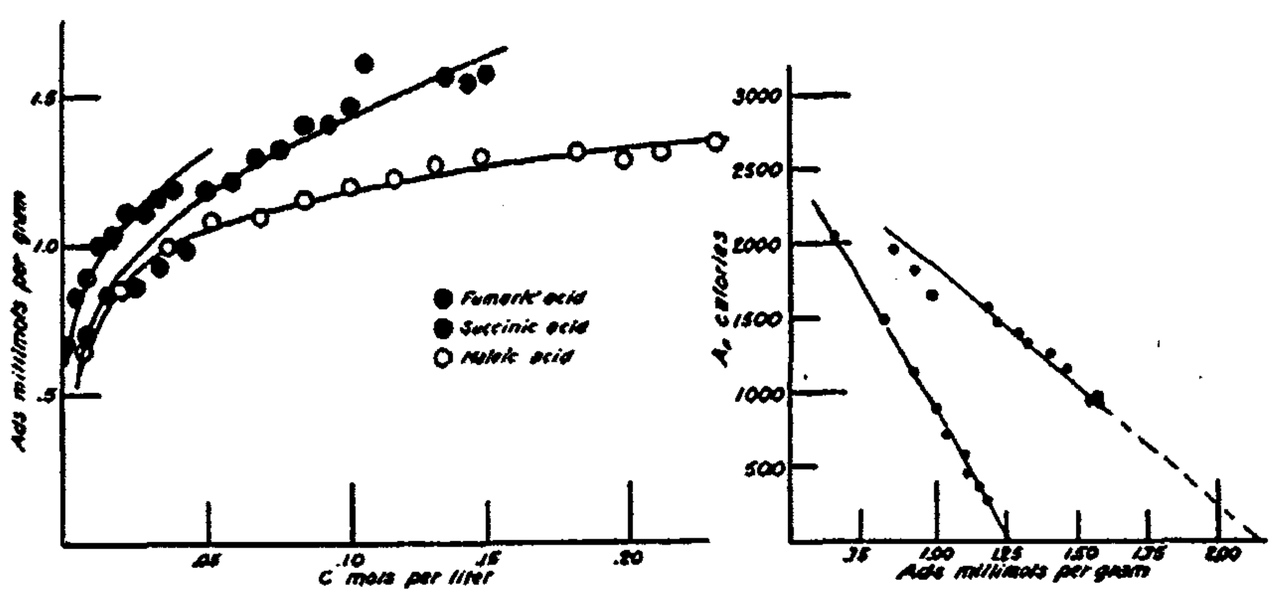


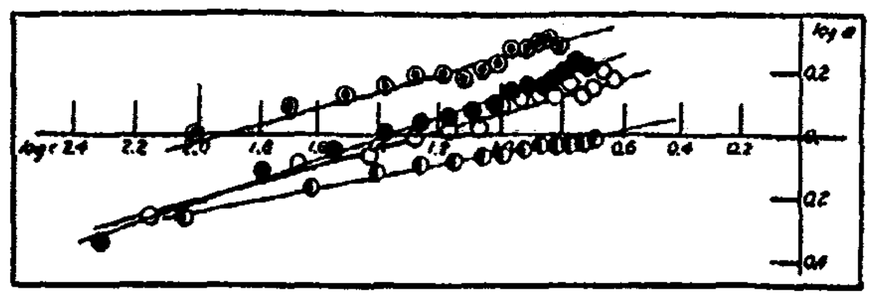
FIG. 5. ADSORPTION ISOTHERMALS SHOWING THE EFFECT OF THE DOUBLE BOND AND OF *cis* AND *trans* ISOMERISM ON ADSORPTION

The graph in the lower left of the figure represents the curves for values plotted arithmetically; in the upper right, logarithmically. Affinity curves for fumaric and succinic acids are given in the lower right of the figure.

The method employed in the present study was to make use of the experimentally determined β, the maximum adsorption values for each acid under our experimental conditions. Accordingly the areas calculated apply with certainty only to this study and may not represent the absolute areas. It is believed, however, that they are valid for comparison *inter se*. The assumptions upon which the calculations were based are: (1) At maximum adsorption a monomolecular layer is formed. (2) The fatty acids have approximately the same adsorption maximum. (3) The average β (1.889) of these acids represents the millimoles adsorbed per gram of adsorbent in the monomolecular film. (4) The molecules of the various

acids are similarly oriented at the interface. (5) The value given by Langmuir for the cross-sectional area of higher fatty acids applies to these shorter chain normal aliphatic acids.

If it is assumed that the cross-sectional area of the fatty acid is 21 sq. A.U., then the area of adsorbent[2] = $21 \times 6.06 \times 10^{20} \times 1.889$. On this basis the area per gram of Norite is 24×10^{21} sq. A.U. (240 square meters). This value is within the range of that found for charcoal by other investiga-



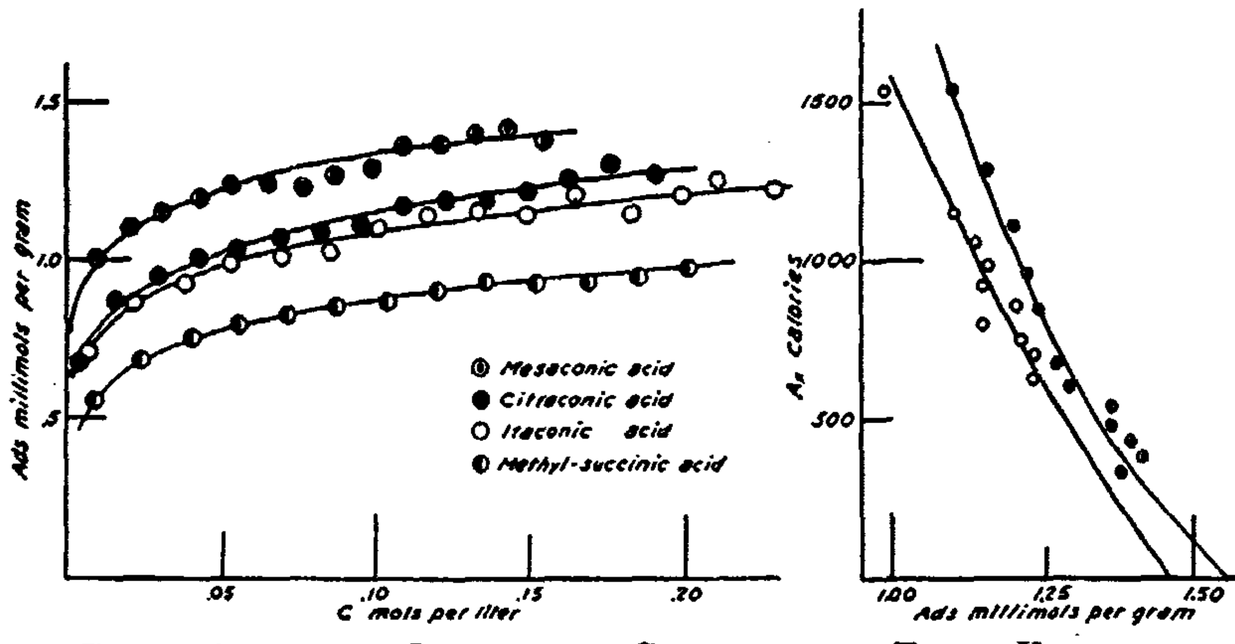


FIG. 6. ADSORPTION ISOTHERMALS COMPARING THE THREE UNSATURATED ACIDS, ITACONIC, CITRACONIC, AND MESACONIC ACIDS, WITH METHYLSUCCINIC ACID

Values are plotted arithmetically in the graph in the lower left of the figure; logarithmically in the upper right. The curves in the graph in the lower right represent the values of the affinity plotted against the values of the adsorbed acid at the same equilibrium concentration for mesaconic and itaconic acids.

tors, and has been used to calculate the molecular cross-sectional areas occupied by the various solutes used in this study. These values are listed in table 10.

Table 10 and its summary table 11 show how definite a rôle the configuration of the molecule plays in determining the amount of solute adsorbed

[2] The value for Avogadro's constant is 6.06×10^{20} in this case, since 1.889 is expressed in millimoles.

at maximum adsorption. The introduction of such groupings as the hydroxyl, the keto, the aldehyde, and the carboxyl groups into the straight

TABLE 9

Showing the extrapolated value of a (maximum adsorption) when the affinity (A_x) equals zero, as it will when the concentration (C) is that of a saturated solution; and the agreement of experimentally determined β and the calculated a (maximum)

ACID	WHEN $A_x = 0$ a EQUALS	β	a (MAXIMUM) (CALCULATED)	PER CENT ERROR BETWEEN COLUMNS 2 AND 3
Butyric	2.24	1.96		13.0
Valeric	2.40	2.15	2.07	10.9
Isovaleric	1.80	1.80	1.75	
Caproic	1.97	1.89	1.86	4.1
Succinic	2.18	1.85	1.78	16.4
Adipic	1.17	1.25	1.17	6.6
Fumaric	1.26	1.22	1.18	3.2
Mesaconic	1.5[illegible]	1.44	1.40	8.0
Itaconic	1.46	1.29	1.27	12.4

TABLE 10

Approximate cross-sectional areas of solute molecules on the surface of the carbon interface

These are calculated on the assumption that the cross-sectional area of the fatty acid molecule is 21 sq. A.U.

ACID	CROSS-SECTIONAL AREA OF MOLECULE	ACID	CROSS-SECTIONAL AREA OF MOLECULE
	sq. A. U.		*sq. A. U.*
Fatty series	21.0	Acetic	21.0
Isobutyric	22.3	Glycolic	41.4
Isovaleric	22.0	Propionic	21.0
		Lactic	37.6
Oxalic	29.9	Glyceric	48.2
Malonic	32.2	Succinic	21.4
Succinic	21.4	Malic	42.8
Glutaric	33.3	Tartaric	57.7
Adipic	31.9		
Methylsuccinic	36.2	Acetic	21.0
Maleic	28.4	Glyoxylic	17.4
Fumaric	32.4	Propionic	21.0
Mesaconic	27.6	Pyruvic	23.7
Citraconic	29.7	Levulinic	30.4
Itaconic	30.7	Monobromosuccinic	27.3
Citric	75.7	Dibromosuccinic	31.7

chain acid materially changes total adsorption. It should be emphasized that we believe that the *relative* values are valid, since the data have re-

sulted from studies on a single and comparable substrate. Subject to the assumptions made, it is seen from table 10 that the affinities of the molecules for water and the orientation of the molecules at the liquid-carbon interface is altered by the introduction of specific polar groups, so that the areas occupied in the interface by the molecules of the structurally different organic acids are varied, whereas structurally similar organic acids tend to approximate similar areas.

The ratios in table 11 are interpreted as representing the relative areas taken up at the interface by the different solute molecules. There is relatively little variation between the areas calculated for the iso acid as compared with that assumed for the normal acid. The dicarboxylic acids occupy approximately 1.5 times the area of the monocarboxylic acids, with the notable exception of succinic. This latter compound is apparently oriented at saturation in a fashion similar to the monocarboxylic acids, since the area per molecule (21.4 sq. A.U.) differs inappreciably from the average of the latter. The effect of the first hydroxyl group added to the straight chain of the fatty acids and succinic acid increases the area by twice the original value. As is to be expected, the effect of the second hydroxyl is greater than that of the first, and is approximately 2.5 times that of the straight hydrocarbon chain. The introduction of a double bond has lessened the adsorption (increased the polarity), as anticipated, as is shown by a comparison of succinic, fumaric and maleic acids.

TABLE 11

Summary of approximation in table 10

ADSORBATE	MEAN VALUE	PER CENT ERROR BETWEEN MEAN AND	
		Low value	High value
Fatty acids	21*		
Iso acids	22	0.9	0.9
Dicarboxylic acids†	32	2.1	4.1
Monohydroxy acids	41	8.3	4.4
Dihydroxy acids	53	9.1	8.9
Geometric isomers (unsaturated)	30	5.5	7.7

* Assumed value.

† Succinic excepted.

The ratios are as follows:

(1) Normal fatty acids: iso acids = 1:1.

(2) Normal fatty acids: dicarboxylic acids = 1:1.5.

(3) Acid: monohydroxy acid: dihydroxy acid = 1:2:2.5.

Comparison of the β of the Langmuir equation of the mono- and di-carboxylic acids with their melting points

An examination of the values of β of the dicarboxylic acids (table 2) reveals an alternation in values between successive members of homologous

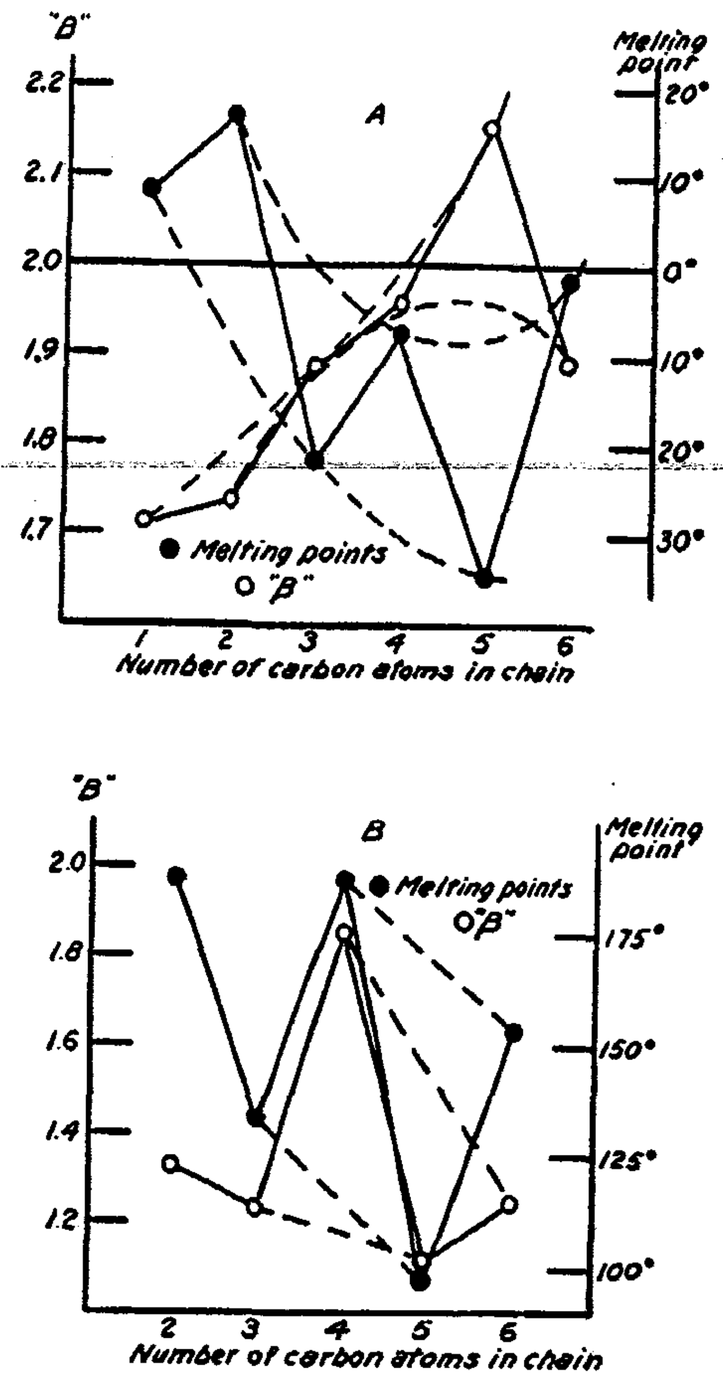


FIG. 7. SHOWING THE ALTERNATIONS IN THE VALUES OF β (LANGMUIR'S EQUATION) AND THOSE OF THE MELTING POINTS FOR HOMOLOGOUS SERIES OF THE MONO- AND DI-CARBOXYLIC ACIDS

A, the monobasic fatty acids; B, the dibasic acids

series. This is also true, as has long been known, of both the solubilities and melting points of the members of these series. When the values of β (table 2) are plotted against the number of carbon atoms in their corresponding acids and the points representing the "odd" and "even" acids are connected it will be observed that the curves so produced (figure 7) are very similar to those obtained either from melting point or solubility data. The

results in themselves perhaps are not particularly striking, but when comparison is made with curves drawn from similar data of the homologous series of the fatty acids it becomes apparent that there is some significant relationship between the melting points and β. Figure 7A shows these relationships. In the case of the fatty acids the plot of β against the number of odd carbon atoms (1, 3, 5) produces a line which is similar in general trend, although opposite in direction to the line produced by plotting the 1, 3, 5 carbon atoms against the melting points of the compounds. The same is true for the lines plotted for carbons 2, 4, 6 against β and carbons 2, 4, 6 against melting points. These observations likewise hold for the dicarboxylic acids (figure 7B).

The *alternation in melting points* is characteristic of the *solid state* of both the mono- and di-carboxylic acids. In the case of the higher fatty acids Garner and Randall (8) and Garner and Ryder (9) have shown that between odd and even acids alternation is more characteristic of the crystalline state than of the liquid state. They have shown such alternation in specific heat and molecular volume. Jensen and Gortner (18) report an odd–even carbon atom effect for the electrokinetic potential of homologous series of the lower members of the normal fatty acids, and their esters at an organic liquid–Al_2O_3 interface. Müller and Shearer (26) have suggested on the basis of x-ray studies that the molecules in the crystal are arranged end to end in opposite directions. Garner and Randall (8) carry this suggestion further and speculate as to possible arrangements similar in character to orientation. In respect to the nature of thin films of higher fatty acids at an interface Rideal (37) says: "The behavior of the higher fatty acids in thin films may well be compared with that of smectic or string-like anisotropic crystalline liquids: these liquids consist of molecules of a chain type and exhibit the property of orientation." The present study adds confirmation to the view that not only do the higher fatty acids in thin films possess this "crystalline" structure, but that the lower members of the series, too, as thin films adsorbed on a solid interface, are held there in "crystalline" form, and probably in the form of a *solid*, close-packed oriented layer of molecules. It is interesting to note that the "liquid" fatty acids, as well as the "liquid" esters studied by Jensen and Gortner (18), when adsorbed at an interface are apparently in the *solid state*.

IV. DISCUSSION

Difficulties attending attempts at comparison from too limited data

Earlier in this paper attention has been called to the fact that results obtained by making comparisons at only one equilibrium concentration do not necessarily represent values which would be obtained over a range of concentrations and that they may be valid only at the point chosen.

For example Shilov and Nekrassov (41) have published data on the per cent adsorption of an homologous series of the fatty acids and the dibasic acids. The fatty acids were studied at an initial concentration of $M/100$, the dibasic acids at a concentration of $M/200$. Their data are shown in

TABLE 12

Values from data of Shilov and Nekrassov (41) for the "per cent adsorbed" and the differences between successive members of an homologous series*

($C_1 = M/100$)	FATTY ACIDS	
	A*	$(A_{n+1} - A_n)$
Formic	13.3	
		2.7
Acetic	16.0	
		6.3
Propionic	22.3	
		13.2
Butyric	25.5	
		15.8
Valeric	51.3	
		15.8
Caproic	67.1	
		11.3
Caprylic	78.4	

* "Per cent adsorbed" $= A = \frac{C_1 - C_2}{C_1} \times 100$ where C_1 = initial concentration and C_2 = equilibrium concentration.

TABLE 13

Values for "per cent adsorbed" obtained from calculations comparable to those of Shilov and Nekrassov (recorded in table 12) for acetic and propionic acids, utilizing data of this study

C_1	A		$A_{n+1} - A_n$
	Acetic acid	Propionic acid	
0.02	2.65	4.04	1.39
0.04	1.86	2.54	0.68
0.06	1.46	1.92	0.46
0.08	1.24	1.59	0.35
0.10	1.08	1.37	0.29
0.15	0.83	1.03	0.20
0.20	0.68	0.83	0.17
0.25	0.57	0.69	0.08

table 12 where their values for per cent adsorbed and the difference between successive members of the homologous series are recorded.

Table 13 shows comparable calculations made from our data on acetic and propionic acids. It will be observed that, whereas Shilov and Nekrassov found a value of 16 per cent adsorption for acetic acid and 22.3 per cent for propionic acid with a difference of 6.3 per cent, the more extensive series of data taken over a range of concentration yield values for acetic

acid varying from 2.7 to 0.6 per cent and for propionic acid from 4.0 to 0.7 per cent with differences of 1.4 to 0.08 per cent. Obviously single point observations may lead to erroneous conclusions.

Furthermore, in figure 8, acetic and glyoxylic acids present an interesting example. If comparison is made at from 0.01 to 0.03 molar equilibrium concentration, one would say that the two were adsorbed to about the same extent within experimental error. Above these values the two curves sharply diverge from each other. Again, if one applied a basis for com-

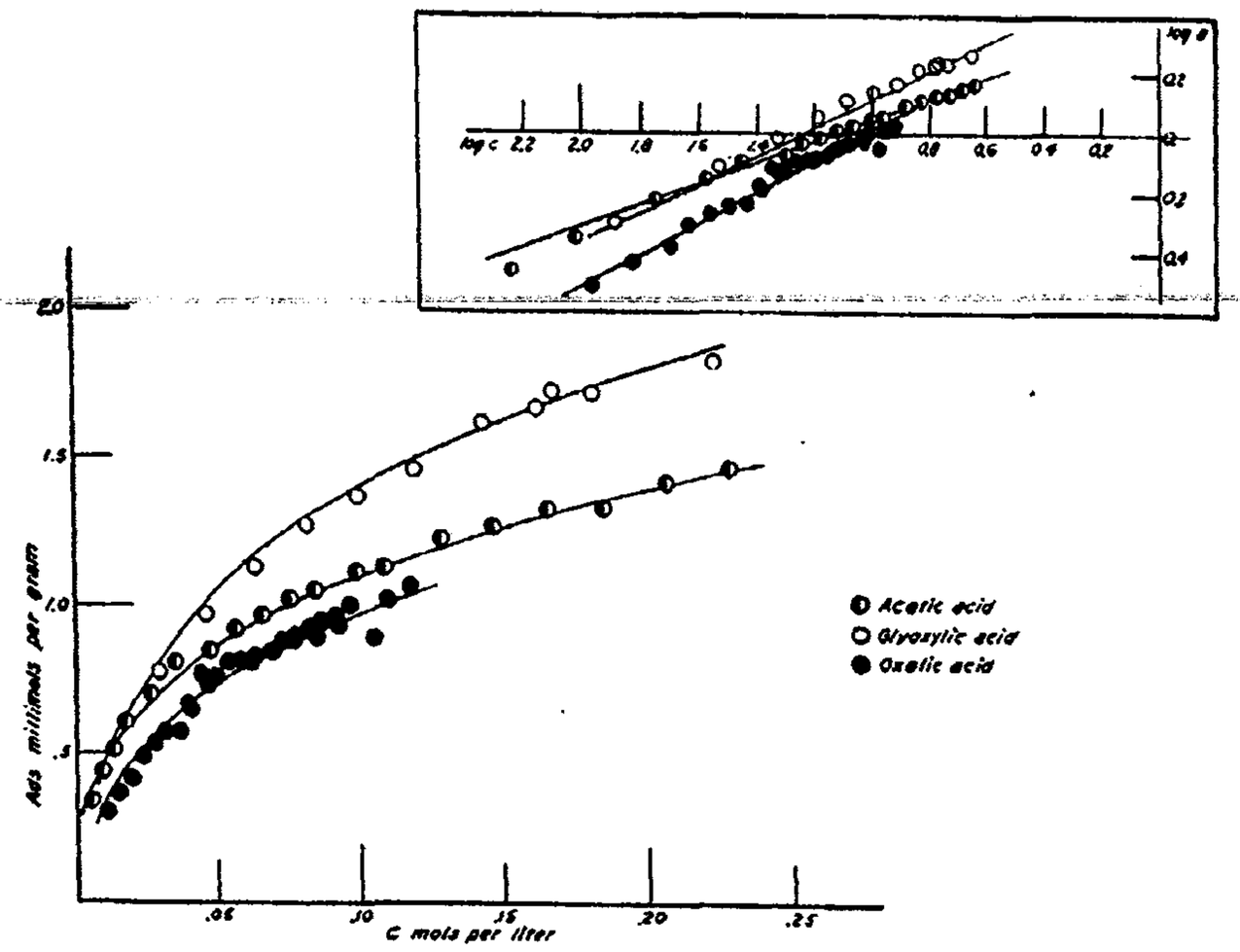


FIG. 8. ADSORPTION ISOTHERMALS FOR ACETIC, GLYOXYLIC, AND OXALIC ACIDS, SHOWING THE EFFECT OVER A DEFINITE CONCENTRATION RANGE OF SUBSTITUTING THE ALDEHYDE AND CARBOXYL GROUPS FOR THE METHYL GROUP

In the graph in the lower left of the figure the values are plotted arithmetically; in the upper right, logarithmically.

parison on the per cent adsorbed, it is evident that the values would be widely divergent at 0.03 and 0.25 molar concentration. The curves for the dicarboxylic acids (figure 9) present the same general difficulties. Below 0.025 molar equilibrium concentration, the adsorption of the members of the series increased definitely with increasing number of carbon atoms. It is plainly evident from figure 9 that above this concentration this is no longer true, and that with the exception of oxalic acid points may be chosen by means of which no essential change in adsorption between one member and the next higher member can be demonstrated. The last

case which will be cited refers to figure 5 in which isotherms for succinic, maleic, and fumaric acids are given. Langmuir (21) and Harkins (14, 15) have pointed out that the double bond increases the polarity of the compound. This should mean decreased adsorption of maleic acid and its *trans*-isomer, fumaric acid, when these are compared with succinic acid. Our data show that over the range studied maleic acid is less adsorbed than is succinic, but that fumaric acid is more greatly adsorbed up to the limits of its solubility. Furthermore, Alekseevskii (1) from a few series of point studies came to the conclusion that fumaric acid is always more greatly

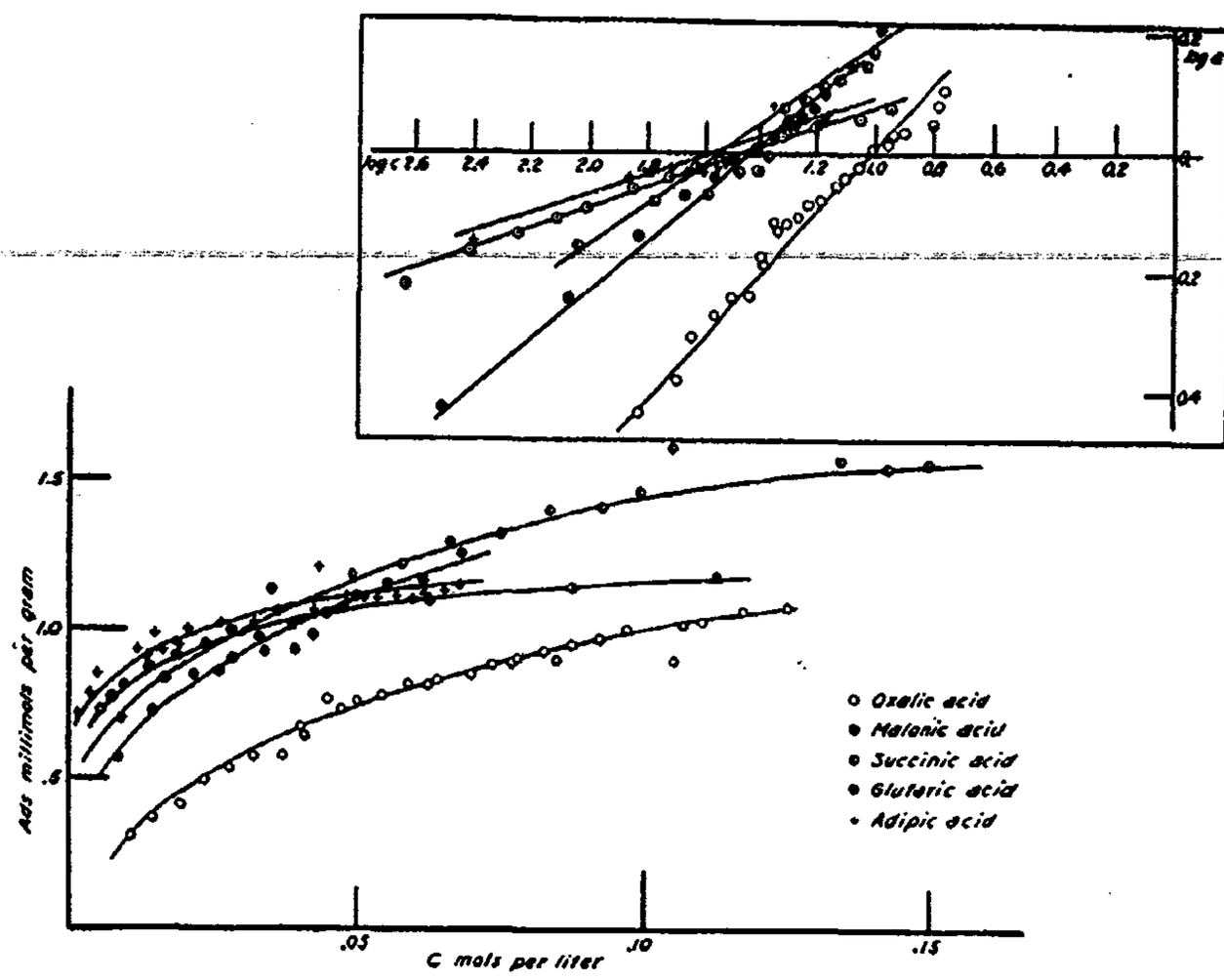


FIG. 9. ADSORPTION ISOTHERMALS FOR THE DICARBOXYLIC ACIDS

In the graph on the lower left the values are plotted arithmetically; in the one on the upper right, logarithmically.

adsorbed than is maleic. In general, our data substantiate this, yet one cannot but feel that such comparisons, although they may possess validity, are not so desirable as those made when the surface is saturated, i.e., when the equilibrium concentration is that of a saturated solution. Comparisons of β which give the maximum amount adsorbed show that a smaller number of millimoles of the acids, fumaric and maleic, is adsorbed per gram of adsorbent when the surface is "full" than is the case with succinic acid. This is in accord with the ideas of Langmuir and Harkins. Further, we find on the basis of our assumptions that fumaric and maleic acids

are about equally adsorbed at saturation, since they vary only some 0.17 millimole per gram of adsorbent. It seems more logical, therefore, to attempt to make comparisons when adsorption is at a maximum as we have already done, for while one must grant the accuracy of "single point" studies it must be admitted that they can hardly lend themselves to a general study of structural comparisons.

The arrangement of molecules in the interface

The assumptions on which the calculations of the cross-sectional areas are based have been stated. It was our intention to point out by a statement of these assumptions that values obtained are purely *relative* among themselves and may not represent absolute areas. We have pointed out, however, that the surface area of the adsorbent obtained by calculation is within the range of other experimental values. Paneth and Radu (29) report values for various carbons varying from 46.2 to 268.0 square meters. The value obtained in these experiments for Norite is 240 square meters.

Bearing in mind the relative character of the values reported in table 9, we can only theorize as to the nature of the arrangement of molecules on the surface. The assumption has been made that the cross-sectional area possessed by the fatty acids is 21 sq. A.U. Such an area may be predicted by the head group when the adsorbent surface is filled. It seems likely on comparing the relative areas of isobutyric and isovaleric acids with butyric and valeric acids, respectively, that only one $—CH_3$ is held at the solid interface and that the —COOH group in the water determines the area. The ratio between the cross-sectional areas of the normal and iso acids is approximately 1:1. Alekseevskii (1) has pointed out that the normal acids are of such a structure that the —COOH or $—CH_3$ may be at the surface, so that at complete filling there will be a larger adsorption of the normal than of the iso acid. He concludes this from a study of two series made from initial concentrations of 0.28 and 0.43 molar solutions. Shilov and Nekrassov (41) by a similar type of experimentation have shown iso acids to be less adsorbed than normal acids. We believe, however, that our data more nearly show what condition is approximately approached at complete filling.

With the exception of succinic acid the dicarboxylic acids have an average covering of the surface of the adsorbent of about 30 sq. A.U. This value is about 1.5 times that of the monocarboxylic acids. At saturation, then, could one not consider that two carbon atoms are in the surface of the adsorbent with the —COOH groups out into the aqueous phase? There are two possible explanations, which are perhaps interdependent, for the fact that in such an arrangement the area is not twice that of a monocarboxylic acid. The forces holding the two carbon atoms together are primary valence forces, and because of them the two carbons in the

molecule are in much closer proximity than are adjacent carbon atoms of two molecules of the monocarboxylic acids. Then again, it may be that the alignment of surface forces is such that only a portion of them can be effective in the case of the dicarboxylic acids. The latter reasoning is weak, perhaps, because there is apparent regularity between the differences the values demonstrate. Why succinic acid is oriented apparently in the same fashion as the monocarboxylic acids is unanswerable in view of the above. Another indication of orientation of such a type as discussed with

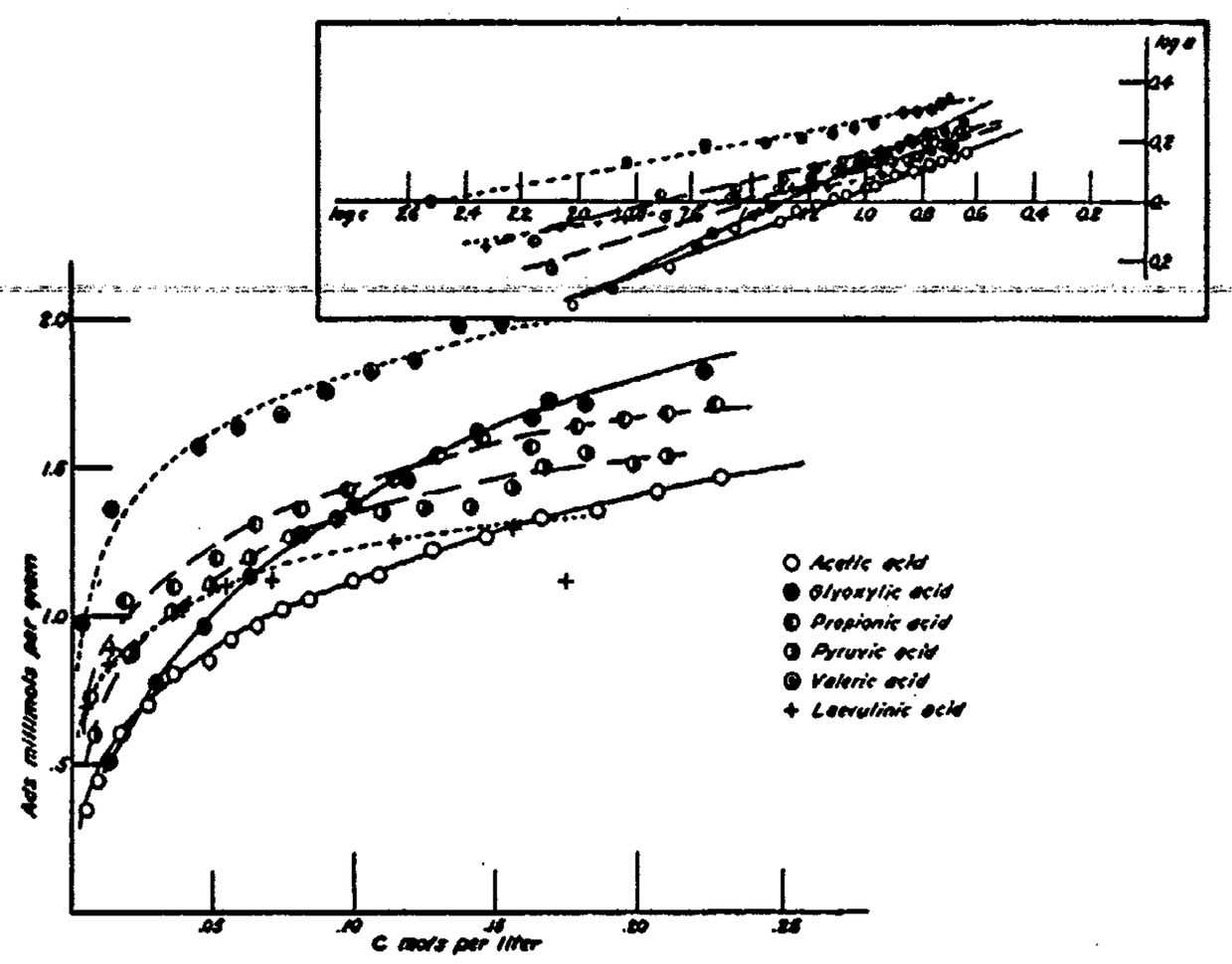


FIG. 10. ADSORPTION ISOTHERMALS COMPARING ACETIC, PROPIONIC, AND VALERIC ACIDS WITH THEIR RESPECTIVE ALDEHYDE OR KETO DERIVATIVES

The graph in the lower left of the figure represents the values plotted arithmetically; in the upper right, logarithmically.

the dicarboxylic acids is the behavior of citric acid. This acid is adsorbed to a much lesser extent than is adipic acid, which contains the same number of carbon atoms. The ratio between caproic, adipic, and citric acids all containing the same number of carbon atoms is approximately 2:3:7.5. It appears probable that the molecule of citric acid is held to a greater degree along its length with the polar groups oriented out into the aqueous phase.

We find that glyoxylic acid at saturation takes up a smaller relative area than does acetic acid, from which it is derived. Surely one should assume

that the substitution of the aldehyde group for the methyl group of acetic acid will increase the polar character of the molecule and that, therefore, a smaller quantity should be adsorbed. The maximum adsorbed quantity for acetic acid is 1.74 millimoles per gram of adsorbent, while that for glyoxylic is 2.28. The only accounting for such a difference must be on the basis of closer packing of the glyoxylic molecules in the interface. It seems probable that such can be taking place since there is a possibility of the effect of stray valence out from the aldehyde grouping which will influence an adjacent molecule and make for greater packing. Figures 8

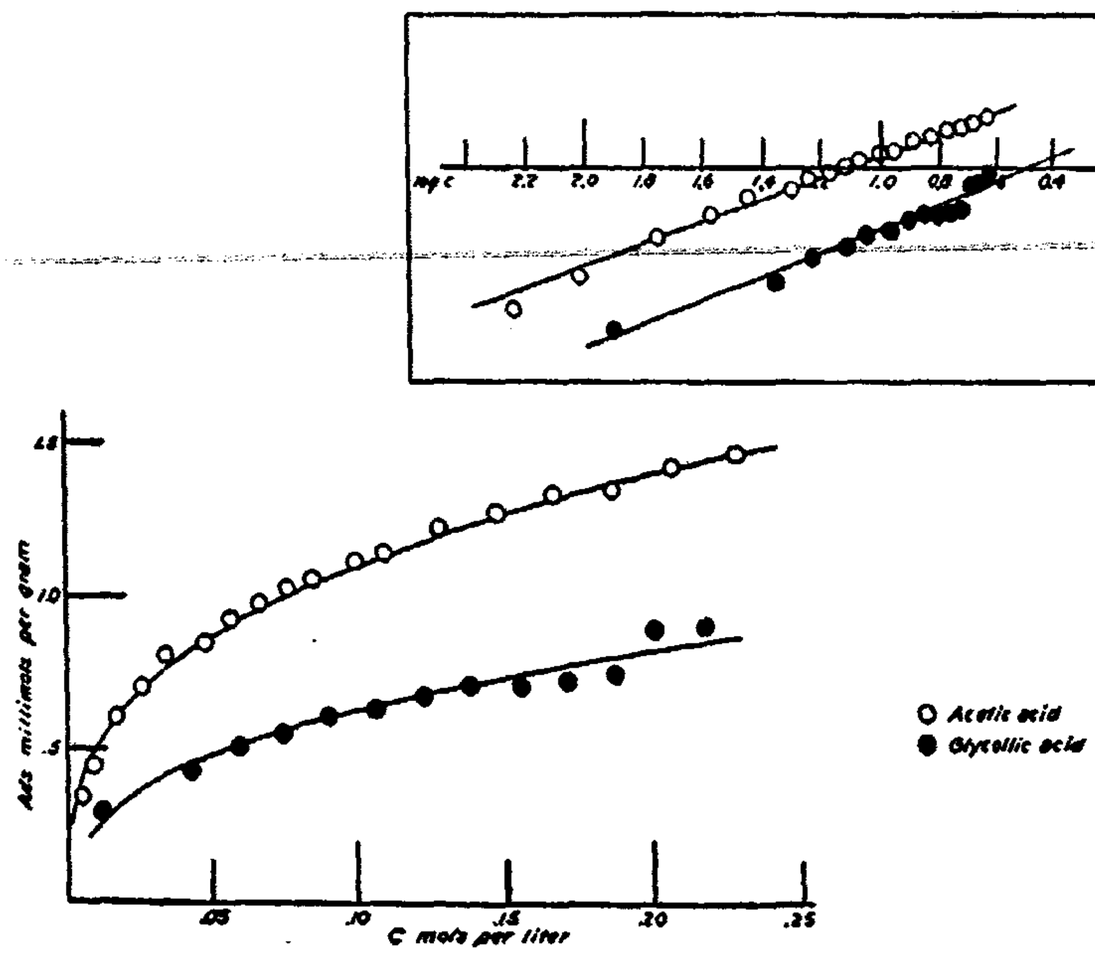


FIG. 11. ADSORPTION ISOTHERMALS SHOWING THE EFFECT OF THE HYDROXYL GROUP: ACETIC AND GLYCOLIC ACIDS

The graph on the lower left represents the plot arithmetically; on the upper right, logarithmically.

and 10 show that in the low concentrations of these compounds there are small differences between the two and that only as the concentrations increase does glyoxylic acid give evidence of closer packing. This is in accord with the picture just given.

Two examples are given of the effect of the keto group on adsorption of acids. Pyruvic and levulinic acids are compared with propionic and valeric acids. Propionic acid at saturation has a relative area of 21 sq. A.U. and pyruvic acid 23.7 sq. A.U., while valeric and levulinic acids have areas of 21 and 30.4 sq. A.U., respectively. The position of the keto group

evidently plays a rôle in the adsorption of these derivatives, for pyruvic acid derived from a shorter chain acid than levulinic acid has such a group on the α-carbon atom, while levulinic acid is a γ-keto acid. The keto group, apparently, has small influence when the molecule possesses a short hydrocarbon chain. Stray valence forces are apparently brought more decidedly into play when the keto group occupies a position considerably removed from the carboxyl, as is the case with levulinic acid. These influences may be between the oxygen of the keto group and that of the carboxyl group, so that at "close packing" a condition exists which is

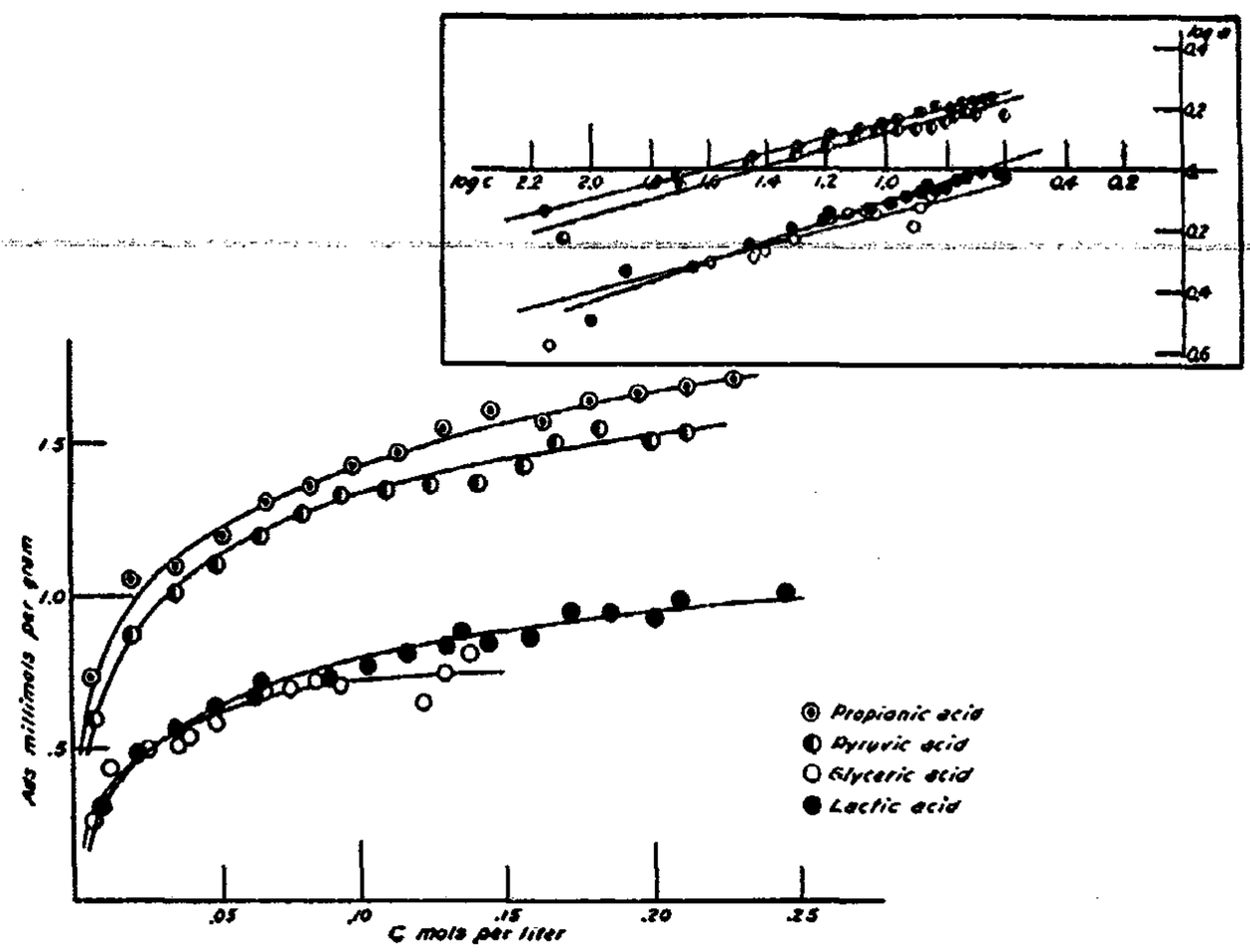


FIG. 12. ADSORPTION ISOTHERMALS FOR PROPIONIC ACID, ITS MONO- AND DI-HYDROXY DERIVATIVES AND ITS KETO DERIVATIVE

In the graph in the lower left of the figure values are plotted arithmetically; in the upper right, logarithmically.

similar in character to the dicarboxylic acids. This is even more evident since the ratio between the relative areas of valeric and levulinic acids is the same as that for the mono- and di-carboxylic acids, i.e., 2:3. One may be tempted to say that these stray valences are of maximum influence between the oxygen atoms of the keto and carboxyl group within the molecule, since even at low concentrations the adsorption of levulinic acid is materially less than is that of valeric acid (figure 10).

The ratio between the saturated and unsaturated acids (i.e., succinic and its *cis*- and *trans*-isomers) is approximately 2:3. The average area given in

table 11 is 30 sq. A.U. This value is about 6 per cent higher than the area obtained for the head group —CH = CHCOOH determined by other investigators, which value has a magnitude of 28.7 sq. A.U. (Rideal (37)). One can suppose in this case that at the packing of not only fumaric and maleic acids but mesaconic, citraconic, and itaconic acids as well, the head group determines the area of the molecule. All of the acids on the basis of our calculations have a relative area of fair constancy, so that it appears that the area of the —CH = CH—COOH group prevents any closer pack-

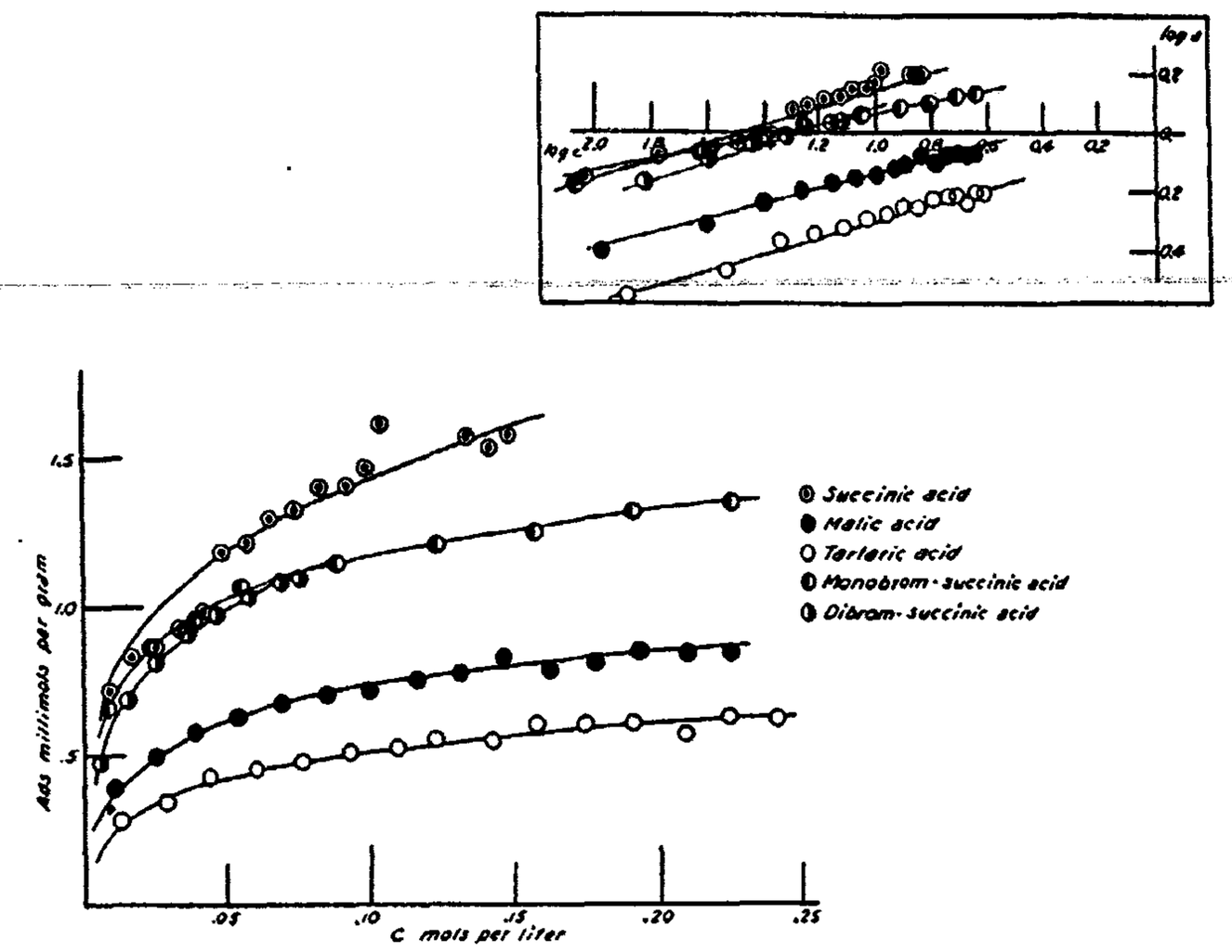


FIG. 13. ADSORPTION ISOTHERMALS COMPARING THE ADSORPTION OF THE MONO- AND DI-HYDROXY DERIVATIVES OF SUCCINIC ACID WITH THE MONO- AND DI-BROMO ACIDS

The curves in the lower left of the figure represent the values of C and a plotted arithmetically; those in the upper right the values plotted logarithmically.

ing at the saturation point. Evidently the substitution of the methyl group for a hydrogen atom in the fumaric and maleic acid molecules makes an insignificant change in adsorption maxima and is no more a deciding factor in the quantity adsorbed than has been found in the case of the normal and iso acids discussed above.

V. SUMMARY

Adsorption studies have been carried out with a series of structurally related compounds on a single and comparable substrate. For this study

a large sample of decolorizing carbon, Norite, was used. Members of the homologous series of fatty acids used were formic, acetic, propionic, butyric, valeric, caproic, and caprylic acids; members of the homologous series of dicarboxylic acids used were oxalic, malonic, succinic, glutaric, and adipic acids. To demonstrate the effect of various groupings in the molecules compounds were chosen and adsorption studies made as follows: for the grouped chain, isobutyric, isovaleric, and methylsuccinic acids; for the hydroxyl group, glycolic, lactic, glyceric, malic, and tartaric acids; for the carboxyl group, acids of the two homologous series listed above and citric acid; for aldehyde and keto groups, glyoxylic, pyruvic, and levulinic acids; for the double bond and variations due to *cis*-and *trans*-isomers, fumaric, maleic, mesaconic, itaconic, and citraconic acids; and for halogen substitutions mono-and di-bromosuccinic acids.

From these series of studies the following generalizations and conclusions are drawn:

1. The Freundlich adsorption isotherm is applicable to the data of these experiments and has been applied in calculating the areas under the curves for the various fatty acids. Ratios between the area under one isotherm between definite limits and that corresponding to the next higher member in the homologous series of fatty acids have been shown to have a better constancy than those obtained by the method suggested by Freundlich.

2. The Langmuir equation is applicable to these data.

3. Agreement has been shown between the β of Langmuir's equation (the maximum amount adsorbed when the equilibrium concentration is that of a saturated solution) and a obtained by substituting for C of the Langmuir equation the saturated concentration of the acid in question.

4. By a graphical method suggested by Polanyi and Heyne, and Polanyi and Goldman, the a at maximum C has been demonstrated to be of the general magnitude of β.

5. It is suggested that a more valid method for comparing the effect of molecular structure on adsorption is by comparison of the maximum value of the adsorbed, i.e., a when equilibrium concentration is that of a saturated solution.

6. Relative areas for the acids studied when a is a maximum have been calculated, based on definite assumptions, and by reference to these areas variations have been shown in adsorption due to the introduction of polar groups into the molecule.

7. The branched chain has little effect on the maximum adsorption of an acid.

8. As the number of carboxyl groups is increased the adsorption decreases greatly.

9. The introduction of the hydroxyl group has been shown to decrease markedly the total amount of acid adsorbed. A second hydroxyl group tends to decrease the adsorption to a still greater extent.

10. Adsorption is decreased by the introduction of the keto group into the molecule, the decrease being dependent on the length of the chain and the position of the polar group in the chain.

11. Glyoxylic acid is adsorbed to a greater extent than is acetic acid.

12. Little difference in total adsorption of *cis*- and *trans*-isomers has been demonstrated at maximum adsorption. The double bond, however, has been shown to have a decided tendency to decrease adsorption.

13. An alternation exists among the values of β (Langmuir's equation) for odd and even acids of the homologous series of both the mono- and di-carboxylic acids. Such alternation is characteristic of the solid state. This adds confirmation to the view that the lower members of the homologous series of the mono- and di-carboxylic acids are adsorbed in the solid state.

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A NEW INTERPRETATION OF THE ADSORPTION ISOTHERM

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Received June 14, 1934

To date, the most satisfactory theory which has been advanced to account for the relation of gas adsorption to pressure is that of Langmuir (1). This theory assumes that the time rate of condensation is proportional to the pressure and to the amount of surface remaining bare, and that the time rate of evaporation is proportional to the amount of gas adsorbed, which is in turn proportional to the amount of surface covered (assuming a monomolecular film). A mathematical equation is derived which is fairly simple for a surface made up of only one kind of elementary spaces, but becomes quite complex with an increase in the number of kinds of elementary spaces; so that, even for a surface comprising only two kinds of spaces, the evaluation of the constants in the mathematical equation becomes, in the words of Langmuir, "a somewhat laborious method of trial."

As Langmuir has pointed out, the above theory is not to be condemned simply because the equations are complicated. However, it is the purpose of this paper to propose a theory which is susceptible to a less complicated mathematical analysis and which, instead of requiring an intimate knowledge of the nature of the adsorbing surface in order to establish the mathematical function, will, if the theory be valid, give valuable information concerning the nature of the surface. This theory requires a slightly different picture of the kinetics of the adsorption process from that assumed by Langmuir.

Let us assume, as does the Langmuir theory in its simplest form, that the adsorbing surface may be divided into elementary spaces, each capable of holding one gas molecule. That is, an elementary space may be defined as a space whose attractive, or adsorbing, force is entirely satisfied by the adsorption of one gas molecule. Contrary to the Langmuir theory, however, instead of assuming that an actual *collision* between a gas molecule and such a space must take place entirely through the inherent kinetic energy of the molecule, let it be assumed that it is only necessary for the gas molecule, through its molecular motion, to come within a certain *radius of attraction* of one of the spaces. This seems to be a reasonable assumption, for, if a space on the surface has enough attractive force to hold a molecule after a collision, it surely can attract the molecule through a small

distance. As soon as a gas molecule comes within this radius of attraction, it will be adsorbed and the attractive force will be temporarily satisfied. However, that will not prevent a second adsorbable gas molecule from coming within the required distance of the elementary space while the first is still held. As soon as the first molecule is released, the second will be adsorbed. At a given pressure, a certain fraction of the elementary spaces having a given adsorbing force will always have at least one gas molecule within their radii of attraction, which, on the basis of this theory, is tantamount to saying that at a given pressure a certain fraction of these spaces always have gas molecules adsorbed upon them.

From this point of view, the kinetic treatment proposed by Langmuir does not hold for the reason that the time rate of desorption, that is, the number of spaces actually becoming bare per unit time, is not independent of the pressure.

The chance for a given elementary space to be covered depends upon the chance of its having an adsorbable gas molecule within its radius of attraction. This is proportional to the pressure.

The theory may be developed mathematically in the following manner: Let the different kinds of elementary spaces on the adsorbing surface be classified merely on a basis of the pressures at which they become saturated, the saturation pressure of a given kind being defined as the lowest pressure at which there is always an adsorbable gas molecule within the range of attraction of every elementary space comprising that kind.

Let it be assumed that the amount of gas adsorbed upon each kind of spaces is proportional to the pressure and to the total number of spaces comprising that kind.

Let X = total amount of gas adsorbed at pressure P,
x_1 = amount adsorbed on first kind of elementary spaces,
x_2 = amount adsorbed on second kind of elementary spaces, and
x_n = amount adsorbed on n^{th} kind of elementary spaces.

Then, up to P_{n_s}, the pressure at which the nth kind of space becomes saturated,

$$x_n = C_n A_n P \tag{1}$$

where C_n is a constant for the given kind of space, and A_n is the total number of spaces comprising the kind, and is constant for the given quantity of adsorbent. That is, CA is a parameter constant for a given kind and different for different kinds. It will be referred to as the coefficient of adsorption for the given kind of spaces.

Then, for the given kind of space, $\frac{dx_n}{dP}$ = constant, and

$$\frac{dX}{dP} = \frac{dx_1}{dP} + \frac{dx_2}{dP} + \cdots \frac{dx_n}{dP} \tag{2}$$

including all kinds of spaces not saturated at pressure P. However, $\frac{dX}{dP} \neq$ constant, but diminishes as the respective kinds of spaces become saturated.

It should be theoretically possible to express the total number of elementary spaces belonging to each kind as a function of the saturation pressure. However, that would require, in order to establish the mathematical equation, a knowledge of the value of the constant, C, for each kind. The values of C are different for different kinds of spaces, because the attractive forces are different; if the attractive forces were not different, all spaces would become saturated at the same pressure. In order to obviate the above difficulty, it is convenient to express CA, rather than A, as a function of the saturation pressure, that is, to let

$$CA = f(P) \tag{3}$$

We then have

$$\frac{dX}{dP} = \sum_{P}^{P_s} \frac{dx}{dP} = \sum_{P=P}^{P=P_s} CA = \int_{P}^{P_s} f(P) \tag{4}$$

and

$$dX = \int_{P}^{P_s} f(P)dP \tag{5}$$

where P_s is the pressure at which the entire surface becomes saturated. At any given pressure P, X, the total adsorption, is the sum of the amounts adsorbed on all kinds of spaces up to pressure P. Therefore

$$X = \int_{0}^{P} \int_{P}^{P_s} f(P)dPdP \tag{6}$$

As a matter of convenience in demonstrating the application of the theory, let it be hypothetically assumed that the distribution of the adsorption coefficients with regard to pressure follows the probability law (2). That is, let

$$CA = \frac{K}{\sqrt{\pi}} e^{-K^2P^2} \tag{7}$$

where the pressure is measured positively and negatively from the value corresponding to the maximum value of CA, or

$$CA = \frac{K}{\sqrt{\pi}} e^{-K^2(P-P_m)^2} \tag{8}$$

where the axes have been shifted to avoid negative values of P and P_m

is the new coördinate of the pressure corresponding to the maximum value of CA. Then

$$X = \int_0^P \int_P^{P_s} \frac{K}{\sqrt{\pi}} e^{-K^2(P-P_m)^2} \mathrm{d}P\mathrm{d}P \tag{9}$$

Since the probability equation may be integrated only by expanding into an infinite series and integrating each term separately, it is more convenient to integrate mechanically. Figure 1, curve 1, shows the distribution of CA with regard to saturation pressure when K in equation 9 is arbitrarily assigned a value of 0.5. Theoretically, of course, $P_m = \infty$.

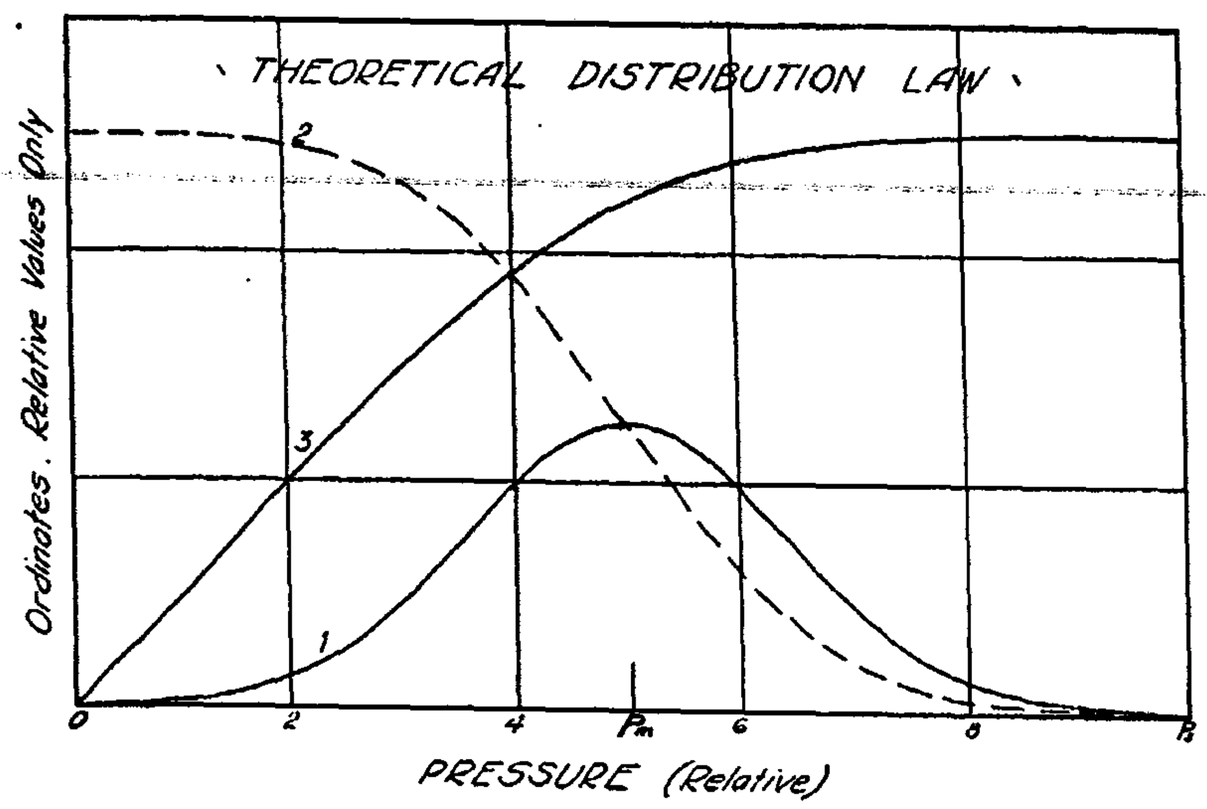

FIG. 1. HYPOTHETICAL CURVES

Curve 1, distribution of adsorption coefficients with respect to saturation pressures. Curve 2, $\frac{\mathrm{d}X}{\mathrm{d}P}$ versus P. Curve 3, adsorption isotherm, X versus P.

However, in the figure, the origin has been shifted to that pressure at which $CA = 0$ within the limitations of the scale.

Figure 1, curve 2, is obtained by plotting against pressure, P, the area under curve 1 from P to P_s, the pressure at which the entire surface becomes saturated. It represents the relation of $\frac{\mathrm{d}X}{\mathrm{d}P}$ to P. Figure 1, curve 3, is obtained by plotting the area under curve 2 from 0 to P. It represents the relation of X to P or, in other words, is the hypothetical adsorption isotherm. Only the central part of this curve resembles an actual isotherm curve, which means, of course, that the hypothetical assumption is not the correct one. By a method of trial, curve 1 doubtless could be altered in such a way as to make curve 3 more nearly resemble an isotherm

curve. This is unnecessary, however, for it is more convenient to attack the problem in the following manner:

Since curve 2 is obtained by integrating curve 1 and curve 3 by integrating curve 2, in any actual case curve 2 may be obtained from curve 3 and curve 1 from curve 2 by the reverse process of differentiating. In other words, in figure 1 curve 3 represents X versus P, curve 2 represents $\frac{dX}{dP}$ versus P, and curve 1 represents $-\frac{d^2X}{dP^2}$ versus P, the minus sign being introduced on account of the fact that $\frac{dX}{dP}$ decreases as P increases.

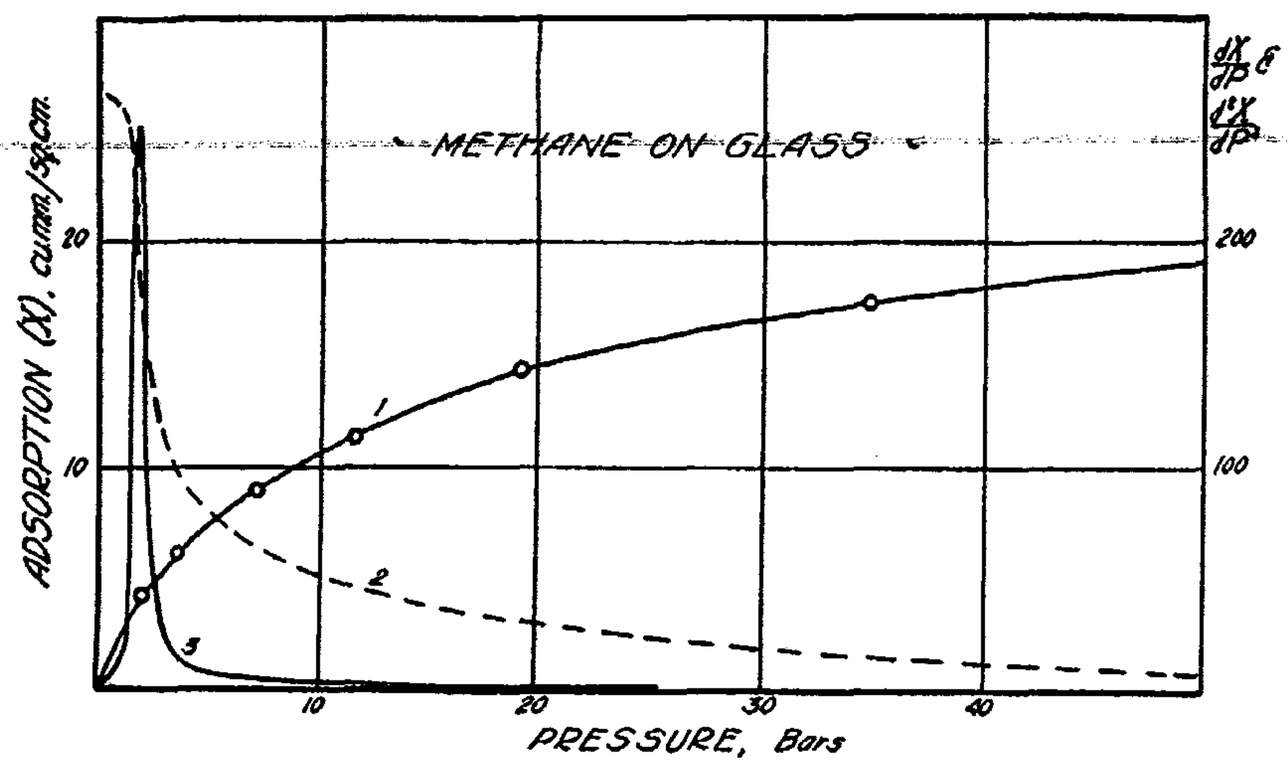

FIG. 2. ADSORPTION OF METHANE ON GLASS (LANGMUIR)

Curve 1, adsorption isotherm. Curve 2, $\frac{dX}{dP}$ versus P. Curve 3, $-\frac{d^2X}{dP^2}$ versus P, i.e., relation of adsorption coefficients to saturation pressures.

Figure 2, curve 1, represents the isotherm for the adsorption of methane on glass, taken from the data of Langmuir (1). Figure 2, curve 2, represents $\frac{dX}{dP}$ versus P and figure 2, curve 3, represents $-\frac{d^2X}{dP^2}$ versus P, the differentiation being done mechanically in each case. This shows a maximum value of the adsorption coefficient (negative of second derivative) at a saturation pressure of approximately 1.7 bars, which means that there is a maximum amount of adsorption on spaces becoming saturated at that pressure. Since the curve is so steep on either side of that pressure, the glass surface may be regarded as composed of elementary spaces which are nearly all of the same kind.

Figure 3 represents a similar treatment of the data of Langmuir for the

adsorption of methane on mica. There are two maxima in the $-\frac{d^2X}{dP^2}$ versus P curve, indicating two principal kinds of elementary spaces on the mica surface. The same conclusion was reached by Langmuir by his method of treatment.

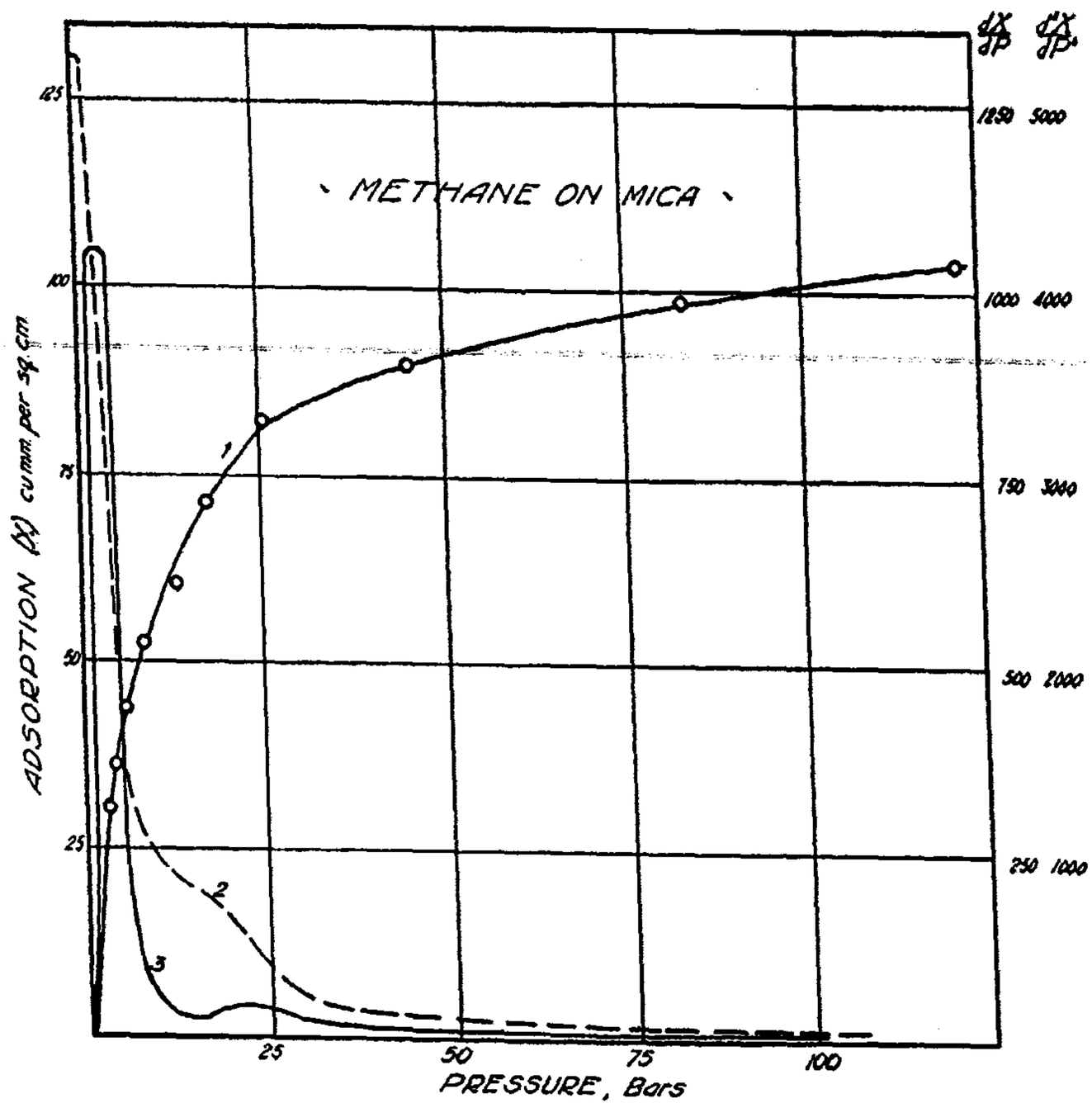

FIG. 3. ADSORPTION OF METHANE ON MICA (LANGMUIR)

Curve 1, adsorption isotherm. Curve 2, $\frac{dX}{dP}$ versus P. Curve 3, $-\frac{d^2X}{dP^2}$ versus P, i.e., relation of adsorption coefficients to saturation pressures.

Figure 4 represents a similar treatment of the data of Langmuir for the adsorption of nitrogen on mica. Curve 3 again shows two principal kinds of elementary spaces on the mica surface, whereas the Langmuir equation is satisfied by assuming only one kind. Since the mica specimens for the two experiments were prepared in exactly the same way, it is not unreasonable to expect similar adsorption phenomena for two inert gases.

If the theory proposed in this paper be correct, the CA–P distribution should be represented by the negative of the second derivative of any equation, theoretical or empirical, which absolutely satisfies the adsorption isotherm. The Langmuir equation applied to this case is of the form

$$X = \frac{abP}{1 + aP} \tag{10}$$

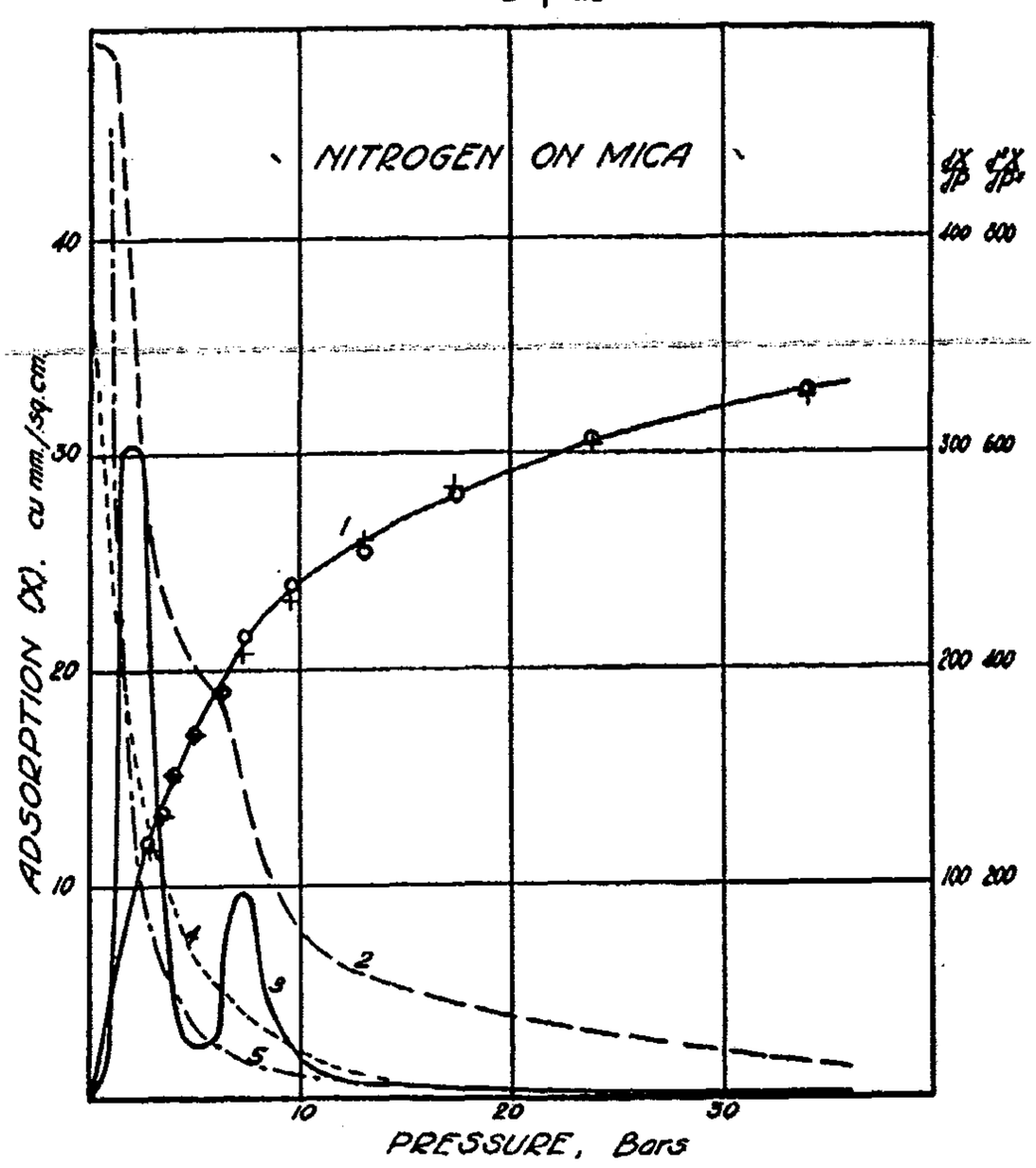

FIG. 4. ADSORPTION OF NITROGEN ON MICA (LANGMUIR)

Curve 1, adsorption isotherm: o, experimental values; +, Langmuir's calculated values. Curve 2, $\frac{dX}{dP}$ versus P. Curve 3, $-\frac{d^2X}{dP^2}$ versus P, i.e., relation of adsorption coefficients to saturation pressures. Curve 4, negative second derivative of Langmuir equation versus P. Curve 5, negative second derivative of Freundlich equation versus P.

where a and b are constants for the given case, and the second derivative of this equation simplifies to

$$\frac{d^2X}{dP^2} = \frac{-2a^2b}{(1 + aP)^3} \tag{11}$$

whence

$$-\frac{d^2X}{dP^2} = \frac{2a^2b}{(1 + aP)^3} \tag{12}$$

The o's in figure 4, curve 1, represent experimental values, whereas the +'s represent the values calculated from equation 10 by letting $a = 0.156$ and $b = 38.9$, the values determined by Langmuir. Figure 4, curve 4, is obtained by plotting equation 12. By smoothing out curve 1 in accordance with equation 10, the inflection in curve 2 and the second maximum in the CA curve are lost entirely, and the first maximum in the CA curve is reached at $P = 0$. It is thus seen that in the case under discussion the equation used by Langmuir is reasonably applicable to the present theory only at pressures greater than approximately 10 bars. (Curve 4 practically coincides with curve 3 at pressures greater than 15 bars.)

Moreover, this discussion brings to light the fact that the Langmuir equation fails also to agree with the Langmuir theory in an important respect. One of the principal claims for the Langmuir equation is that it explains the fact that the adsorption is practically a linear function of pressure at low pressures. Without reference to the present theory of adsorption, it is a mathematical fact that the second derivative of a rectilinear equation is zero. The second derivative of the Langmuir equation not only is not approaching zero at low values of P, but its negative actually has its maximum value of $2a^2b$ at zero pressure. It therefore seems, when the equation is analyzed in this way, that it does not justify this claim made for it, which, however, probably has been amplified in text books, more than the originator intended.

On the other hand, the theory proposed in this paper is flexible in that respect, since the isotherm begins to bend downward at the pressure at which an appreciable number of elementary spaces become saturated, whether that pressure be zero or not. The accuracy of the interpretation in this and all other pressure ranges depends solely upon the accuracy of the experiments.

The limited applicability of the empirical Freundlich equation,

$$X = KP^n \tag{13}$$

may be represented as follows: From equation 13,

$$-\frac{d^2X}{dP^2} = \frac{Kn(1 - n)}{P^{(2-n)}} \tag{14}$$

Letting $K = 8.4$ and $n = 0.417$, the values assigned by Langmuir, and plotting equation 14 gives curve 5, figure 4. From this equation, the negative second derivative is infinitely large at zero pressure. A study of this curve indicates that by the proper evaluation of the constants the

Freundlich equation may be made to conform approximately to the facts only at pressures greater than that corresponding to the maximum value of the adsorption coefficient. This is a lower pressure in some cases than others, and therefore the empirical equation will apply over a wider pressure range in some cases than others. It will be most applicable in those cases in which a large number of elementary spaces become saturated at low pressures.

Further use of the data of Langmuir has not been made for the reason that in the other cases cited by him the number of experimental values given in the tables is not considered sufficient to warrant an assumption as to the exact shape of the isotherm curve. The data chosen were believed to be the most accurate available, and it is believed that the present theory explains them better than does the Langmuir theory.

The opportunity has not been available for a search for suitable data in other sources and the author therefore invites other workers dealing with adsorption isotherms to plot the negative second derivatives of those curves and criticise the theory accordingly. The treatment given in this paper is not regarded by the author as a finished product, but is offered in the hope that it may prove to be the nucleus of extended work in the field.

SUMMARY

A new theory of the kinetics of gas adsorption has been proposed.

It is assumed that, in order to be adsorbed, a gas molecule must only come within a certain range of attraction of the adsorbing surface, rather than actually collide with the surface through its molecular motion.

The amount of gas adsorbed upon a given kind of elementary surface space is proportional to the pressure.

Different kinds of elementary spaces become saturated at different pressures.

A mathematical treatment has been derived which is in better agreement with published data than is the Langmuir equation.

The applicability of the Langmuir equation to the present theory has been discussed and a discrepancy between the Langmuir equation and the Langmuir theory has been pointed out.

The applicability of the empirical Freundlich equation to the present theory has been briefly discussed.

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THE RELATION BETWEEN HEAT CONDUCTIVITY AND STRUCTURE IN SILICA AEROGEL

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Received June 14, 1934

The structural units of jellies have dimensions of such an order that they have failed to yield to the ordinary methods of mensuration. Electrical conductivity, diffusion, and adsorption measurements have yielded figures of questionable accuracy on account of the uncertainties involved in the interpretation of the results. Ultramicroscopic studies in optically empty jellies are fruitless, while a measurement of the Rayleigh scattering of light, when it is intense enough to be measured, can at best give only qualitative results because the elements of structure are far too close together to obey Rayleigh's equations. The situation is somewhat better with gelatinous membranes where ultrafiltration of colloidal particles and Bechold's bubble test are available, but in the former case one is far from certain that the maximum diameter of particle that passes the membrane is within a factor of 10 of the actual average diameter of channel through which it passes, and a corresponding uncertainty enshrouds the bubble test, owing to the fact that only the largest passages can be thus estimated and also owing to uncertainty of the surface tension at small radii of curvature. X-ray methods can indicate only the size of crystal in crystalline gels, but can in no way indicate the relation between size of crystal and size of structural units, e.g., fibrils, platelets, spheres, etc., from which the gel is constructed.

The development of a process for the replacement of the liquid in a jelly by a gas with little or no change in its structure (2) has made available a powerful new measuring rod, the mean free path of the gas molecules. The kinetic theory of gases has received such substantiation and acceptance in the past two-thirds of a century that the mean free path may be regarded as one of the well-established physical quantities.

Two methods of associating dimensions within the aerogel with the mean free path of a gas have been used in this laboratory. By forcing a gas through an aerogel at different absolute pressures, the pressure at which the type of flow through the gel changes from viscous to molecular can be found and related to the average size of opening through which the gas passes. The results of this work will be published later. The second

method relies upon the linear relation between heat conductivity of a gas and its mean free path, other quantities being held constant.

RELATION BETWEEN MEAN FREE PATH AND HEAT CONDUCTIVITY OF A GAS

According to the kinetic theory of gases, thermal conductivity of a gas is associated with the mean free path by the equations

$$k = Bc_v\eta \tag{1}$$

and

$$\eta = 0.35\,\rho v l \tag{2}$$

where k is the coefficient of heat conductivity, B is a constant, c_v is the specific heat of the gas at constant volume, η is the viscosity, ρ the density, v the arithmetical average velocity of the molecules, and l the mean free path. The constant 0.35 is due to Boltzmann. The coefficient k can then be represented by the expression

$$k = k'l \tag{3}$$

where k' is a function of the pressure, temperature, and composition of the gas.

Since we know nothing of the nature of the fine structure in an aerogel except that the free spaces are much larger than the elements of structure themselves (aerogels with 98 per cent void space have been produced), we will think of a large number, N, of molecules randomly distributed through the aerogel, starting from rest and moving in straight lines in all directions until they collide with structural elements of the gel. If the structure is random, which we must assume, the fraction $\frac{dn}{N-n}$ of the molecules that have not yet struck surfaces will impinge within the distance dx, where n is the number that have already struck. Therefore

$$dn = \frac{N-n}{L}\,dx \tag{4}$$

where $\frac{1}{L}$ is the proportionality factor. Integration gives

$$n = N\left(1 - e^{-\frac{x}{L}}\right)$$

which is the familiar equation connecting the number of impacts between molecules with distance in a gas, and L can now be defined as the mean free path of a highly attenuated gas within the aerogel. In other words, $\frac{e-1}{e}$ or 63 per cent of the molecules will hit surfaces in the distance L.

In the same manner one finds that when the pressure is sufficiently high many molecules strike others in going between surfaces,

$$dn = \left(\frac{N-n}{L} + \frac{N-n}{l}\right) dx = \frac{(N-n)(l+L)}{Ll} dx$$

and the mean free path of the gas in the aerogel is

$$l_a = \frac{Ll}{L+l} \tag{5}$$

Now substituting equation 5 into equation 3

$$k_a = k'l_a = k' \frac{lL}{L+l} = k \frac{L}{L+l} \tag{6}$$

where k_a is the conductivity coefficient for the gas while in the aerogel. It was in this approximate form that the equation was used in a former publication (3).

More careful consideration of the mechanism of heat transfer through an aerogel indicates that the coefficient B in equation 1 should be different for the gas in the aerogel than for the free gas under the usual measuring conditions where the mean free path is very small with respect to the distance apart of the calorimeter plates. Where the molecules are moving in straight lines between surfaces with only occasional impacts in between, as is the case within aerogels at low pressures, it is readily shown that

$$k = \frac{Mc_vIl}{6.06 \times 10^{23}}$$

where M is the molecular weight and I is the number of impacts of molecules on unit area in 1 sec. Measuring length in centimeters and pressure in millimeters of mercury,

$$I = 1.99 \times 10^{16} \frac{P}{\sqrt{MT}}$$

which yields

$$k_a = 0.058 \sqrt{\frac{M}{T}} C_v l_0 \frac{L}{L + \frac{l_0}{p}} \tag{7}$$

where l_0 is the normal mean free path of the gas at the given temperature and a pressure of 1 mm.

Equation 7 assumes that with every impact a molecule comes to thermal equilibrium with the surface on which it strikes before it departs. If one

assumes that only the fraction a of the molecules comes to thermal equilibrium and that the fraction $1 - a$ is specularly reflected, the equation becomes

$$k_a = 0.058\, a \sqrt{\frac{M}{T}}\, c_v l_0 \frac{L^2}{\frac{2Ll_0(1-a)}{p} + aL\left(L + \frac{l_0}{p}\right)} \tag{8}$$

Equations 7 and 8 neglect the correction factor proposed by Chapman (1) as being inoperative under these conditions.

EXPERIMENTAL PROCEDURE AND RESULTS

The calorimeter and method of operation were described in a former paper (3).

The gel was made by mixing E Brand water glass, kindly furnished by the Philadelphia Quartz Company, diluted to a specific gravity of 1.20, with an equal volume of 4.3 N acetic acid and casting over mercury in paraffined crystallizing dishes. After 48 hours the cakes were removed, washed free of salts, and extracted in a Soxhlet extractor with 95 per cent alcohol until the water content of the cakes was less than 10 per cent. They were then placed in an autoclave with excess alcohol and heated to 260°C., at which temperature the alcohol was allowed to escape. The cakes of very nearly the same thickness were next trimmed with a sharp knife to shapes that could be fitted closely together on the lower plate of the calorimeter. The calorimeter was then assembled and evacuated to less than 0.01 mm. for half an hour in order to remove adsorbed moisture.

Following the evacuation the gas to be used was admitted and measurements made at pressures differing from each other roughly by a factor of 2. The lowest pressure used was generally in the neighborhood of 10 mm. to avoid making measurements at pressures so low that the conductivity of gas films between the pieces of silica aerogel and the calorimeter plates would be affected.

As was pointed out in the earlier publication in which measurements were reported on powdered aerogel, reproducibility of results is good. Only occasionally does a reading in a series fall far from a smooth curve, and those occasions have been traced to a drift of the zero point on the high sensitivity galvanometer that controls the temperature of the guard ring.

The results of the measurements with three gases, air, carbon dioxide, and dichlorodifluoromethane, are presented in table 2 and the figure. These three gases were chosen since they represent three very distinct types and possess mean free paths, as calculated by equation 2, differing by a factor of 3. Measurements were also made with hydrogen, but were not satisfactory on account of the high thermal conductivity between guard ring

and disc and the consequent uncertainty of readings due to the unusually bad zero point drift of the galvanometer. When the galvanometer suspension has been replaced, this series will be repeated and the results reported later.

Table 1 gives the calculated constants required in equation 7 for the three gases. The required data were obtained from the International Critical Tables except for the last gas, for which the data were obtained from the literature (4) and from Mr. A. L. Henne. The average temperature of

TABLE 1

Calculated constants for air, carbon dioxide, and dichlorodifluoromethane

GAS	l_0	$0.058\sqrt{\frac{M}{T}}c_v l_0$
Air	7.46×10^{-3}	2.27×10^{-5}
CO_2	5.04×10^{-3}	1.67×10^{-5}
CCl_2F_2	2.46×10^{-3}	1.20×10^{-5}

TABLE 2

Observed conductivity of silica aerogel

AIR		CO_2		CCl_2F_2	
P	Conductivity $\times 10^5$	*P*	Conductivity $\times 10^5$	*P*	Conductivity $\times 10^5$
mm.		*mm.*		*mm.*	
740	4.85*	745	4.33*	740	3.71*
363	4.16	397	3.84	406	3.38
183	3.63*	206	3.42	259	3.18
2	2.93	100	3.06*	123	2.86*
43	3.10	49	2.98	59	2.63
94	3.26	24	2.80	29	2.59
206	3.61	9	2.65	8	2.68
387	4.06				
743	4.83				

* Values used in calculating the results given in table 3.

measurement was 33.3°C. Conductivities are reported as $\frac{\text{cal.}}{\text{cm.} \times \text{sec.} \times °\text{C.}}$ To demonstrate the reproducibility of the data, two series of measurements were taken on air and distinguished in the figure by crosses and circles.

CALCULATIONS

Owing to the difficulty of obtaining good thermal contact between the calorimeter plates and the cakes of aerogel, there is a constant thermal resistance in series with that of the aerogel itself. The series conductivity

will be called k_2. Also in parallel with the conductivity due to the gas in the aerogel, there is a constant conductivity, k_3, due to the continuous structure of silica and to the gas in the small spaces between the cakes. The overall conductivity, k, as measured in the calorimeter, is related to the other conductivities by the equation

$$\frac{1}{k_g + k_3} + \frac{1}{k_2} = \frac{1}{K} \tag{9}$$

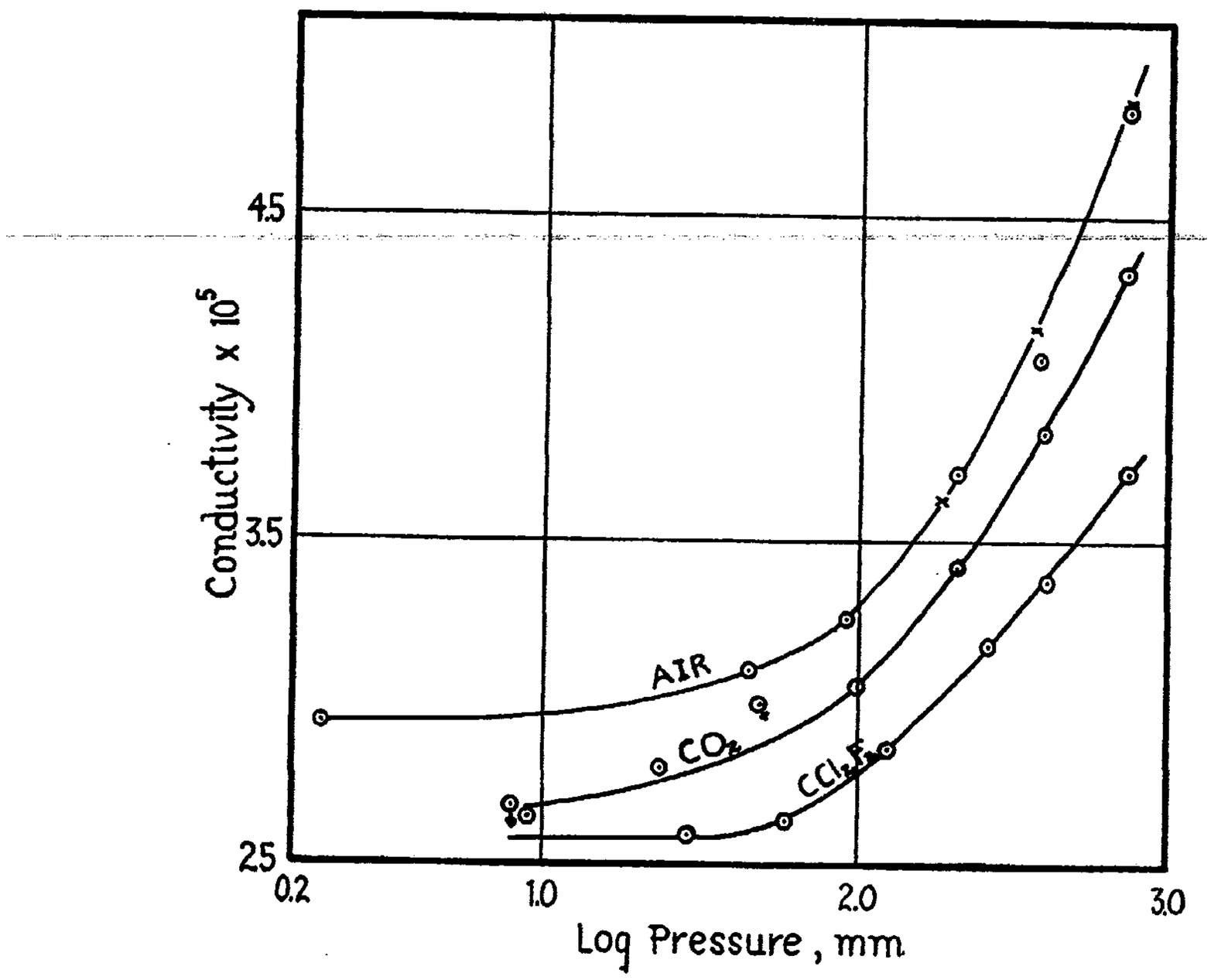

FIG. 1. CONDUCTIVITY OF SILICA AEROGEL

To be perfectly general it is evident that equation 8 should be used for k_g in order to allow for a possible accommodation coefficient a less than 1. From what is known of a gel surface, however, it seems permissible, at least as a first approximation, to establish $a = 1$ and therefore gain the decided advantage of the simplicity of equation 7.

From the curves in the figure, one can estimate the value of k_3 for each gas as the asymptotic value at low pressures. This quantity combined

with the calorimetric conductivities at two other pressures enables one to solve equation 7 for L. Table 3 gives the results of such calculations, using the values of K starred in table 2.

It is gratifying that by the use of three such different gases one should obtain such concordant results, and it gives one confidence both in the method and in the verity of the conclusions. The average distance apart of the structural elements in this batch of silica aerogel whose apparent density was 0.184 g. per cubic centimeter must lie very close to 5×10^{-6} cm., or 500 A.U.

There is one second-order source of error in these calculations that must eventually be mathematically evaluated. In the derivation of the coefficient 0.058 in equation 7, it was assumed that all of the impacts experienced by gas molecules within the aerogel are with surfaces. This assumption is a very close approximation, particularly at the lower pressures, but at the higher pressures, where there are more direct impacts between gas molecules, the coefficient should increase slightly. This dependence of the

TABLE 3

Calculated free spaces within the aerogel

GAS	k_2	L
		cm.
Air	2.9×10^{-5}	4.8×10^{-6}
CO_2	2.6×10^{-5}	5.1×10^{-6}
CCl_2F_2	2.5×10^{-5}	5.1×10^{-6}
Average		5.0×10^{-6}

coefficient upon pressure will slightly increase the calculated value of L. Nevertheless, as a first approximation and as a very acceptable value until this function can be evaluated, the average of table 3 can stand.

SUMMARY

The heat conductivity of silica aerogel of density 0.184 filled with three different gases at various pressures has been measured. The relation between heat conductivity, mean free path of the gas molecules, and the average distance separating the elements of structure in the aerogel has been derived from kinetic theory, and the last quantity has been evaluated at 5.0×10^{-6} cm.

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MOLECULAR DIFFUSION INTO WOOD[1]

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Received June 14, 1934

I. STATEMENT OF PROBLEM

One of the purposes of the study of molecular diffusion into a gel has been to obtain information about the structure of the gel. Thus, in spite of the fact that early investigators had assumed the gel to have no effect on the diffusion, it is now a matter of record that mechanical blocking, wall friction, and viscosity effects do modify the rate at which a simple solute molecule can diffuse across an interface and into such a solid. It appeared possible to us that the methods which have been successful in the study of gels could be extended to the porous solids. Therefore it was decided to measure the rate of diffusion, from dilute aqueous solutions, of the neutral molecules urea, glycerol, and lactose into wood samples, with the expectation that these diffusion data could be used to estimate the effective mechanical blocking. Wood samples were chosen because through the efforts of the scientists at the U. S. Forest Products Laboratory and elsewhere the capillary dimensions for certain species are quite accurately known. This report describes the results obtained in a somewhat extended series of experiments and discusses their significance.

A number of interesting experiments have followed the successful analyses by March and Weaver (8) and by Langer (7) of the mathematical problem involved in a diffusion experiment in which the process is allowed to take place across the interface formed by a stirred liquid in contact with a gel or porous solid. As a result of experiments based upon this analysis Friedman and Kraemer (3) have been able to make observations of the diffusion of non-electrolytes into gelatin gels, Friedman (2) and Klemm and Friedman (4) have been able to extend the work to agar and cellulose

[1] A more complete account of this work is to be found in the thesis of L. C. Cady, presented to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy and filed in the Library of the University of Wisconsin in August, 1934.

acetate gels, and Wolkowa (14) has obtained data for the diffusion of glucose into silica gels. In all these cases the diffusion into the gel is slower than it is into pure water at the same temperature. Friedman and Kraemer considered three causes for the retarded diffusion: a mechanical blocking by the gel substance, an additional resistance due to the proximity of the diffusing molecule to the capillary walls, and an increased viscosity of the dispersion medium due to the solution in it of a certain amount of the gel substance. Correction for these effects was made by the use of an equation of the form,

$$D_w = D_s (1 + \pi) (1 + 2.4\, r/R) (1 + \alpha) \qquad (1)$$

In this equation,

D_w is the diffusion coefficient of the substance into water,
D_s is the diffusion coefficient of the substance into the gel or porous solid,
π is the correction factor for mechanical blocking,
r is the radius of the diffusing molecule,
R is the radius of the pore through which the diffusion is taking place, and
α is the correction factor for changed viscosity.

In the treatment of our experimental data we shall prefer to make use of another equation, as follows:

$$D_w (1 - \pi) = D_w \cdot A = D_s (1 + 2.4\, r/R) (1 + \alpha) \qquad (2)$$

Our work has been done with wood samples, and R is now to be interpreted as the effective radius of the pit membrane pores. Since mechanical blocking serves to reduce the unit area through which the diffusion can take place, it has seemed logical to compare D_s and D_w for a process taking place across equal areas. This necessitates the adjustment of D_w to the reduced open cross-sectional area of the porous substance. Thus, the mechanical blocking may be taken into account by multiplying D_w by a factor A, which is the fraction of the area unobstructed by the solid substance. Then differences between D_w values which have been adjusted in this way for reduced cross-sectional area and D_s are due to other factors, including the anisotropic character of the wood.

Aside from microscopic measurements with extremely thin sections there is no direct method by which the amount of open area in a given surface can be evaluated. The method of attack most frequently used is based upon a determination of the partial pore volume of a sample, using density measurements. If the partial pore volume is represented by S, then $S = 1 - g/d$. In this definition, g is the weight of the gel or porous solid per cubic centimeter, and d is the density of the solid material forming the structure.

Thus, the problem becomes one of expressing the factor A in terms of S. There are two conditions which any equation relating A and S should fulfil. When the partial pore volume is zero the substance is solid throughout, the area is completely blocked, and the factor A becomes zero. Likewise, when the partial pore volume is unity there is no mechanical blocking, none of the area is obstructed, and A becomes unity. The mechanical blocking factor has been obtained in different ways by interested investigators. In order to collect in one place a few of the results, table 1 and figure 1 have been prepared.

Buckingham's equation was based upon his observations of the resistance experienced by carbon dioxide and oxygen diffusing through soil. The Dumanski expression resulted from an attempt to calculate by theory the area in a single plane of the sections of spherical molecules forming the disperse phase. It was applied by Dumanski to the correction of both electrical conductivity and diffusion data for gels. To correct conductivity data which were obtained with samples of wood, Stamm modified

TABLE 1

Evaluation of mechanical blocking factor A

VALUE OF A	INVESTIGATOR	REFERENCE
S^2	Buckingham	U. S. Department of Agriculture, Bur. Soils, Bulletin No. 25 (1904)
$1 - (1 - S)^{2/3}$	Dumanski	Kolloid-Z. **3**, 210 (1908)
S	Stamm	J. Phys. Chem. **36**, 312 (1932)

the equation, because in this case the structural units are elongated rather than spherical in shape. The diffusion problem was not considered by the latter investigator.

Since Friedman and his associates have adopted the Dumanski relationship for their work it may be remarked that their use of equation 1 is equivalent to a definition of the mechanical blocking factor such that,

$$A = \frac{1}{1 + (1 - S)^{2/3}}$$

This equation does not meet the condition that A must be zero when the partial pore volume is zero, therefore it cannot have any general validity. The reason why its use with gel systems which have very large values of partial pore volume has not led to apparent difficulties is evident from an inspection of figure 1.

The correction to be made for the increased frictional resistance to the movement of a molecule in the neighborhood of a wall has been studied at some length by Ladenburg (6), Arnold (1), and many others. The correc-

tion used in the diffusion equations (1, 2) is that of Ladenburg. The effect of the proximity of the wall surface on spheres falling in cylindrical glass vessels was measured, and Stokes' law of fall was modified to take it into account. Arnold confirmed the Ladenburg correction and showed that it is independent of the viscosity of the liquid in which the molecule or particle is moving.

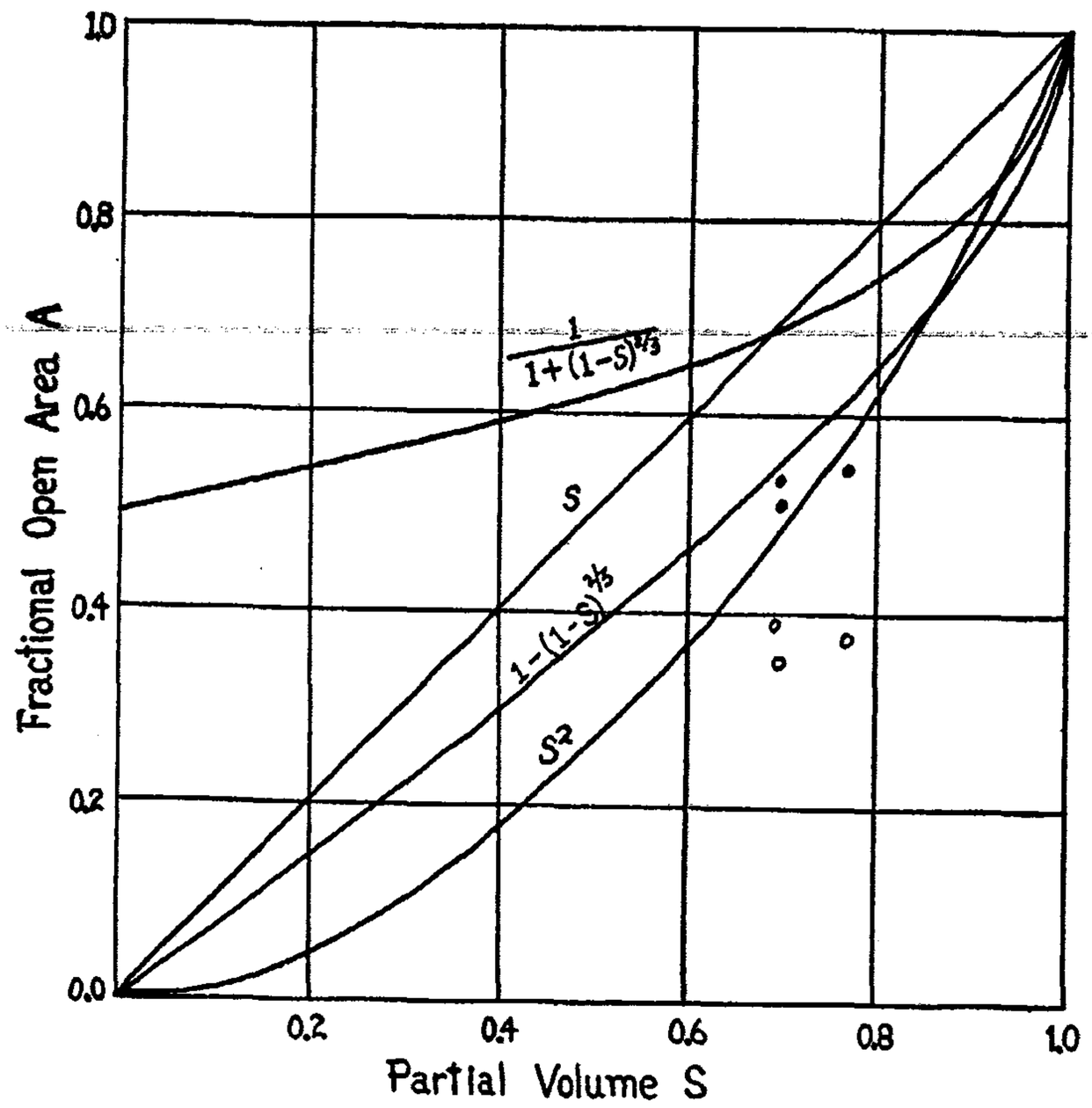

FIG. 1. EVALUATION OF MECHANICAL BLOCKING FACTOR

In order to correct the law of Stokes the viscosity was multiplied by the factors $(1 + 2.4\, r/R)$ and $(1 + 3.3\, r/h)$. In these factors h is the length of the capillary, and r and R have the significance already assigned them. The second factor becomes appreciable in the case of short tubes with closed ends and may be disregarded in the gel and wood problems. For wood, h would be twice the diameter of a lumen which is about one thousand times the value of r.

Obviously the additional resistance to motion caused by the proximity of the wall will manifest itself for a limited range of values of r/R. When

r/R is large, one is dealing with a condition approaching ultrafiltration, but when r/R is very small, the wall is so far removed that the condition is one of free fall, or in the case of a diffusion, one of free diffusion. The data of Ladenburg indicate that this ratio should have values between 1/90 and 1/11 if the first factor is to be applicable without modification. Arnold's curves place the lower limit in the neighborhood of 1/100, with the upper limit at about 1/10.

The correction factor α for increased viscosity of dispersion medium is obtained from the difference between D_s at zero concentration of solid and D_w. Since there is only one "concentration" of wood substance when the voids or capillaries are filled with water, it is not possible to estimate α by an extrapolation of the kind resorted to when synthetic gels are being considered. For reasons which cannot be given at this time it seems reasonable to conclude that the factor α can be considered to be negligible in our work with wood sections.

If this correction factor for increased viscosity of medium can be neglected, diffusion experiments of the type to be reported here can give considerable information with regard to the magnitude of the mechanical blocking effects, because the radii of the diffusing molecules and the average radii of the pores of the pit membranes are known with some degree of accuracy. Stamm (13) has summarized the results for R obtained by using several independent methods. In this way it should be possible to differentiate between the several equations proposed to calculate the magnitude of the mechanical blocking coefficient. In addition, differences between observed values and values obtained by calculation with the equation adjudged to be most nearly correct can be ascribed to the anisotropic character of the capillary spaces and to the presence of lumen pores without outlet.

It might be assumed that diffusion studies of the kind we are to report would make possible an estimate of an average radius of the pit membrane pores in wood sections, but when it is realized that the principal cause of the reduction of diffusion is the mechanical blocking, the difficulties involved become apparent. We have little exact information about several factors which determine the effective area available for the diffusion. Furthermore, since the effects due to mechanical blocking are very large compared to those which result from the additional frictional resistance to motion due to the proximity of the walls, small errors in the A factor would lead to large errors in the determination of the ratio r/R, and therefore in the effective capillary area of the pores of the pit membranes.

II. MATHEMATICAL FORMULATION AND EXPERIMENTAL PROCEDURE

The coefficient of diffusion or diffusion constant is defined as the quantity of matter which in unit time moves through a unit of cross section

under unit concentration gradient. In this work it was required to determine the constant for various solute molecules, moving across the interface formed by the stirred solution in contact with a wood section, from observations of the decrease in concentration of the solution with time. March and Weaver showed that the diffusion constant, D_s, of a solute moving into the solution contained in a porous solid is given by the expression

$$D_s = \frac{a^2T}{t} \tag{3}$$

In this equation D_s is the diffusion constant expressed in cm.^{2} per second, and a is the thickness of the solid and also the depth of the solution above the solid. The value of T is found from the equation,

$$V = \frac{1}{2} - (0.327e^{-4.117T} + 0.0766e^{-24.14T} + 0.0306e^{-63.68T} + 0.0160e^{-123T} + 0.0100e^{-200T} + 0.0067e^{-299T} + \cdots)$$

In this expression V is the fraction of the total amount of solute which has diffused into the void spaces of the solid. In our experiments this quantity was found by determining the concentration of the solution above the block of wood with an immersion refractometer. At any time, t,

$$V = \frac{R_0 - R_t}{R_0 - R_w} \tag{4}$$

Here R_0 is the reading of the refractometer for the solution at time, $t = 0$,
R_t is the reading at time t, and
R_w is the reading for the solution originally filling the void spaces of the solid.

In order that equation 3 be exact it is required that the depth of solution and thickness of the solid be the same, and that the solution be maintained at uniform concentration throughout. In order to use equation 4 in the form given, it is necessary to assume the concentration of solute to be directly proportional to the refractive index of the solution.

In practice, values of T were assumed and the corresponding values of V were calculated. A plot of V versus T was then made and values of T for any experimentally determined value of V were read from the curve.

In an experiment a block of wood was saturated with water and fitted into a thermostated brass diffusion chamber. The solution containing nearly spherical solute molecules was placed in contact with the block, and the change of concentration with time, as the solute diffused into the block of wood, was observed.

Samples of cedar and white fir were obtained from freshly felled trees

about 15 in. in diameter. The sample of white pine was a kiln-dried piece, and results with it were obtained largely while developing the technique

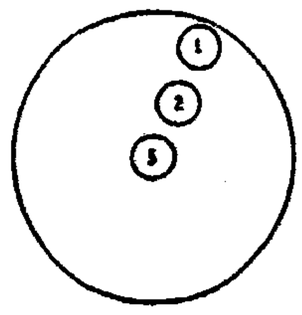

FIG. 2. LOCATION OF SAMPLES TAKEN FROM TREE

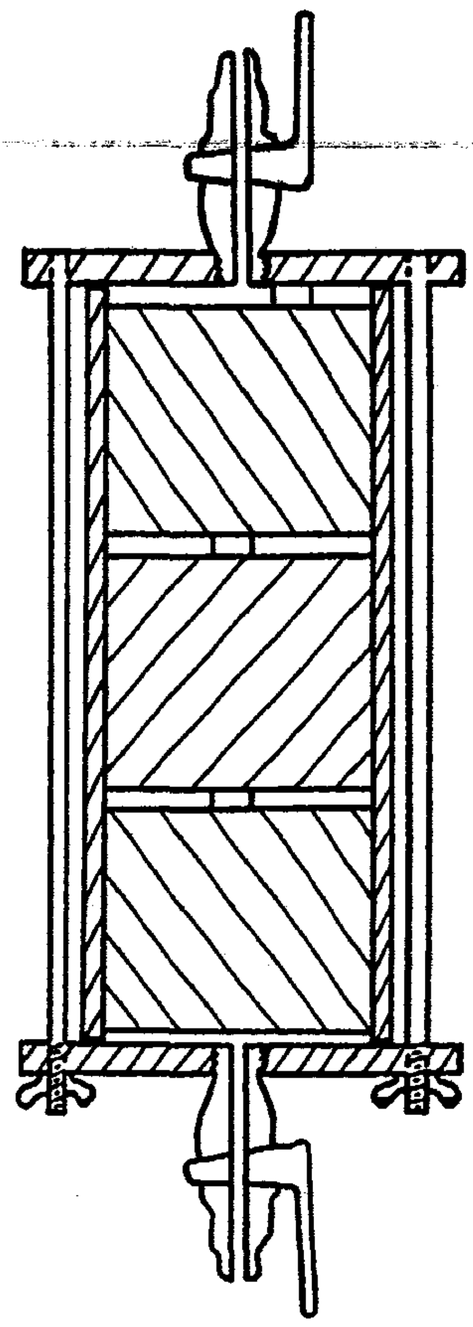

FIG. 3. EVACUATION CELL

of the method. The Western hemlock sample was furnished by the U. S. Forest Products Laboratory. Sections taken from these were numbered

as shown in figure 2. All samples were turned to the required size in a lathe and the ends were coated with paraffin to prevent drying and checking. To lower the humidity to a sufficient extent to avoid growth of molds, the samples were kept over a saturated solution of barium chloride.

The turned wood samples were cut into cylindrical blocks of the desired length, which varied from 1.5 to 4.0 cm. The exact thickness was measured with a micrometer caliper. The samples were placed in an evacuation cell whose construction is indicated by figure 3. This cell was a brass

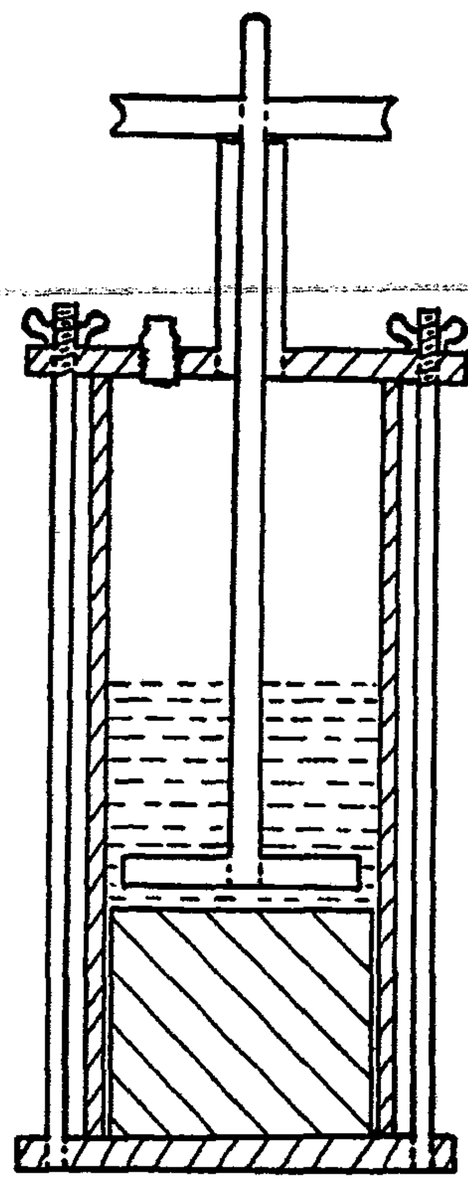

FIG. 4. DIFFUSION CELL

cylinder 5 in. long and 2 in. in diameter. Cover and bottom, provided with brass stopcocks, were arranged so that they could be clamped to the cylinder. The upper stopcock was connected to a vacuum pump and the lower one was attached to a mercury manometer. Rubber gaskets between the cylinder and the cover and bottom sealed the apparatus. The cylinder, with block in place, was maintained for about twenty-four hours at a pressure of 4 to 5 mm. of mercury. Water was introduced through the lower stopcock of the cell in order to fill the evacuated void spaces in

the block of wood. The sample was then kept for four weeks or longer in a vacuum desiccator filled with water, from which the air was exhausted at intervals.

The diffusion apparatus proper is shown in figure 4. It resembled the evacuation cell in form except that it had no stopcocks and the cover piece was provided with a stirrer and tapped hole to permit removal of the sample.

Since diffusion was to take place only across the upper surface of the block, it was necessary to make it impossible for the solution to come into contact with the sides and bottom of the block. This was accomplished by painting the block on these faces with an aluminum–glyptal paint, and then coating them with a layer of paraffin to such a thickness that the block would not quite slip into the cylinder. The cylinder was then warmed and the paraffined block forced into it. On cooling, the block was firmly imbedded in the paraffin. The apparatus was tested for tightness by allowing it to stand full of water overnight. Any seepage of water along the sides of the block could be detected in this way. After inversion to remove the excess water, the cell was clamped firmly to a brass frame by means of which it was possible to lower the cell in fixed position into the thermostat. The temperature chosen for the experiments was 25°C. To start an experiment an amount of the solution, such that its height in the cell was equal to the height of the wood block, was introduced into the diffusion cell.

The choice of solute molecule was restricted for several reasons. The molecule should be nearly spherical in shape and of such radius that the ratio r/R falls within the limits mentioned in the previous section. The refractive index of the aqueous solution should be such that it varies linearly with the concentration of the solute. The solution should not cause change in any of the constituents of the wood. The molecules urea, lactose, and glycerol met these requirements fairly well. The concentration of the glycerol solution used was 4 per cent, while that of the urea and lactose was 5 per cent, by weight. The concentrations were kept as low as possible in order to avoid a "solute hindered" diffusion, but at the same time the concentration was great enough to allow a difference of reading of 15 to 20 immersion refractometer units between the solution and water at the beginning of the experiment.

Refractometer readings were taken at the beginning of the experiment and at intervals of from twelve to twenty-four hours. The diffusion was allowed to continue until successive readings indicated that equilibrium had been reached. Six to twelve values of the diffusion constant were determined for each block. In this way it was possible to obtain a representative value provided the variations between individual figures were not excessive. Preliminary experiments showed that there was no change

of refractometer reading due to leakage, seepage, oil from the stirrer, or solution of material from the cylinder or paraffin. Further, no measurable sorption of solute by the wood substance was found. Before the start of all experiments the blocks were saturated as nearly as could be determined by weighing at intervals to constant weight. The rate of stirring was so adjusted that the solution was kept at uniform concentration without producing a vortex effect above the block. A stirrer speed of 275 R.P.M. was maintained.

The initial refractive index of the water saturating the block depended upon the amount of material extracted from the block and varied with the species of wood. It was assumed that the solution filling the void spaces of the wood and the solution covering the block had reached equilibrium during the time that the block was in the vacuum desiccator. The refractometer reading, R_w, was taken as the value obtained for the solution in which the block was saturated.

III. EXPERIMENTAL RESULTS

Data obtained in a typical diffusion measurement are presented in table 2. The values of D_s in this table check each other unusually well, but in practically all cases the mean deviation from the average value is less than 0.01.

The length of the block which could be used was fixed within definite limits by the dimensions of the diffusion cell, the amount of solution that could be stirred adequately, and the effect of sample removal upon the concentration of the remaining solution. It is evident from table 3 that the length of the block may be changed by 100 per cent without changing the diffusion coefficient to an appreciable extent.

Additional experiments were made in which the wood was saturated with the solution so that a diffusion of the solute into water above the block took place. When glycerol diffused into the seasoned heartwood of white pine a value of $D_s = 0.66 \times 10^{-5}$ was obtained. Reversing the experiment with glycerol diffusing into the water above the block the value $D_s = 0.63 \times 10^{-5}$ resulted. However, experiments in which the solute diffused out of the block into the water above it offered several difficulties and were not generally used.

When the pore dimensions of the wood blocks were larger, the values for the diffusion constants increased. In all, there could be distinguished: (1) hindered diffusion, in which the ratio r/R was not too small to be of significance; (2) free diffusion, in which the effective pores were small enough to prevent mixing of the water in the block with the solution, but large enough to allow *practically* unrestricted diffusion of the solute molecules; and (3) stirred diffusion, in which the pores were so large that mechanical mixing with the liquid in the pores of the wood block took place

as the solution was stirred. There is involved a mechanical blocking in all three cases. Results of experiments typical of the three kinds of diffusion have been collected to form table 4. The solute used was urea, for which $D_w = 1.3 \times 10^{-5}$ at 25°C.

There have been summarized in table 5 the data for diffusion studies made on wood sections cut in the transverse direction. In the table heartwood is represented by the symbol Hw and sapwood is designated by Sw. Numbers in parenthesis after the kind of wood refer to the positions indicated by the chart, figure 2, which gives the location of the sample in the tree. The sample labeled 3a was taken next to the center but not concentric with it. Each figure in the table represents the average value of from six to twelve diffusion coefficients obtained from experiments on two to six samples of wood.

TABLE 2

Diffusion data for lactose into heartwood of white fir

Length of block = 3.14 cm.; R_w = 14.00; R_0 = 31.50

HOURS	R_t	$R_0 - R_t$	V	T	$D_t \times 10^5$
22.8	29.00	2.50	0.143	0.0205	0.248
46.8	28.10	3.40	0.194	0.0414	0.244
70.8	27.48	4.02	0.228	0.0615	0.240
94.8	27.00	4.50	0.257	0.0828	0.240
119.8	26.55	4.95	0.282	0.1062	0.244

TABLE 3

Effect of length of block on diffusion coefficient of glycerol into white fir heartwood (2)

BLOCK LENGTH	$D_t \times 10^5$
cm.	
1.35	0.46
1.38	0.45
1.41	0.46
2.09	0.44
3.14	0.44

It may be concluded from these data that a reproducible hindered or nearly free diffusion, of the type required for estimation of the mechanical blocking effect, results when observations are made on the *heartwoods* of pine, cedar, hemlock, and fir. It is also indicated that the structure of the sapwood in these species is too coarse to give consistent and reproducible diffusion constants.

The above data have been obtained with wood samples cut in the trans-

verse direction. Diffusion into radial sections was also investigated and much lower diffusion constants resulted. Space does not permit the

TABLE 4

Effect of pore size in determination of type of diffusion

Figures given are diffusion constants for urea, D_s

TIME INTERVAL	WHITE FIR HEARTWOOD (3) HINDERED DIFFUSION	WHITE FIR HEARTWOOD (2) APPROACHES FREE DIFFUSION	WHITE FIR SAPWOOD (1) STIRRED DIFFUSION (SLOW STIRRING)	WHITE FIR SAPWOOD (1) STIRRED DIFFUSION (RAPID STIRRING)
1	0.34×10^{-5}	0.64×10^{-5}	1.38×10^{-5}	1.66×10^{-5}
2	0.36×10^{-5}	0.66×10^{-5}	1.34×10^{-5}	1.61×10^{-5}
3	0.34×10^{-5}	0.65×10^{-5}	1.31×10^{-5}	1.55×10^{-5}
4	0.35×10^{-5}	0.63×10^{-5}	1.19×10^{-5}	1.38×10^{-5}

TABLE 5

Diffusion data for wood samples cut in transverse section

WOOD	SOLUTE	SAMPLES	$D_s \times 10^5$	TYPE OF DIFFUSION
Cedar Sw (1)	Lactose	6	0.85–2.4	Stirred
Cedar Sw (1)	Glycerol	3	0.76–1.2	Stirred
Cedar Hw (2)	Glycerol	5	0.43	App. free
Cedar Hw (2)	Lactose	3	0.20	App. free
Cedar Hw (3a)	Lactose	3	0.13	Hindered
Cedar Hw (3)	Glycerol	2	0.25	Hindered
Cedar Hw (3)	Lactose	6	0.12	Hindered
Cedar Hw (3)	Urea	3	0.38	Hindered
Western hemlock Sw	Glycerol	2	0.26–0.93	Stirred
Western hemlock Hw	Lactose	2	0.18	App. free
Western hemlock Hw	Glycerol	3	0.43	App. free
White fir Sw (1)	Urea	3	0.86–1.55	Stirred
White fir Sw (1)	Lactose	3	0.52–1.51	Stirred
White fir Sw (1)	Glycerol	6	0.40–0.63	Stirred
White fir Hw (2)	Urea	3	0.67	App. free
White fir Hw (2)	Glycerol	6	0.44	App. free
White fir Hw (2)	Lactose	4	0.22	App. free
White fir Hw (3)	Glycerol	3	0.30	Hindered
White fir Hw (3)	Urea	3	0.36	Hindered

presentation and discussion of these data at the present time. Purely tangential sections of required length could not be cut from the trees

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from which the sample blocks were taken. Several experiments with semi-tangential sections also gave much lower diffusion constants.

IV. DISCUSSION OF RESULTS

In the experiments in which a hindered or nearly free diffusion took place we assume D_t to be smaller than D_w for two reasons. The first and more important reason is the effect of the mechanical blocking, the second is the additional resistance to motion due to the proximity of the pit membrane pore walls to the diffusing solute molecule. Values of the fractional open area A have been calculated by the use of equation 2. In these

TABLE 6

Fractional open area of transverse heartwood sections

SPECIES	SOLUTE	D_t	r/R	S	A
Western cedar (3)	Glycerol	0.25	0.05		0.32
Western cedar (3)	Lactose	0.12	0.10	0.70	0.32
Western cedar (3)	Urea	0.38	0.04		0.32
Western cedar (3a)	Lactose	0.13	0.10	0.70	0.36
Western cedar (2)	Glycerol	0.43	0.03	0.72	0.56
Western cedar (2)	Lactose	0.20	0.10		0.54
Western hemlock (Hw)	Glycerol	0.43	0.05	0.71	0.55
Western hemlock (Hw)	Lactose	0.18	0.08		0.48
White fir (3)	Glycerol	0.30	0.03	0.77	0.36
White fir (3)	Urea	0.36	0.02		0.30
White fir (2)	Glycerol	0.44	0.03		0.54
White fir (2)	Lactose	0.22	0.05	0.77	0.54
White fir (2)	Urea	0.67	0.02		0.54

calculations α is assumed to be zero and the pit membrane pore radii, based on Stamm's values, are for Western red cedar, 8 mμ, for Western hemlock, 12 mμ, and for white fir, 15 mμ. The values of A have been collected to form table 6. These values are shown by the points on figure 1.

The values of A fall into two regions, one at about 0.35 and the other at about 0.55, depending upon the distance from the center of the tree at which the sample was taken. Samples of heartwood taken at some distance from the center (region 2) give blocking coefficients which are but slightly below those required by the Dumanski equation. The differences between observed values and values obtained by calculation with the

Dumanski equation are probably due, in large measure, to the anisotropic character of the capillary spaces in the wood, and to aspirated tori. These samples are representative of the major area of the heartwood.

Samples of heartwood taken from the center (region 3) have A values lying much below the expectation based upon the use of the Dumanski equation, and even below that required by the Buckingham relation. These low values are not surprising when it is realized that the percentage of aspirated tori is high at the center of the tree. Furthermore, the actual effective value of the radii of the pores of the pit membranes is probably smaller than the value actually used in the calculations. A reduction of pit membrane pore radius for red cedar from 8 mμ to 4 mμ would cause an increase in blocking of 0.06 unit. Further, it must be recognized that the blocking factor changes more from the center to the periphery of the tree than would be expected from density measurements alone.

It is worthy of note that the data of table 6 are not inconsistent with rough estimates of the relative amounts of open and closed area of a wood section as determined by running a planimeter over photomicrographs of transverse wood sections. These estimates, made on photomicrographs which have been reproduced in articles by Ritter (12), indicate a fractional open area varying from 0.35 to 0.40.

The data obtained, therefore, may be considered to indicate the essential correctness of the theoretical deductions of Dumanski for the calculation of the mechanical blocking factor in a diffusion experiment involving a porous solid. We are not prepared to say as to whether or not the deviation between experiment and theory can be completely accounted for on the basis of the considerations presented above, because the apparent diffusion constants may be affected by the particle size and other factors not yet taken into account. The matter is deserving of further experimental work and theoretical analysis.

Finally, the data of this article are not without interest in connection with recent studies of Northrup and Anson (11) and of McBain (9, 10), in which the diffusion process has been caused to occur across thin porous membranes of alundum or glass powders, the idea being that the process would be greatly accelerated owing to the maintenance of a high concentration gradient, and at the same time, troublesome convection currents would be avoided. As Northrup and Anson point out, the pores must be small enough to prevent convection currents in the liquid held in them and large enough to allow free diffusion of the particles or molecules of the solute. It is evident from our table 4 that there is, between the two extremes, such a favorable capillary pore size in some wood sections for the diffusion of solute molecules of radius comparable to that of urea. It is only reasonable to suppose that there can be found other membranes having pore sizes to permit free diffusion of any given solute molecule and at the same time prevent convection currents.

In the method of Northrup and Anson a membrane is standardized against some solution, the diffusion constant of which is known, much after the fashion of the determination of the constant of a conductance cell. When the membrane constant for the diffusion apparatus with a particular diaphragm has been determined, it is used to obtain the diffusion coefficient for unknown substances. In this way any effects due to what we have termed mechanical blocking are eliminated.

Among other things this determination of membrane constant assumes invariable effective area of the pores. It would seem, therefore, that there still remains some uncertainty as to what effect, if any, there will be when the radius of the diffusing molecule is varied over such wide limits as has been the case in the investigations which have been carried out in this manner. At the present time we are inclined to agree with Kraemer (5), who writes, "This technic, however, combines the theoretical complications of osmotic pressure and free diffusion so that results obtained in this way for D, if presumed to be quantitative, can only be accepted as provisional until independent confirmation is obtained."

SUMMARY

1. Diffusion experiments in which the process is allowed to take place across the interface formed by a stirred liquid in contact with a gel have been extended to porous solids. The coefficients of diffusion at 25°C. of urea, lactose, and glycerol from aqueous solution into transverse sections of samples of white fir, Western hemlock, and Western red cedar wood have been determined.

2. From the data obtained it has been possible to distinguish three kinds of diffusion. They have been described as hindered diffusion, free diffusion, and stirred diffusion. Attention has been called to results of experiments which are typical of each. These data are of interest in connection with recent methods which have been proposed for the determination of the diffusion coefficient of a solute from its rate of passage through a thin porous membrane.

3. Fractional open areas for heartwood sections have been calculated by using a modified theory, when it could be shown that the diffusion constant was not influenced by the rate of stirring. Comparisons of the experimentally observed mechanical blocking factors with those calculated by the theoretical and empirical equations already existent in the literature have been made.

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A STUDY OF CERTAIN FACTORS INFLUENCING THE MOVEMENT OF LIQUIDS IN WOOD[1]

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Received June 14, 1934

Early workers in the fields of plant anatomy and physiology did not believe there were any direct openings between the cells of wood. To explain the movement of viscous organic substances, preserving oils for example, Tiemann (21) advanced the hypothesis that the wood was made permeable by checks which developed in the cell wall during seasoning. Weiss (22) modified this hypothesis to explain why a greater penetration of preserving oils was obtained in the dense summerwood of longleaf pine. Information was later submitted by Bailey (1, 2) which led him to conclude that the intercellular movement of preserving fluids was through small openings in the pit membranes. Scarth (14), after an examination of coniferous wood impregnated with mercury, also concluded that the effective intercellular communication was localized in the bordered pits.

Assuming that the pit membrane pores were the means of intertracheid flow, Stamm (15) has used physical methods to obtain the dimensions of the pit perforations. The range in average diameters (of true circles having the same effect as the openings of unknown shape) of the pit perforations in two species was found to be 11 mμ to 23 mμ. The range in maximum diameters for five woods was found to be 68 mμ to 184 mμ. Stamm (16) also has recently made determinations of the ratio of the effective capillary length to the effective capillary cross section of the pores in the pit membranes.

The influence of certain of the gross structural features of wood upon the

[1] From the Divisions of Forestry and Agricultural Biochemistry of the University of Minnesota. Published with the approval of the Director as Paper No. 1288 of the Journal Series, Minnesota Agricultural Experiment Station. Condensed from a thesis presented by Stanley J. Buckman to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1933.

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movement of liquids has been investigated by a number of workers. Griffin (5, 6) and MacLean (13) have obtained evidence that the position of the tori of the bordered pits influences the permeability of wood. Teesdale (18) and Teesdale and MacLean (19) found that the distribution of resin canals and the freedom of vessels from obstructions are other structural features which influence the impregnation of wood. These studies clearly showed, however, that wood of similar gross structure may react quite differently to impregnation.

Investigations have been made of the effect of pressure upon the rate of flow of liquids through wood. Johnston and Maass (9), referring to the influence of pressure, state: "The rate of flow in greenwood and sapwood tends to increase in proportion to the pressure when the system is in a stable state, but in seasoned wood, flow increases more rapidly especially at the higher pressures, when even sapwood departs from a linear relationship." On the other hand Sutherland, Johnston, and Maass (17) have reported that the rate of flow of water through seasoned and unseasoned white spruce and the unseasoned heartwood of black spruce was approximately proportional to the pressure. For the unseasoned heartwood of Norway pine, cedar, tamarack, balsam fir, and white pine a disproportionate increase in rate of flow was obtained for increased pressures.

Teesdale and MacLean (20), in an early work, found no apparent relationship between viscosity (expressed in Engler numbers) and the ease of movement of mixtures of coal-tar creosote and coal tar in the heartwood of longleaf pine. Bateman (3) recalculated their data and concluded that when the viscosity was expressed in centipoises a definite relationship between the viscosities of the preserving oils and their penetrations into wood did exist. MacLean (10, 11, 12, 13) in later work emphasized the importance of the relationship between absolute viscosity and the penetration into wood of aqueous solutions of zinc chloride, mixtures of coal-tar creosote and petroleum, and coal-tar creosotes. Howald (7, 8) found, however, that the penetrations of certain petroleums and mixtures of coal-tar creosote and petroleum could not be predicted from their viscosities. Likewise Johnston and Maass (9) have observed deviations from purely viscosity considerations for aqueous solutions of neutral sulfites when the rates of flow of these solutions were compared with water, and Sutherland, Johnston, and Maass (17) have obtained similar results for aqueous solutions of glucose.

EXPERIMENTAL

The problem

We have studied certain of the relationships governing the pressure movement of liquids in wood. These were: (1) the influence of moisture content of wood below the fiber-saturation point upon the relative effec-

tiveness of the intercellular openings, (2) the influence of pressure upon the rate of flow of water through wood, and (3) the movement of organic liquids and salt solutions through wood.

Apparatus and methods

The effect of moisture content upon the pressure necessary to overcome the surface tension of benzene in the maximum effective intercellular openings in wood was determined with an apparatus similar to that described by Stamm (15).

The rate of flow of different organic liquids through wood and the rate of flow of water at different pressures was determined by the use of an ap-

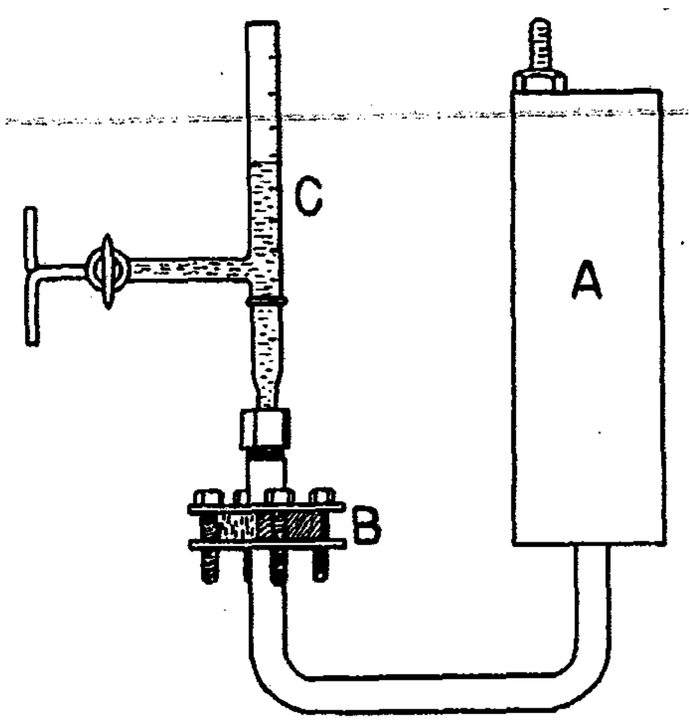

FIG. 1. THE ESSENTIAL FEATURES OF THE APPARATUS USED IN DETERMINING THE RATE OF FLOW OF LIQUIDS THROUGH WOOD

paratus made of brass. A similar apparatus made from glass was employed for the study of the movement of salt solutions. The two sets of apparatus were composed of the essential parts shown in figure 1.

Air pressure was applied to the liquid in the supply tank, A, which forced it through the wood section held in place at B (the area of the section exposed to the path of flow of the liquid was 0.35 sq. cm. for the brass apparatus and 1.93 sq. cm. for the glass apparatus), and into the buret, C. An air pressure gauge sensitive to 0.05 kg. per square centimeter and a mercury manometer were employed for measuring the applied air pressure.

The temperature was not controlled. However, each time a reading was taken the room temperature was recorded. These results showed that the normal fluctuations in temperature of the room did not appear to influence materially the relationships obtained.

The viscosity of the kerosene was determined with an Ostwald viscometer. The viscosities of the other organic liquids were determined by interpolation from values obtained from the International Critical Tables.

The moisture content given in all cases is expressed in terms of percentage of the oven-dry weight, which was determined by drying to constant weight at 105°C. at atmospheric pressure in an electric oven.

Materials

Seven kinds of wood were used: namely, balsam (*Abies balsamea* (Linneaus) Miller), Norway pine (*Pinus resinosa* Solander), white spruce (*Picea glauca* (Moench) Voss), Northern white cedar (*Thuja occidentalis* Linnaeus), Western red cedar (*Thuja plicata* D. Don), and Eastern hemlock (*Tsuga canadensis* (Linnaeus) Carrière).

All Norway pine, balsam fir, and white spruce sections were sawed from freshly felled logs. The Northern white cedar, Western red cedar, and Eastern hemlock sections were sawed from air-dry material, the past history of which was unknown. In all cases transverse sections more than one tracheid length in thickness, sawed from clear pieces of wood cut parallel with the grain, were employed. The numbers by which the wood sections in each group are designated indicate their relative positions in the original piece of wood.

The following liquids and chemicals were used: water (freshly distilled), hexane (Eastman, Practical Grade), nitrobenzene (Eastman, C.P.), bromobenzene (Eastman, C.P.), kerosene ("composed of predominantly straight chain hydrocarbons" furnished by The Atlantic Refining Company), benzene (C.P., thiophene-free), and inorganic salts (C.P.).

THE EXPERIMENTAL FINDINGS

The influence of moisture content upon the permeability of wood

In all of Stamm's work (15), dealing with the determination of the maximum effective diameters of the pores in the pit membranes of coniferous wood, water was the liquid displaced from the pit membrane capillaries. The pore sizes consequently were those existing at the fiber-saturation point. It seemed of interest therefore to investigate the influence of varying amounts of water present in the cell wall upon the maximum effective diameters of the openings between the cells. This was done by determining the pressure necessary to overcome the surface tension of benzene in sections of balsam fir heartwood (1.40 cm. in thickness) which were at different moisture contents. These sections were sawed from a freshly felled log and slowly dried to approximately 6 per cent in moisture content. They then were transferred to three chambers in which different relative humidities were maintained, and were permitted to take up moisture until

they had reached approximate equilibrium. Taken from the different humidity conditions the sections were immediately submerged in benzene, and determinations made of the gas pressure necessary to overcome the surface tension of benzene in the maximum effective intercellular openings. The values obtained in this manner may be used for comparative purposes as being inversely proportional to the maximum effective openings through the wood section. The data are shown graphically in figure 2. The result for each moisture content is an average for five wood sections.

Another method of ascertaining the influence of moisture content upon the effective size of the openings between the cells of wood also was employed. This consisted of determining the rate of flow of an organic liquid

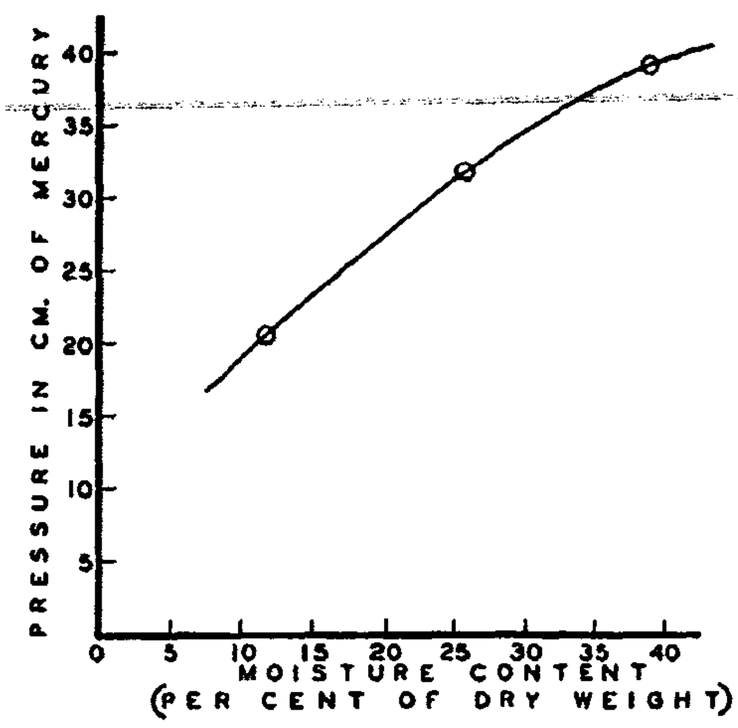

FIG. 2. THE EFFECT OF MOISTURE CONTENT UPON THE PRESSURE REQUIRED TO OVERCOME THE SURFACE TENSION OF BENZENE IN THE MAXIMUM EFFECTIVE INTERCELLULAR OPENINGS OF BALSAM FIR HEARTWOOD

through wood sections which had been previously brought to equilibrium with different relative humidities. This method gives a basis of comparison for the change in effectiveness of the average diameters of the openings between the cells of wood; the more rapid the rate of flow the greater the effectiveness of the average diameters.

Sections of Norway pine (1.3 cm. in thickness) were sawed from freshly felled logs and slowly dried to approximately 6 per cent moisture content. After drying the sections were permitted to take up moisture to equilibrium with different relative humidities. These sections then were taken from the different relative humidities, submerged in the organic liquid, and determinations made immediately of the rate of flow of the organic liquid through them. The average rate of flow in cubic centimeters per

minute for the first 10 cc. forced through the section was taken as the measure of permeability. Care was taken not to allow any appreciable exposure of the sections to the air; while the sections were in the apparatus they were surrounded by a bath of the organic liquid which prevented any appreciable loss of moisture.

The results obtained for the rate of flow of benzene, a non-polar organic liquid, through Norway pine sapwood are shown graphically in figure 3. The rate of flow for each moisture content is an average for two wood sections. A pressure of 26.0 cm. of mercury was used for all of these determinations.

The data for the rate of flow of nitrobenzene, a polar organic liquid, through Norway pine sapwood at different moisture contents are given in

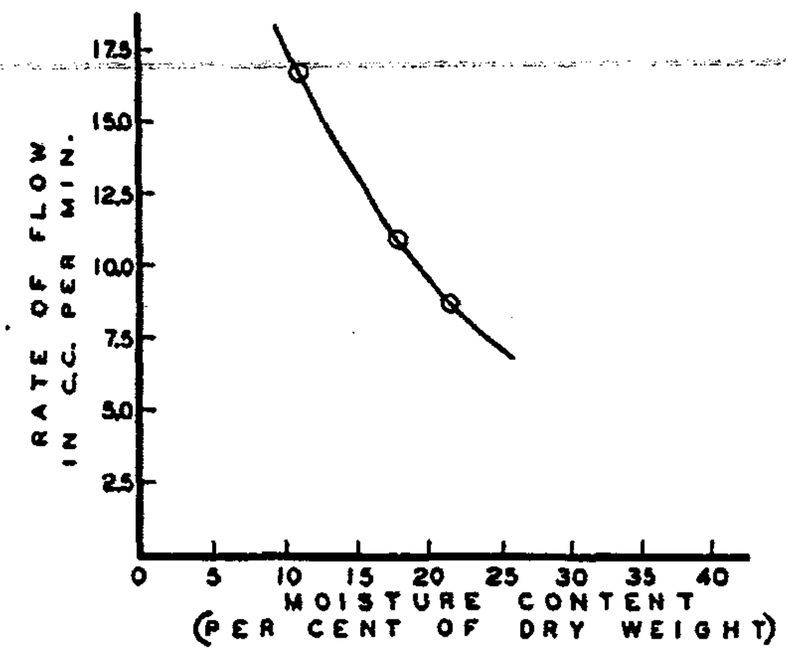

FIG. 3. THE EFFECT OF MOISTURE CONTENT UPON THE RATE OF FLOW OF BENZENE THROUGH NORWAY PINE SAPWOOD

Pressure, 26.0 cm. of mercury

table 1. A pressure of 119.8 cm. of mercury was used for all of these determinations.

Assuming that the intercellular openings in wood are through the membranes of the pits, the data in figures 2 and 3 and table 1 show that the maximum and average effective diameters of the pores in the pit membranes became smaller with increasing moisture content of the wood below the fiber-saturation point. The results do not, however, offer an exact measure of the change in effectiveness of these openings with moisture content. Factors such as slight changes in moisture content during the handling of the sections and the possibility of flow through the resin canals of Norway pine would tend to modify the relationship between the effective diameters of the openings in the pit membranes and moisture content. The results can therefore only be interpreted as illustrating the

trend of the influence of the moisture content of wood below the fiber-saturation point upon the effective diameters of the openings in the pit membranes.

Influence of pressure upon the rate of flow of water through wood

Sections of balsam fir (1.10 cm. in thickness), Norway pine sapwood (1.24 cm. in thickness), white spruce sapwood (1.33 cm. in thickness), Northern white cedar (1.24 cm. in thickness), Western red cedar (1.18 cm. in thickness), and Eastern hemlock (1.35 cm. in thickness) were used in these experiments. The balsam fir, Norway pine, and white spruce sections were obtained from freshly felled logs. Paired sections of each of the three woods were divided into two groups. Sections of one group were

TABLE 1

Effect of moisture content upon the rate of flow of nitrobenzene through Norway pine sapwood

Pressure 119.8 cm. of mercury

NUMBER OF THE SECTION	MOISTURE CONTENT OF THE SECTION*	RATE OF FLOW
	per cent	*cc. per minute*
9	Av. = 6.56	6.70
24		21.05
34		10.43
		Av. = 12.73
2	Av. = 15.65	2.54
22		5.31
33		4.69
		Av. = 4.18

* The moisture content given is an average obtained for three sections similarly treated.

given a seasoning treatment, while those of the other group were immediately placed in distilled water. The Norway pine and white spruce sections designated as seasoned, were slowly dried to approximately 4 per cent moisture content. The balsam fir sections designated as seasoned were first dried to approximately 4 per cent moisture content and then were dried to a constant weight at 105°C. (a 6-hour drying period was used). The Northern white cedar, Western red cedar, and Eastern hemlock sections were obtained from air-dried material which had a moisture content of approximately 8 per cent at the time of preparation. These sections, together with the seasoned sections of balsam fir, Norway pine and white spruce, were placed in distilled water.

Both the seasoned and unseasoned sections were allowed to soak for at least two weeks before testing their permeability. The soaking was car-

ried out in a desiccator, and an intermittent vacuum was applied to facilitate the complete removal of air from the cells.

After the soaking period the sections were placed in the apparatus and water forced through them until an approximately constant rate of flow was obtained. In attaining the constant rate of flow a decreasing rate of flow with time from the initial rate was observed in all cases except in several runs with white spruce sapwood. In these runs it was observed that the decreasing rate of flow was preceded by an increase from the initial rate. After a constant rate of flow had been obtained, higher pressures were applied and the new rate of flow determined for each of the pressures. Values for the rate of flow then were obtained by decreasing the pressure and observing the rate of flow at lower pressures. The values obtained in this manner were in close agreement for the same pressure whether the rate of flow was determined by going from a lower to higher pressure or *vice versa*, providing that sufficient time was allowed for the sections to return to a constant rate with the lower pressures. In the case of white spruce and Norway pine it was observed that the return to the constant rate of flow was very rapid. In the case of balsam fir and the other woods which gave a pronounced disproportionate rate of flow with increased pressures, it was observed that longer periods of time were required to return to a constant rate of flow with the lower pressures. The results obtained for the rate of flow of water through both seasoned and unseasoned woods are given in table 2. The value given in each case is an average of the results for three sections of each wood both seasoned and unseasoned.

The data given in table 2 and figure 4 show that the influence of pressure on the rate of flow is characteristic of the kind of wood. Seasoning of the wood previous to use did not significantly alter the relationship between pressure and the rate of flow for white spruce, Norway pine, and balsam fir. This is particularly illustrated by the results for balsam fir, because the unseasoned sections of this wood were not dried after they were sawed from a freshly felled log, while the seasoned sections were oven-dried. Table 3 gives the results for both the seasoned and unseasoned individual sections of balsam fir heartwood.

Likewise seasoning did not appear to cause any pronounced permanent changes in the permeability of the woods to water. This would seem to indicate that when the sections were seasoned in the manner previously described, either seasoning did not increase pit aspiration in the manner observed by Griffin (5) or more importance has been attributed to this condition than it deserves. In fact, in the cases of balsam fir and white spruce the rate of flow was more rapid at any pressure for the seasoned than for the unseasoned wood. For Norway pine the situation was reversed; the unseasoned wood was the more permeable. However, the

TABLE 2

Influence of pressure upon the rate of flow of water through seasoned and unseasoned coniferous woods

KIND OF WOOD	TREATMENT	PRESSURE	RATE OF FLOW	RATE OF FLOW
		kg. per sq. cm.	*cc. per minute*	*per cent*
Balsam fir heartwood	Seasoned (oven-dried)	1.8	0.092	2.56
		3.5	0.534	14.85
		5.3	1.553	43.19
		7.0	3.596	100.00
Balsam fir heartwood	Unseasoned	1.8	0.062	2.34
		3.5	0.429	16.19
		5.3	1.186	44.75
		7.0	2.650	100.00
Norway pine sapwood	Seasoned	1.8	2.35	16.78
		3.5	5.83	41.64
		5.3	9.66	69.00
		7.0	14.00	100.00
Norway pine sapwood	Unseasoned	1.8	3.01	20.62
		3.5	6.60	45.21
		5.3	10.61	72.67
		7.0	14.60	100.00
White spruce sapwood	Seasoned	1.8	0.171	25.15
		3.5	0.345	50.73
		5.3	0.507	74.56
		7.0	0.680	100.00
White spruce sapwood	Unseasoned	1.8	0.141	25.59
		3.5	0.289	52.45
		5.3	0.425	77.13
		7.0	0.551	100.00
Northern white cedar heartwood	Seasoned	1.8	0.082	4.83
		3.5	0.392	23.09
		5.3	0.971	57.18
		7.0	1.698	100.00
Western red cedar heartwood	Seasoned	1.8	0.237	3.66
		3.5	1.580	24.39
		5.3	3.722	57.46
		7.0	6.477	100.00
Eastern hemlock heartwood	Seasoned	1.8	0.157	5.27
		3.5	0.725	24.34
		5.3	1.657	55.64
		7.0	2.978	100.00

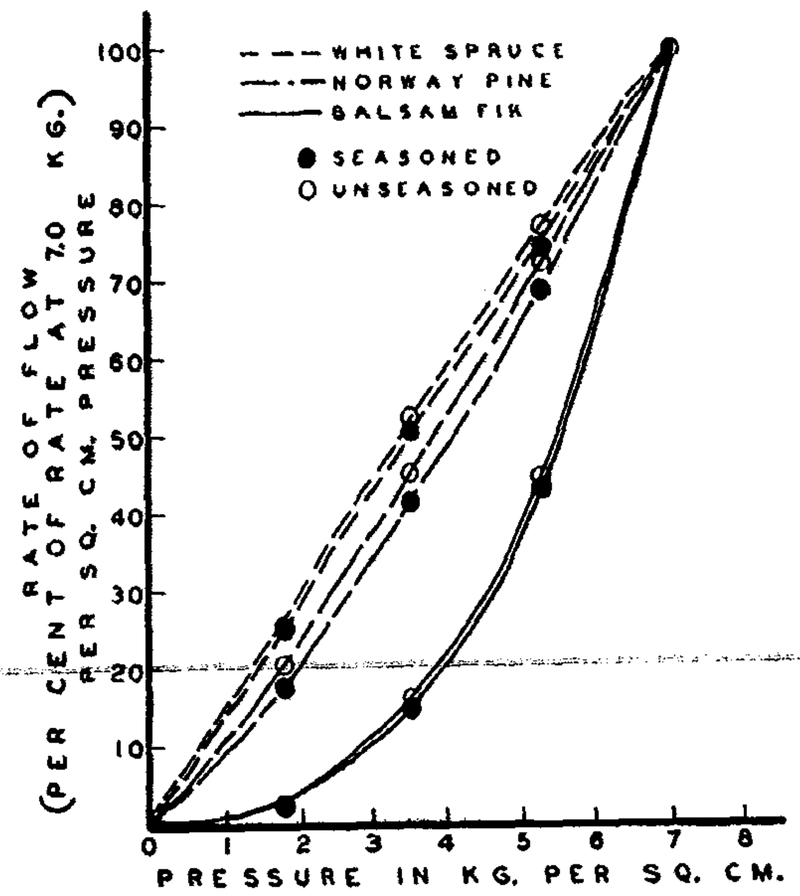

FIG. 4. THE EFFECT OF PRESSURE UPON THE RATE OF FLOW OF WATER THROUGH SEASONED AND UNSEASONED BALSAM FIR HEARTWOOD, NORWAY PINE SAPWOOD, AND WHITE SPRUCE SAPWOOD

TABLE 3

Variability of the influence of pressure upon the rate of flow of water through seasoned and unseasoned balsam fir heartwood

TREATMENT	PRESSURE	RATE OF FLOW					
		Section No. 19		Section No. 21		Section No. 26	
	kg. per sq. cm.	*cc. per minute*	*per cent*	*cc. per minute*	*per cent*	*cc. per minute*	*per cent*
Unseasoned	1.8	0.084	1.90	0.058	2.61	0.044	3.26
	3.5	0.722	16.30	0.333	15.00	0.231	17.11
	5.3	2.009	45.36	0.969	43.65	0.580	42.96
	7.0	4.429	100.00	2.220	100.00	1.300	100.00
		Section No. 16		Section No. 20		Section No. 22	
		cc. per minute	*per cent*	*cc. per minute*	*per cent*	*cc. per minute*	*per cent*
Seasoned (oven-dried)	1.8	0.132	2.52	0.081	2.79	0.064	2.41
	3.5	0.771	14.74	0.441	15.20	0.391	14.72
	5.3	2.213	42.30	1.301	44.85	1.145	43.11
	7.0	5.232	100.00	2.901	100.00	2.656	100.00

differences in observed permeability were within the limits of variation of individual samples treated in the same manner, and for this reason caution is necessary in the interpretation of the results.

The results obtained for the relationship between pressure and the rate of flow of water through Norway pine, white spruce, balsam fir, and Northern white cedar are in general agreement with those reported by Sutherland, Johnston, and Maass (17) for heartwood of the same four woods. Sutherland, Johnston, and Maass concluded that the different relationships between pressure and rate of flow obtained for different woods perhaps could be explained on the basis of a varying thickness of the effective pit membranes. They reasoned that pressure would cause a stretching of the thin pit membranes, resulting in an increase in size of the pit membrane pores, and consequently the relative importance of this effect of pressure would vary for pit membranes of different thickness.

It also seems possible that the effect of pressure on the rate of flow of liquids through coniferous wood may be modified somewhat by the presence of structures such as resin canals. Of the six woods used in this study Norway pine and white spruce possess resin canals, while the other woods do not. If we assume, as has been done in this study, that the flow of liquids between tracheids is through the pores in the pit membranes, it follows that for woods which do not possess resin canals the flow was entirely of this type. For white spruce and Norway pine the resin canals may have contributed to the flow. If this is the case, then it is certainly conceivable that a different relationship between pressure and rate of flow exists when a portion of the liquid is moving through a comparatively large opening such as a resin canal, than when the movement is confined to the small openings in the thin pit membranes.

The movement of organic liquids and aqueous salt solutions through wood

Sections of balsam fir heartwood (1.00 cm. in thickness) and Norway pine sapwood (1.33 cm. in thickness) sawed from freshly felled logs were used in these determinations.

The sections used with the organic liquids were gradually dried to equilibrium under controlled humidity. Moisture determinations made after the sections had attained equilibrium showed that two samples of Norway pine sapwood had moisture contents of 24.63 per cent and 24.71 per cent, and two samples of balsam fir heartwood had moisture contents of 21.08 per cent and 21.01 per cent.

The sections were taken from the humidity chambers and transferred to the apparatus in weighing bottles. Thus the sections were not exposed to the air for any appreciable length of time. The term "initial rate of flow" is used to designate the rate of flow after 1 cc. of the liquid had been forced through the section.

TABLE 4

Rate of flow of several organic liquids and water through balsam fir heartwood

Pressure 1.8 kg. per square centimeter

TIME		HEXANE		BENZENE		WATER		BROMOBENZENE		KEROSENE		NITROBENZENE	
		Section No. 2	Section No. 11	Section No. 4	Section No. 12	Section No. 6	Section No. 7	Section No. 8	Section No. 14	Section No. 5	Section No. 9	Section No. 1	Section No. 10
		Rate of flow in cc. per minute											
hours	*minutes*												
0	00	2.500	2.308	1.600	1.429	1.091	0.800	1.200	1.463	0.984	0.923	0.282	0.209
0	30	2.222	2.069	1.429	1.333	0.582	0.385	0.800	1.071	0.698	0.606	0.0977	0.0904
1	30	2.143	1.936	1.367	1.250	0.375	0.235	0.594	0.800	0.606	0.526	0.0640	0.0549
2	30	2.105		1.333	1.200		0.167		0.667	0.556	0.456	0.0526	0.0400
3	30		1.875			0.239	0.142				0.415	0.0456	0.0310
4	30							0.432				0.0319	0.0243
5	30						0.120	0.417					0.0210
		Rate of flow in percentage of the initial rate											
0	00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
0	30	88.88	89.64	89.31	93.28	53.34	48.12	66.67	73.20	70.94	65.66	34.64	43.25
1	30	85.72	83.88	85.44	87.47	34.37	29.38	49.50	54.68	61.59	56.99	22.69	26.27
2	30	84.20		83.31	83.97		20.88		45.59	56.50	49.40	18.65	19.14
3	30		81.24			21.91	17.75				44.96	16.17	14.83
4	30							36.00				11.31	11.63
5	30						15.00	34.75					10.05
Viscosity at 25°C. in centipoises		0.33		0.60		0.89		1.07		1.23		1.85	

The results for the rate of flow through balsam fir heartwood are given in table 4. A pressure of 1.8 kg. per square centimeter was used for all of these determinations.

The values given in table 4 for the rate of flow in cubic centimeters per minute of nitrobenzene (section No. 10), kerosene (section No. 9), and

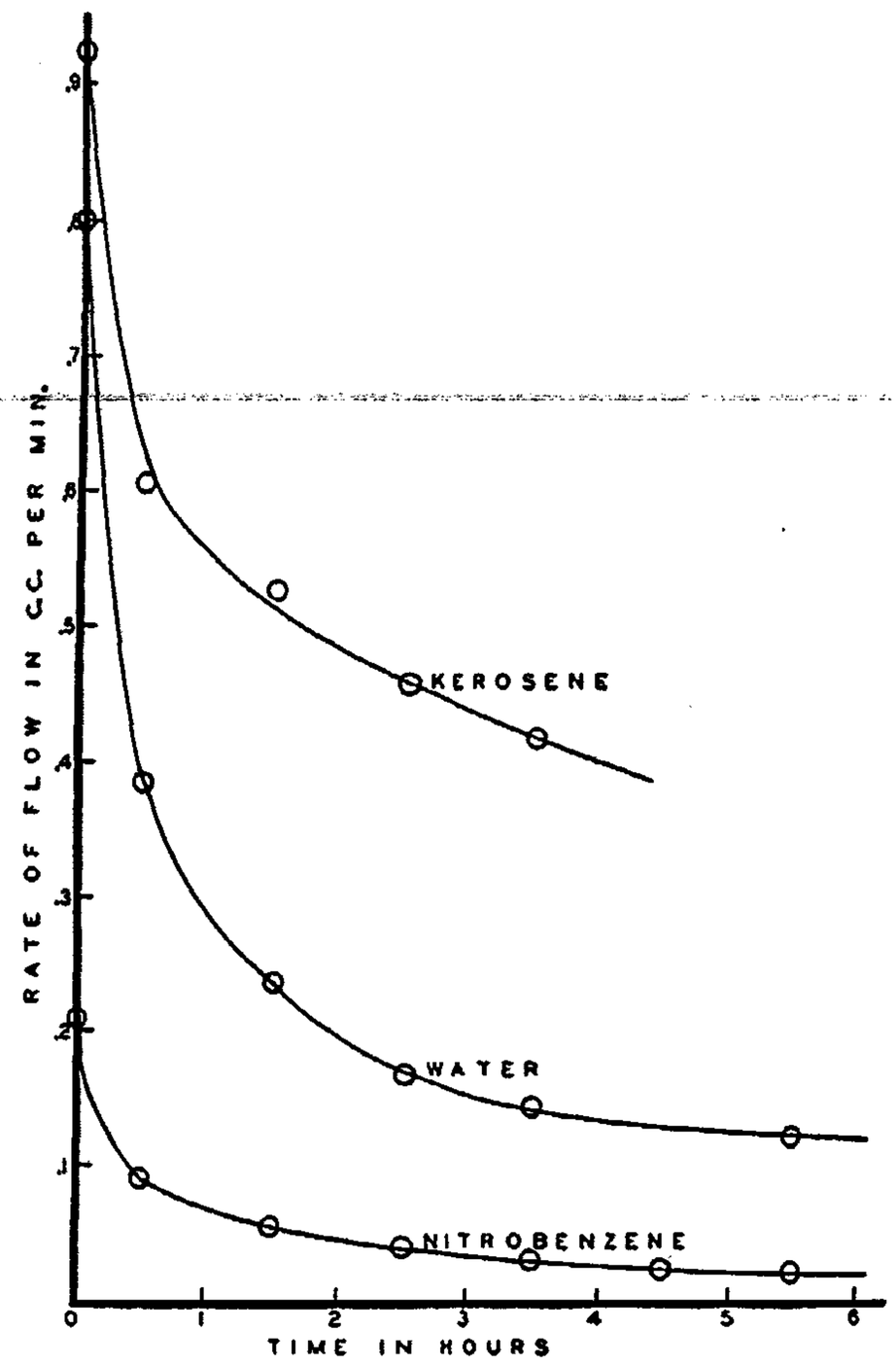

FIG. 5. RATE OF FLOW OF KEROSENE, WATER, AND NITROBENZENE THROUGH BALSAM FIR HEARTWOOD

Pressure, 1.8 kg. per square centimeter

water (section No. 7) are shown graphically in figure 5. The values given in table 4 for the rate of flow in percentage of the initial rate for sections Nos. 7, 8, 9, 10, 11, and 12 are shown graphically in figure 6.

Table 5 gives the data for the rate of flow of benzene, kerosene, and nitrobenzene through Norway pine sapwood. A pressure of 23.0 cm. of mercury was used for all of these determinations.

The balsam fir heartwood sections used with the aqueous salt solutions were submerged in distilled water immediately after preparation and allowed to soak for at least two weeks under the influence of an intermittent vacuum. The sections then were placed in the apparatus and water forced through them, under a pressure of 76.5 cm. of mercury, until an equilibrium rate of flow was obtained. The water then was replaced with the desired salt solution. The initial rate of flow and the change in rate of flow with time were determined for the salt solution. The initial rate of flow in this case was the value observed after approximately 0.5 cc. of

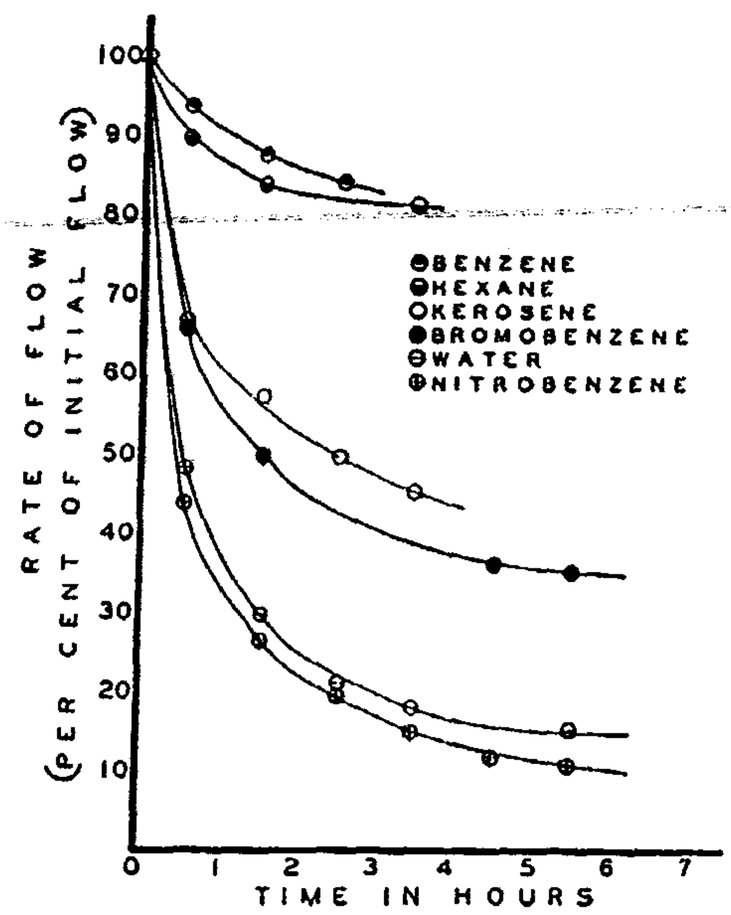

FIG. 6. CHANGES IN THE RATE OF FLOW WITH TIME OF WATER AND SEVERAL ORGANIC LIQUIDS THROUGH BALSAM FIR HEARTWOOD
Pressure, 1.8 kg. per square centimeter

the solution had been forced through the section. The salt solutions used were 0.1 normal solutions of zinc chloride, potassium chloride, mercuric chloride, and aluminum chloride, and a 0.01 normal solution of thorium chloride. The results for the different salt solutions are shown graphically in figure 7. The rate of flow is expressed as a percentage of the equilibrium rate of flow for water.

The data given in tables 4 and 5 and figures 5, 6, and 7 show that the rate of flow of liquids of widely different properties through wood cannot be predicted necessarily from their viscosities. The data in table 4 show that kerosene having a viscosity of 1.23 centipoises gave an initial rate of

flow approximately four times that for nitrobenzene and a rate of flow at the end of 3.5 hours about thirteen times that for nitrobenzene. Water with a viscosity of 0.89 centipoise, had an initial rate of flow slightly less than that for kerosene and a rate of flow at the end of 3.5 hours approximately one-third the rate for kerosene and four times the rate for nitrobenzene. From the standpoint of a direct viscosity relationship, the rate

TABLE 5

Rate of flow of several organic liquids through Norway pine sapwood

Pressure 23.0 cm. of mercury

TIME		BENZENE		KEROSENE		NITROBENZENE	
		Section No. 37	Section No. 40	Section No. 38	Section No. 39	Section No. 28	Section No. 36
Rate of flow in cc. per minute							
hours	*minutes*						
0	00	7.500	5.854	4.000	2.670	1.163	1.463
0	30	8.570	5.333	3.200	2.449	0.566	0.895
1	30	8.450	5.217	2.105	1.644	0.486	0.674
2	20	7.321	5.217	1.644	1.333	0.392	0.529
3	30			1.558	1.121	0.344	0.400
4	30			1.500		0.314	0.360
5	30					0.289	0.322
6	30						0.312
Rate of flow in percentage of the initial rate							
0	00	100.00	100.00	100.00	100.00	100.00	100.00
0	30	114.57	91.10	80.00	91.72	48.67	61.18
1	30	112.67	89.12	52.62	61.57	41.79	46.07
2	30	97.61	89.12	41.10	49.92	33.71	36.16
3	30			38.95	41.98	29.58	27.34
4	30			37.50		27.00	24.61
5	30					24.85	22.01
6	30						21.33
Viscosity at 25.0°C. in centipoises		0.60		1.23		1.85	

of flow for water should be about twice the rate for nitrobenzene, but the value actually obtained was about four times the rate. Also on the basis of purely viscosity considerations the rate of flow of benzene should have been about three times the rate for nitrobenzene, yet the initial rate for benzene was about six times and at the end of 2.5 hours was about twenty-seven times the value for nitrobenzene.

The relationships obtained for Norway pine sapwood, table 5, are in

general agreement with those obtained for balsam fir heartwood. However, the differences in rates of flow of the different liquids were not of the same magnitude as those for balsam fir heartwood.

The data given in figure 7 show that pronounced deviations from purely viscosity considerations exist for the flow of different salt solutions through

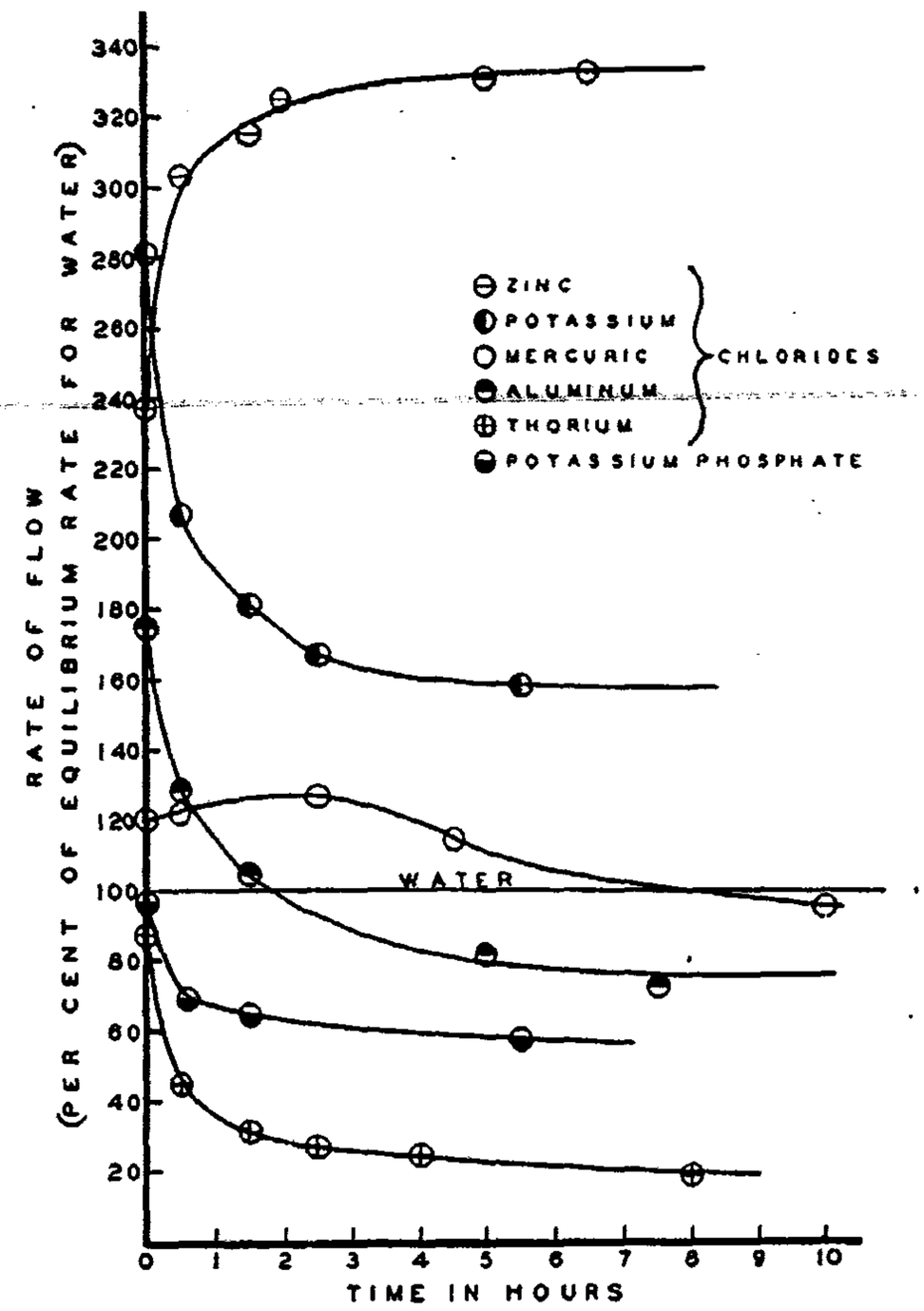

FIG. 7. CHANGES IN THE RATE OF FLOW WITH TIME OF SEVERAL SALT SOLUTIONS THROUGH BALSAM FIR HEARTWOOD

Pressure, 76.5 cm. of mercury

balsam fir heartwood. The zinc chloride solution flowed through the wood sections more than three times as rapidly as water, while the rate of flow of the thorium chloride solution was only about one-sixth as rapid as water. These differences are more pronounced if the two salt solutions are compared. When considered in this manner, the rate of flow of the zinc chloride solution through balsam fir heartwood was approximately eight-

een times that of the thorium chloride solution, yet the viscosities of the different salt solutions, for the concentrations used, are not greatly different from that of water.

The results obtained for the flow of organic liquids and salt solutions through coniferous wood show that factors other than viscosity determine in a considerable measure the rates of flow through wood of liquids possessing widely different properties. Factors such as the influence of the liquids upon the effective diameters of intercellular openings must be considered. Shrinking, swelling, or a solution of materials from these openings would alter the rate of flow of liquids through wood. Bull (4) also has pointed out that with small capillaries (0.1 μ) electrical "back pressure" may play an important rôle in the flow of organic liquids such as nitrobenzene. In addition, polar liquids such as nitrobenzene should be expected to be strongly adsorbed and highly oriented on the surface of the pit membrane capillaries. It may well be that these adsorbed oriented molecules are an effective agent in reducing the area of the pores in the pit membranes; certainly they, as well as the tetravalent thorium ions, will materially affect the surface electrical properties of such capillary openings.

A comparison of the results obtained for the flow of organic liquids through Norway pine sapwood and balsam fir heartwood indicates that the relative importance of factors other than viscosity would vary with the kinds of wood. It seems that different woods may be expected to show different behavior. The presence and effectiveness of structures such as resin canals, variation in the size of the pores in the pit membranes, and the presence of extraneous materials such as resins in the effective openings of the pit membrane pores are perhaps only some of the factors which would tend to make one wood behave differently from another.

SUMMARY

1. A study was made of: (1) the relative effectiveness of the maximum and average pore diameters of the openings in the pit membranes for wood at different moisture contents, (2) the influence of pressure upon the rate of flow of water through wood, and (3) the movement of organic liquids and salt solutions through wood.

2. The maximum and average effective diameters of the pores in the pit membranes were found to vary with the moisture content of the wood: below the fiber-saturation point effective pore diameters decreased with increasing moisture content.

3. The influence of pressure upon the rate of flow of water through wood is a characteristic of the kind of wood.

4. The relationship between pressure and the rate of flow of water through wood perhaps is influenced by factors such as the thickness of the pit membrane and the presence and effectiveness of resin canals.

5. The relationship between pressure and the rate of flow of water through several woods was not changed significantly by drying of the wood previous to use.

6. Drying previous to use did not appear to cause pronounced permanent changes in the permeability of the woods to water.

7. The rate of flow of organic liquids and aqueous salt solutions could not be predicted necessarily from the viscosities of these liquids. The same was true for the rate of flow of organic liquids through Norway pine sapwood.

8. Evidence was obtained which indicates that the magnitude of the deviations from a viscosity relationship for the flow of organic liquids would be different for different kinds of wood.

9. The decrease in rate of flow with time through balsam fir heartwood for benzene, bromobenzene, and nitrobenzene increased with increasing polarity of the liquid.

10. It would seem that the movement of liquids of widely different properties in wood cannot be predicted necessarily from the viscosity alone. Other factors such as the influence of the liquid upon the effective capillary dimensions of the openings in wood and the possible effect of electrical "back pressure" on the flow of polar organic liquids must be considered. The relative importance of factors other than viscosity can perhaps be expected to vary with the kinds of wood and the properties of the liquids.

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THERMODYNAMICS OF THE SWELLING OF WOOD

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Received June 14, 1934

Although the swelling of a number of colloidal materials has been studied intensely, little attention has been given the thermodynamic aspects of swelling. This lack of attention is perhaps because the major part of sorption and swelling data are not subject to thermodynamic calculations. Katz (2) has pointed out that thermodynamics deals only with true equilibrium conditions and hence such effects as those of sorption and swelling hysteresis and changing surface of sorption during a single cycle must be eliminated in order that the results have theoretical significance.

Katz (2) has compared the differential heats of swelling in water obtained from thermal data with the changes in free energy of swelling calculated from moisture content–vapor pressure data for cotton, wood, and casein, using the equation

$$-\Delta F = \frac{RT}{M} \ln \frac{P}{P_0} \tag{1}$$

in which $-\Delta F$ is the change in free energy in gram-calories occurring when 1 g. of liquid is added to an infinite amount of swelling material at a moisture content in equilibrium with the relative vapor pressure $\frac{P}{P_0}$, R being the gas constant, T the absolute temperature, and M the molecular weight of the liquid. Since the differences between the differential heats of swelling and the changes in free energy of swelling were small, he concluded that they were within the range of experimental error and that consequently the entropy change was negligible.

Fricke and Lüke (1), however, have shown that this is by no means the case. They determined both the integral heat of swelling at different moisture content values and the moisture content–relative vapor pressure relationship at two different temperatures for agar-agar, casein, and keratin

[1] Maintained at Madison, Wisconsin, by the Forest Service of the U. S. Department of Agriculture, in coöperation with the University of Wisconsin.

swelling in water. They were thus able to calculate the differential heat of swelling, using the integrated form of the Clausius-Clapeyron equation

$$\Delta H = \frac{RT_1T_2}{M(T_2 - T_1)} \ln\left(\frac{P_2}{P_1} - \frac{P_{0_2}}{P_{0_1}}\right) \tag{2}$$

in which ΔH is the change in the heat of swelling in gram-calories occurring when 1 g. of the liquid is added to an infinite amount of swelling material at a moisture content in equilibrium with the vapor pressure P_2 at the temperature T_2 and the vapor pressure P_1 at the temperature T_1, P_{0_2} and P_{0_1} being the corresponding saturation vapor pressures and the other symbols having the same significance as in equation 1. In these calculations as well as in those for obtaining $-\Delta F$ the averages between desorption and adsorption moisture contents corresponding to each relative vapor pressure were used as an approximate means of eliminating the effects of hysteresis. The values for ΔH calculated in this way agreed very well with the values obtained from the thermal measurements, thus substantiating the validity of the theoretical equation. Values of $-\Delta F$ calculated from the vapor pressure data were in all cases less than the corresponding values of ΔH, showing that a definite entropy change ΔS accompanies swelling; thus

$$\Delta S = \frac{\Delta H - (-\Delta F)}{T} \tag{3}$$

Katz (3) has recently admitted the validity of Fricke and Lüke's findings, and suggests that the increase in entropy occurring during swelling is due to an orientation or compression of the water molecules, which become adsorbed on the surface of the swelling material, or to an association of these molecules.

In connection with a study of the seasoning of wood, the Forest Products Laboratory recently had occasion to collect moisture content–relative vapor pressure–temperature data on the drying of wood. As these data were obtained under conditions which practically eliminate hysteresis effects, it seemed worth while to subject them to thermodynamic analysis.

The equilibrium moisture content determinations were made in four specially designed drying chambers, each of which had a capacity of about 16 cu. ft. The chambers were equipped with electrically driven blowers which moved the air uniformly through the drying compartments at a rate of about 100 ft. per minute. The wet- and dry-bulb temperatures in each kiln were under the control of a thermostat of the vapor tension type. The drying conditions in the chambers were read frequently through glass windows.

The dry-bulb temperature oscillated on an average about ¼°F. above and below the desired value, while the wet-bulb temperature had a total positive and negative amplitude of about ½°F. The wet- and dry-bulb cycles would sometimes be out of phase 180°, with the result that the wet-bulb depression was sometimes ¾°F. greater or less than desired. The maximum amplitude of relative vapor pressure oscillations at the higher temperatures was from 1.5 to 3.0 per cent for different vapor pressures, and at the lower temperatures from 4.0 to 8.0 per cent.

From twenty-five to forty strips of green flat-sawed Sitka spruce were used in determining the equilibrium moisture content for a given temperature and relative vapor pressure. The strips were cut about 3 mm. thick and weighed from 100 to 125 g. each when in an oven-dry condition. The specimens were suspended from lead stoppers located in the roof of the chambers and were weighed *in situ* during the drying process to 0.05 g.

The hysteresis phenomenon encountered in desorption and adsorption measurements made on very small specimens under the most carefully controlled vapor pressure conditions was largely eliminated in these measurements. The specimens used were sufficiently large to permit the setting up of moisture gradients across the sections during the process of drying. This combined with the oscillations in vapor pressure permit alternate desorption and adsorption to take place, thus tending to establish an intermediate moisture content equilibrium. The appreciable reduction in hysteresis obtained in this way is illustrated in figure 1 by the oscillating vapor pressure–desorption curve. The normal desorption and the adsorption curves shown in figure 1 were obtained by Seborg and Stamm (5) by using very small cross sections of wood suspended from quartz helical balances in thermostatically controlled (25° ±0.02°C.) tubes through which air humidified over saturated salt solutions was passed. These carefully controlled conditions tend to promote the maximum hysteresis effect. All the available drying data obtained under industrial control conditions on other softwood species also gave curves which fell within this hysteresis loop. The oscillating vapor pressure–desorption curve approaches more nearly the normal desorption curve at high relative vapor pressures and the adsorption curve at low relative vapor pressures. This would be expected on the basis of Urquhart and Williams' (8) explanation of the hysteresis loop. In the initial desorption the maximum number of the hydroxyl groups of the amylene oxide chains of cellulose are satisfied by water. When the material approaches the dry state these hydroxyl groups are drawn closer and closer together as a result of shrinkage, and they finally mutually satisfy each other. On adsorption part of these hydroxyl groups are not freed for water adsorption, thus accounting for the decreased moisture equilibrium values. Oscillating vapor pressure conditions at high relative vapor pressures hence have only a

slight tendency to cause the hydroxyl groups of the cellulose mutually to satisfy each other, whereas this tendency becomes appreciable at low relative vapor pressures.

The dotted line in figure 1 connecting the origin with the saturation point represents the sorption conditions that would be attained if Henry's law were followed. This line is tangent at the origin to the curve for hysteresis-free sorption, showing that Henry's law is obeyed at infinitesimal concentrations.

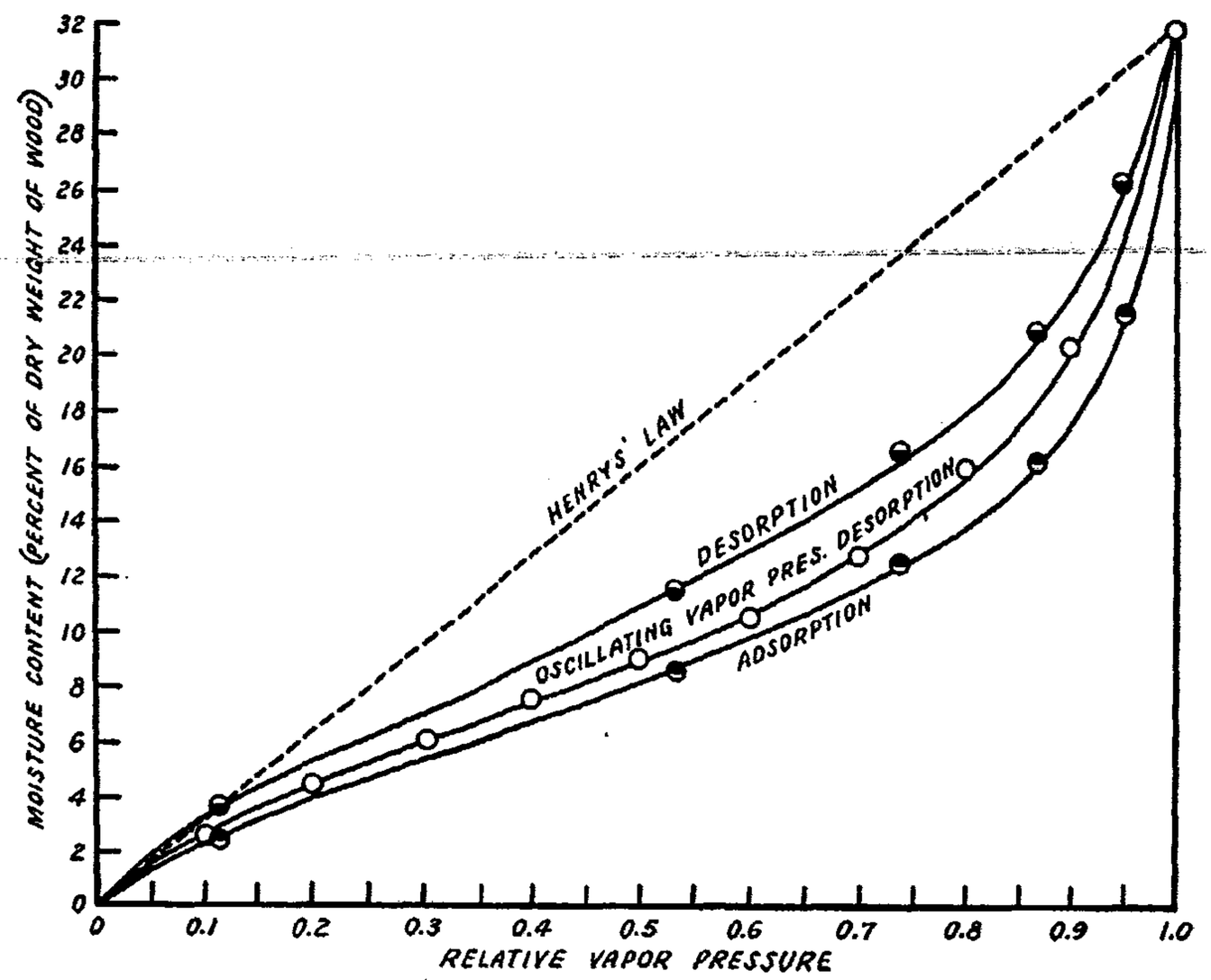

FIG. 1. MOISTURE CONTENT–RELATIVE VAPOR PRESSURE RELATIONSHIP FOR SITKA SPRUCE UNDER NORMAL DESORPTION AND ADSORPTION CONDITIONS AND UNDER OSCILLATING VAPOR PRESSURE DESORPTION CONDITIONS AT 25°C.

In figure 2 the moisture content–relative vapor pressure isotherms for Sitka spruce are plotted for 10°F. temperature intervals from room temperature to the boiling point of water. The changes in the fiber-saturation points (saturation moisture content) with temperature are given in figure 3. The fiber-saturation points change linearly with the temperature, increasing approximately 0.1 per cent for a decrease in temperature of 1°C.

In figure 4 are plotted the differential heats of swelling calculated with the aid of equation 2 from the data of figure 2 together with differential

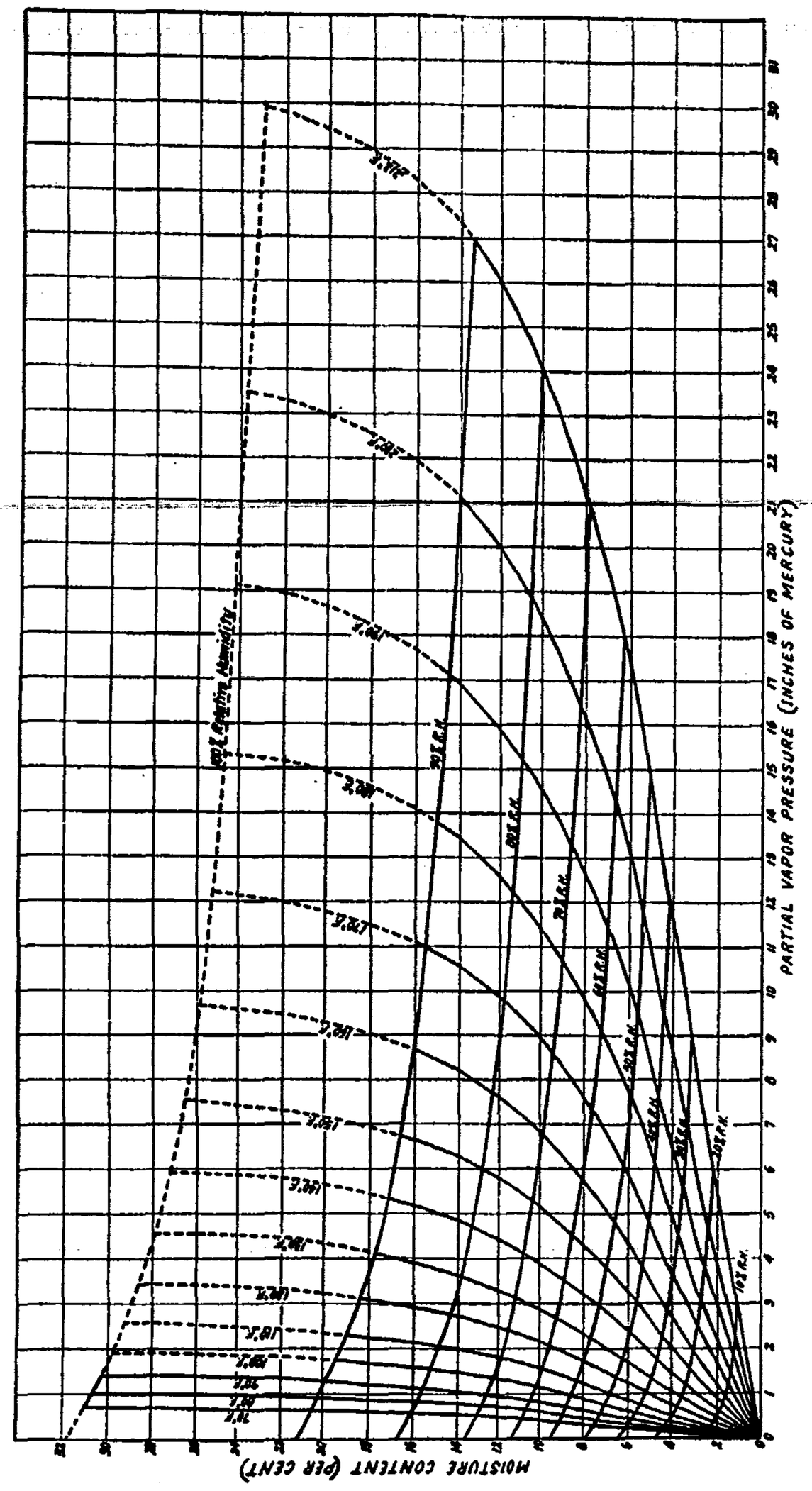

FIG. 2. THE MOISTURE CONTENT OF SITKA SPRUCE AT EQUILIBRIUM WITH VARIOUS TEMPERATURES, PARTIAL VAPOR PRESSURES, AND RELATIVE HUMIDITIES UNDER OSCILLATING VAPOR PRESSURE CONDITIONS

The solid lines in the curves are based on experimental data; the dotted parts of the lines are calculated

heat of swelling obtained from the integral heat of swelling data of Volbehr (9). The 87.8°C. curve was calculated from the 200° and 180°F. isotherms, the 71.1°C. curve from the 200° and 120°F. isotherms, and the 54.4°C. curve from the 140° and 120°F. isotherms. The 0°C. curve is the experimental curve of Volbehr. Below 6 per cent moisture content the curves are all identical within experimental error. Above this moisture content the values of ΔH increase with a decrease in temperature. Volbehr's experimental values for pine are in complete accord with the calculated values given for Sitka spruce. The agreement between species is not surprising, as practically all softwoods have almost identical fiber-saturation points (7) and would be expected to have similar adsorptive powers.

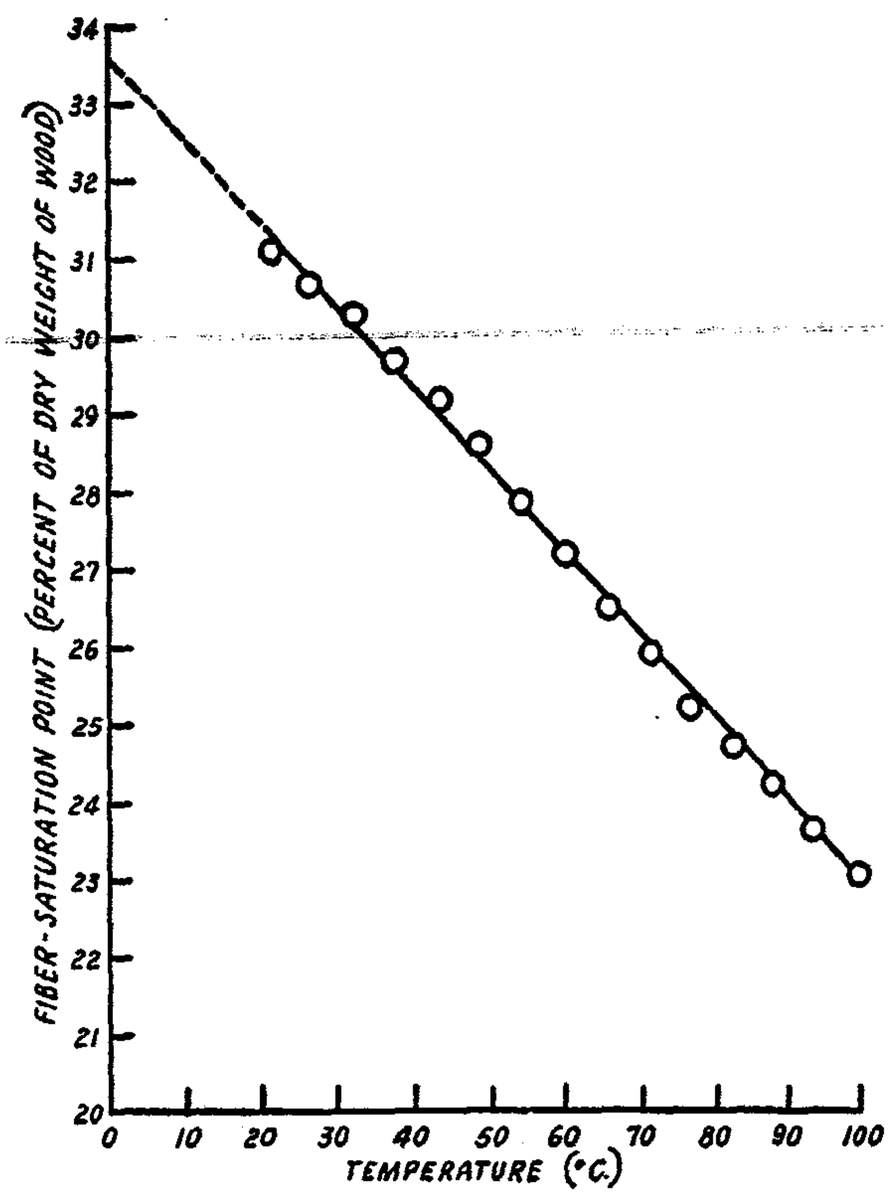

FIG. 3. CHANGE IN FIBER-SATURATION POINT WITH TEMPERATURE FOR SITKA SPRUCE

In figure 5 are plotted the isosteres, logarithm of vapor pressure against the reciprocal of the absolute temperature, for a number of different moisture content values from the data of figure 2. The linear isosteres at the

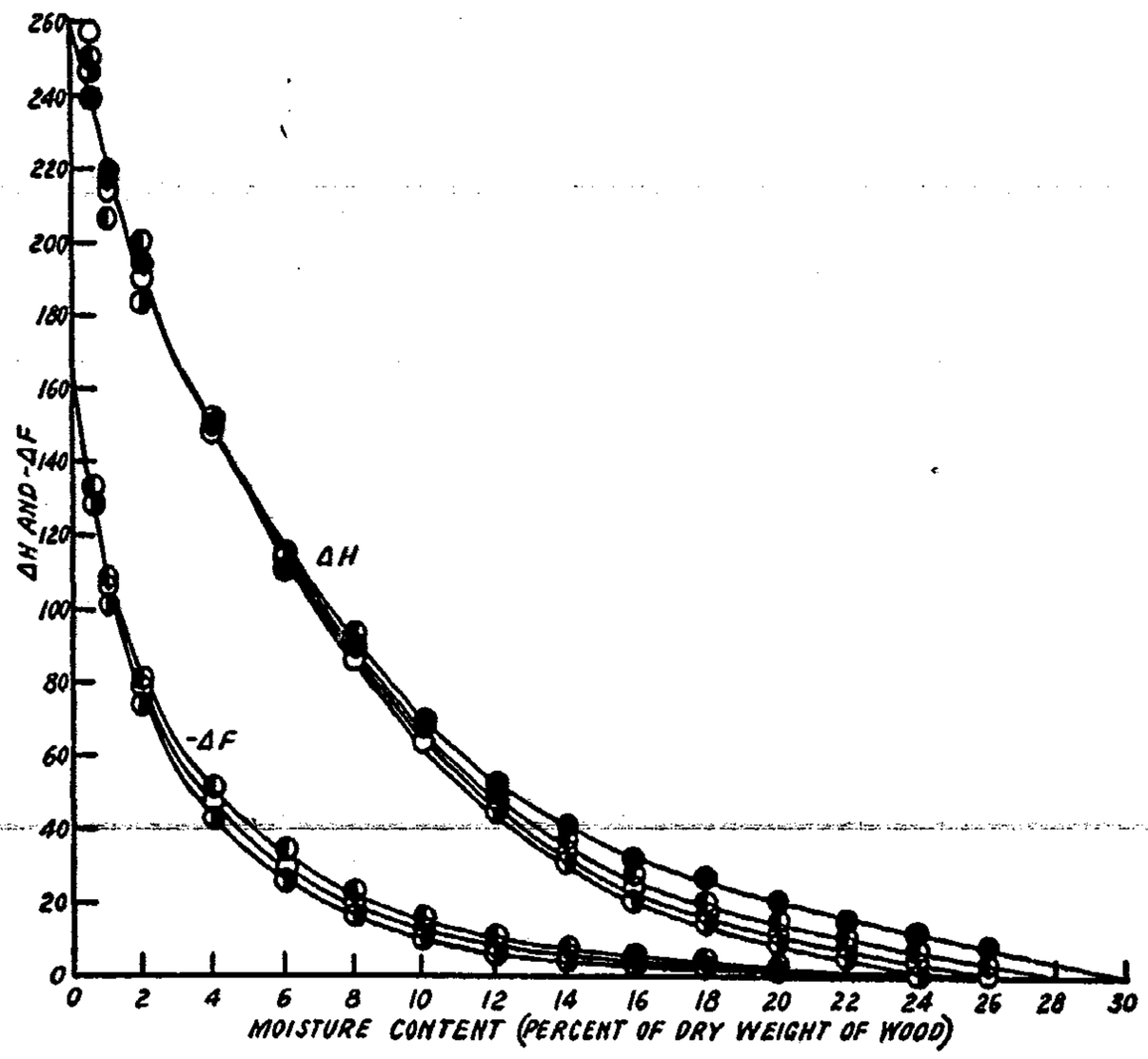

FIG. 4. DIFFERENTIAL HEAT OF SWELLING AND FREE ENERGY CHANGE WITH MOISTURE CONTENT FOR SITKA SPRUCE

● Experimental curve of Volbehr at 0°C.
◐ Calculated curve of authors at 54.4°C.
○ Calculated curve of authors at 71.1°C.
◑ Calculated curve of authors at 87.8°C.

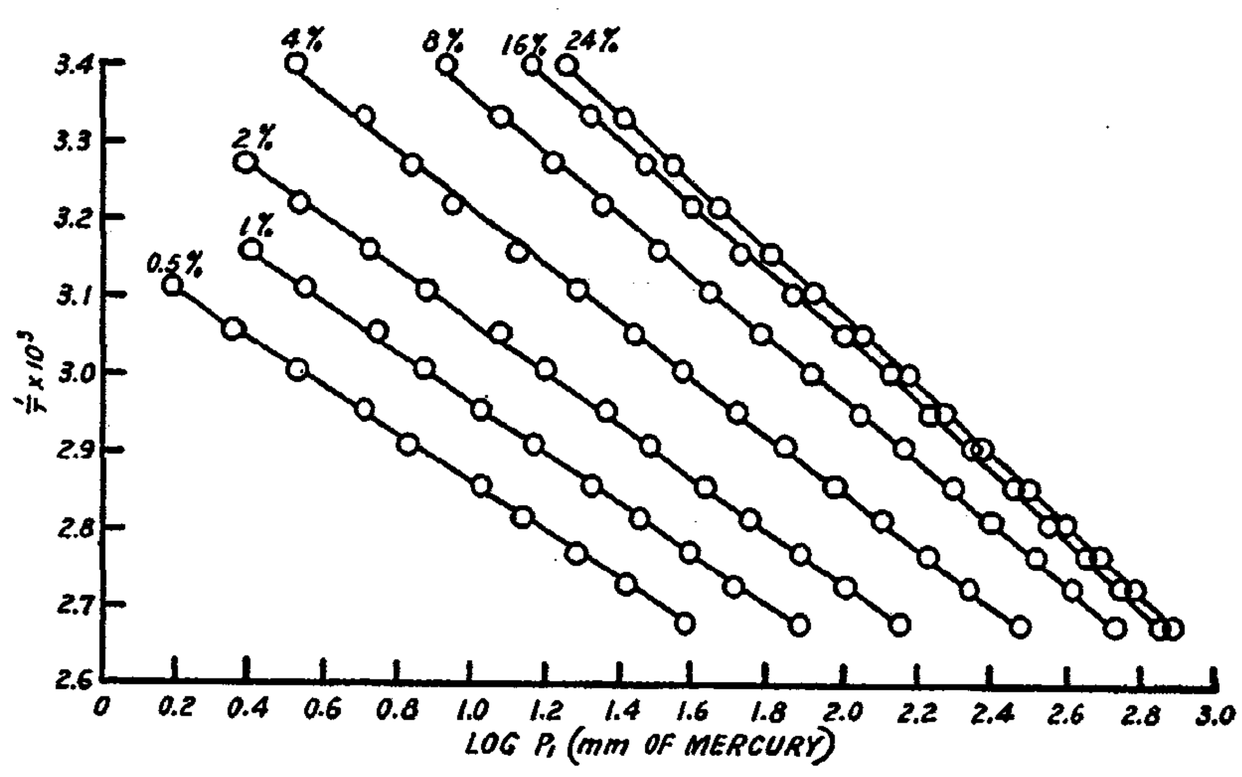

FIG. 5. LOGARITHM OF VAPOR PRESSURE-RECIPROCAL OF THE ABSOLUTE TEMPERATURE ISOSTERES FOR SITKA SPRUCE AT THE INDICATED MOISTURE-CONTENT VALUES

lower moisture content values indicate that the temperature coefficient of the heats of swelling is zero. The slight convex curvature of the isosteres at higher moisture contents indicates that the ΔH values increase slightly with a decrease in temperature. This agrees with ΔH curves in figure 4. The heat of swelling can also be calculated from these isosteres by taking the difference between the slope of any isostere and the saturation isostere thus:

$$\Delta H = -\frac{R}{M}\left(\frac{d \ln P_1}{d\frac{1}{T}} - \frac{d \ln P_0}{d\frac{1}{T}}\right) \tag{4}$$

The isosteres for the lowest moisture content values approach parallelism. This would be strictly true only if Henry's law were obeyed.

The changes in the free energy of swelling calculated with the aid of equation 1 are plotted in figure 4 together with the heat of swelling curves. These were calculated from the 190°, 160°, and 130°F. isotherms, respectively. The $-\Delta F$ values increase very slightly with a decrease in temperature.

In figure 6 are plotted the entropy change curves calculated with the aid of equation 3. They show that a definite entropy change accompanies swelling up to the fiber-saturation point. The entropy changes for the moisture content values below 6 per cent are unaffected by the temperature. At higher moisture content values there is a definite increase in the entropy change with a decrease in the temperature.

The ΔH, $-\Delta F$, and ΔS curves are all smooth curves which show no sign of a sharp transition between the bound or surface adsorbed water and the capillary condensed water or water held by van der Waals forces, although the ΔS curves show a slight inflection at low moisture content values. This is in keeping with the moisture content–relative vapor pressure curves which also lack a sharp discontinuity. The points of adsorption must thus vary in activity as in the case of a metal catalyst. The attractive force at the weakest of these adsorption points must be of the same order of magnitude as the van der Waals force exerted by the most active adsorption point at a distance of at least one molecular diameter from the surface. Such a gradual transition, with perhaps a slight overlapping, from surface-bound water to water held by the van der Waals forces has been recently illustrated in a diagrammatic manner by Sheppard and Newsome (6). It is also very similar to the two-phase adsorption theory of Pierce (4) who, however, believes that a dynamic equilibrium is set up over the whole sorption range between the surface-bound water and water held by van der Waals forces such that the fraction of the total water taken up that goes into the bound phase is proportional to the ratio of unoccupied true adsorption positions to the total

number of adsorption positions. According to these conceptions the inflection point in the moisture content–relative vapor pressure curves corresponds approximately to the transition point between the surface-bound water and the water held by van der Waals forces. It is interesting to note from figure 2 that this inflection point occurs at a relative vapor pressure of about 0.30 for all of the temperatures. This relative vapor pressure

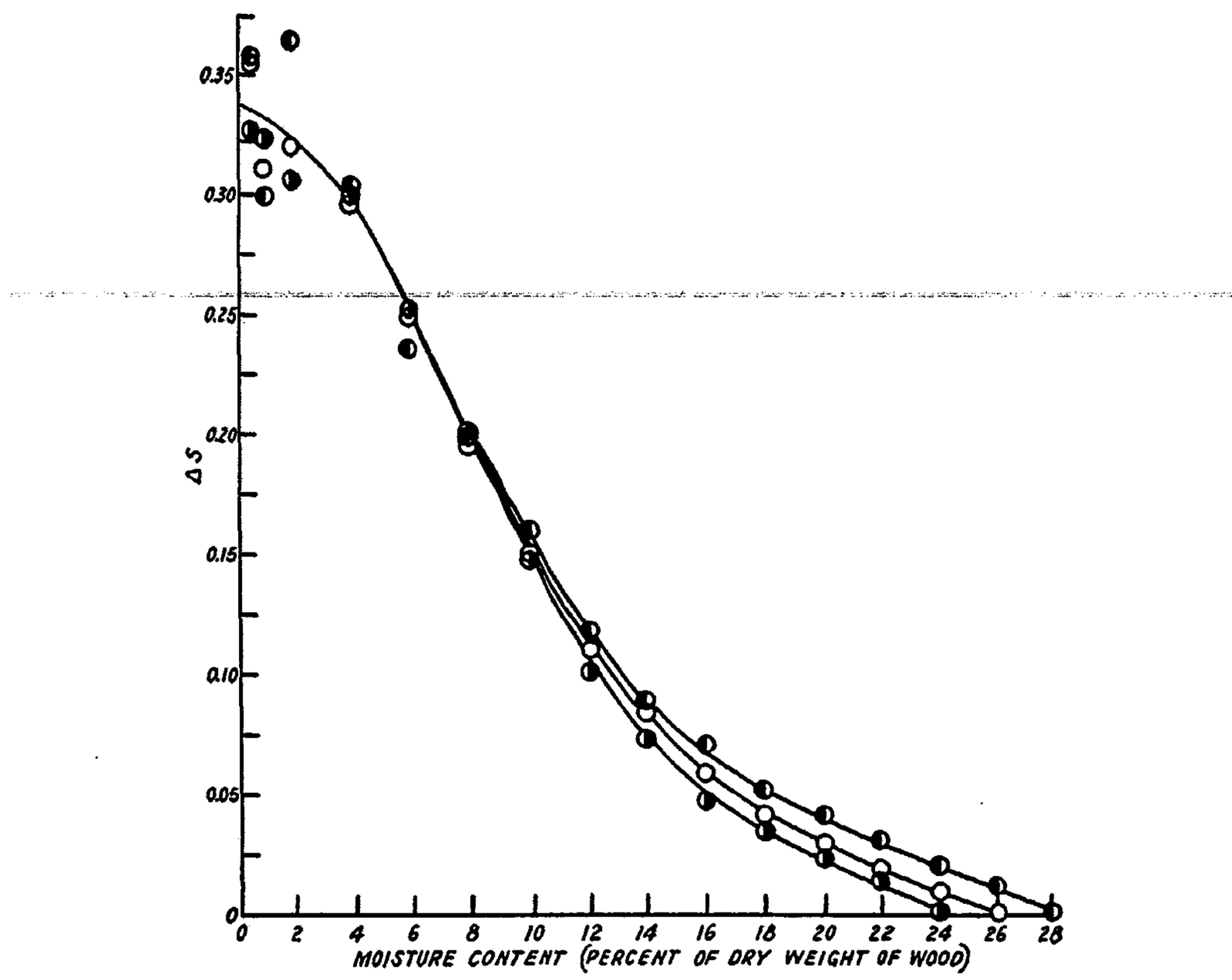

FIG. 6. CHANGES IN ENTROPY WITH CHANGES IN MOISTURE CONTENT OF SITKA SPRUCE

◐ 54.4°C. ○ 71.1°C. ◑ 87.8°C.

further gives a capillary radius when applying Kelvin's equation for the relationship between meniscus curvature and vapor pressure that is only 2.3 times the molecular diameter. This is very near the limiting distance expected for primary molecular attraction, and should represent the limiting size of capillary in which capillary condensation can take place.

In figure 7 are plotted the ΔH, $-\Delta F$, and ΔS versus moisture content curves for soda-boiled cotton calculated from the adsorption data of Ur-

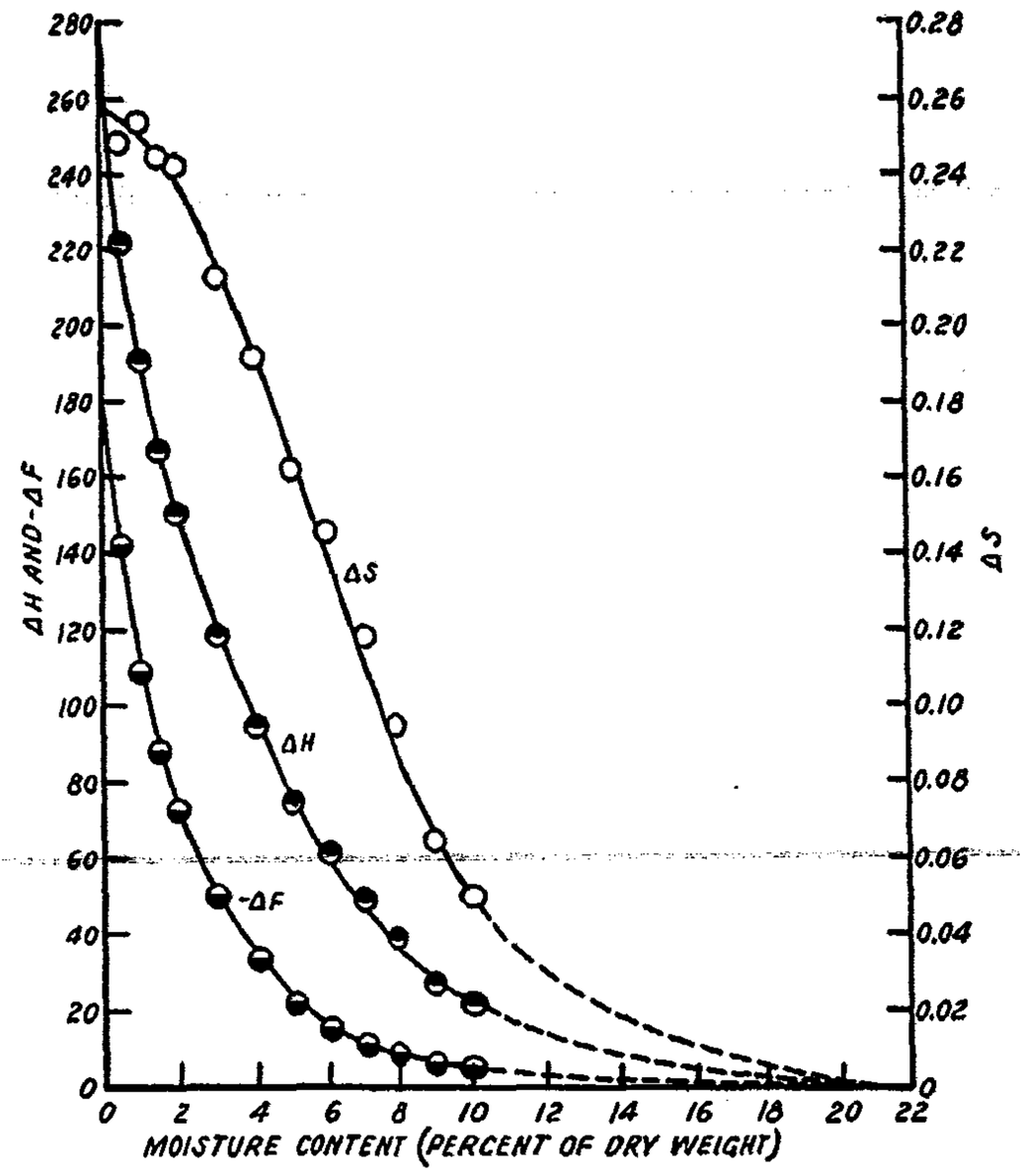

FIG. 7. DIFFERENTIAL HEAT OF SWELLING AND FREE ENERGY AND ENTROPY CHANGES WITH MOISTURE CONTENT AT 50°C. FOR SODA-BOILED COTTON CALCULATED FROM THE DATA OF URQUHART AND WILLIAMS

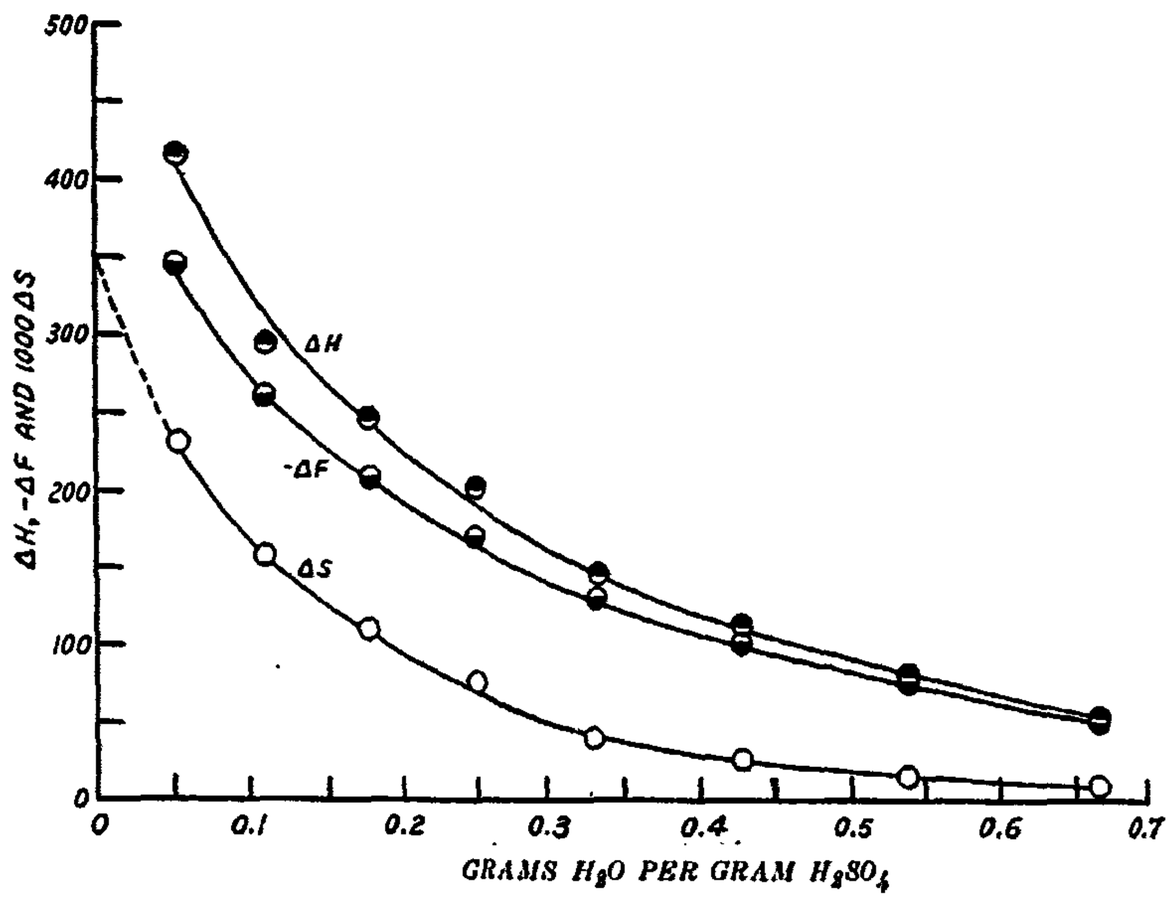

FIG. 8. HEAT OF SOLUTION AND FREE ENERGY AND ENTROPY CHANGES FOR SULFURIC ACID–WATER MIXTURES AT 50°C., CALCULATED FROM DATA TAKEN FROM THE INTERNATIONAL CRITICAL TABLES

quhart and Williams (8). The ΔH values were calculated from the 60° and 40°C. moisture content–relative vapor pressure isotherms and the $-\Delta F$ values from the 50°C. isotherm. It was not possible to correct for the effect of hysteresis; hence the values should be considered only approximations. All three curves are very similar, however, to those for wood. Urquhart and Williams (8) also give isosteres similar to those of figure 5. All of them, however, show a very slight convex upward curvature.

In figure 8 are plotted the ΔH, $-\Delta F$, and ΔS versus moisture content curves for sulfuric acid–water mixtures calculated from data obtained from the International Critical Tables. As Katz (2) has pointed out,

TABLE 1

Thermodynamic constants for the swelling and solution of various materials in water expressed in gram-calories per gram of water added to an infinite amount of the material at the moisture content indicated in the subscripts

MATERIAL	SOURCE OF DATA	ΔH_0	ΔS_0	$\Delta H_{4.0}$	$-\Delta F_{4.0}$	$\Delta S_{4.0}$
Wood:						
Sitka spruce	Stamm and Loughborough	270	0.34	150	46	0.30
Pine	Volbehr (9)	260		150		
Cotton	U. and W. (8)	280	0.26	95	33	0.19*
Cotton	Katz (2)	390				
Starch	Katz (2)	320				
Nuclein (from yeast)	Katz (2)	200				
Casein	F. and L. (1)			166	70	0.35
Casein	Katz (2)	200				
Agar-agar	F. and L. (1)			222	125	0.35
Keratin	F. and L. (1)			150	90	0.22
Sulfuric acid	International Critical Tables			440	365	0.23
Sulfuric acid	Katz (2)	550				

* No correction made for hysteresis effect.

there is a close analogy between solution and swelling. Unfortunately, the data do not extend to moisture content values sufficiently low to determine if the ΔS curve has an inflection point.

Table 1 gives the initial heat of swelling or solution, the initial entropy change, and also the differential heat of swelling and free energy and entropy changes at 4 per cent moisture of a number of materials in water. Although the variation in ΔH and $-\Delta F$ values among the different materials is as great as five to ten times, the variation in ΔS values is less than twofold, showing that the non-reversible work of sorption is fairly constant for a wide variation of materials.

SUMMARY

1. Relative vapor pressure–moisture content desorption isotherms from room temperature to the boiling point of water have been determined for the system wood–water under conditions which minimize the hysteresis effect.

2. The fiber-saturation points decrease with an increase in temperature in a linear manner, the fiber-saturation point being reduced 0.1 per cent for each rise in temperature of 1°C.

3. Differential heats of swelling and free energy and entropy changes were calculated over the entire sorption range. All give smooth curves with zero values at the fiber-saturation point.

4. The nature of the curves with respect to the mechanism of sorption is discussed.

5. Comparisons are made between heats of swelling and free energy and entropy changes for the swelling and solution of various materials in water.

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ADSORPTION COMPRESSION ON CELLULOSE AND WOOD. I

Density Measurements in Benzene

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Received June 14, 1934

INTRODUCTION

The apparent density of an adsorbent material with a large extent of internal surface varies with the nature of the displaced medium used for making the measurements. Harkins and Ewing (9) attributed the phenomenon in the case of charcoal to varying degrees of adsorption compression of the displaced liquid in the capillary structure. They obtained the greatest densities in the most compressible liquids. The size of the molecules of the displaced liquid and the ratio of their surface tensions to viscosities showed no correlation with the densities. They concluded that the differences in the density values could not be due to differences in penetration. Lamb and Coolidge (13) calculated compressive force values as high as 37,000 atmospheres from their heats of adsorption measurements on charcoal, by assuming that all of the heat evolved is due to compression of the liquid. Cude and Hulett (5) made measurements of the density of charcoal in various liquids which they injected into the charcoal under pressure to facilitate penetration, and Howard and Hulett (10) made measurements in helium gas which they showed to be nonadsorbed on the charcoal. The helium gas gave quite similar values to those obtained in the various liquids, thus indicating that any adsorption compression taking place in the liquids would have to be much less than the values predicted by Lamb and Coolidge.

Davidson (6) determined the specific volume of cotton in helium gas, water, and several organic liquids. Non-polar organic liquids gave the highest values, the helium gas values were but slightly less, and the water values were still smaller. He concluded that the helium gas gives the true values and that the slightly higher values in the non-polar organic liquids are due to incomplete penetration, while the low values in water are due to adsorption compression. He calculated values for the average compression of the sorbed water of approximately 2000 atmospheres on

[1] Maintained at Madison, Wisconsin, by the Forest Service of the U. S. Department of Agriculture, in coöperation with the University of Wisconsin.

the basis of the compression taking place entirely in the water. This assumption seems justified, especially in the case of cellulose, because of the fact that x-ray measurements show no change in the x-ray diagrams on swelling of the cellulose in water (11, 12).

Similar measurements on wood have been made at the Forest Products Laboratory (16). Helium gas gave intermediate density values between those obtained in water and in non-polar organic liquids as in the case of Davidson's measurements, but the helium gas values were nearer to the water values than to the non-polar liquid values. In the light of more recent findings these helium gas values appear high. Measurements in this medium are now being repeated. A series of organic liquids gave the greatest density values in the most polar liquids which cause swelling and the lowest density values in the non-polar liquids which do not cause swelling. No relationship between the density values and the compressibilities of the liquids was obtained. Water, a slightly compressible liquid, gave the greatest density. These results for hydrophilic cellulose may appear to be in conflict with those of Harkins and Ewing (9) for hydrophobic carbon, but this is by no means the case. The internal surface of contact for non-swelling carbon is constant except for possible slight variations in penetration, while in the case of cellulose and wood, which are subject to swelling, it may vary from several hundredfold to a thousandfold. For example, the estimated internal swollen surface of cellulose and wood varies from 3×10^5 to 10^7 square centimeters per gram (14), while the coarse capillary surface of unswollen wood (total lumen area) varies from 1 to 5×10^3 square centimeter per gram. The extent of the surface on which compression can take place, rather than the magnitude of the compression per unit of surface, thus appears to be the prime factor in causing the variation in the density values of swelling solids obtained in different liquids.

Filby and Maass (7) have made measurements in helium gas of the density of cellulose with various amounts of adsorbed water present by an ingenious combined gas expansion and moisture sorption method. From the few measurements which they reported they drew several very far-reaching conclusions: First, that the compression takes place only within the first 8 to 10 per cent of moisture adsorbed; second, that a constant maximum compression is reached at moisture content values below about 4 per cent; and third, that the initial compression amounts to 0.6 cc. per gram of water adsorbed. An externally applied compressive force of about 100,000 atmospheres would be required to give this compression. The first two conclusions are not in harmony with moisture content–relative vapor pressure data or heats of swelling data (17). Vapor pressure depressions and differential heats of swelling are obtained at all moisture content values up to the fiber-saturation point, which varies from

15 to 35 per cent for the different fibrous materials. It thus seems unreasonable that the compression, which is a related property, should not be effective up to these higher moisture content values. Further, the moisture content–vapor pressure and the moisture content–entropy change data show inflection points at presumably the transition point between the bound and capillary held water, but they do not indicate a constancy of attractive force of all of the sorption points (17) as in the case of the data of Filby and Maass. The extremely high compression obtained by these investigators would require that the work of adhesion of cellulose and water be seven to eight times the work of cohesion of water. This, too, is at variance with other data. Bartell and Osterhof (2) and Bartell and Jennings (1) have shown from adhesion tension measurements that the work of adhesion for a solid wetted by water is but 1.00 to 1.05 times the work of cohesion of water. The work of adhesion of mercury and water according to Harkins (8) is only 1.25 times the work of cohesion of water.

Because of these irreconcilable results of Filby and Maass and the general unsettled opinions as to the magnitude of adsorption compression, the Forest Products Laboratory undertook this research with the hope of settling this point, which has considerable bearing on the general problem of sorption.

EXPERIMENTAL

The measurements of Davidson (6) show that the specific volume of cellulose determined in toluene is only a little over 1 per cent greater than in helium gas. The difference must be due entirely to incomplete penetration by the toluene, as toluene is practically a non-swelling liquid in which the compression can be only 0.01 to 0.001 of that in a swelling liquid. Such a small compression would be outside the range of experimental measurement. It further seemed reasonable to assume that the small amount of void structure of cellulose or wood inaccessible to benzene or toluene would be filled by the first few per cent of water added, so that density measurements in these liquids of cellulose or wood containing appreciable amounts of sorbed water should give results free from the error introduced by incomplete penetration. Only in the case of dry or relatively dry cellulose or wood should an error be introduced by making density measurements in a non-swelling liquid.

For these reasons the density measurements of cellulose and wood containing sorbed water were made in benzene, thus greatly simplifying the measurements and increasing their accuracy.

Benzene was chosen in preference to toluene for the measurements because it caused no measurable swelling of wood, whereas toluene caused a very slight swelling. Although water is very slightly soluble in benzene, only in the case where the moisture present exceeds the fiber-saturation

point of cellulose or wood could the benzene become saturated because of the vapor pressure depression caused by the cellulose or wood. The error caused by using dry benzene for the measurements should hence be small and will be shown later to be entirely negligible. The benzene used was a chemically pure benzene, thoroughly dried over phosphorus pentoxide, and then distilled.

The adsorbent materials used were Sitka spruce and white spruce heartwood sawdust of 40 to 60 mesh, from which the extractives had been removed by extraction with a mixture of benzene and alcohol, cotton linters alpha-cellulose, a normal spruce sulfite pulp, and the same pulp beaten for 20 hours to a "highly hydrated" condition. Beaten pulp when dried by ordinary methods becomes hard and horny. The water was hence replaced by alcohol and the alcohol, in turn, replaced by ether and then the pulp dried from this latter solvent. By drying in this way practically normal porous texture is obtained, and the sealing up of voids is prevented.

The measurements were made in 50-cc. and 100-cc. pycnometer flasks brought to thermal equilibrium in a thermostatic water bath held at 30°C. ±0.02°C. The volume of the pycnometers was obtained from their weight filled with water, and the density of the benzene was determined. The pycnometers were then half filled with cellulose or wood (3 to 10 g.) that had been brought to moisture equilibrium in rooms controlled at 97, 90, 75, 65, and 30 per cent relative humidity and 80°F., or partially dried over calcium chloride, weighed, and covered with anhydrous benzene. The air was removed from the submerged fibrous materials by carefully applying a vacuum and releasing until no sign of air bubbles was obtained up to a vacuum which caused boiling of the cold benzene. Experience showed that the cellulose and the wood could be completely freed from air after a few hours treatment. After bringing the pycnometers containing the adsorbent, water and benzene to thermal equilibrium and volume in the thermostatic bath, they were rapidly weighed. The weights in general could be checked to 0.5 mg. The excess of benzene was then decanted off, and the materials dried at 105°C. to constant weight.

The compression of the water was calculated with the aid of the following equation:

$$C = \frac{\dfrac{w_w}{d_w} - \dfrac{W_b - (W - m_1)}{d_b}\dfrac{m_0}{D}}{m_0}$$

in which C is the decrease in volume due to compression in cubic centimeters per gram of dry adsorbent material, d_w the normal density of the water, d_b the density of the benzene, and D the true density of the adsorbent material, w_w the weight of sorbed water, m_0 the weight of the dry adsorbent material and m_1 the weight of the wet adsorbent material, W_b the weight

of the pycnometer filled with benzene alone, and W the weight of the pycnometer filled with wet adsorbent material and benzene.

In figure 1 are plotted the apparent adsorption compressions for several cellulosic materials calculated on the basis of the density of the dry material as determined in benzene being the true density. The average densities of each of the materials determined in benzene are Sitka spruce 1.449, white spruce 1.459, sulfite pulp 1.529, beaten sulfite pulp 1.543, and cotton 1.549. The integral curves give the relationship between the total compression occurring in the water adsorbed on a gram of cellulosic material and the moisture content. The differential curves obtained by graphically determining the slope of the integral curves give the compression per gram of

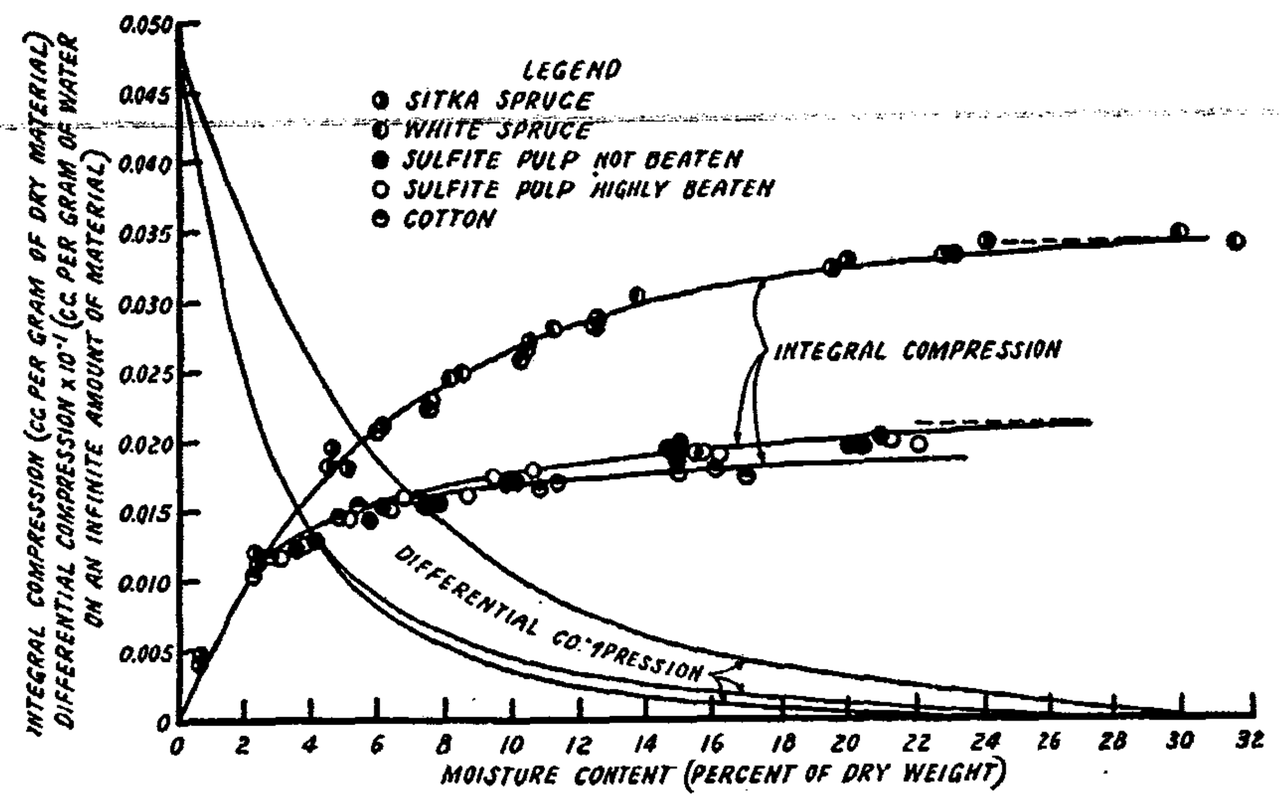

FIG. 1. APPARENT ADSORPTION COMPRESSIONS OF WATER ON VARIOUS CELLULOSIC MATERIALS AS DETERMINED IN BENZENE

water adsorbed on an infinite amount of cellulosic material containing different amounts of water. The initial compressions, the compressions occurring when 1 g. of water is added to an infinite amount of dry material, are identical for all the cellulosic materials tested. The integral compressions increase up to maximum values which correspond to the maximum compressions calculated from the difference in the specific volume of the cellulosic material determined in water alone and in benzene. For example, the apparent specific volume of the normal sulfite pulp in water is 0.632 cc. and in benzene 0.653 cc. The difference, 0.021 cc., represents the decrease in volume due to compression of water. As an excess of water is present in these measurements, it is impossible to tell from them alone within what moisture content the compression takes place. The fact that

the line representing this compression (dotted line in figure 1) becomes tangent to the integral compression curve at 27 per cent moisture content, which is the fiber-saturation point for this particular pulp, indicates that compression takes place up to the fiber-saturation point. It also indicates that the error introduced by neglecting the solubility of water in benzene in the compression measurements is negligible and that penetration is complete in the cellulosic material–water–benzene systems at high moisture contents.

It is of interest that not only the two similar species of wood give identical compression curves but that highly beaten and unbeaten pulp also give identical curves. This offers further proof of the fact that beating a pulp

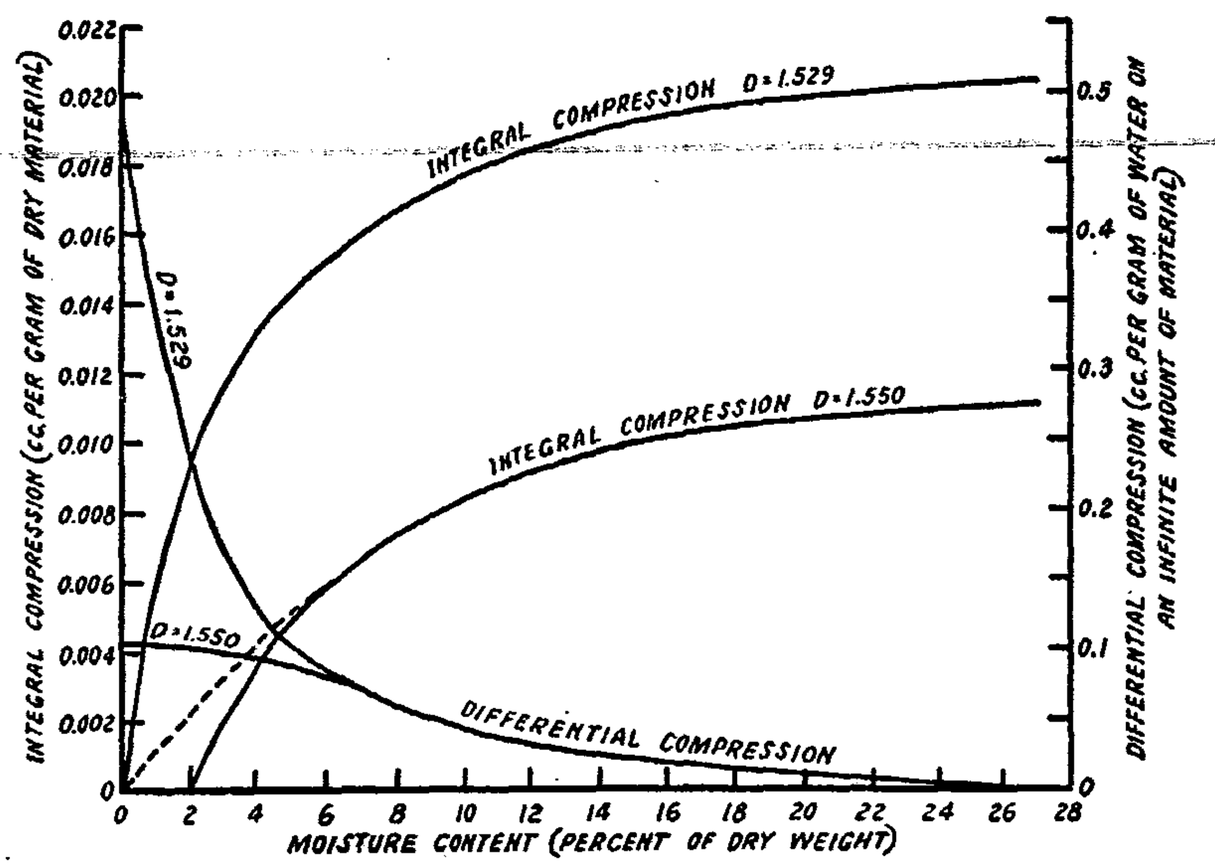

FIG. 2. EFFECT OF CHANGES IN THE VALUE OF THE ABSOLUTE DENSITY OF SULFITE PULP UPON THE CALCULATED ADSORPTION COMPRESSION

does not increase the surface available for the adsorption of water (4, 14, 15).

As was pointed out earlier, these compression values are liable to be too high because of incomplete penetration of the cellulosic materials by the benzene at low moisture content values. If, for example, the true density of the sulfite pulp were higher than the value determined in benzene, the compression would be appreciably decreased, as is shown in figure 2. The upper integral compression curve is the same curve as that plotted in figure 1, using 1.529 for the density, while the lower curve was obtained on the basis of the true density being 1.4 per cent higher, which is higher by practically the same amount that Davidson's values (6) determined in

helium gas are higher than his values determined in toluene. These two curves are identical except for an additive shift of the ordinates. The lower curve does not pass through the origin, indicating in this case that no compression could take place below a moisture content of 2 per cent and that it would then suddenly become appreciable. Such a condition is ridiculous. The curve must pass through the origin without exhibiting an inflection point to avoid such a condition of reversal in compression. The dotted curve through the origin and tangent to the compression curve would avoid this difficulty. Assuming that the dotted curve represents the true conditions at low moisture content values, then the upper curve must be in error below 6 per cent moisture content, presumably because of incomplete penetration which would cause a reduced apparent compression.

The differential curves were obtained from both the upper curve and the lower curve with the dotted extension to the origin. They are identical down to a moisture content of 6 per cent, but deviate greatly below this point. The initial compression from the upper curve is 0.48 cc. per gram of water adsorbed on an infinite amount of dry pulp which corresponds, according to the extrapolation of the compression data of Bridgman (3), to an externally applied compressive force of over 100,000 atmospheres, while the lower curve gives an initial compression of only 0.105 cc., which corresponds to an externally applied compressive force of 3440 atmospheres. As this tremendous difference in the calculated compressive force results from a change of the value taken for the absolute density of the pulp substance of only 1.4 per cent, it is obvious that accurate values for this density must be known before even approximate values for the initial force of compression can be obtained.

The following analogy as well as other previously mentioned considerations, however, indicates that the latter value is perhaps a better estimate of this force than the former.

Katz (11) has pointed out the similarity between the sorption of water vapor by a solid and the mixing of sulfuric acid and water. In this latter case the difficulty of distinguishing whether changes in the specific volume of the system are due to differences in penetration or differences in compression become meaningless. The system sulfuric acid–water is hence an ideal one to examine from the standpoint of the compression phenomenon. In figure 3 the compression values for the system sulfuric acid–water are plotted on three different bases. The integral compression and molal compression curves were plotted from data for the density of various concentrations of sulfuric acid taken from the International Critical Tables. The differential curve was obtained by determining graphically the slope of the integral curve as before.

The compression occurring in this system is not entirely due to the

compression of water, as in the case of adsorption by cellulose and wood, for part of the compression takes place in the sulfuric acid. This is demonstrated by the molal compression curve in which the compressions per unit volume of solution are plotted against the mole fraction. The compression increases practically linearly with an increase in the moisture content up to proportions slightly in excess of 1 mole of water to 1 mole of sulfuric acid. Compression presumably takes place in these proportions. When equal molal proportions of sulfuric acid and water are mixed the compression takes place in all of the solution. In any other proportions either part of the acid or part of the water is in excess and is not compressed. Concentrated sulfuric acid is only 0.73 as compressible as water per unit of volume at 166 kg. per cubic centimeter (International Critical Tables).

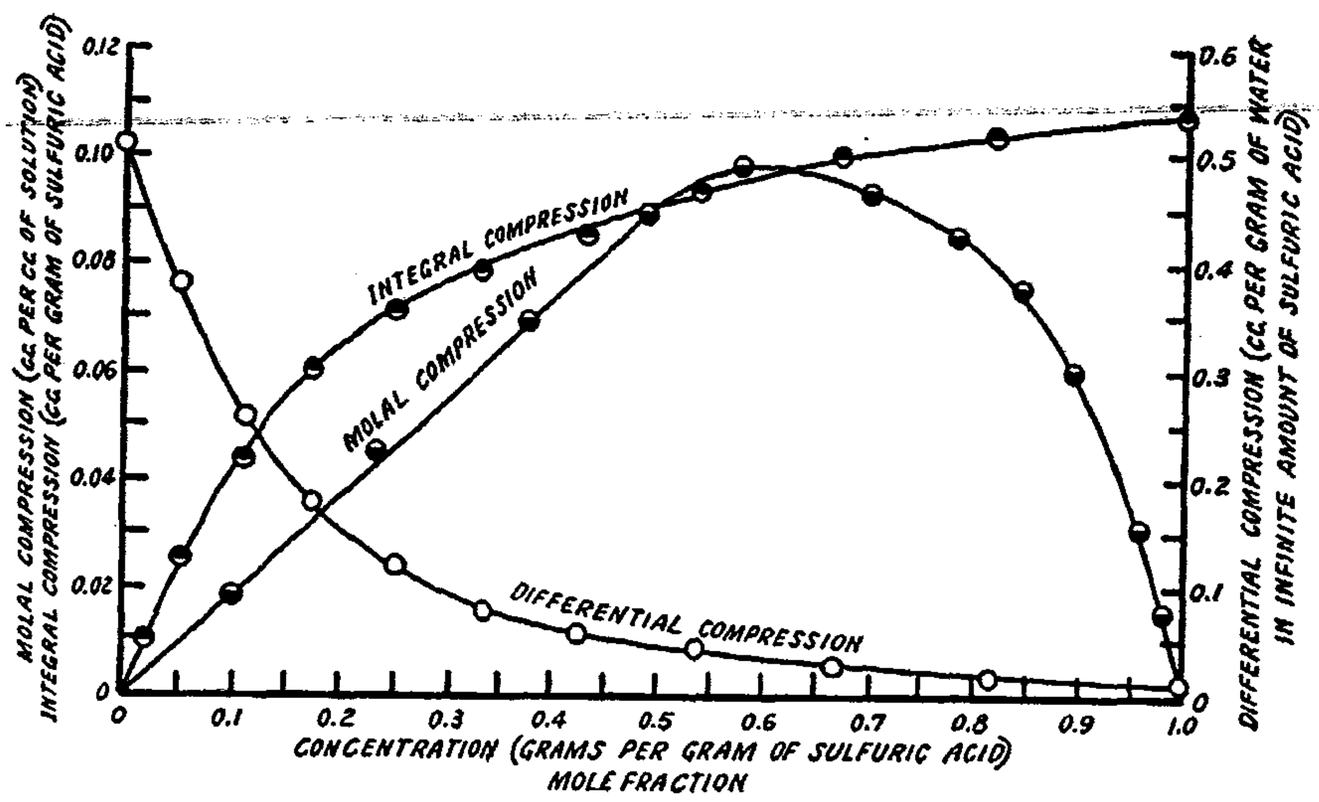

FIG. 3. COMPRESSION TAKING PLACE ON SOLUTION OF WATER IN SULFURIC ACID

If this ratio remains constant at all pressures, then the compression occurring in equal molal proportions per unit of pressure will be 3.21 times that in the contained amount of water alone. Thus the compression values given in the differential curve should be divided by 3.21 to obtain the compression that occurs in the water alone. The initial compression value would hence be 0.159 cc., rather than 0.51 cc. for the water. This compression, according to the data of Bridgman, would result from a compressive force of 6750 atmospheres. The differential compression of the water at equal molal proportions is 0.053 cc., which, in turn, would be obtained under a compressive force of 1450 atmospheres. These compressive forces are of the same order of magnitude as those obtained for the pulp by assuming that the true density of pulp is 1.4 per cent greater

than the value determined in benzene. It thus seems probable that the densities of dry cellulosic materials as determined in benzene are slightly lower than the true densities, as was found by Davidson (6), and that Filby and Maass' compression values are too high. Measurements are now being made of the density of dry cellulosic materials in helium gas to confirm this point. These measurements together with thermodynamic considerations of compression will be given in a subsequent publication.

Although the data presented in this publication are insufficient to determine the magnitude of the adsorption compression of water on cellulosic materials at low moisture content values, they do give the true values at moisture contents above which penetration is complete and show quite definitely that compression continues to the fiber-saturation point. This is not in agreement with Filby and Maass' (7) contention that compression extends only to a moisture content of 8 to 10 per cent. Filby and Maass' own data, however, tend to disprove their contention, as the maximum compression calculated from their specific volumes in water and in helium gas alone correspond to the compression value of their extrapolated compression-moisture content curve at 22 per cent moisture content, which should be approximately equal to the fiber-saturation point of their cotton.

SUMMARY

1. The apparent adsorption compression of water on cellulosic materials has been determined in benzene.

2. The effect of small variations in the value used for the true density of the cellulosic material on the resulting compression is illustrated. Evidence indicating that the compressive force is of the order of a few thousand atmospheres rather than 100,000 atmospheres, is given.

3. It is demonstrated that actual adsorption compression values can be obtained by this method at higher moisture content values, and that adsorption compression extends to the fiber-saturation point.

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SOME PROPERTIES OF CELLULOSE ESTERS OF HOMOLOGOUS FATTY ACIDS

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Received June 14, 1934

In a previous paper (7) attention was drawn to the utility of working with homologous series of compounds in the effort to obtain quantitative characteristics of the solubilities of certain cellulose esters. In this paper the procedure is reversed, in so far that it is the cellulose esters themselves which here form the homologous series. The data recorded here for the most part apply to the triesters of cellulose. They are only strictly comparable on the assumption that the degree of polymerization of the cellulose remained the same through any given series, or, in other words, that the average molecular weight of the cellulose portion remained the same. In the series of compounds prepared in our own laboratories, where the same original cellulose material was used, we have reason to regard this as substantially the case, and the same may be regarded as equally probable for the material of other investigators cited. But while the comparisons in a *series* may be regarded as justified, it is not permissible to consider any given triester of investigator A as necessarily the same as that of investigator B. Identical in composition, they might differ considerably in average molecular weight.

With this reservation made, we can proceed to collate the data showing the progressive changes produced in cellulose esters as the molecular weight of the fatty acid is increased.

MEASUREMENTS OF PHYSICAL PROPERTIES

The melting points were determined by heating the sample in a glass capillary tube placed in a copper block.

The densities were determined by using methyl alcohol as the displacement liquid. Methyl alcohol wets the esters, especially the higher ones, much better than water and gives a higher density value than water. The esters were dried by evacuation at room temperature.

The data are shown in table 1 and figures 1 to 4.

The densities of the esters decrease regularly with increase in number of carbon atoms, corresponding to the behavior of the free acids (see table 2).

The melting points of the cellulose esters pass through a minimum at

cellulose caprate, whereas the melting points of the normal fatty acids pass through a minimum at valeric acid, thus showing the influence of the cellulose residue.

There is no definite evidence of an alternation in the melting points of the esters with odd and even numbers of carbon atoms as is the case with the free acids. This effect, which is more pronounced for the lower acids, is apparently minimized by the presence of the cellulose residue—large in comparison to three hydrogen atoms. Since the alternating effect is attributed to differences in crystal structure (2), the presence of the cellulose residue should lower the degree of orientation and therefore reduce the magnitude of the alternation.

TABLE 1

Properties of cellulose triesters at 25°C.

ESTER	NO. OF CARBON ATOMS	DENSITY	MELTING POINT	PER CENT MOISTURE REGAIN		CONTACT ANGLE VS. WATER	WORK OF ADHESION VS. WATER
				50 per cent R.H.	100 per cent R.H.		
			degrees C.			*degrees*	*ergs*
(Cellulose)	0	1.618		5.6	18.8		
Acetate	2	1.377	Decomposes at 245	2.3	10.0	50	117
Propionate	3	1.268	239	1.3	4.4	78	87
Butyrate	4	1.178	183	0.7	3.5	84	79
Valerate	5	1.178	160	0.5	1.7	90	72
Caproate	6	1.110	87	0.3	0.9	93	68
Heptoate	7	1.081	97	0.2	0.8	100	59
Caprylate	8	1.058	85	0.1	0.9	99	61
Pelargonate	9	1.032	66	0.1	1.0	100	59
Caprate	10	1.026	64	0.3	1.5	100	59
Laurate	12	1.004	80	0.3	1.4	101	58
Myristate	14	0.991	87		1.5	104	55

The moisture regain apparently passes through a minimum near cellulose heptoate. The reason for this is not known. It appears that the moisture regain should continue to decrease with increase in number of carbon atoms in the side chains.

The contact angle against water steadily increases with increase in length of the hydrocarbon chain and approaches that of a long chain hydrocarbon—pure paraffin having an angle of 108° and work of adhesion of 50 ergs.

The method used for the determination of the contact angle, and therefore of adhesion tension or work of adhesion, was by measurement of the height of a drop of water placed on a horizontal surface of the solid (5).

The contact angle is given by the equation

$$h = a\sqrt{2} \sin \theta/2$$

where $a = \sqrt{\frac{2T}{g\rho}}$, h = height of drop in cm., T = surface tension of liquid, g = gravity, and ρ = density of liquid. The drop should be at least 1.5 cm. in diameter. Glass plates were coated uniformly with the various esters, from solutions of these in chloroform. The height of the drop was determined with a spherometer.

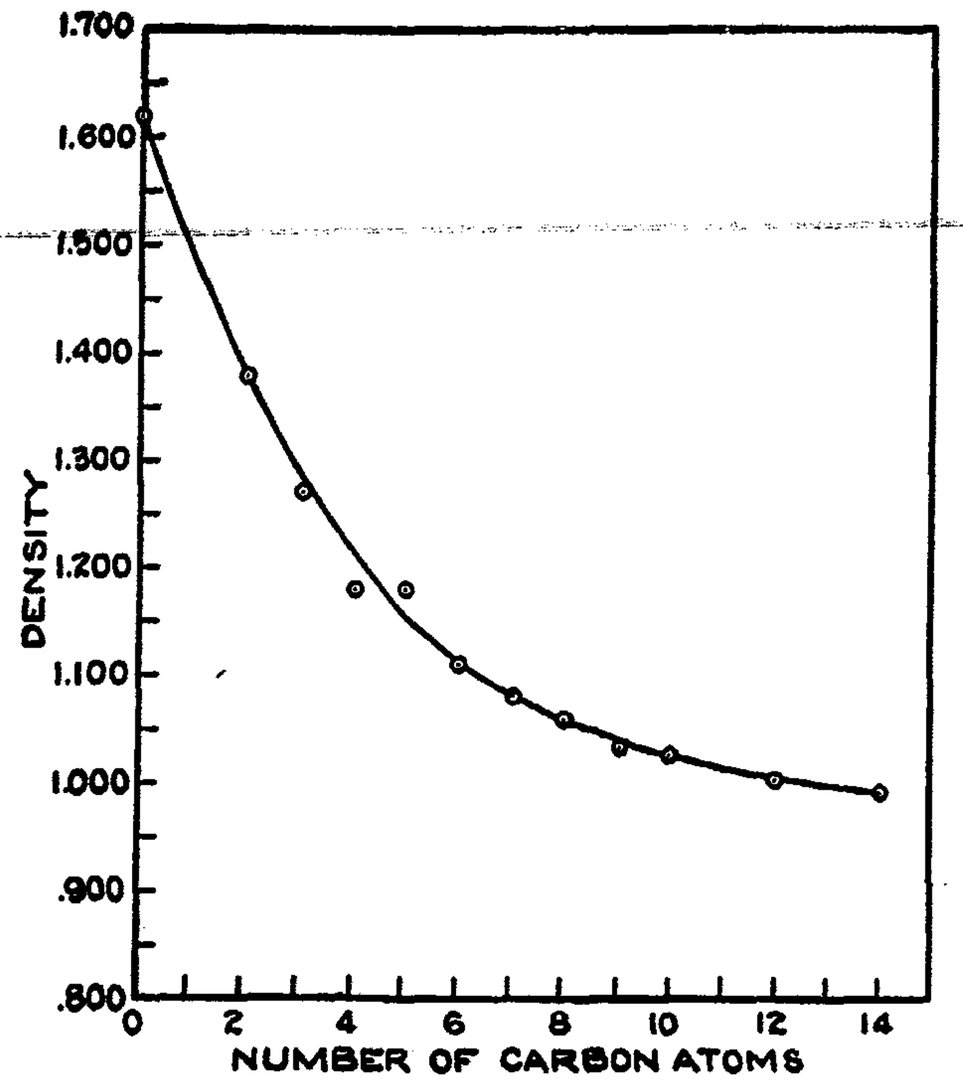

FIG. 1. DENSITY OF CELLULOSE TRIESTERS AT 25°C.

The work of adhesion is obtained from the contact angle θ by the formula

$$W = T_{LA} (1 - \cos \theta)$$

where T_{LA} is the surface tension, liquid to air.

It will be noticed that the values of the work of adhesion of water for the fatty acid esters of cellulose appear to fall steadily, finally approaching that of paraffin. On the other hand, A. H. Nietz (6) found for the fatty acids themselves a minimum value, in the neighborhood of twelve carbon atoms. Nietz discusses various molecular and thermodynamic explanations for this minimum, which are, however, unnecessary. The actual

reason is the fact that the lower fatty acids (up to pentadecylic) have appreciable solubility in water, and therefore appreciable lowering of the surface tension T_{LA}. Consequently, while the contact angle θ rises more or less steadily (there is an alternating effect not found with the cellulose esters), the surface tension is at first nearly constant at a lowered value, then rises suddenly to be nearly equal to that of pure water above pentadecylic acid. Hence the minimum for the expression

$$W = T_{LA}(1 - \cos\theta)$$

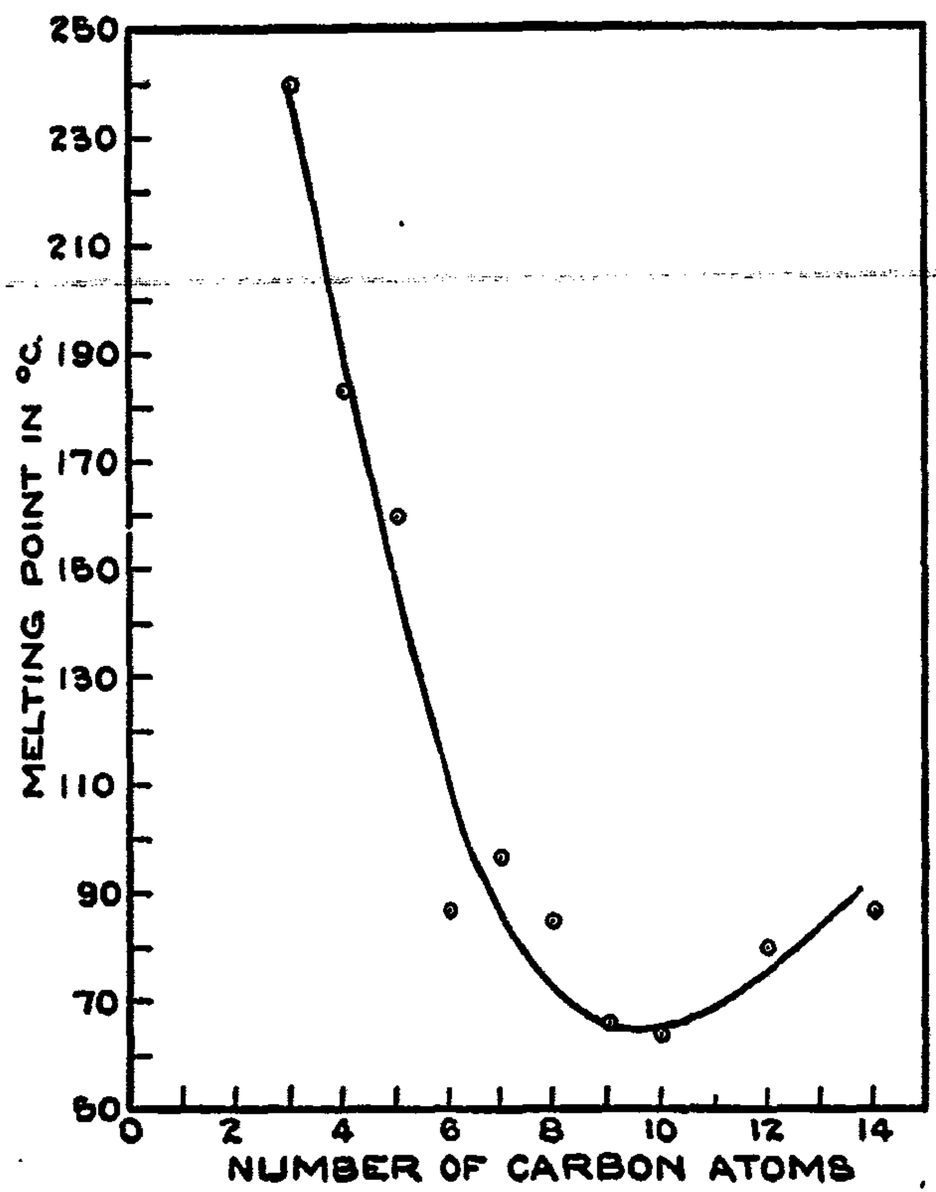

FIG. 2. MELTING POINT OF CELLULOSE TRIESTERS

SOLIDIFICATION AND MOLECULAR ORIENTATION

If the surface layers of molecules of these substances were completely oriented, as in a monomolecular film (4), then in accordance with Langmuir's theory of surface structure, we should expect to find either very high wetting (for the cellulose esters) or a very low (paraffin) value. The progression of values from high to low wettability indicates a—probably kinetic—effect of the chain length (in the case of the cellulose esters, side chain length) on the surface orientation on solidification.

In the case of the fatty acids themselves, Nietz found, using stearic acid, that the surface orientation on solidifying the melt depended decisively upon the medium in contact, i.e., the contiguous liquid or gas phase. High humidity or liquid water produced a surface of much higher adhesion tension, showing orientation of the polar groups to the water.

The increasing domination of the properties of the cellulose ester aggregate by the aliphatic side chains is well brought out in the studies of N. K. Adam (1) on the spreading of films of these substances on water,

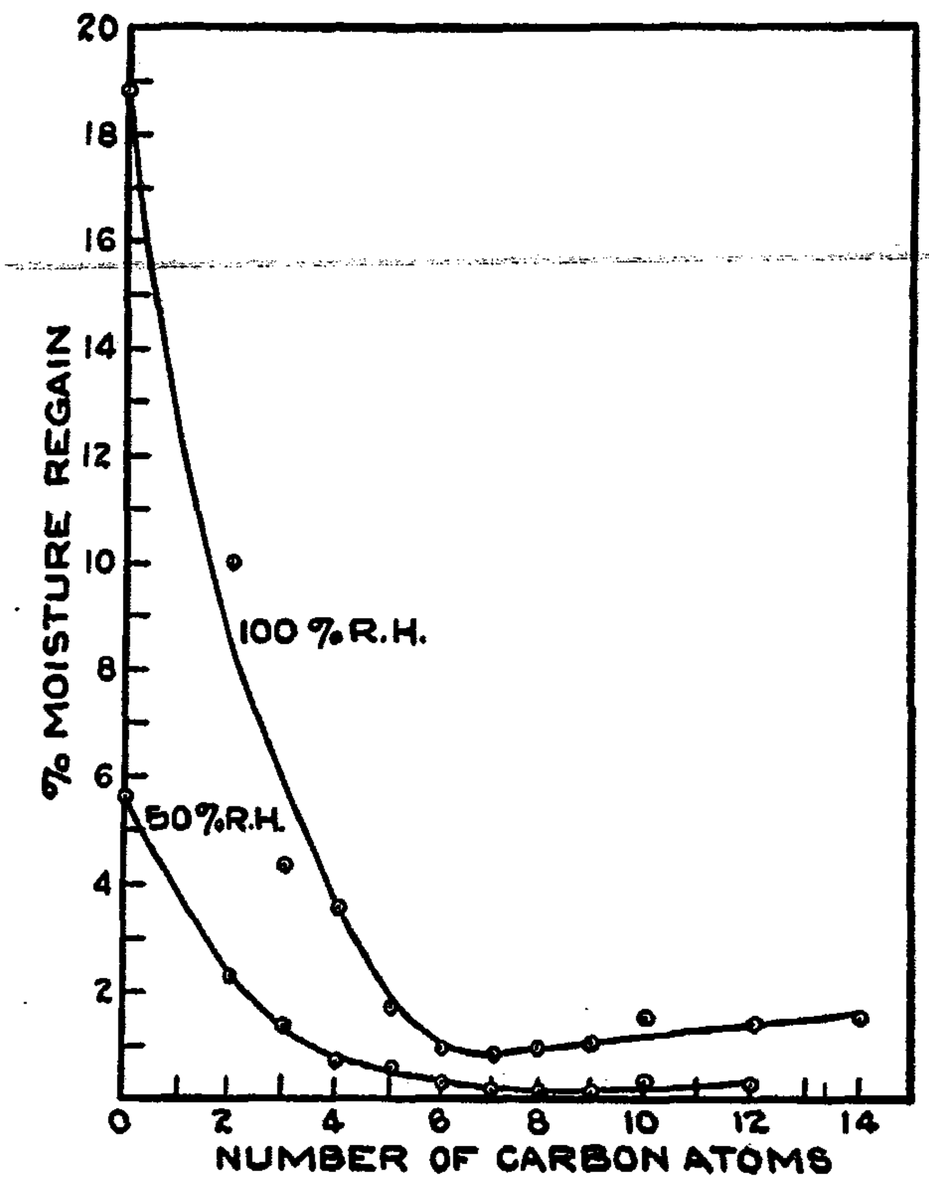

FIG. 3. MOISTURE REGAIN OF CELLULOSE TRIESTERS AT 25°C.

and in those of J. J. Trillat (9) on their x-ray spectroscopy. In figure 5 is reproduced Adam's data for the spreading of a number of fatty acid esters of cellulose.

There is observable an increased "molecular" area covered as the length of the fatty acid chain increases (48 sq. A.U. for triacetate, ca. 78 sq. A.U. for tristearate). Adam concludes that "the hexose ring, lying *flat* on the surface of the water, occupies an area greater than that of the three eighteen carbon chains [also presumed to be flat on the water?]; and that lateral

compression of the film allows some rearrangement of the hexose rings next the water, which form the base of the film, the *super*structure of which no doubt *consists of the long chains arranged at a fairly steep angle to*

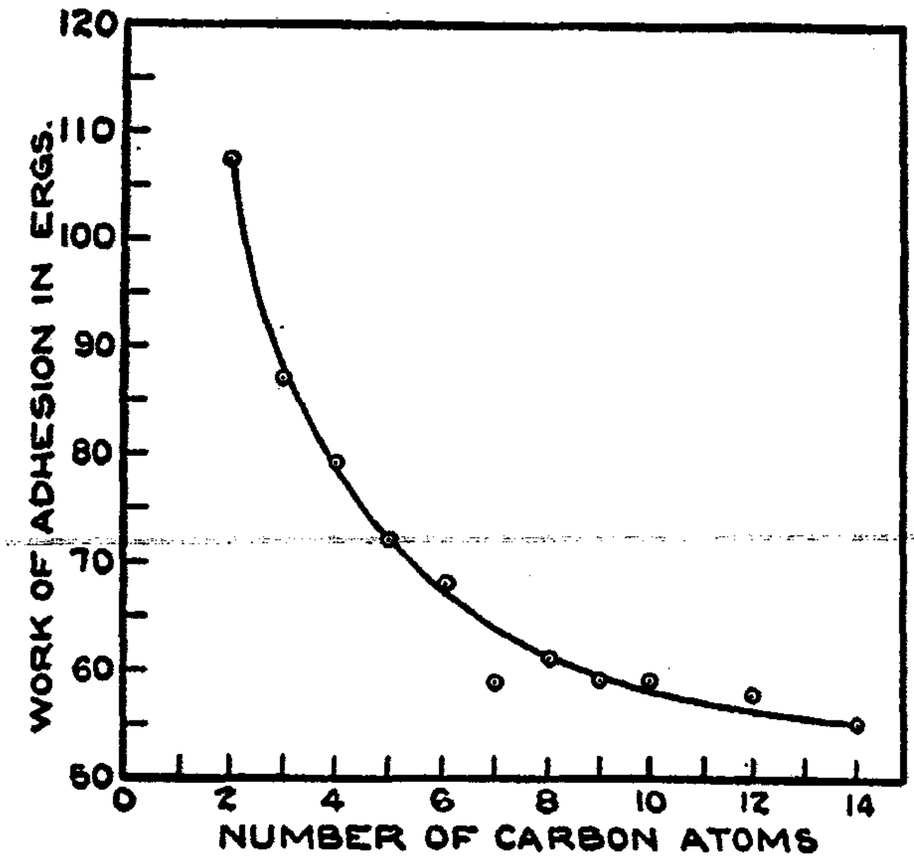

FIG. 4. WORK OF ADHESION OF CELLULOSE TRIESTERS AGAINST WATER

TABLE 2

Densities and melting points of normal fatty acids

ACID	DENSITY AT 20°C.	MELTING POINT
		degrees C.
Formic	1.220	8.4
Acetic	1.049	16.6
Propionic	0.992	−22.0
Butyric	0.959	−7.9
Valeric	0.942	−34.5
Caproic	0.929	−9.5
Heptylic	0.922	−10.0
Caprylic	0.910	16.0
Pelargonic	0.907	12.0
Capric	0.895	31.0
Lauric	0.883	48.0
Myristic	0.858	58.0
Stearic	0.847	69.3

the surface.[1] The lateral adhesion between the long 18-carbon chains is not sufficient to counteract the tendency of the hexose rings to lie flat."

[1] Our italics.

These conclusions do not seem to us to be entirely tenable in the light either of general x-ray evidence on the structure of the cellulose macromolecule, or more specifically of Trillat's (9) results with the same series of fatty acid esters of cellulose whose properties were described here. This

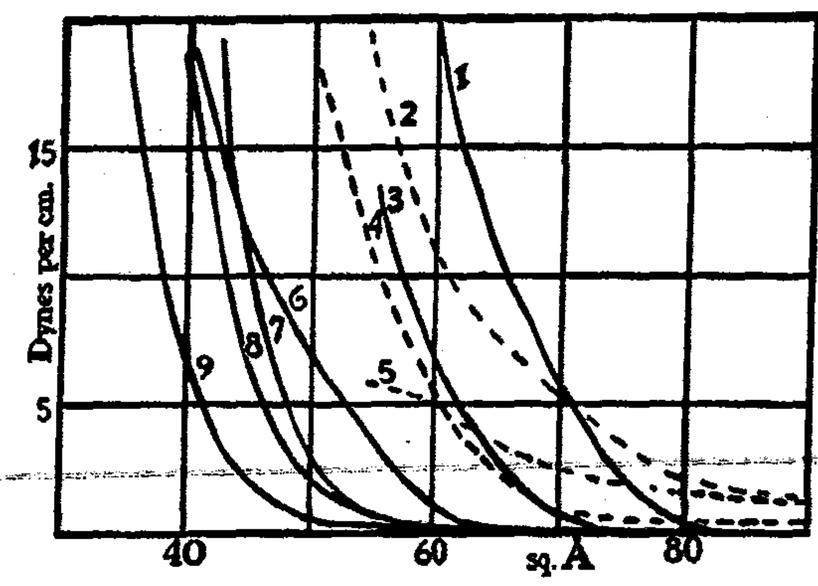

FIG. 5. FATTY ACID ESTERS OF CELLULOSE NOT FULLY SPREAD ON WATER

1. Tristearate
2. Tripropionate on sodium hydroxide
3. Dilaurate
4. 2½ Butyrate on sodium hydroxide
5. Triacetate on sodium hydroxide
6. 2½ Butyrate
7. Distearate
8. Tripropionate
9. Triacetate

N. K. Adam

TABLE 3

Tensile strength and total elongation of cellulose ester sheets

CELLULOSE ESTER	TENSILE STRENGTH	TOTAL ELONGATION IN PER CENT
	*kg. per mm.*²	
Acetate	9–12	15–25
Propionate	6–7	10–15
Butyrate	5–6	8–10(?)
Valerate	4–5	18–25
Caproate	2.5	60
Pelargonate	3.5–4.0	20–30
Laurate	0.8–1.0	100–130
Stearate	0.5	140
Naphthenate	0.3	110

investigator found that the Debye-Scherrer transmission diagrams showed a structure greatly modified by the fixation of the long aliphatic chains. In brief, there were reproduced the diagrams of the fatty acids, or their metal salts, superposed on a (fading) cellulosic pattern. While the lower

members (triacetate, tripropionate, tributyrate) have a definitely crystalline structure, the higher members show structure more and more mesomorphic.

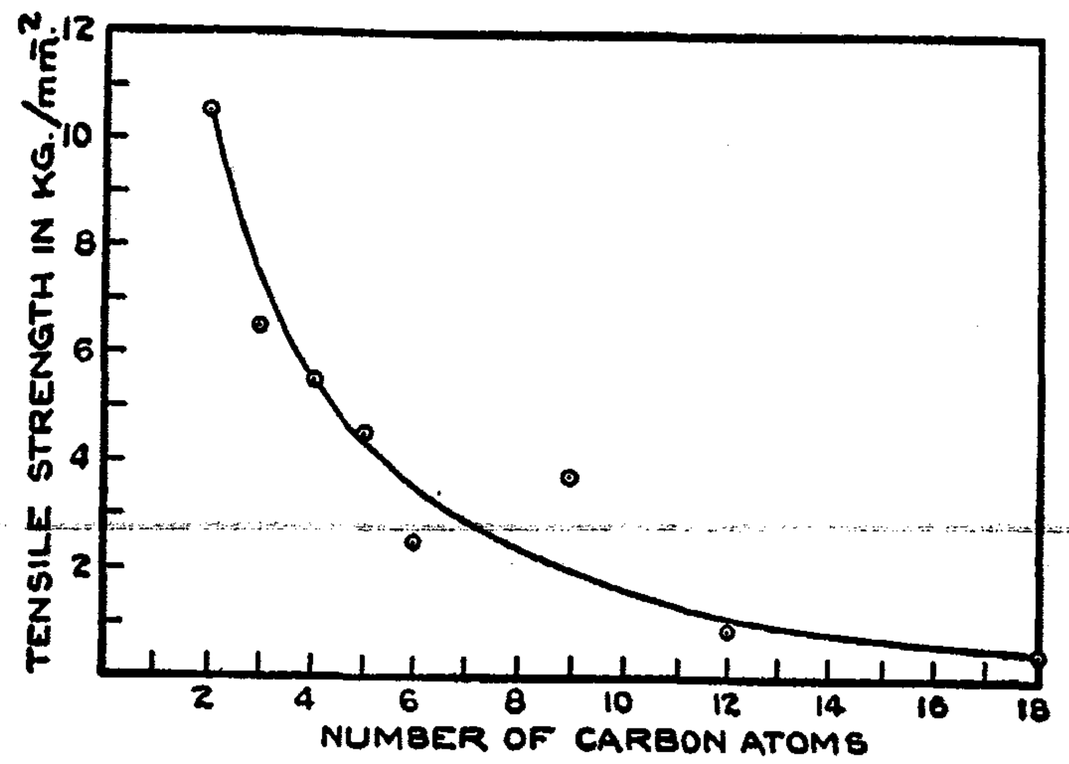

FIG. 6. TENSILE STRENGTH OF CELLULOSE ESTER SHEETS

Hagedorn and Moeller

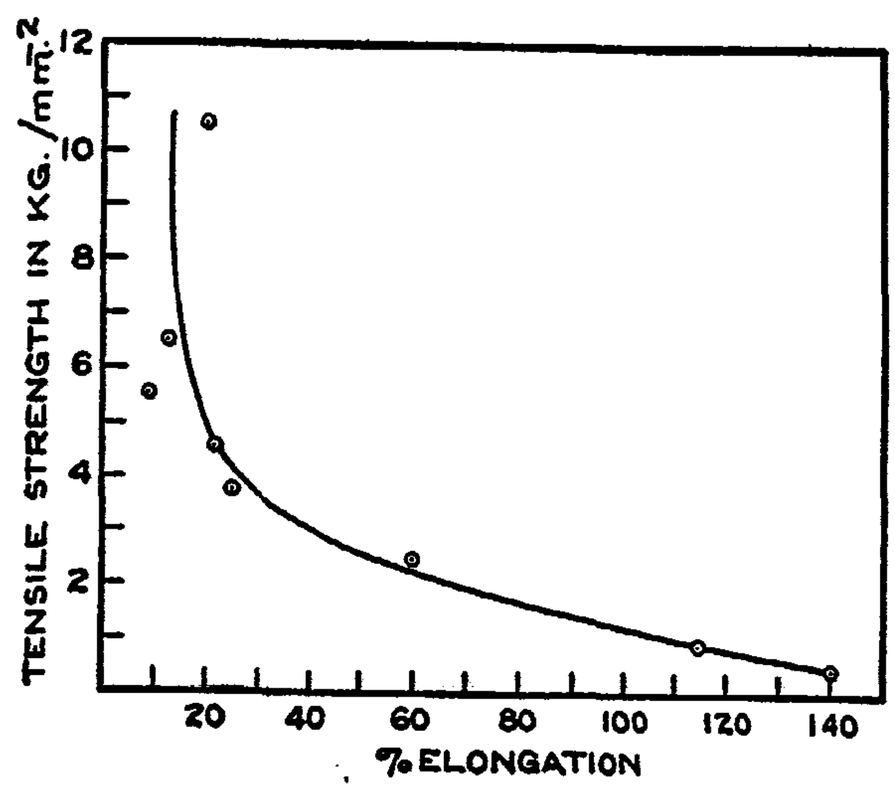

FIG. 7. TENSILE STRENGTH AND ELONGATION OF DIFFERENT CELLULOSE ESTER SHEETS

Hagedorn and Moeller

Using the rotating crystal method for thin films of the esters compressed on glass sheets, it was found that in the degree that the side chain length

increased, there appear reflexions of planes separated by intervals varying with the number of carbon atoms, planes parallel to the surface of the glass. "This indicates that the aliphatic chains, when their length is sufficient, orient themselves parallel to the direction of pressure, perpendicular to the plane of the support."

The aliphatic chains are placed perpendicularly, or nearly so, to the direction of the cellulose chain, that is, to the plane of the glucosan (or pyranose) ring. Further, there will be an alternation of direction of the two secondary substituents and the one primary.

In this way it is easy to see the mutual orientations as attractions of the cellulosic chains submerged and lost as the aliphatic chains increase in length. But also, this structure is difficultly compatible with that of Adam for the spreading on water. For the pyranose rings to lie flat on the water, there would have to be, not only a superstructure of hydrocarbon chains, but also an identical substructure extending down into the water. That does not seem very probable. Moreover, if this took place, the area in compression should remain substantially the same, *independent* of the length of the side chains.

For these reasons it seems more probable that the main valence chain must lie either edgewise or very much tilted on the water surface.

This progressive submergence of the cellulose skeleton by an adipose carcass is again brought out in the figures for elasticity and mechanical strength.

The tensile strength and total elongation at the breaking point of cellulose triesters are shown in table 3, and figures 6 and 7 as determined by Hagedorn and Moeller (3). The tensile strength decreases with increase in the number of carbon atoms in the side chain and the total elongation increases.

SOLUBILITY

The solubility of the higher fatty acid esters of cellulose has been discussed already by G. S. Whitby (10) at a previous symposium. He concluded that they were less polar than cellulose acetate, because of the longer hydrocarbon residues. But this does not seem a necessary conclusion, since according to Smyth (8) the polar moment need not change with length of chain. We do not propose to discuss this subject further here, beyond saying that the solubilities of the series of homologous triesters of cellulose do not support a theory of solubility based solely, or even mainly, on polarity and polar moment.

SUMMARY

A study has been made of the physical properties of a series of triesters of homologous fatty acids, from the acetate to the stearate. It shows the

"cellulose" character being progressively submerged as the length of the side chain is increased. The structure of the solids is interpreted from x-ray data and from spreading and wetting experiments.

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VOLUME 39, NUMBER 2

Page 106. For 1.46 in the 9th line, read 0.66.
For 1.74 in the 10th line, read 0.58.

THE MOLECULAR WEIGHTS OF CELLULOSE AND CELLULOSE DERIVATIVES[1]

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B3C-247

Received June 14, 1934

INTRODUCTION

The nature of the solutions of the lyophilic colloids has long been a favorite subject for investigation by colloid chemists. Evidence has gradually accumulated from many sources to show that the well-known typical lyophilic colloids such as the proteins, rubber, gutta percha, starch, cellulose, and other polysaccharides and their derivatives, are polymeric materials of high molecular weight (45). In recent years a large number of synthetic high polymers possessing also the properties of lyophilic colloids have been prepared and carefully studied, particularly in the laboratories of Staudinger (55) and of Carothers (9). Many of the high polymers, both synthetic and natural, are now recognized to be "linear polymers;" i.e., the molecule is a single chain of recurring structural units bound together by primary valences. When, as is sometimes the case, the number of recurring groups in a molecule attains the magnitude of hundreds, it is indeed a giant or "macro" molecule. In many cases there is good reason to believe that these macromolecular substances are dispersed in solution to the individual molecule, and to a considerable degree the physical and colloidal properties of the solutions appear to be determined by the size and shape of the molecule. A substantial part of our understanding of the lyophilic colloids has come out of the study of the synthetic high polymers, which constitute excellent models for their better-known, naturally occurring prototypes.

A problem of fundamental importance in the interpretation of the behavior of macromolecular materials is the determination of their molecular weights. Numerous efforts have been made to employ the various colligative properties of solutions in accordance with classical methods for de-

[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

Communication No. 144 from the Experimental Station. Second paper in the series on The Molecular Weight of Linear Macromolecules by Ultracentrifugal Analysis. The first paper appeared in J. Am. Chem. Soc. 55, 4319 (1933).

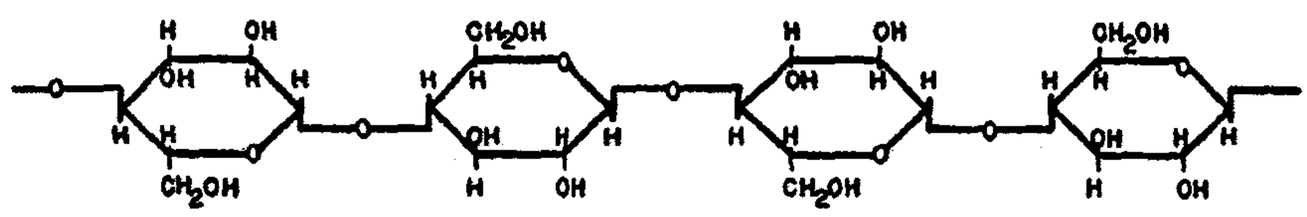
termining molecular weights, but the results have frequently been uncertain or inconclusive. Whenever the molecular weight exceeds a few thousand, the change in freezing point, boiling point, or vapor pressure is too small to be measurable with sufficient precision at the low concentrations necessary for satisfactory molecular weight determinations. Many of the values in the literature obtained by these methods for the naturally occurring high polymers and their derivatives are undoubtedly erroneous for one reason or another. A number of investigators have made limited use of osmotic pressure measurements, but the most comprehensive and conclusive work hitherto carried out on the problem is without question that of Svedberg and his associates for the proteins, using the Svedberg ultracentrifuge (58). Although these investigations have demonstrated the superiority of the ultracentrifuge over other methods, relatively little application of the method has yet been made to high polymers other than the proteins, partly because there are only two laboratories possessing the necessary equipment. The sum total of data obtained by other methods for proteins as well as other macromolecular substances is relatively meager, and the individual items are difficult to assess. In spite of this fact, it has become clear that protein solutions, at least for the cases that have been carefully studied, differ from most other macromolecular solutions in that the dissolved protein molecule is approximately spherical in form, whereas for other high polymers the solute unit is highly elongated. The difference is particularly strikingly manifested by the marked difference in viscosity characteristics, dilute protein solutions commonly having viscosities relatively independent of the molecular weight and in approximate agreement with Einstein's equation for spherical particles. On the other hand, the viscosities of most other macromolecular materials are very sensitive to molecular weight differences and are much greater than would be the case for spherical molecules (33).

The theory for the influence of highly elongated, perhaps flexible, molecules upon the free energy of a solvent has not yet been worked out, and it is therefore not known how far conventional methods for estimating molecular weights are applicable to polymers of the high-viscosity type. Having recently shown, however, that for one such case the molecular weight can be correctly determined with the ultracentrifuge (34), and taking into account the experimental efficacy of the instrument, we believe that it provides the most reliable and most effective method now known for estimating the molecular weights, in solution, of linear macromolecules of all kinds. We have accordingly selected this method of study for what we hope will eventually be a comprehensive investigation of cellulose and its derivatives.

Cellulose and its derivatives represent, next to the proteins, the most thoroughly studied class of high polymers and typify the high-viscosity

group. For theoretical investigations concerning the nature of lyophilic colloids and their solutions, cellulose and its derivatives are particularly valuable. As will be seen, in certain cases they permit chemical conversions with little if any change in the length of the molecule. They offer several chemically related series of derivatives of considerable chemical stability for comparative studies. Many of them are soluble in a wide variety of solvents and permit avoidance of the ionic complications so characteristic of protein solutions. The molecular weight may be varied at will over very wide limits without a detectable change in chemical composition. Finally, x-ray crystal analysis has provided an unusual amount of valuable correlative information concerning the solid forms of cellulose and its derivatives.

It is now very generally agreed that the cellulose molecule is a long chain of anhydroglucose residues linked together by 1,4 glucosidic oxygen (reference 45, p. 91), in accordance with the following scheme:



On each glucose residue in the chain there are three hydroxyl groups which react with suitable reagents to give the various cellulose derivatives. Presumably, on one end of the chain the terminal glucose residue possesses four alcoholic hydroxyl groups, and at the opposite end there is a hemiacetal group. The length of the chain may vary within wide limits, probably being very long in native cellulose and passing through all intermediate lengths, as depolymerization occurs by breaking the oxygen links, until the final product is glucose. Whether the chains of native cellulose are uniform in length is not known, but in all probability, the length (or molecular weight) of degraded celluloses and derivatives is never uniform. This is a general characteristic of high polymers. Usually, therefore, when reference is made to chain length or molecular weight, an average value is meant. When comparing various celluloses and derivatives with respect to their molecular lengths, it is useful to specify the "degree of polymerization" (D.P.), by which is meant the number of glucose residues per molecule. For many years, industrial chemists interested in products manufactured from cellulose have assumed in a rather vague way that molecular "degradation" (without specification as to its chemical nature) of cellulose and its derivatives leads to reduction of the relative viscosity of their solutions (4, 48). As will be discussed in more detail below, it now appears that the viscosity characteristics of dilute solutions in good solvents are primarily determined by the degree of polymerization.

PREVIOUS INVESTIGATIONS OF THE MOLECULAR WEIGHT OF CELLULOSE AND CELLULOSE DERIVATIVES

Every method for the estimation of the molecular weight of macromolecules that we are aware of has been applied to cellulose and its derivatives. In a number of investigations, particularly the earlier ones in which freezing point or boiling point methods were usually used, values were obtained ranging from a few hundred to a few thousand (3, 5, 8, 29, 32, 46). In many cases later work failed to confirm these results, and in the light of present knowledge, it may be assumed either that the experimental technic was faulty (2, 17, 22, 44; 55, p. 453), or that the cellulosic materials were far more degraded than was suspected. Calculations of molecular weights by means of Einstein's equation for the diffusion coefficient of spherical molecules (24, 61) are now realized to be invalid, because the diffusion of cellulose and cellulose derivatives does not obey Fick's law and the solute particles are non-spherical (27, 38). On the basis of the breadth of the lines in the x-ray diffraction pattern, Mark (reference 42, pp. 163, 197) has inferred that the length of the crystallite in native ramie cellulose is about 600 A.U. Assuming that the length of the cellulose molecule is not longer than the length of the crystallite, and taking into account data from other sources, he has concluded that the molecule probably contains one hundred and fifty to two hundred glucose residues. Although this is an interesting speculation, it is admittedly not the only possible interpretation of the x-ray observations.

The most significant results hitherto made public have been obtained by means of osmotic pressure measurements, ultracentrifugal analysis, end-group determinations, and viscosity measurements. Even with these methods, there are gross discrepancies in the results, and there is not, as yet, general agreement as to which results are correct. The principal data are summarized in tables 1, 2, and 3.

In addition to molecular weights, the tables summarize the available data concerning the viscosity characteristics, in order to reveal to what extent a quantitative relationship exists between molecular weight and viscosity. Since the viscosity characteristics were not expressed by the various investigators in a uniform manner, the data were reduced to a common basis for comparative purposes by calculating $[\eta]$ defined by the expression[2]

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_r - 1}{c} \right)$$

[2] For more detailed discussion of the advantages of comparing viscosities in infinitely dilute solutions, see references 36, 45 (p. 175), and 55 (p. 56).

where η_r is the viscosity of the solution relative to that of the solvent, and c is the concentration in grams per 100 cc. of solution. Extrapolation to zero concentration was made by means of Fikentscher's equation (14, 37). As Staudinger has shown, $[\eta]$ is directly proportional to the molecular weight for linear molecules of considerable length.[3]

Osmotic pressure results

Examination of table 1 shows that with a single exception the molecular weights of the cellulose ethers and esters as determined by the osmotic pressure method fall in the range 15,000 to 204,000, with most of the values falling between 25,000 and 100,000. In most cases the materials were commercial products or fractions thereof. The outstanding discrepancy is provided by the results of Hess and Ulmann (31) for Hess's crystalline cellulose triacetate II ("biosan acetate") by a modification of the method of Frazer and Patrick (15), in which the vapor phase serves as membrane. Inasmuch, however, as the authors report several quite unusual effects, such as a greater vapor pressure for a solution than for the solvent (60) and a remarkable reversible depolymerization of the triacetate, for which there are at present no generally accepted interpretations, the results cannot for the time being be considered as conclusive. In addition, Hess's crystalline triacetate does not display the properties characteristic of high polymers (e.g., large value of $[\eta]$, swelling behavior, and film-forming capacity) and is undoubtedly a relatively low molecular weight degradation product corresponding to a cellodextrin acetate (2, 16, 17, 19, 23, 44; 55, p. 460).

An important fact brought out by the osmotic pressure investigations is the non-uniformity of the cellulose derivatives with respect to molecular weight. The fractionation studies of Duclaux and Wollman (13) and of Medvedev (43) for cellulose nitrate, of Herzog and Deripasko (25) and of

[3] In view of the increasing recognition of the value of characterizing the viscosity of solutions of macromolecular materials by the quantity $[\eta]$, there would be considerable advantage if investigators in this field could agree upon a suitable name for the quantity. In analogy to specific conductivity, specific volume, specific refraction, specific rotation, and the like, "specific viscosity" would serve very well. Unfortunately, the expression is already in use with two different meanings. It has long been used by Duclaux (10, 12) in referring to the constant k in Arrhenius's logarithmic equation ($\log \eta_r = kc$). Berl (4) refers to k as the "specific viscosity constant." If natural logarithms are used, $k = [\eta]$ for infinitely dilute solutions. Staudinger later adopted the term, "specific viscosity," for the quantity $\eta_r - 1$, but proposed no name for the more useful quantity, $[\eta]$. In passing, it may be pointed out that Staudinger's expression η_{sp}/c is equal to our quantity $[\eta]$ multiplied by one-tenth the weight of the structural unit of the particular linear polymer to which it refers, e.g., $\eta_{sp}/c = 162[\eta]/10$ for cellulose, the difference being due to the fact that Staudinger's concentrations are expressed in molarity with respect to the structural unit.

TABLE 1

Molecular weights of cellulose derivatives from osmotic pressures

CELLULOSE DERIVATIVE	MOLECULAR WEIGHT	D. P.	[η]	D. P./[η]	AUTHOR AND REFERENCE
Nitrocellulose	51,000	200			Duclaux and Wollman (12)
Nitrocellulose	21,000 to 70,000	80 to 270	1.5 to 3.1	50 to 100	Duclaux and Wollman (13)
Nitrocellulose	13,000 to 50,000	50 to 200	0.5 to 2.4	50 to 100	Duclaux and Nodzu (11)
Nitrocellulose	7,000 to 50,000	25 to 190	0.3 to 2.8	70 to 100	Grard (21)
Nitrocellulose	19,000 to 204,000	70 to 770	0.5 to 5.2	130 to 165	Buchner and Steutel (7)
Nitrocellulose	25,000 to 75,000	100 to 280	1.4 to 2.1	70 to 160	Medvedev (43)
Cellulose acetate	21,000 to 64,000	80 to 250	0.9 to 2.3	93 to 108	Herzog and Deripasko (25)
Cellulose acetate	20,000 to 152,000	110 to 600	1.0 to 2.3*	120 to 260	Herzog and Herz (26)
Cellulose acetate	23,000 to 34,000	90 to 130	1.2 to 2.1	55 to 85	Grard (20)
Cellulose acetate	33,000 to 45,000	130 to 180	0.9 to 1.8	80 to 145	Buchner and Samwel (6)
Cellodextrin acetate	576 to ∞				Hess and Ulmann (31)
Benzylcellulose	29,000	84			Herzog and Spurlin (28)
Ethylcellulose	14,000 to 63,000	60 to 270	0.7 to 3.4	35 to 90	Okamura (47)

* These viscosity measurements were made by ourselves.

Herzog and Herz (26) for cellulose acetate, and of Okamura (47) for ethylcellulose (see table 1) all agree in showing that the original materials contained a mixture of molecules of different weight. Numerous investigators have in other ways also demonstrated the heterogeneity of cellulosic products (39, 40, 49, 50).

The accuracy of the results, so far as revealed by internal evidence, varies somewhat for the different investigations. In most cases the ratio of pressure to concentration increases with concentration, i.e., the molecular weight apparently decreases with increasing concentration, and there is some question concerning the correctness of the extrapolation to zero concentration, particularly when the concentrations used were 1 per cent or more (6, 7, 20, 21). In other cases, where an effort was made to use low concentrations (25, 26), there was considerable irregularity in the resulting molecular weights. Notwithstanding, the values obtained are perhaps of the right order of magnitude.

Ultracentrifugal analysis

The data obtained from osmotic pressure measurements all refer to cellulose derivatives and leave the question of the molecular weight of cellulose itself entirely open. The only effective solvent for cellulose with a limited degrading action is Schweitzer's reagent, commonly referred to as cuprammonium solvent, but its complexity precludes its usefulness for osmotic pressure measurements. The molecular weight of cellulose dissolved in cuprammonium solvent has however been investigated by means of the ultracentrifuge by Stamm (54) and by ourselves (35). With respect to sedimentation equilibrium, the ultracentrifuge method is in basic theory similar to the osmotic pressure method as mentioned above. An important advantage, however, of the ultracentrifugal method is the fact that it yields information concerning the homogeneity of the sample being studied.

By the sedimentation equilibrium method, as recorded in table 2, Stamm found the molecular weight of the cellulose–copper complex formed in cuprammonium solvent,[4] and calculated cellulose molecular weights therefrom, on the assumption of one atom of copper per glucose residue. For a cotton-linters alpha-cellulose he obtained an average value of 56,000 for the copper complex or 40,000 on a copper-free basis, with no evidence for appreciable non-uniformity. Approximately the same value was obtained by the sedimentation velocity method. Wood celluloses of various sources were, on the other hand, found to be non-uniform, containing more or less relatively low molecular weight material in addition to various

[4] Strictly speaking, Stamm's method of calculating his results does not yield an exact value of the molecular weight of the cellulose–copper complex because of the difference between the specific volumes of the cellulose–copper complex and of cellulose.

amounts of the constituent characteristic of cotton cellulose and a second constituent with a molecular weight of about 20,000 on a copper-free basis.

As reported last year (35), we were unable to confirm Stamm's results and obtained a much larger value for the same cotton cellulose: 300,000 for the cellulose–copper complex or about 220,000 on a copper-free basis, as calculated by Stamm's method. Even degraded and regenerated celluloses gave values of 100,000 and greater. Although it is not certain, we believe that degradation inadvertently occurred during Stamm's measurements and, perhaps, that sedimentation equilibrium was not attained. On the basis of our investigation of a synthetic high polymer of known molecular weight, the results obtained by the sedimentation velocity method are of doubtful reliability as absolute values (34).

End-group determinations

Molecular weights by osmotic pressure and ultracentrifuge methods depend upon the state of dispersion of the solute in a solvent and are affected by association and solvation, with the consequence that the values so obtained may not correspond to the true molecular weight in the ordinary sense of the term. In contrast, the end-group method is independent of the laws of solutions, but depends upon knowledge concerning the chemical structure of the substance being studied. In principle, it is simply necessary to determine by suitable analytical means the proportion of glucose residues showing some chemical property characteristic of a terminal residue, from which the average number of glucose residues per molecule may be estimated. Two types of end-group determination may be used for cellulose or derivatives: one depending upon the terminal hemiacetal group, the other depending upon the terminal tetrahydroxyglucose residue.

The so-called copper number measures the reducing power of cellulose and presumably is due, at least in part, to the hemiacetal groups. The determination, unfortunately, is very sensitive to the conditions of experimentation, and the calculated molecular weights can scarcely be considered reliable (42, p. 192; 55, p. 491).

Bergmann and Machemer (2) developed an iodometric method for determining the hemiacetal content of cellodextrin acetates and used it in estimating molecular weights (see data of table 3). Unfortunately, the authors give no viscosity or other independent data indicative of the state of degradation of the products. In the discussion at the symposium of the Faraday Society, Machemer (41) reported that the iodometric method and the Haworth and Machemer method, involving the nonreducing end group, gave concordant results for cellodextrins with molecular weights in the range of 3000, but admitted that end-group determinations are not satisfactory for high-viscosity cellulosic products. Staudinger (reference 55, pp. 463, 491) was not able to obtain consistent results with this method for celluloses in any case, and only for highly

TABLE 2

Molecular weights of celluloses in cuprammonium by ultracentrifugal analysis

CELLULOSE	METHOD	MOLECULAR WEIGHT (CELLULOSE-Cu)	D. P.	[η]	D.P./[η]	AUTHOR AND REFERENCE
Cotton celluloses	Sedimentation equilibrium	56,000	250	4.33	58	Stamm (54)
	Sedimentation velocity	56,000 + f*		4.15		
	Sedimentation velocity	56,000 + ff*		2.79		
Wood celluloses	Sedimentation velocity	2A† + 1B + ff		3.65		
	Sedimentation velocity	1A + 3B + ff		2.63		
Cotton celluloses	Sedimentation equilibrium	300,000	1300	5.05	260	Kraemer and Lansing (35)
	Sedimentation equilibrium	200,000	890	3.40	260	
	Sedimentation equilibrium	110,000	490	1.83	270	

* f indicates a small amount and ff indicates a considerable amount of a fine fraction of relatively low molecular weight.

† A represents a component with a molecular weight of 56,000, and B represents a component with a molecular weight of 28,000.

TABLE 3

Molecular weights by end-group determinations

END GROUP	TYPE OF CELLULOSE	D. P.	[η]	D. P./[η]	AUTHOR AND REFERENCE
Hemiacetal	Cellodextrin acetates	8 to 11			Bergmann and Machemer (2)
	"Biosan" acetate	8 to 13			
	Native celluloses	70 to 175			Mark (42, p. 196)
	Regenerated cellulose	75 to 155			
	Cellulose acetate	105			
	"Biosan" acetate	13	0.15	87	Staudinger (55, pp. 463, 491)
	Special triacetates	9 to 35	0.07 to 0.45	97 ±10	
	Native cellulose	50			Freudenberg et al. (18)
	Cellodextrins	30 to 40			
Carboxyl	ClO_2-purified cellulose	96			Schmidt et al. (51)
Tetramethylglucose	"Biosan" acetate	12 to 25			Haworth and Machemer (23)
	Special acetate	100 to 200			

degraded triacetates with molecular weights not exceeding about 10,000 were the results apparently satisfactory. Hess also has found this method to give erratic results (30). On the basis of considerable experience with the method, Mark considers his results, given in table 3, to be of questionable reliability as absolute values (reference 42, p. 196).

Haworth and Machemer (23) have employed the terminal tetrahydroxyglucose residue for molecular weight determinations. Cellulose acetate was converted to a completely methylated cellulose which was then completely hydrolyzed and the yield of tetramethylglucose determined. From this value the molecular weight of the methylcellulose may be calculated to be about 35,000. Unfortunately, the method does not appear to be applicable to cellulose acetates in general, or to other derivatives.

Although, strictly speaking, an end-group determination in the above sense is apparently not involved, Schmidt and coworkers (51) have applied analogous principles to the calculation of molecular weight from their determinations of the acidity (i.e., free carboxyl groups) of various celluloses. Schwarzkopf and Weiss (52), however, deny the suitability of the analytical method, which involved conductometric titration of a heterogeneous system. Regardless of the accuracy of the acidity determination, it is highly improbable that the molecular weights of the different types of celluloses studied by Schmidt et al are really equal, as they infer.

Considering all the end-group determinations, it must be admitted that the results so far obtained are rather meager. The reactions involved are complicated and of limited applicability and the accuracy in the best of cases is not sufficient for the high molecular weights possessed by the technically important materials.

Viscosity method of Staudinger

Although, as pointed out above, it had been generally believed for a good many years that the viscosity of solutions of cellulose derivatives depends upon the molecular weight, no general quantitative relations were formulated until Staudinger discovered that $[\eta]$ for linear polymers of low molecular weight (i.e., having molecular weights within the range of freezing or boiling point methods) is to the first approximation directly proportional to the molecular length and for many cases is relatively independent of the chemical composition. Thus, Staudinger found that $[\eta]$ for solutions of cellodextrin triacetates in *m*-cresol was related to the degree of polymerization, as calculated from molecular weights by the freezing point and Bergmann-Machemer end-group methods, in accordance with the equation[5]

[5] This is equivalent, within the limits of experimental error, to Staudinger's equation (reference 55, p. 466)

$$\text{Mol. Wt.} = \frac{\eta_r - 1}{CK_m}$$

where $K_m = 11 \times 10^{-4}$ and C is expressed as molarity of glucose residues.

$$D.P. = 90\ [\eta]$$

The same acetates were carefully saponified with alcoholic potassium hydroxide and the viscosities of the resulting regenerated cellodextrins in cuprammonium were determined. Upon the assumption that no scission of the cellulose chain occurred during regeneration, i.e., that the degree of polymerization of each triacetate and the corresponding cellodextrin was the same, it was found that

$$D.P. = 100\ [\eta]$$

The regenerated cellodextrins were also nitrated and the viscosities in butyl acetate measured, and again upon the assumption that no degradation occurred, it followed that

$$D.P. = 77\ [\eta]$$

The methylated derivatives, prepared by the method of Haworth and Machemer, gave somewhat discordant results in that the constant of proportionality varied from 50 to 75, depending on the solvent used (57). Although no actual molecular weight determinations by freezing point or other direct methods were reported for the cellodextrins, nitrates, or methyl derivatives, the approximate constancy of the factor of proportionality (the experimental error being probably ± 10 per cent) is in agreement with Staudinger's viscosity laws and thus confirms the assumption that the chemical conversions did not affect the molecular lengths.

The same close relationship was found between the viscosities of cellulose acetates having $[\eta]$ up to 4 and of the regenerated celluloses and nitrates made therefrom (reference 55, p. 506). Since molecular weights by the Bergmann-Machemer method (over the range where it appeared satisfactory) and the osmotic pressure results of Herzog and Deripasko and of Buchner and Samwel (56) indicated that the direct proportionality between D.P. and $[\eta]$ extended for cellulose acetates to $[\eta]$ = ca. 2.8, Staudinger concluded that the linear relationship extends to the highest values of $[\eta]$ and is applicable to all cellulose derivatives. On this basis, he has estimated the degree of polymerization or molecular weight of many cellulosic materials from viscosity measurements. Thus, he has deduced the degree of polymerization of native cellulose carefully purified in absence of oxygen to be 750 (molecular weight of 120,000), of rayons to be 100 to 200, of so-called high-viscosity nitrocelluloses to be 500 to 2600.

At the present time, it is impossible to predict on theoretical grounds whether there should be a direct proportionality between degree of polymerization and $[\eta]$ of cellulose derivatives or not. The justification for the calculation of molecular weights from viscosity data must rest entirely upon an experimental correlation of viscosity characteristics and molecular weights determined by absolute methods. In so far as cellulose and its

derivatives are concerned, the results on this point are promising but not entirely concordant. Although the osmotic pressure results of Herzog and Deripasko and of Buchner and Samwel appear to confirm Staudinger's conclusions, other apparently equally reliable data, summarized in tables 1 to 3, fail to agree. Even in the cases cited, the confirmation may be apparent rather than real, for the measurements of Buchner and Samwel were all made at concentrations too high to give accurate results, and, according to Ubbelohde (59), the viscosity measurements of Herzog and Deripasko are vitiated by a kinetic energy error. A definite parallelism between $[\eta]$ and degree of polymerization is nevertheless evident, and in view of the recognized difficulties in accurately determining high molecular weights, there is reason to suspect that the inconstancy in the values for the viscosity coefficient (D.P./$[\eta]$) obtained by various workers is due to experimental errors.

ULTRACENTRIFUGAL ANALYSIS OF CELLULOSE DERIVATIVES

In order to establish the relationship between viscosity and molecular weight more definitely, we have extended our ultracentrifugal investigations of cellulose to a group of technical cellulose acetates and nitrates. The acetates were acetone-soluble "secondary" acetates having values of $[\eta]$, in acetone solution, ranging from 0.80 to 2.32. Several members of the acetate series were fractionated samples prepared and used by Herzog and Herz (26) in their osmotic pressure investigations.[6] The nitrates contained 12.0 per cent nitrogen and had values of $[\eta]$ ranging from 1.41 to 2.20, corresponding to viscosities of 5 to 71 seconds in 12.2 per cent concentration by the A.S.T.M. standard method (1). For both acetates and nitrates, ultracentrifugal determinations and viscosity measurements were made at 25.0°C. on acetone solutions about 0.1 g. per 100 cc. in concentration. In all cases, the molecular weights found were converted to degrees of polymerization and values of $[\eta]$ were calculated.

Both acetates and nitrates, including the fractionated products, were found to be distinctly non-uniform with respect to molecular weight. The average values, obtained by an approximate method, nevertheless showed a proportional relation to $[\eta]$ corresponding within experimental errors (about ± 10 per cent) to the expressions D.P. $= 230\ [\eta]$ for the acetates and D.P. $= 270\ [\eta]$ for the nitrates. As shown in table 3, our results on celluloses in cuprammonium solvent are given by the expression D.P. $= 260\ [\eta]$. Thus the degrees of polymerization found by means of the ultracentrifuge are from $2\frac{1}{3}$ to $3\frac{1}{2}$ times as great as predicted by Staudinger, his factors of proportionality being respectively 90, 77, and 100.

In interpreting the differences between our results and those of other

[6] We are much indebted to Professor Herzog for furnishing us with these samples so that their molecular weights might be determined by two independent methods.

investigators, it is necessary to consider the effects of non-uniformity. For heterogeneous materials, different methods for determining molecular weights give different "average" values. Thus, it may be shown that freezing point, osmotic pressure, and end-group methods, when applied properly to an ideal mixture, result in an average value defined by the expression

$$M_n = 1 \Big/ \sum \frac{f_i}{M_i}$$

where f_i is the fractional weight of the constituent of molecular weight M_i in the mixture, and the summation is to be applied to all constituents present. This average may be designated as a "number-average molecular weight." On the other hand, the viscosity method, according to Staudinger's theory, should give an average value defined by the expression

$$M_w = \sum f_i M_i$$

which corresponds to a "weight-average molecular weight." The ultracentrifugal method gives a weight-average value. As a consequence, the osmotic pressure method should give a lower apparent molecular weight for a mixture than the viscosity method or the ultracentrifuge method. If the non-uniformity is marked, the difference in the two average values is surprisingly large. In order that the viscosity method for estimating degree of polymerization may give useful results for practical cases where non-uniform products are inevitably involved, it is essential that "weight-average" molecular weights be used in determining the proportionality factor. Staudinger's factors were determined with molecular-weight methods giving "number-averages," and are therefore too small. The improved consistency between viscosity and molecular weight by the freezing point method after fractionation of his samples was taken by Staudinger to mean that the fractionated products were substantially uniform. However, they were probably still distinctly non-uniform (53), and the greater consistency of results really was due to a more nearly constant ratio between the number-average and the weight-average molecular weights following fractionation. Without quantitative information concerning the distribution of molecular weights for a given specimen, it is not possible to convert number-average to weight-average or vice versa, so the magnitude of the error in Staudinger's values due to this factor alone cannot be definitely estimated.

Solvation is another factor affecting molecular weight determinations in various ways. In the case of osmotic pressure measurements in dilute solutions, solvation to the extent of 100 per cent or so has a negligible effect on the calculated molecular weight. The same is true for ultracen-

trifuge determinations unless the partial specific volumes of the solvated and unsolvated molecules differ, whereupon there is a corresponding error in the calculated molecular weight. For cellulose esters and ethers in organic solvents, the effect is probably not marked. $[\eta]$, on the other hand, is decidedly sensitive to solvation, but the moderate variation in $[\eta]$ with different solvents (10) and the approximate equality of the viscosity coefficients indicate that the solvation of cellulose acetates and nitrates is not large nor greatly different. In fact, if $[\eta]$ is reduced to a volume basis by division by the partial specific volume of the solute (acetate, 1.46; nitrate, 1.74), as should logically be done when comparing different solutes, the results for cellulose acetates and nitrates in acetone may be expressed by the single equation

$$\text{D. P.} = 156\,[\eta]_{\text{vol.}}$$

Association also may be involved in molecular weight determinations of high polymers, as so often is the case for ordinary small molecules. Osmotic pressure and the ultracentrifuge should give the weight of the associated molecule, other disturbing factors being absent. The effect of association upon the viscosity depends, according to Staudinger's theory, upon the relative positions of the molecules associating together. If compact bundles of parallel molecules are formed, the viscosity is supposed not to be affected, but if two molecules associate end to end, the effect on viscosity is supposed to be twice as great as in the absence of association.

With so many factors influencing molecular weight determinations and viscosities of solutions of celluloses or derivatives, irregularities in the relationship between viscosity and molecular weight probably will persist even with accurate values for molecular weights. Much accurate data for various solvents and at various temperatures must be obtained before the effects of complicating factors can be properly unscrambled. On account of unavoidable non-uniformity, the ultracentrifuge is the only means at present available for obtaining molecular weight information with the necessary detail. Useful information can be secured by osmotic pressure methods, but the experimental technique needs further refinement so that reasonably accurate results can be obtained at low concentrations (e.g., 0.1 per cent or less). In the meantime we believe that the equations we have stated above may be used for estimating the degree of polymerization of technical celluloses, cellulose acetates, and cellulose nitrates by the viscosity method over the range of $[\eta]$ we have studied and with the solvents we have used.

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THE SORPTION OF BROMINE AND IODINE BY SILICA GEL

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Received April 26, 1934

In the literature on the adsorption of gases and vapors by porous adsorbents there is lacking a reasonably complete study on the halogens. There is recorded a set of measurements by Magnus and Müller (3) on the adsorption of chlorine by silica gel in an all-glass system at 0°, 20° and 40°C. They obtained adsorption isotherms which were slightly concave toward the pressure axis. However their results did not fit the Freundlich equation. Some time ago one of us decided to undertake a rather complete study on the sorption of the halogens and the hydrogen halides on various surfaces. This and the following paper give the results for bromine and iodine sorption on silica gel and charcoal.

APPARATUS AND MATERIALS

Measurements of the sorption were made by the static method. The vapor pressure of pure halogen vapor in a glass and quartz system was controlled, and the sorption determined by means of a McBain sorption balance (4).

Figure 1 shows the essential portions of the apparatus. The quartz spring balance was suspended from a hook on a glass ball resting upon three projections in the sorption tube, A. The sorbent was contained in a small glass bucket (1), S, and was suspended from the spring by a quartz fiber. The pressure in the apparatus was determined by the 4.5 turn Bodenstein quartz spiral gauge, B, using this instrument as a null point indicator. The pressure in the jacket of the gauge was varied until the index needle coincided with the fixed reference point viewed in the field of a low-power microscope. The reference point, which was an integral part of the gauge, was attached with wax to the end of a glass tube sealed through the bottom of the jacket in order to prevent damaging vibration. The gauge was mounted in the jacket with a graded seal.

Pressures were read from the large bore, closed-end, mercury manometer with a cathetometer. The manometer readings were corrected to 0°C.

[1] The material here presented formed a part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Angus E. Cameron in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1932.

Zero readings were taken with the apparatus evacuated or the halogen frozen out with liquid oxygen and the quartz gauge at the temperature at which a run was to be made.

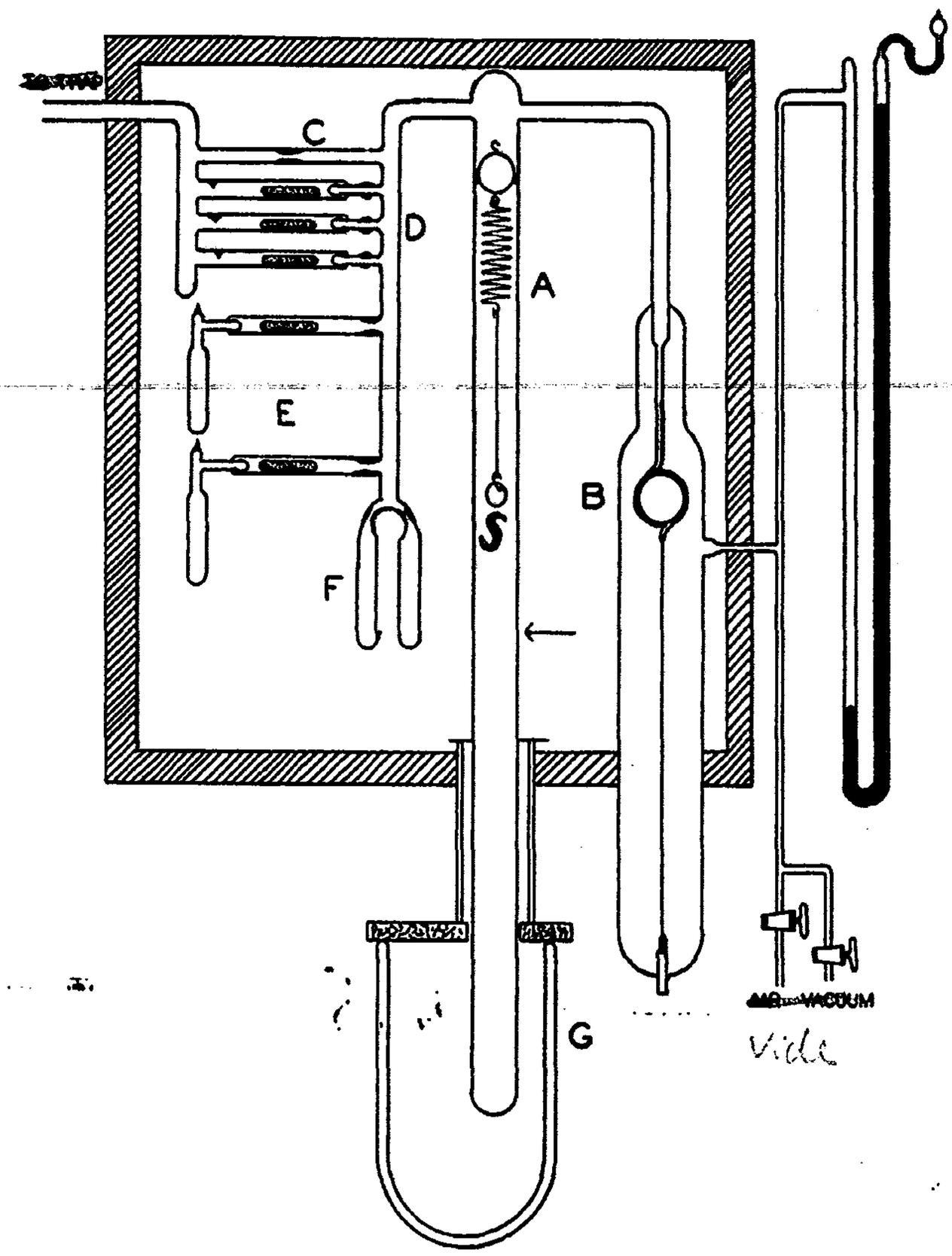

FIG. 1. SORPTION APPARATUS

The entire apparatus, with the exception of the lower portion of the sorption tube, A, and the bottom of the quartz gauge, was enclosed in an air bath built of wood and lined with asbestos. A multibladed fan at

the top of the bath blew air down through a grid of resistance wire. A long, thin-walled glass regulator bulb filled with mercury and connected through a capillary to a control "U" was inserted through the wall of the oven, and operated a thermionic relay device to vary an external resistance in series with the heating grid.

The halogen was introduced into the bottom of tube, A, as will be described, and its temperature was controlled by means of a thermostated bath in a half-gallon Dewar jar. The space between the lid of this small bath and the bottom of the air bath was insulated by a glass tube of large diameter, which was wound with asbestos paper. A resistance wire wound on the inside of this tube permitted heating of this portion of the tube to prevent condensation of halogen when working at high vapor pressures.

The small bath was stirred by a multibladed paddle driven by an induction stirring motor. A special thermoregulator bulb, with large external surface and filled with toluene or mercury, operated a thermionic relay device to control the bath temperature. Above room temperature a small, direct-immersion heating element with a series resistance was used. Water or paraffin oil were used as bath liquid, depending upon the temperature to be obtained. Below room temperature the temperature was controlled by an automatically operated cryostat (2).

The sorption tube was cut at the point indicated by the arrow, and a quartz fiber of sufficient length to extend below the floor of the oven was attached to the one already hanging from the spring. This fiber was shielded from air currents inside the oven by a glass tube of somewhat greater diameter attached to the sorption tube with a ring of cork. A mica pan, weighing about 0.03 g., was hooked to this fiber, and calibrated fractional gram weights were placed upon the pan. The long fiber and pan were weighed on an analytical balance.

Measurements of the spring length were made with a traveling microscope rigidly mounted on a vertical rod supported permanently on the side of the air thermostat. Observations were made through a narrow glass window. Other windows permitted observations of the interior of the thermostat. To reduce thermal disturbances on the inside the latter were double windows. Illumination for reading the spring points was furnished by a long show-case bulb behind an opal glass plate. The opal plate was removed for the studies with iodine vapor and the filament of the bulb lined up behind the spring points.

The traveling microscope was especially designed for vertical mounting and was constructed in the instrument shop of the University of Minnesota. The screw was cut with a 1-mm. pitch and the micrometer head was marked with 100 divisions. The total useful range of the instrument was 100 mm.

The spring was calibrated at the various temperatures both before and after each run. The second calibrations were used in calculations of the sorption. The calibration was carried out in steps of 0.1 g. The sensitivity of the spring, expressed in milligrams per 0.01 mm. elongation, was calculated for each 0.1 g. interval at the different temperatures (see table 1). This sensitivity and the calibration points were used to determine the load on the spring from the observed length.

The weight of the bucket was determined by hanging it on the short fiber and measuring the spring length. About 0.2 g. of sorbent was added to the bucket; after hanging it in place the sorption tube was sealed together. The system was evacuated through tube C. The vacuum system consisted of an ordinary and a high speed Langmuir mercury vapor pump operating in series, with the customary McLeod gauge and liquid air trap.

The portion of the sorption tube in which the sorbent hung was heated with a small resistance tube furnace operated at 500–550°C. During

TABLE 1

Spring calibration

LOAD	LENGTH	DIFFERENTIAL SENSITIVITY
grams	*mm.*	*mg. per 0.01 mm.*
0.33958	57.051	
0.43944	62.666	0.17783
0.53967	67.272	0.17880

evacuation the connecting tubing was flamed over as much of its length as possible. The system was evacuated at 10^{-5} mm. pressure for 24 hours, and tube C was sealed. The halogen in one of the ampoules, E, was frozen with liquid air, and the breakoffsky operated by a small direct current solenoid which had been placed around the tube before it was sealed in place.

The halogen was allowed to remain in contact with the sorbent for at least twelve hours. During this time the furnace was held at a sufficiently high temperature to prevent excessive condensation on the sorbent. The temperature was raised to 500°C. several times during the twelve hours to aid in the displacement of foreign gases from the sorbent surface. The ampoule E, containing most of the halogen, was then sealed off, and the system opened to the vacuum line through one of the bank of breakoffskies, D, after the remaining halogen had been frozen out in a seal-off bulb, F, with liquid oxygen.

Evacuation and activation were continued as before for 48 hours, at which time the open breakoffsky was sealed and the second sample of

halogen admitted, distilled into the bottom of tube A, and the empty bulb sealed off. The activation furnace was removed when all the halogen had been frozen down in the bottom of tube A, the air bath was brought up to temperature, and the vapor pressure thermostat was assembled and brought into operation. At the completion of a run the halogen was frozen into the remaining bulb, F, and sealed off before opening the system to the vacuum line.

The temperature of the oven was read on a calibrated thermometer suspended beside the sorption tube. The temperature was constant to ±0.15°C., at any setting from 60°C. to 220°C. When working with bromine the temperature of the liquid bath was read on a 100°C. thermometer graduated in 0.1°C. steps and calibrated against thermometers with Bureau of Standards certification. A similarly calibrated 220°C. thermometer reading in 0.2°C. steps was used in the work with iodine. Below 0°C. the temperature of the bath was determined with a calibrated toluene thermometer which for later work was replaced with a ten-junction copper–constantan thermocouple. The temperature of the bath was held to ±0.01°C. above room temperature and to within ±0.03°C. from room temperature to 0°C. Below 0°C. the variation was found to be over a range not greater than 0.08°C.

The same quartz spring was used throughout this work. It consisted of twenty-one turns and was 1.5 cm. in diameter. Its sensitivity was approximately 0.18 mg. per 0.01 mm. elongation. The calibration of the spring was found to be remarkably reproducible, spring lengths measured two months apart checking within a few thousandths of a millimeter under the same load and at the same temperature.

The bromine used was prepared from analytical reagent quality bromine. Further purification was carried out according to the directions given by Scott (6), shaking the bromine twice with 1 *N* potassium hydroxide and once with 0.5 *N*. It was then distilled once from dilute potassium hydroxide solution in an all-glass still with a short fractionating column, and again from the same still after cleaning and drying. The middle portion of the bromine was twice distilled in high vacuum through phosphorus pentoxide which had been resublimed in a current of oxygen. The pentoxide tube was then sealed out of the all-glass apparatus and the bromine thrice fractionated in high vacuum before being distilled into the capsules and sealed off.

The iodine was of C.P. quality and was sublimed once in air from an intimate mixture with C.P. potassium iodide and calcium oxide. The sublimed iodine was then ground with more potassium iodide and calcium oxide, and introduced into the bottom bulb of a series of four bulbs joined by strictured tubing. The column was pumped out and about two-thirds of the iodine driven into the second bulb by heating with boiling water.

TABLE 2

Sorption of bromine by silica gel

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isothermal at 58.0°C.		
mm.	*millimoles per gram sorbent*	*hours*
0.0	0.0000	3.0
3.7	0.0384	1.5
16.1	0.1238	2.0
38.2	0.2585	1.5
68.6	0.4337	16.0
88.6	0.5514	1.7
113.8	0.7094	3.7
144.7	0.9291	3.0
178.1	1.2134	2.5
239.0	1.8908	10.0
219.1	1.6580*	3.7
198.4	1.4130*	4.7
160.2	1.0650*	3.0
127.2	0.8188*	2.7
99.9	0.6347*	3.5
68.9	0.4433*	6.0
68.7	0.4423*	11.2
58.7	0.3629*	3.0
20.7	0.1705*	2.2
9.0	0.0890*	2.0
5.3	0.0635*	2.0
0.6	0.0230*	1.7
Isothermal at 79.0°C.		
0.0	0.0000	2.0
2.4	0.0105	1.0
11.5	0.0473	1.2
69.8	0.2342	12.7
112.5	0.3601	1.0
162.4	0.5034	1.2
218.6	0.6911	1.7
267.7	1.0144	11.0
326.9	1.0942	2.5
395.4	1.4103	4.0
458.0	1.7697	2.5
520.5	2.1890	1.7
566.6	2.5863	13.0
617.7	3.0396	4.0
671.6	3.6238	4.0
718.7	4.3252	7.0
756.0	4.6483	6.0

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isothermal at 79.0°C.—*Cont.*		
mm.	*millimoles per gram sorbent*	*hours*
795.1	5.2766	6.0
693.6	4.4618*	5.0
640.2	3.6289*	12.0
547.0	2.4475*	5.5
501.2	2.0126*	5.0
426.8	1.5788*	12.5
365.1	1.2778*	8.2
293.7	0.9758*	2.0
244.2	0.7935*	13.0
174.4	0.5615*	3.5
137.7	0.4511*	3.5
108.5	0.3674*	3.5
64.4	0.2382*	15.0
10.2	0.0516*	3.7
3.9	0.0256*	2.0
0.0	0.0000*	10.0
Isothermal at 99.9°C.		
1.7	0.0036	2.5
12.9	0.0267	0.7
72.6	0.1443	1.2
118.3	0.2210	4.2
151.3	0.2770	1.5
214.2	0.3801	2.0
265.9	0.4665	5.0
324.4	0.5649	3.0
392.6	0.6828	1.0
455.6	0.8028	1.0
336.1	0.5934*	3.0
488.4	0.8752	2.0
564.9	1.0350	3.2
629.6	1.1930	18.0
694.7	1.3616	4.5
744.4	1.4505	3.5
793.0	1.6324	11.0
673.8	1.2929*	26.5
567.0	1.0495*	3.0
473.4	0.8498*	2.0
364.9	0.6466*	6.0
289.2	0.5149*	10.5
235.1	0.4271*	2.0

* Desorption readings.

TABLE 2—*Concluded*

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isothermal at 99.9°C.—*Cont.*		
mm.	*millimoles per gram sorbent*	*hours*
173.9	0.3262*	1.7
139.6	0.2698*	1.5
86.6	0.1670*	1.7
68.0	0.1443*	3.0
27.1	0.1081*	2.0
0.0	0.0000*	4.5
Isothermal at 117.5°C.		
0.0	0.0000	11.0
67.7	0.0809	9.5
110.2	0.1262	2.7
139.4	0.1585	2.0
174.2	0.1889	1.5
215.7	0.2295	1.0
266.0	0.2846	3.7
323.5	0.3423	1.5
392.0	0.4076	1.7
470.6	0.4852	2.0
563.1	0.5780	2.0
669.3	0.6888	4.0
790.4	0.8315	1.5
740.0	0.7756*	9.7
614.2	0.6393*	2.5
517.1	0.5330*	2.5
429.8	0.4511*	2.2
356.5	0.3753*	4.0
292.1	0.3118*	8.2
241.2	0.2611*	11.0
194.4	0.2103*	3.2
155.6	0.1806*	1.5
124.0	0.1476*	2.2
74.9	0.1059*	2.5
68.6	0.0838*	10.7
21.1	0.0326*	1.7

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isothermal at 117.5°C.—*Cont.*		
mm.	*millimoles per gram sorbent*	*hours*
3.9	0.0109*	2.0
1.2	0.0054*	2.0
0.0	0.0000*	2.0
Isothermal at 137.7°C.		
0.0	0.0000	3.0
68.1	0.0570	11.0
109.6	0.0857	1.5
139.5	0.1039	1.7
173.3	0.1297	5.5
215.7	0.1577	16.2
257.3	0.1907	3.0
323.0	0.2249	3.0
393.8	0.2663	2.7
472.5	0.3186	3.0
563.4	0.3753	3.5
668.6	0.4429	3.0
789.8	0.5214	10.2
751.6	0.4959*	4.0
613.8	0.4102*	2.7
507.3	0.3412*	2.5
432.2	0.2928*	14.5
356.0	0.2456*	3.7
294.5	0.2071*	5.5
239.3	0.1744*	22.0
193.5	0.1446*	2.0
152.8	0.1199*	1.5
122.9	0.0988*	3.0
67.7	0.0559*	11.0
24.3	0.0280*	2.0
9.3	0.0171*	3.0
1.7	0.0080*	2.0
0.0	0.——*	2.5

The bottom bulb was sealed off and the system further evacuated with a mercury pump protected by liquid air trap. Two-thirds of the iodine was then sublimed into the third bulb and the remainder sealed off. The sample tubes, each with a breakoffsky attached, were previously sealed to the top bulb and the iodine driven into them following a third fractional sublimation.

Silica gel used was of the commercial glassy type. It was thoroughly

TABLE 3

Sorption of iodine by silica gel

PRESSURE (CORRECTED)	X/M	TIME FOR READING
Isotherm at 98.2°C.		
mm.	*millimoles per gram sorbent*	*hours*
0.03†	0.——	1.7
5.6	0.0143	2.0
10.6	0.0231	10.7
18.0	0.0423	3.0
23.3	0.0787	4.0
13.6	0.0294*	1.7
Isotherm at 137.6°C.		
2.2†	0.01462	3.0
47.4	0.03483	2.0
80.0	0.06375	10.0
120.0	0.2011	9.5
99.6	0.1129*	6.2
15.3	0.0217*	11.5
0.03†	0.0009*	5.0
0.00	0.——	3.5
Isotherm at 158.3°C.		
0.03†	0.——	3.0
15.0	0.0041	1.2
48.2	0.0120	1.5
100.0	0.0269	5.5
144.4	0.0492	9.5
199.6	0.1280	3.5
169.7	0.0743*	1.2
0.03†	0.——*	2.7
Isotherm at 178.4°C.		
0.00†	0.——	14.0
2.6	0.0009	1.5
48.0	0.0071	1.2
101.4	0.0156	2.0
235.1	0.0436	1.5
319.1	0.0905	2.5
428.4	0.3411	9.7
368.4	0.2443*	8.5
169.6	0.0278*	2.2

* Desorption readings.

† Values derived from vapor pressure function.

TABLE 3—*Concluded*

PRESSURE (CORRECTED)	X/M	TIME FOR READING
	Isotherm at 198.5°C.	
mm.	*millimoles per gram sorbent*	*hours*
0.03†	0.——	1.0
46.2	0.0043	1.2
108.7	0.0160	10.0
318.2	0.0333	2.5
423.6	0.0530	1.7
560.0	0.1205	3.5
233.3	0.0236*	1.5
119.5	0.0119*	14.0
0.03†	0.——*	2.0

washed with nitric acid and water and electrodialyzed for two days. The gel was dried and air-activated at 600°C. It was crushed in an agate mortar and sieved, the portion passing 60 mesh and retained by 100 mesh being used in this work. A sample of this gel was ignited to constant weight in a platinum crucible and showed a loss in weight of 3.32 per cent.

RESULTS

Measurements on the sorption of bromine by silica gel were carried out with the adsorbent maintained at 58°, 79°, 99.9°, 117.5°, and 137.7°C., respectively. The vapor pressure of the bromine was regulated by the constant temperature cryostat, G. Equilibrium was established rapidly in the case of silica gel at all but higher pressures. However sufficient time was always taken to insure several constant readings before changing the pressure of the bromine. Data for the measurements are given in table 2. It will be noted that sorption studies were always followed by desorption determinations down to zero pressure. The spring calibrations for the measurements at 58°C. are given in table 1. Similar calibrations were made at the other temperatures, but they are not included in the results. A calculation of the correction for the buoyancy effect of the halogen vapor was made assuming the gas laws and it was found to be less than one-half of 1 per cent of the bromine sorbed at atmospheric pressure. Accordingly no buoyancy corrections were made.

Table 3 gives similar results for iodine. The sorption–desorption isotherms were measured at 98.2°, 137.6°, 158.3°, 178.4°, and 198.5°C., respectively. Readings were possible up to about 600 mm. pressure. Above this pressure the density of the iodine vapor rendered it impossible to see the spring points even against the bare filament of the lamp. An experimental determination of the buoyancy correction for iodine showed it to be within the limits of experimental error, so no correction was made for this factor.

DISCUSSION

The five isothermals recorded in table 2 are shown graphically in figure 1 of the following paper. Millimoles of bromine sorbed per gram of silica gel are plotted as ordinates against vapor pressure of bromine as abscissae. Similar results are presented in figure 2, also of the following paper, for the sorption isotherms of iodine on silica gel. It is evident from the results that adsorption and desorption are fully reversible. There is no evidence for the hysteresis so often found in sorptions on silica gel. The curves exhibit more or less convexity toward the pressure axis, which indicates loose binding forces and physical adsorption.

Except for slight discontinuities the isotherms for bromine at the higher temperature are almost straight lines. The discontinuities seem to be greater than the probable experimental error and appear to be real. The isotherms for iodine appear to rise more abruptly, but this is in the main due to the change in the ordinate scale. Under comparable conditions many times as many bromine molecules are sorbed per gram of silica gel as iodine molecules. At its boiling point 1.5 millimoles of bromine are adsorbed per gram of gel under a pressure of 200 mm. Under the same pressure at its boiling point only 0.03 millimole of iodine is sorbed per gram of the gel. The International Critical Tables give the critical temperatures for bromine and iodine as 302°C. and 553°C., respectively. It is evident from the data that the amount of sorption here found is not related to the difference between the critical temperature and the temperature at which the sorption was measured, as is the case in so many sorption studies on silica gel.

The data here presented do not fit the exponential equation of the classical adsorption isotherm. Neither do the data fit the Langmuir equation for monomolecular adsorption. The expression which best fits these experimental results is that given by McGavack and Patrick (5). A fuller discussion of the characteristics of the sorption of bromine and iodine by silica gel will be given at a later date. A rather complete study on the sorption of chlorine by porous sorbents is in progress in this laboratory.

SUMMARY

1. An apparatus combining the sorption balance of McBain and Bakr and a quartz spiral manometer is described.

2. Using this apparatus the sorption of bromine by silica gel was measured at 58°, 79°, 99°, 117.5°, and 137.7°C.

3. Using similar technique the sorption of iodine was measured at 98.2°, 137.6°, 158.3°, 178.4°, and 198.5°C.

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STUDIES ON THE SORPTION OF THE HALOGENS BY SILICA GEL AND CHARCOAL[1]

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Received June 14, 1934

There are recorded in the literature several instances of adsorption studies in which one of the halogens was adsorbed by either silica gel or charcoal. Probably the best work to date is that of Magnus and Müller (4), who studied the sorption of chlorine by silica gel in an all-glass system at 0°, 20° and 40°C. Bosshard (2) determined the retention of bromine by various silica gels when the bromine vapor was carried over the gel by an inert gas. Qualitative measurements on sorptions measured dynamically in the presence of foreign gases constitute most of the other recorded measurements. The great difficulties involved in the sorption of halogen vapors have no doubt hindered successful study in this most important field.

Some time ago it was decided to study rather completely the sorption of the halogens in an all-glass–quartz system. Experimental technique in the handling of gases had advanced to such a point that success seemed possible. In this investigation the helical quartz spring sorption balance of McBain and Bakr (5) was combined with the quartz spiral manometer described by Bodenstein and Katayama (1). The design and operation of the apparatus is fully described by the authors in another publication. In brief, the apparatus of all-glass and quartz was sealed from the vacuum pumps during measurements. The vapor pressure of the halogen was maintained by condensing it into a tube immersed in an automatic cryostat as described by Cameron (3). By proper control of the temperature of the bath, the vapor pressure of the halogen could be varied throughout wide limits. The sorption balance and quartz manometer were maintained at constant temperature during measurements in a specially constructed air thermostat. This thermostat was capable of close temperature regulation up to 220°C.

The silica gel used in this investigation was of the glassy type. It was kindly furnished by the Silica Gel Corporation. This gel was digested with nitric acid and then thoroughly washed and finally electrodialyzed for several days in an electrodialysis cell. Following the dialysis it was

[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

dried and air-activated at 600°C. Granules which passed a standard 60-mesh and were retained by a 100-mesh screen were used in this investigation. The charcoal was prepared from cocoanut shells which had been cleaned and extracted with ether, alcohol, and water in the order named. The shells were coked by bringing the temperature slowly to 550–575°C. and holding it there for half an hour after the last flammable vapors had been generated. The charcoal was crushed and then activated by passing superheated steam over it in a silica tube heated in an electric tube furnace to 850°C. On analysis this charcoal was found to have an ash content of 0.185 per cent.

The bromine and iodine were purified chemically by the best recommended procedure. They were then further purified by successive distillations or sublimations in specially constructed vacuum systems. The middle portions only of the final vacuum purifications were used in this investigation.

Sorption–desorption isotherms were obtained over a wide pressure range for bromine on silica gel at 58°, 79°, 99.9°, 117.5°, and 137.7°C. Figure 1 presents the results graphically. Except for the highest desorption readings at 79°C., the sorption and desorption values seem to be completely reversible. Throughout the temperature and pressure range studied there is no hysteresis evident. Slight irregularities may be noted in the curves, and these may be due to errors in the determination. However they seem to be slightly larger than experimental errors and may be evidence for the type of discontinuity reported recently by Allmand and other investigators. The curves obtained for the two highest temperatures indicate that the sorption of bromine is directly proportional to the pressure at these temperatures. The results for the sorption–desorption of iodine at 98.2°, 137.6°, 158.3°, 178.4°, and 198.5°C. are shown graphically in figure 2. The ordinates of this graph are magnified tenfold as to millimoles adsorbed over figure 1. This makes the curves appear to rise more abruptly in the case of iodine sorption. However the millimoles of bromine sorbed under comparable temperature and pressure conditions were on the average tenfold greater than in the case of iodine. Except at the highest pressures, equilibrium between the silica gel and the halogen vapor was established rather rapidly. There was no evidence for a slow sorption of a different type from the initial rapid sorption. The isotherms for iodine at the two lowest temperatures indicate a slight break in the lowest pressure range. This may indicate a different type of sorption at low pressures.

In the sorption studies on charcoal a very different behavior was found. The rate of sorption was slower than in the case of silica gel, about 24 hours being needed to obtain reasonably constant results. As a result it was decided to determine the rates of sorption and desorption on charcoal. Measurements of this rate were made at constant vapor pressure of the

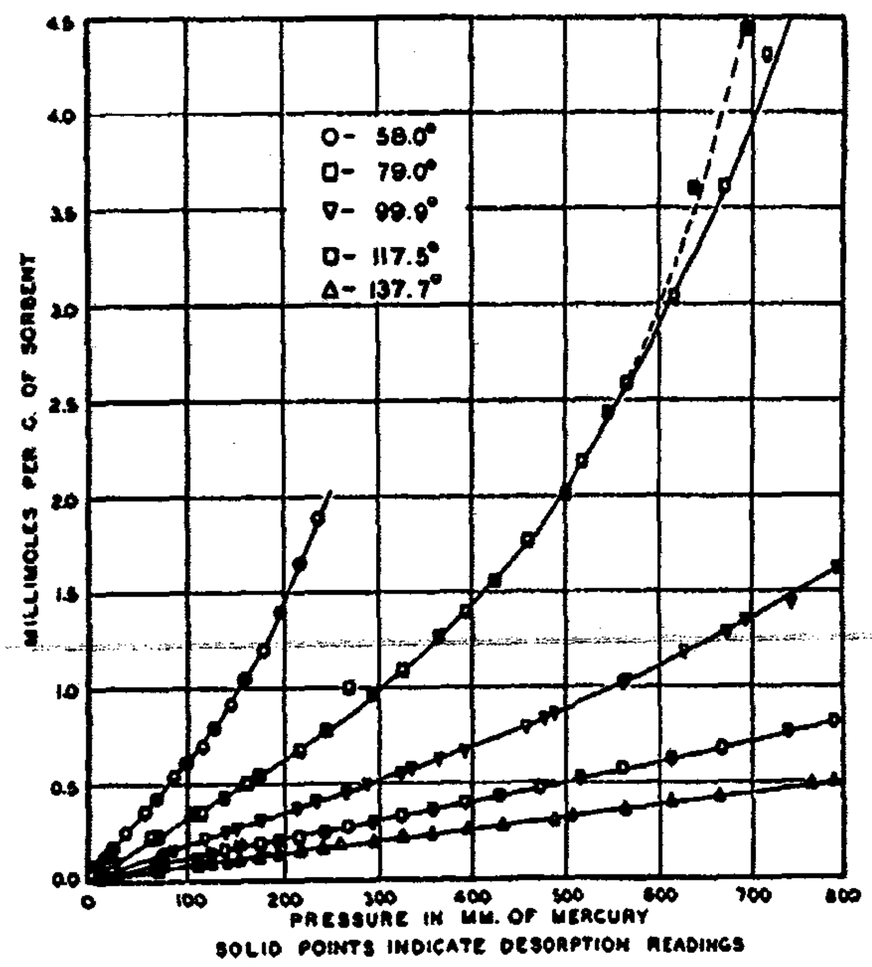

FIG. 1. SORPTION OF BROMINE BY SILICA GEL

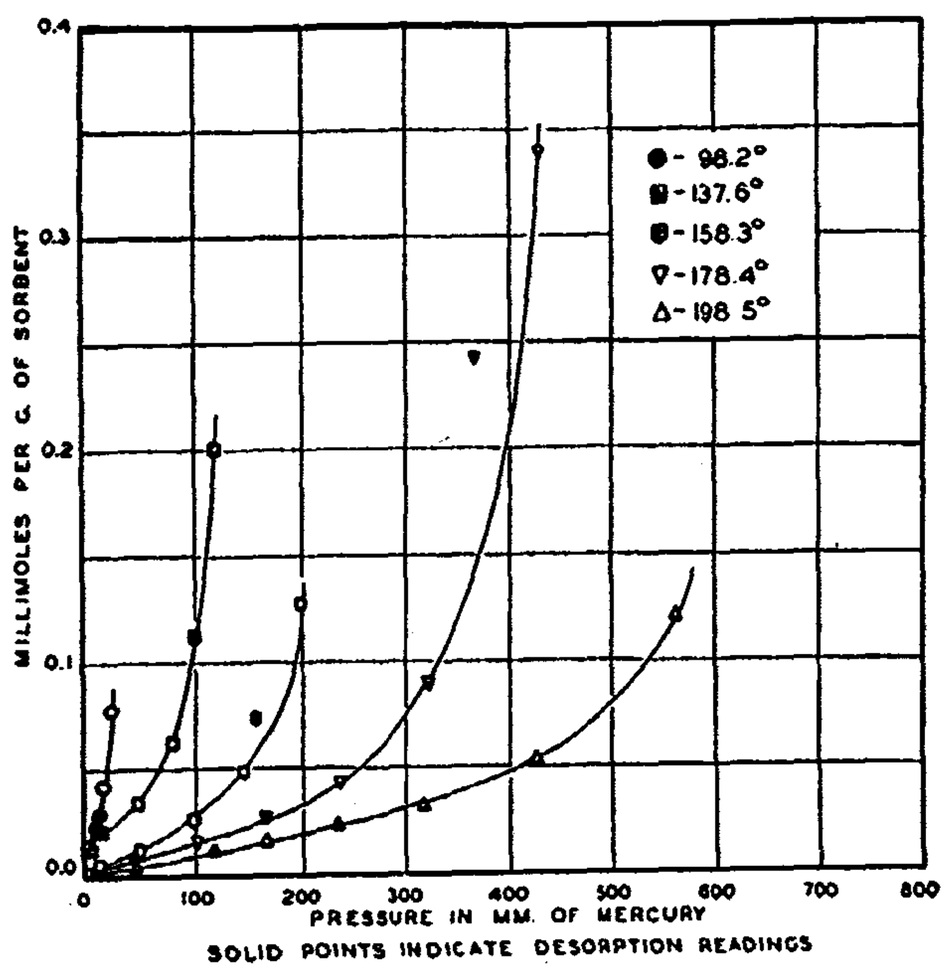

FIG. 2. SORPTION OF IODINE BY SILICA GEL

halogen for 24 hours. The vapor pressure was then increased and the rate of sorption determined for this higher pressure. After sorption at the highest vapor pressure, similar rate studies were made on desorption by successively dropping the vapor pressure of the halogen to the same pressures as were maintained during sorptions. Figure 3 shows graphically the results obtained at 137.6°C. It should be noted that the desorption points reached at the end of the 24-hour period always lie slightly above the corresponding sorption points. It is possible that these points would coincide after a very long time, but the sorption–desorption curves came so close to one another and were so nearly parallel that it was not felt necessary to

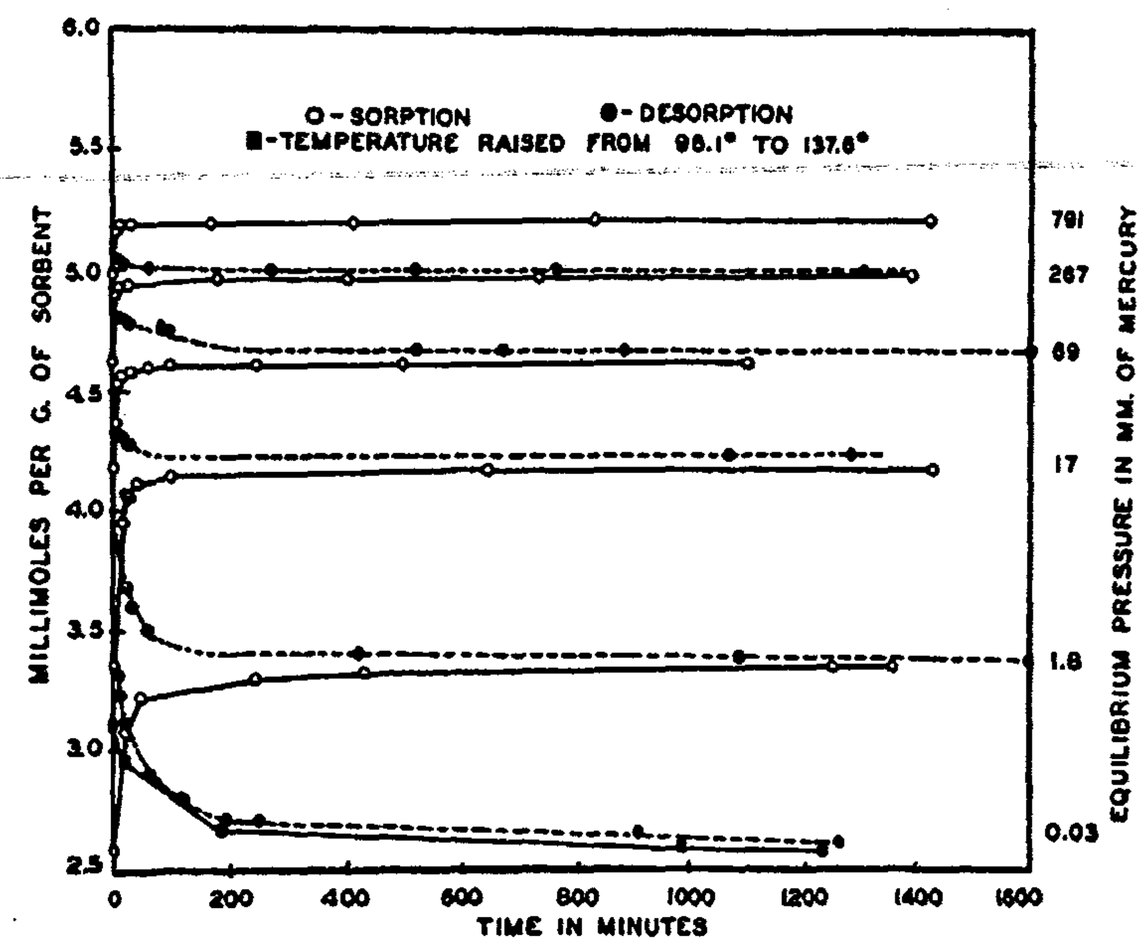

FIG. 3. RATES OF SORPTION OF BROMINE BY CHARCOAL AT 137.6°C.

prolong the study. Rate curves for other temperatures than the one given in figure 3 are much the same. However, the higher the pressure and the higher the temperature the closer to the sorption points lie the desorption points. It should also be noted that more than 2.5 millimoles of bromine remain adsorbed when desorption is carried out at 0.03 mm. pressure. In fact it is impossible to remove all the bromine from the charcoal by thorough evacuation. When the charcoal containing the halogen is heated to about 500°C. and the tube containing the liquid bromine is frozen by immersion in liquid oxygen, equilibrium is reached when slightly more than 2 millimoles of bromine remain sorbed by a gram of charcoal. Under similar heat treatment of the charcoal containing bromine, evacuation of the system was carried out at 10^{-6} mm. pressure. After 24 hours about 0.7

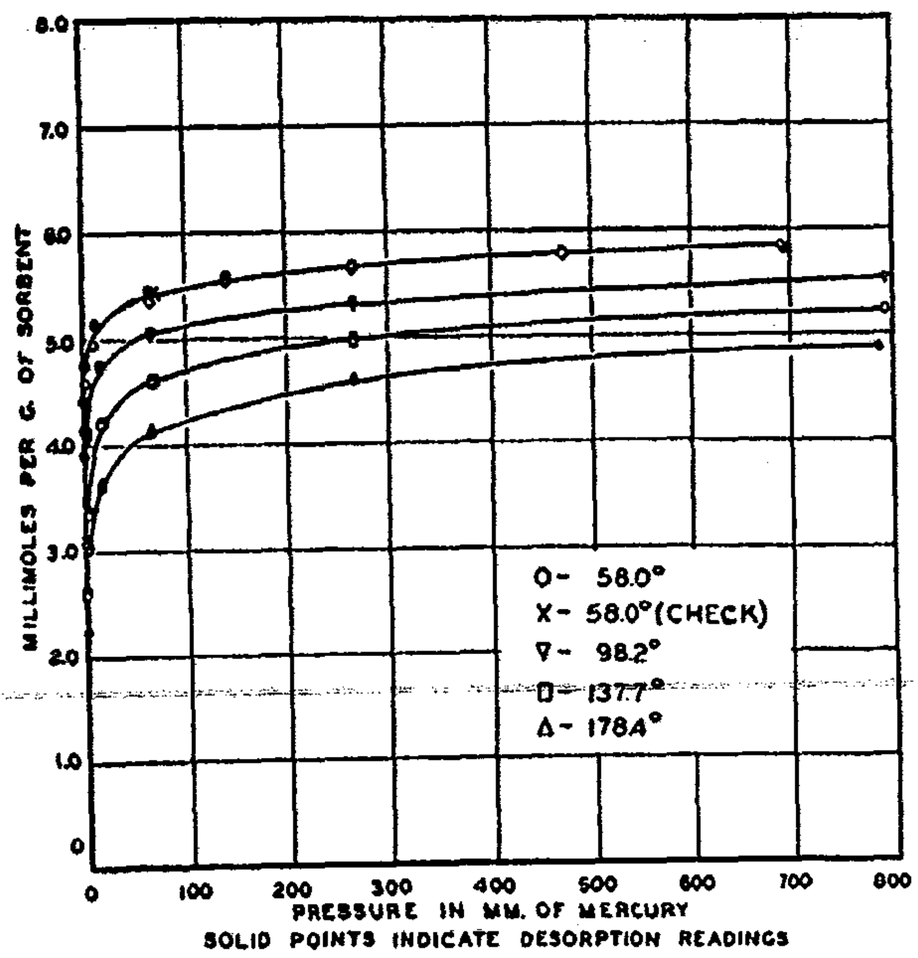

FIG. 4. SORPTION OF BROMINE BY CHARCOAL

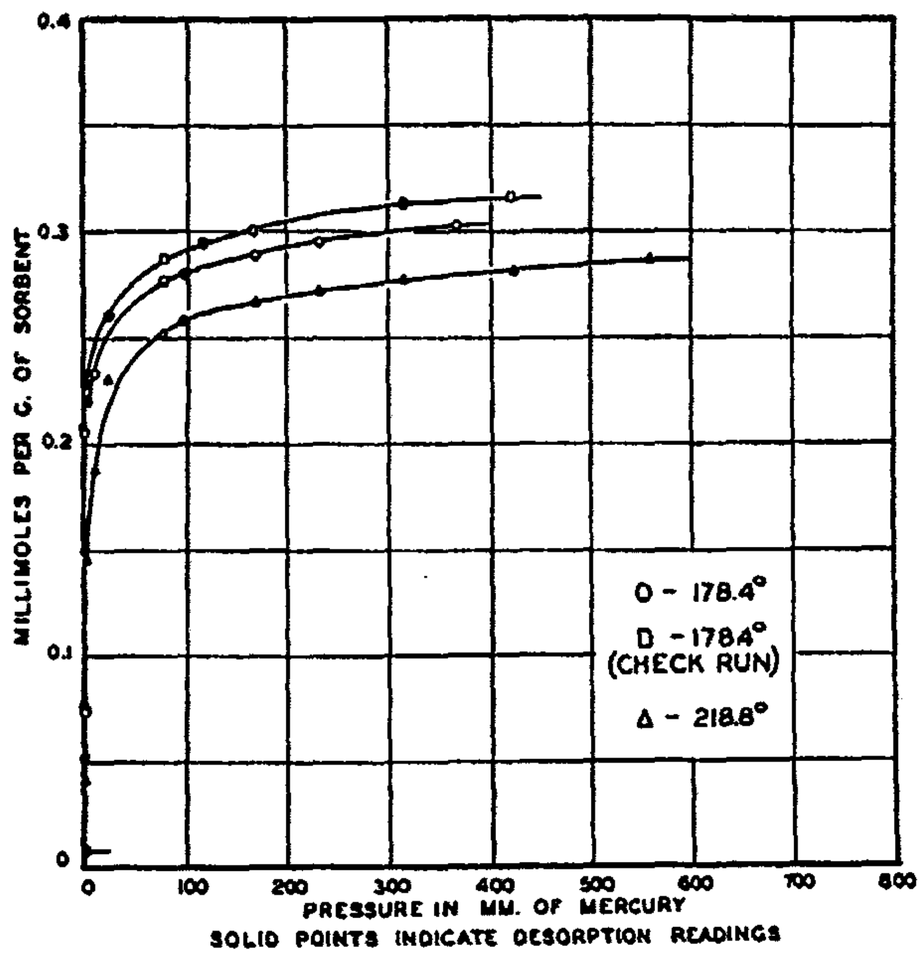

FIG. 5. SORPTION OF IODINE BY CHARCOAL

millimole of bromine remained per gram of charcoal, and at the end of 72 hours this quantity had only been reduced to 0.6 millimole. These results are in agreement with those of Ruff, Rimrott, and Zeumer (6), who found that charcoal must be heated to 1100°C. before the last of the bromine was removed. The products then obtained were hydrogen bromide, bromine, and some carbon-containing bromine compounds.

The isotherms for bromine and iodine sorbed by the charcoal are given in figures 4 and 5. It should be noted that the amount of iodine taken up by the charcoal is much less than the quantity of bromine. However the types of isotherms obtained are similar. The differences in amount of iodine sorbed by the charcoal as compared to bromine are very similar to the differences obtained on silica gel.

DISCUSSION

In considering the character of the sorption of the halogens by two such different porous sorbents, it is important to know the surface area covered by the sorbed gases at various temperatures and pressures. From viscosity measurements Rankine gives the molecular diameters of bromine and iodine as 3.42×10^{-8} cm. and 3.76×10^{-8} cm., respectively. If we assume that the molecules cover an area equal to the square of the diameters, then 1 millimole of bromine would cover 7.1×10^5 cm.^{2} and 1 millimole of iodine would cover 8.58×10^5 cm^2. Multiplying the number of millimoles sorbed at varying pressures by these areas would give the approximate area covered under the different conditions. The data obtained for the sorptions by silica gel do not fit the classical sorption isothermal, neither can they be fitted to the Langmuir expressions. The shape of the curves seems to indicate a rather loose type of physical binding of the van der Waals type, or they may represent capillary condensation. In fact the sorption values fit the expression of Patrick,

$$V = K\left(\frac{P\gamma}{P_S}\right)^{\frac{1}{n}}$$

for capillary condensation better than any other, and even here the agreement is not good at either very high or very low pressure values for bromine. The sorption of iodine shows still less agreement with this expression. In order to test this equation it is necessary to know the volume, V, of the liquid sorbed, the surface tension, γ, of the liquid at the temperature of the isothermal, the equilibrium pressure, P, and the saturation pressure, P_S, at the temperature of the isothermal. The data for all the isothermals should fall on the same straight line, where log V is plotted against log $\frac{P_\gamma}{P_S}$. The values used in checking the Patrick expression were obtained as follows. The values of P_S were read from a plot of log P against $1/T$.

The values of the vapor pressure used in the graphs and of the surface tension and density at 20°C. of bromine were obtained from the International Critical Tables. The constant of the Ramsay-Eötvös-Shields equation was calculated for bromine and found to be 2.074. Using this constant and the values of the surface tension, γ, obtained by straight line extrapolation between 20°C. and t_c^{-6}, the density of bromine at the temperatures of the various isothermals was calculated. The various values so obtained for bromine are given in table 1.

The values of V and $\frac{P_\gamma}{P_S}$ can then be obtained and the logarithms of these values plotted against each other. Figure 6 shows the results so obtained. The points all lie well along a straight line except at the two extremes, where considerable deviation is to be noted. In view of the many assumptions made use of in obtaining the necessary quantities for the Patrick equation, the agreement seems rather good. In addition, if one reads the equilibrium pressures for the same value of X/M for the various isothermals, then it is possible to calculate the differential heats of sorption from the Clausius-Clapeyron equation.

TABLE 1

$\gamma_{20°} = 41.5$ dynes per centimeter; $d_{20°} = 3.119$; $t_c = 302$°C.

$t_{isothermal}$	γ	d_t	P_S
			mm.
58.0	36.0	3.14	740
79.0	32.6	3.04	1340
99.9	29.4	3.11	2631
117.5	27.0	3.148	3881
137.7	23.8	3.12	5650

$$Q = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{P_2}{P_1}$$

The average of eleven such calculations gives the differential heat of sorption as 7719 cal. per mole. The latent heat of vaporization of bromine at the boiling point is given in the International Critical Tables as 7167 cal. per mole. Thus the differential heat of sorption is only slightly larger than the latent heat of vaporization. This difference may be significant, but the sorption forces are apparently not much different from those involved in the formation of the liquid from the vapor phase. Finally the question should be raised as to whether it is necessary to have capillary condensation or not. In these experiments the maximum sorption measured for bromine on silica gel was about 4.5 millimoles at 79°C. $4.5 \times 7.1 \times 10^5$ cm.^{2} gives 31.95×10^5 cm^2. as probably the area covered by bromine. This

is not as great as the total surface area per gram of silica gel as reported by many investigators. However, the shape of the isothermals indicates that the gel will continue to take up more of the halogen as its pressure is increased. It is therefore possible that we have capillary condensation superimposed on loosely acting surface forces.

Calculations similar to those given above were made for iodine, but the results did not agree so well with the Patrick expression as did those for bromine. The average of four calculations of the differential heat of sorption gave a value of 11,340 cal. per mole. The latent heat of vaporization at the boiling point is given in the International Critical Tables as 10,516

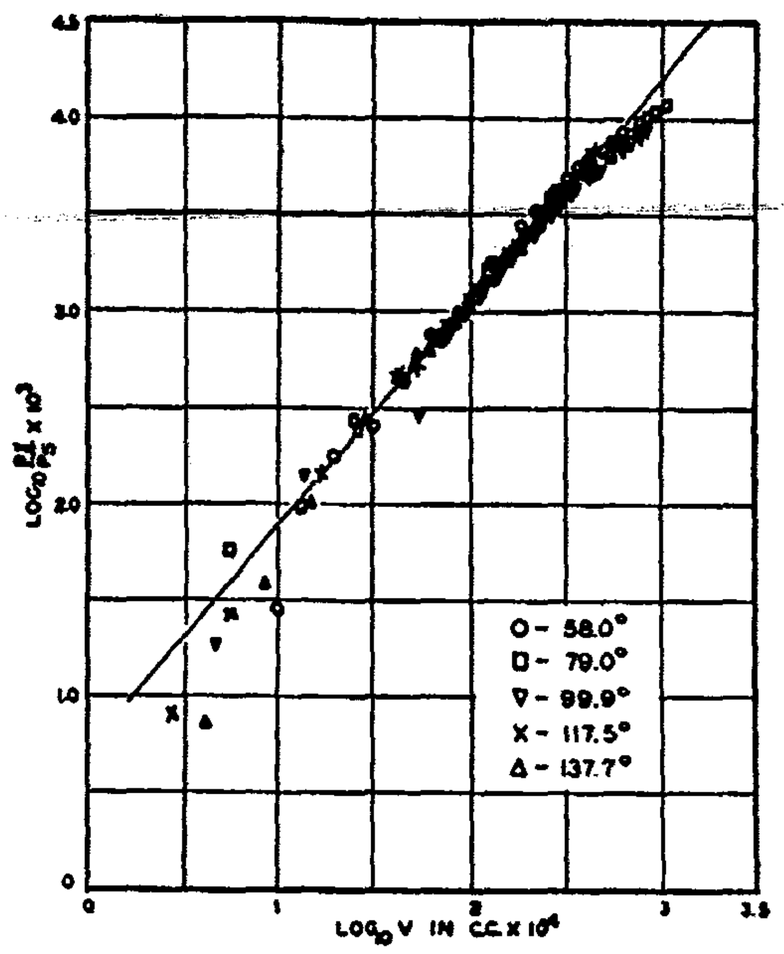

FIG. 6. LOGARITHMIC PLOT OF BROMINE SORPTION BASED ON PATRICK'S EQUATION

cal. per mole. However, the heat of sublimation is of the order of 14,520 cal. The differential heat of sorption is thus only slightly greater than the latent heat of vaporization. Similar physical forces seem to be acting in the case of iodine sorption as was found for bromine.

As already noted, the character of the sorption of the halogens on charcoal is quite different from that on silica gel. By far the largest part of the sorption occurs in the lowest pressure ranges. There is a relatively small difference between the amounts sorbed at the lowest and highest temperatures at the same vapor pressure of the halogen. This is not true in the case of silica gel. The type of isotherm obtained indicates the formation of a monomolecular layer of sorbed molecules. This appears to be followed at higher pressures by slow diffusion into the charcoal.

The average of eleven values of the differential heat of sorption calculated as before was 11,420 cal. per mole for bromine on charcoal. The average of four such calculated values for iodine was found to be 13,500 cal. per mole. The value for bromine is some 4000 cal. per mole higher than the latent heat of vaporization. In the case of iodine it is about 2500 cal. higher. These significantly higher values indicate that some form of activated sorption is taking place.

The simplest form of the Langmuir sorption expression is

$$\frac{X}{M} = \frac{abp}{1 + bp}$$

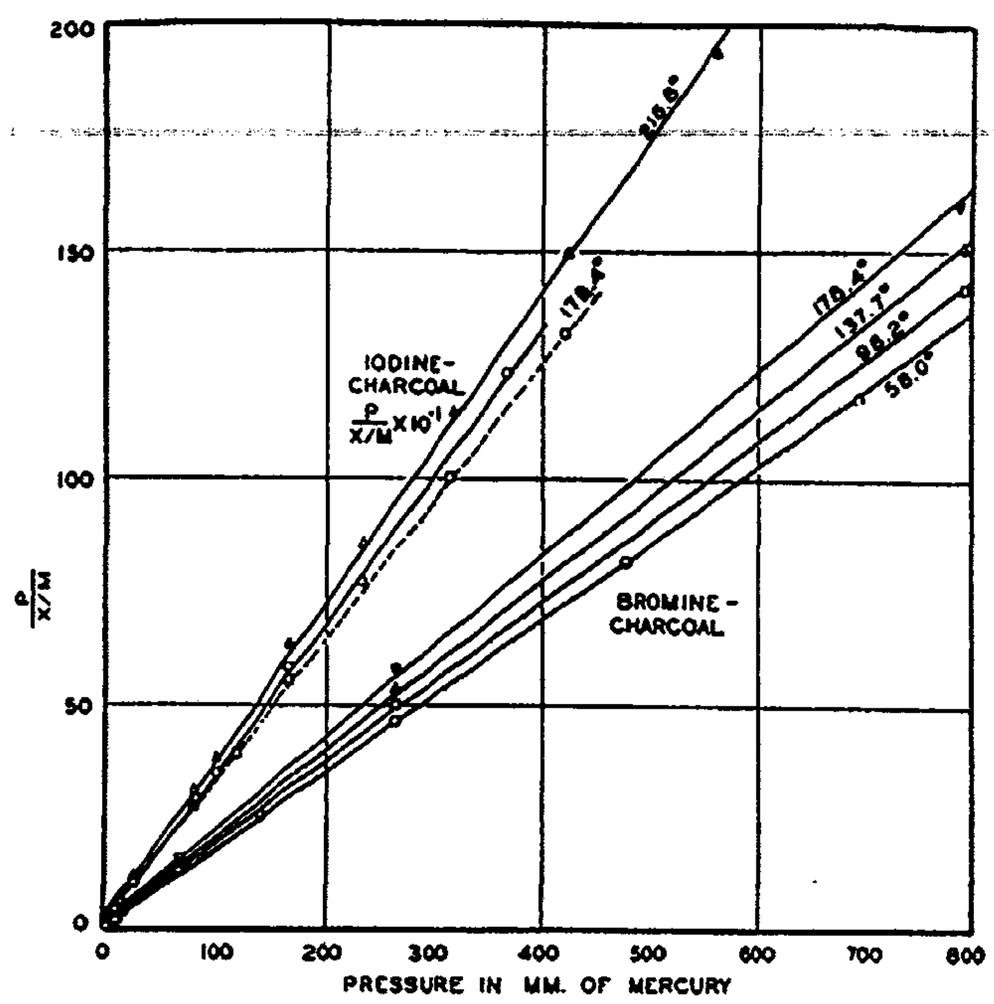

FIG. 7. SORPTION ISOTHERMS OBTAINED BY USE OF THE LANGMUIR EQUATION

which by rearrangement becomes

$$\frac{P}{X/M} = \frac{1}{ab} + \frac{1}{a}P$$

which is the equation of a straight line. The values of $P/X/M$ were calculated from the data and plotted against P. The results are shown in figure 7, and the agreement with the Langmuir equation is excellent. Only when plotted on a much enlarged scale is any deviation from the straight-line relationship found, and this occurs at the very lowest pressure.

It seems evident that the sorption of bromine and iodine by activated charcoal is of the monomolecular type called "persorption" by McBain. In this type of sorption all of the sorbed molecules are bound directly by the atoms of the surface of the sorbent. If the surface of the charcoal is completely covered by bromine molecules, then a simple calculation shows that a gram of this activated charcoal has a surface area of about 350 square meters. This is of the same order of magnitude as found by other investigators.

SUMMARY

1. Sorptions of bromine and iodine on silica gel and activated charcoal have been measured in an all-glass–quartz system at widely different temperatures.

2. Sorptions by silica gel indicate a loose physical binding or capillary condensation.

3. Sorptions by charcoal indicate activated sorption that is monomolecular in depth of layer.

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STUDIES ON OVERVOLTAGE. VIII

Overvoltage at Bright Platinum Electrodes in 2 Normal Sulfuric Acid for Low Current Densities Determined with an Oscillograph[1]

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Received May 3, 1934

In previous articles the authors have described studies on overvoltage at platinized platinum electrodes in 2 N sulfuric acid (a) by means of a commutator in connection with a potentiometer (1, 2, 5, 6), (b) by means of a commutator in connection with an oscillograph (3), and (c) by means of an electromagnetic interrupter in connection with an oscillograph (4).

In the present paper the methods described in the last two papers are used to study the overvoltage phenomena at smooth platinum electrodes in 2 N sulfuric acid solutions. In all respects except for the type of electrodes, the equipment, general methods of procedure, kind of measurements made, method of recording data, and symbols used are the same as in previous papers and therefore will not be described here.

In the fourth paper (2) of this series the results furnished extremely strong evidence that platinized platinum electrodes in 2 N sulfuric acid show no surface resistance of any kind for current densities between 3.8 and 150 ma. With smooth platinum electrodes the decrease in discharge potential was found to be so rapid that satisfactory results could not be obtained with the commutator–potentiometer system. In the fifth paper (3) it was shown that for platinized platinum the commutator–oscillograph method gives results identical with those obtained by the direct potentiometer method; and further confirmation was added to the conclusion previously stated that there is no surface resistance at such electrodes. In the seventh paper (4) an electromagnetic interrupter was used, which made it possible to superimpose various curves in such a manner that a direct comparison could be made between the nature of discharge curves which were known to result only from an IR drop and others which were known to result from an IR drop and depolarization, and the curve of an unknown type which was under investigation and was known to contain

[1] The oscillograph used was purchased with a grant from the Faculty Research Fund of the University of Michigan, which thus made this work possible.

a potential drop due to depolarization and might contain a drop due to surface resistance. It was evident, clearly, from comparisons such as these, that there is no surface resistance at platinized platinum electrodes in 2 N sulfuric acid throughout the range of current densities used.

In the works just referred to, the authors have based their conclusions concerning the non-existence of surface resistance upon the assumption that no part of a discharge potential can result from any portion of the charge potential required to force current through a surface resistance. A second assumption has been made, also, that the rate of discharge of potential of an IR nature is much more rapid than depolarization. It is entirely upon the latter assumption that many other investigators have based their conclusion concerning the existence of surface resistance, i.e., Newbery (8) and Hollar (7) obtained oscillograms showing vertical drops at the beginning of the discharge intervals which they interpreted as due to a resistance at the electrode-electrolyte interface. The work to be described in the present paper indicates that the early part of the discharge curves at smooth platinum electrodes shows as rapid a drop as that due to a pure resistance. It is shown further, however, that this very rapid drop cannot be due to surface resistance.

Figures 1 and 2 show the behavior of the cathode at different current densities. The potential measured between the two reference electrodes is made up only of IR drops between the polarized electrodes and is represented in all figures by I when measured by the commutator–potentiometer method and by I' when measured by the direct method, i.e., while the polarizing circuit is still closed. The corresponding values for the cathode are represented by K and K'. The cathode values are the potentials measured between the cathode and cathode standard and might include an IR drop due to surface resistance if such exists.

It should be noted that for all current densities the I and I' values are identical, which means that all potentials due to resistances must be the same irrespective of the method of measurement. At the cathode, for extremely low current densities, the potential is about 1 millivolt less as measured by the commutator method than by the direct; the authors believe, however, that this difference would disappear if a slightly longer charge interval were allowed; it may be observed that the K curves were still slowly rising at the end of the charge interval. A similar phenomenon was observed at platinized platinum cathodes. The agreement between the values obtained by the two methods is perfect in all other cases. Probably the most striking difference between these curves for smooth platinum and those reported earlier (3) for platinized platinum is the rapid increase in cathode potential with current density and the rate at which depolarization takes place on the smooth platinum. For instance, according to figure 5 of reference 7 the cathode overvoltage at platinized platinum is

less than 2 millivolts for a current density of 0.0084 amp., while from figure 2 of the present article it is about 150 mv. for a current density of only 0.0035 amp.

It is clearly not possible to say from the shapes of the K curves of figures 1 and 2 whether the rapid drop represents depolarization only or whether a part is due to an IR drop over a surface resistance.

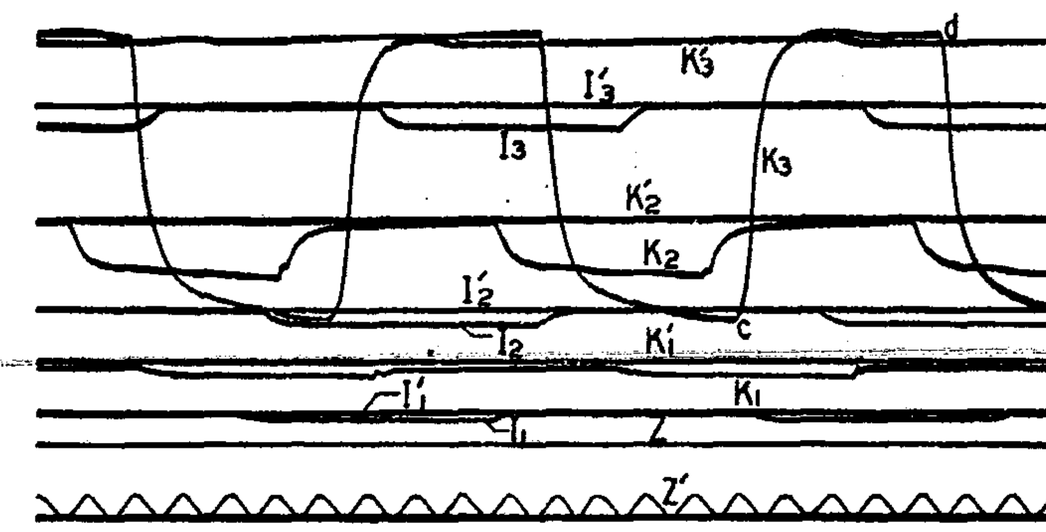

FIG. 1. CATHODE CURVES AND CURVES SHOWING THE IR DROP THROUGH THE SOLUTION AT THE CURRENT DENSITIES 0.0004, 0.0010, AND 0.0016 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

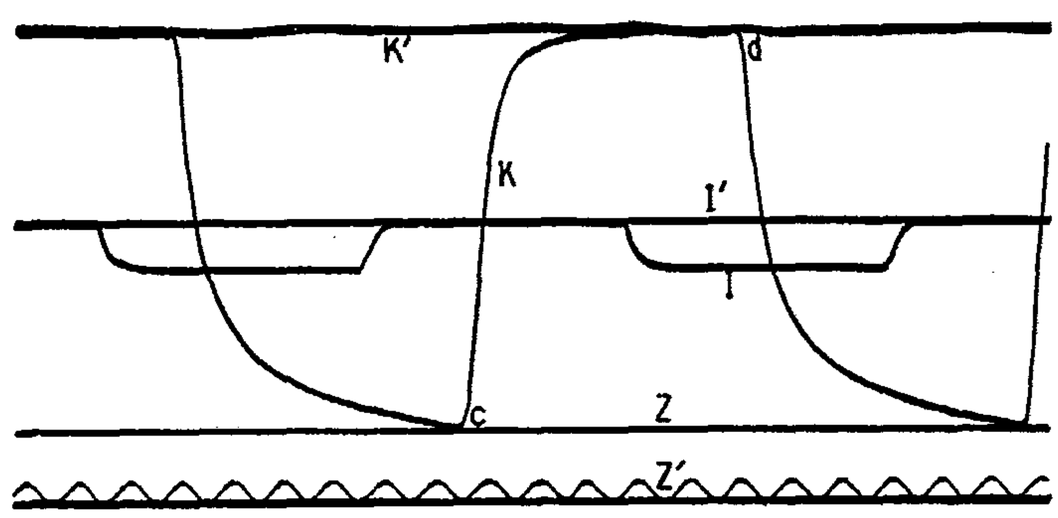

FIG. 2. CATHODE CURVES AND CURVES SHOWING THE IR DROP THROUGH THE SOLUTION AT THE CURRENT DENSITY 0.0035 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

The behavior of the anode at different current densities is represented by the curves in figures 3 and 4. The A_3 curves of figure 3 show that at extremely low current densities the anode, also, gives a slightly lower value by the commutator method than by the direct; in fact it shows no drop at all in potential during the discharge intervals. The overvoltage, therefore, under these conditions appears to be zero. The overvoltage at the anode increases extremely rapidly with current density, as the curves in

figures 3 and 4 show, but the maximum value attained by the commutator method is precisely the same as that given by the direct method in all cases except the lowest current density. The general nature of the discharge curves is such as would be expected to result from depolarization, though it is not possible to say from the appearance of curve A_3, figure 4, that no portion of the discharge is due to an IR drop. It is evident from

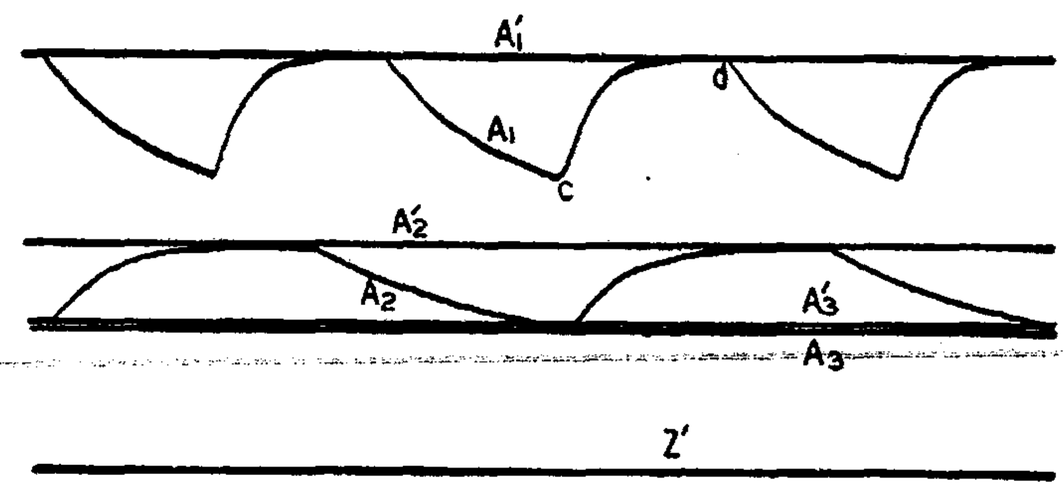

FIG. 3. ANODE CHARGE AND DISCHARGE CURVES AT THE CURRENT DENSITIES 0.000005, 0.00034, AND 0.00071 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

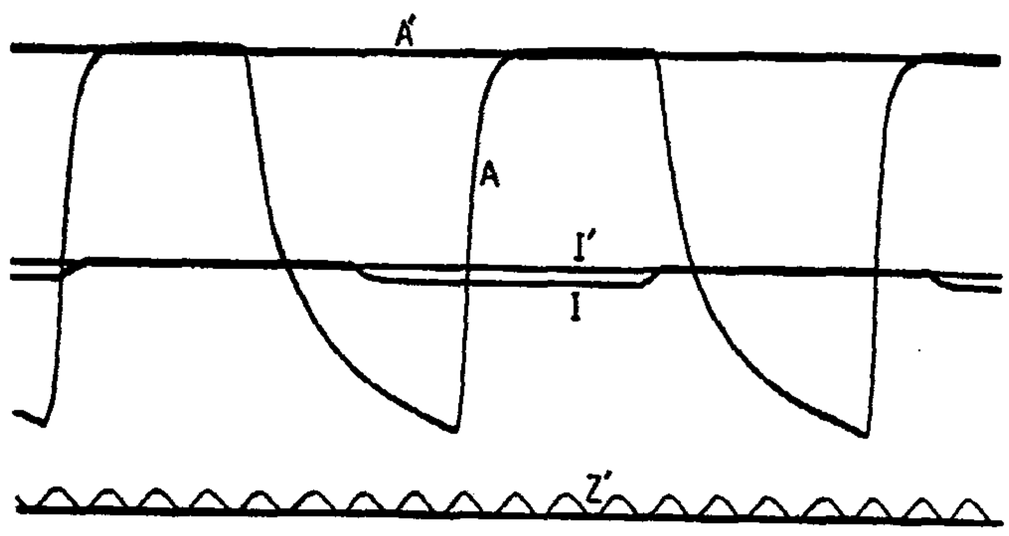

FIG. 4. ANODE CURVES AND CURVES SHOWING THE IR DROP THROUGH THE SOLUTION AT THE CURRENT DENSITY 0.0015 AMP., OBTAINED BY BOTH THE DIRECT AND COMMUTATOR METHODS

these curves that the extent of overvoltage and its general nature is about the same for anode and cathode at smooth platinum electrodes; and the drop in potential is so rapid in both cases that it is not possible to distinguish by means of the commutator between an IR potential and true overvoltage. These observations are distinctly different from those reported for platinized platinum. In order to obtain more information along this line, curves were taken with the electromagnetic interrupter.

The action of the electromagnetic interrupter is described in article VII (4) of this series and therefore no description is given here. By means of this arrangement it is possible to superimpose curves representing potentials of different types and different absolute values, and each may be interrupted at the same point on the film. This makes it much easier to analyze the nature of an unknown potential by comparing the curve given by it with curves given by potentials of known characteristics.

In figure 5 the three anode curves, A_1, A_2, and A_3, were obtained at current densities 0.00024, 0.00032, and 0.00163 amp., respectively. The corresponding curves, I_1, I_2, and I_3, show that the potential due to IR drop between the electrodes was practically zero at these low current densities. There are two timing waves at the bottom; the one showing the higher drum speed corresponds to A_3 and the other to A_1. These anode curves

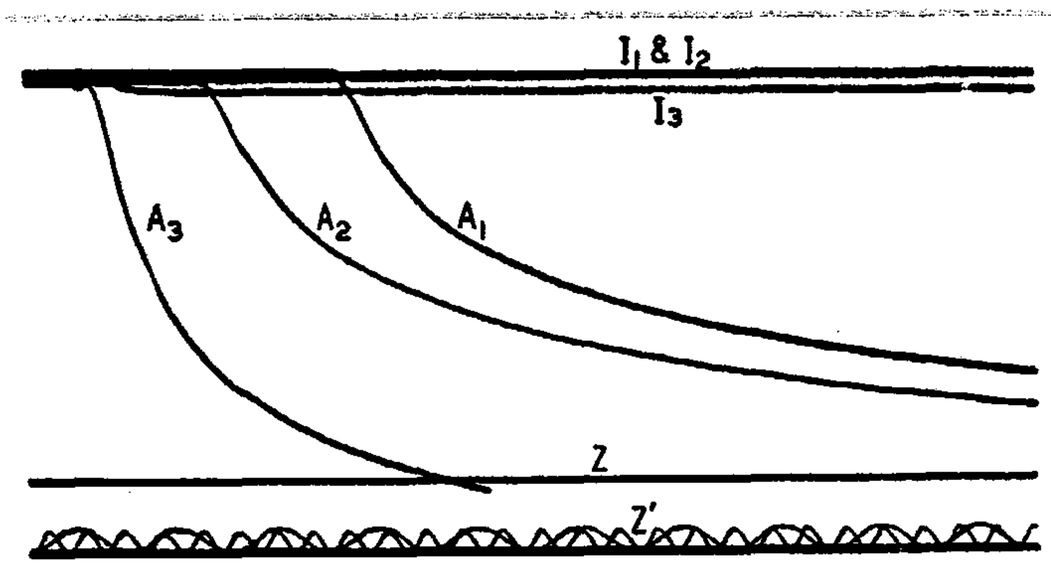

FIG. 5. CURVES FOR ANODE DEPOLARIZATION AND IR DROP THROUGH THE SOLUTION AT THE CURRENT DENSITIES 0.00024, 0.00032, AND 0.00163 AMP.

A_1 and A_3 were obtained at different drum speeds

appear to represent electrode depolarization only, since there is no vertical portion; but one is liable to be misled unless the speed of the drum is considered. As they appear in the figure, A_3 drops at a greater rate than A_1, yet the film in the case of A_3 had a velocity about 3.5 times greater than in the case of A_1. If the speed of the film had been the same for A_3 as A_1, the rate of drop of A_3 would appear much greater. These curves show: (1) that the anode overvoltage increases very rapidly with current density at low current densities, and (2) that the apparent rate of depolarization increases greatly with the amount of polarization.

In figure 6 are curves representing overvoltage values determined by three methods. The straight line A' and the straight portion of A_1 were obtained by the constant deflection of the oscillograph mirror due to a continuous constant potential applied to the anode. Both lines correspond to the same potential, but were taken at different times and with different

balancing potentials which caused them to appear at different positions on the film. At the end of the straight portion of A_1 the polarizing circuit was interrupted by means of the electromagnet and the remainder of the curve represents the depolarization of the electrode. Curve A was obtained with the commutator for the same polarizing potential as used in the two

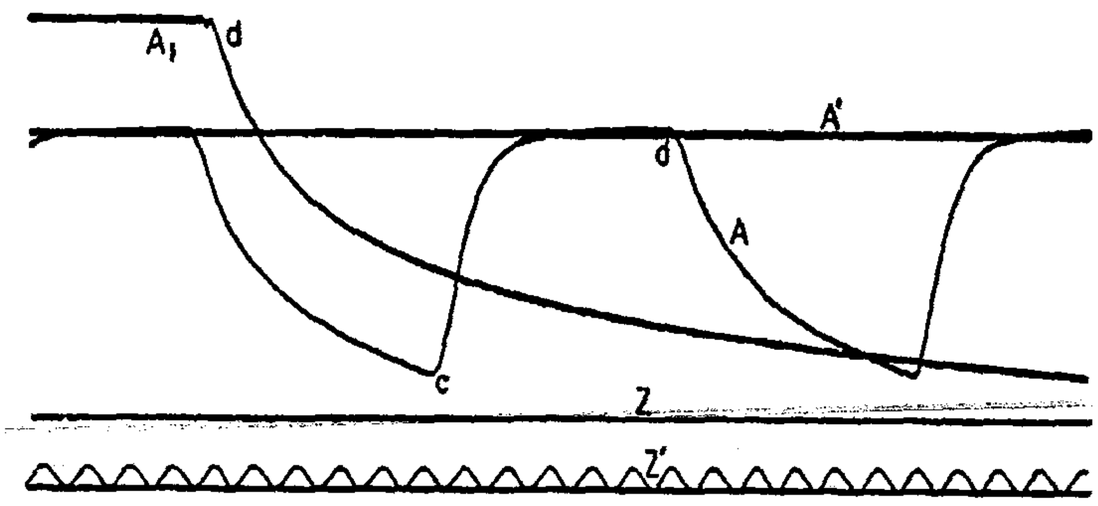

FIG. 6. ANODE CURVES OBTAINED BY THE DIRECT METHOD (A'), THE COMMUTATOR METHOD (A), AND THE ELECTROMAGNETIC INTERRUPTER (A_1)

The same anode potential was used in each case

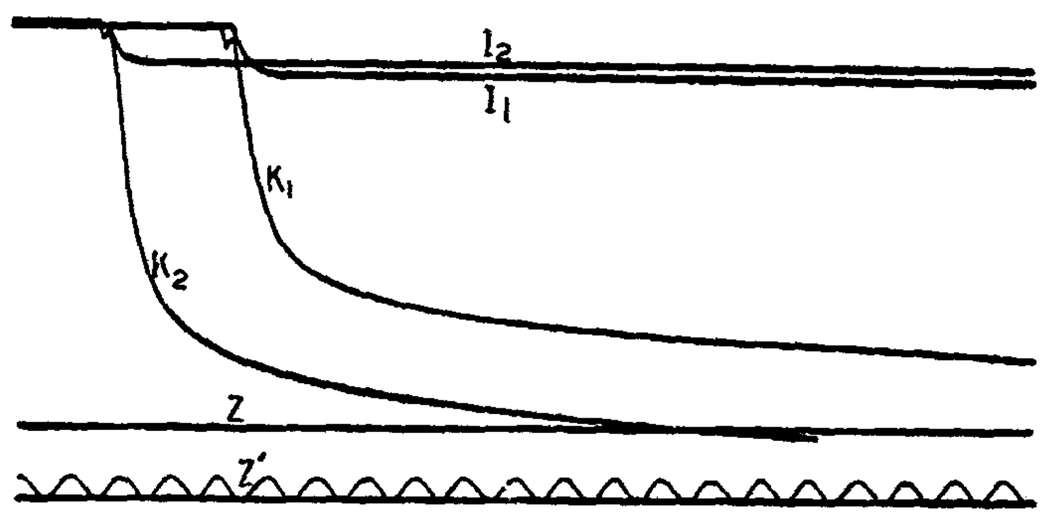

FIG. 7. CURVES FOR CATHODE DISCHARGE AND IR DROP THROUGH THE SOLUTION

The same polarizing potential was used in all cases, but K_2 and I_2 were taken about one half-hour after K_1 and I_1.

previous cases. It is evident that the commutator and electromagnet give identical depolarization curves.

The curves in figure 7 were all taken with the same applied polarizing potential across the cell; the only variable factor was time. The K_2 and I_2 curves were taken about one half-hour after K_1 and I_1. During this time interval the overvoltage increased about 40 mv., and the current density dropped from 0.0029 to 0.0028 amp. The drop in the I_1 and I_2 curves is due to the potential across a pure resistance, that of the solution, while the

drop in K_1 and K_2 is due to depolarization alone, yet the latter is even more rapid than the former at the start.

Curves for slightly higher current densities are shown in figure 8. The same current density, 0.0067 amp., was used for K_1 and I_1 as for K_1' and I_1', the latter being taken a few minutes after the former. The K_2 and I_2 curves were obtained at a current density of 0.0116 amp. The I curves in this figure represent a sufficiently large potential to show accurately the type of curve given by the interruption of a potential over a pure resistance; this is particularly true of I_2. It is very important to keep in mind that the I_2 curve represents or includes all potentials due to IR drops between the cathode and anode of the electrolysis cell. In other words, if there is any transfer or surface resistance at the cathode it must be included as a part of the drop in I_2. When it is remembered that K_2 is made up only of the

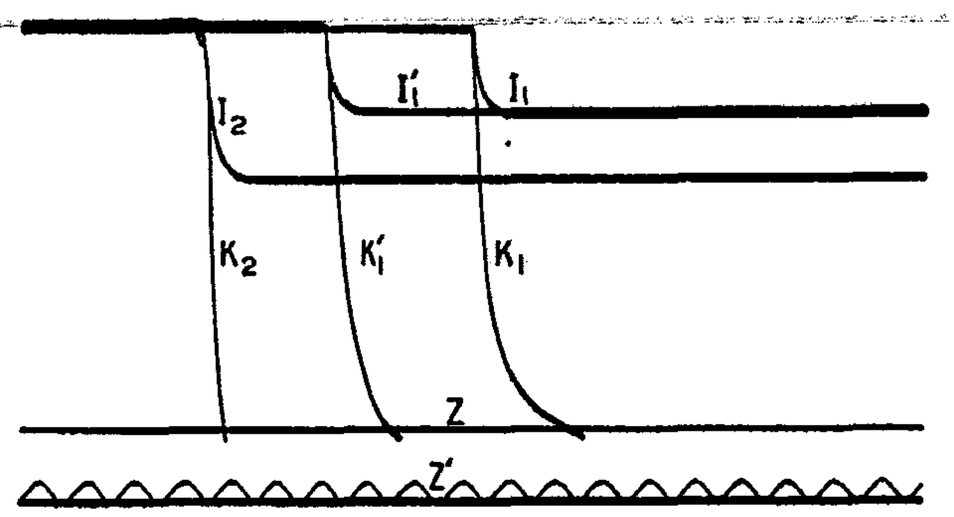

FIG. 8. CURVES FOR CATHODE DISCHARGE AND IR DROP THROUGH THE SOLUTION

K_1' and I_1' were taken at the same current density, 0.0067 amp., as K_1 and I_1, but about five minutes later. K_2 and I_2 were taken at a current density of 0.0116 amp.

sum of I_2 and the true polarization at the cathode, it must be evident that any potential greater than I_2 can be due only to true polarization; or, in other words, all that portion of K_2 below the lower horizontal line of the I_2 curve must be due to cathode depolarization. It is also evident from the curves that there can be no distinction made in the nature of the K_2 curve between the portion above and that below the lower horizontal part of I_2; also, no distinction can be made between the upper part of I_2 and any part of K_2. This all demonstrates that no distinction can be made between a curve representing a fall of potential over a pure resistance and a curve representing pure depolarization for smooth platinum electrodes at the current densities used here. If this conclusion is warranted from the data, then it follows that the oscillograph such as is employed in this work can not be used to disprove the existence of transfer resistance in the case of smooth platinum electrodes merely on the basis of a difference in the shapes

of the curves. The authors wish to point out especially, however, that in all of these figures the I curves include all IR drops, those due to surface resistances as well as electrolytic resistance, and that these drops are small compared with the total drops at the electrodes; also, that current measurements were made in all cases, and when the total resistance was calculated the same value was found irrespective of the total current or whether the electrodes were platinized or smooth.

On the basis of the evidence here presented, therefore, irrespective of the fact that for smooth platinum electrodes it is not possible to distinguish between an IR drop and depolarization because both fall so rapidly, yet it may be concluded that there is no transfer resistance even at the surface of smooth platinum electrodes.

SUMMARY

1. A study is made of overvoltage phenomena at both anodes and cathodes of bright platinum in 2 N sulfuric acid.

2. An oscillograph was used to obtain charge and discharge curves.

3. Curves are obtained which show the influence of time and current density.

4. A comparison is made of the direct method, the commutator method, and the electromagnetic interrupter.

5. An attempt is made to distinguish between discharge curves due to a pure resistance, those due to true depolarization, and those due to a combination of the two.

The junior author wishes to acknowledge his indebtedness to the China Foundation for the Promotion of Education and Culture, for the granting to him of a fellowship which made it possible for him to continue his research work at the University of Michigan.

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THE APPLICATION OF THE RAYLEIGH INTERFEROMETER TO THE MEASUREMENT OF REACTION VELOCITY

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Received May 29, 1934

INTRODUCTION

Duane (6), in 1901, demonstrated that the progress of a reaction in the liquid phase could be determined by measuring the changes in refractive index of the reacting solution. At the same time he showed that the same result could be obtained by measuring the changes in volume of the solution during the course of the reaction. Koelichen (11) had first employed this "dilatometric" method the preceding year. The latter method has since been employed frequently in rate investigations; the former has been almost abandoned. Recently, however, with the increased use of the Rayleigh interferometer, a few investigators (9, 16, 17, 19) have employed that instrument in the determination of rates of reactions. None of these, however, has devoted much space to a description or analysis of his method, which deserves more consideration.

There is a close relationship between the dilatometric and refractometric methods; this is a necessary consequence of the exactness of all the formulas for specific refraction, in which the refractive index is closely inversely proportional to the density. Wagner, Fajans, and Kohner (12), among others, have shown that for completely ionized salts and acids, as well as for unionized substances in aqueous solutions, the molecular refractions calculated from the Lorenz-Lorentz equation and the Biot-Arago law of mixtures are very nearly constants, rarely deviating by as much as 0.5 per cent from their mean values except over very wide ranges of concentration. Since the Lorenz-Lorentz equation is also the soundest, theoretically, of the relations between density and refractive index, we shall employ it in an investigation of the relations between the two aforementioned quantities and the molecular refraction.

For a general reaction

$$A_1 + \ldots A_i + \ldots A_k \rightarrow B_1 + \ldots B_j + \ldots B_l \qquad (1)$$

the Lorenz-Lorentz equation before any interval of the reaction is

$$M = p_s M_s + \sum_1^k p_i M_i + \sum_1^l q_j M_j \qquad (2)$$

and after the interval is

$$M' = p_s M_s + \sum_1^k p'_i M_i + \sum_1^l q'_j M_j \tag{3}$$

where the terms $\frac{(n^2-1)}{d(n^2+2)}$ for the various components are designated by M with sub- and super-scripts as indicated below:

M for the solution before the interval of reaction,
M' for the solution after the interval of reaction,
M_i for the reactant A_i,
M_j for the product B_j and
M_s for the solvent.

p_i and q_j are the weight fractions, respectively, of A_i and B_j before the reaction, and p_i' and q_j' their weight fractions after the reaction.

Subtracting equation 3 from equation 2 we obtain

$$M - M' = \sum_1^k (p_i - p'_i) M_i + \sum_1^l (q_j - q'_j) M_j \tag{4}$$

The weight fractions of the terms remaining on the right-hand side of equation 4 correspond to the quantities consumed and produced according to the stoichiometric equation. That being so,

$$\frac{\text{Mol. wt.}}{p - p'} \quad \text{and} \quad \frac{\text{Mol. wt.}}{q - q'}$$

are the same for all terms.

Multiplying and dividing the right-hand side of equation 4 by this quantity and defining the molecular refraction,

$$R = \frac{\text{Mol. wt.}}{d} \frac{(n^2 - 1)}{(n^2 + 2)}$$

we have

$$M - M' = \frac{p_i - p'_i}{\text{Mol. wt.}_i} \left[\sum_1^k R_i - \sum_1^l R_j \right] \tag{5}$$

The right-hand side of equation 5 we will call K. K is a function only of molecular refractions, which may, in general, be calculated with a fair degree of accuracy, and of concentrations; hence it is readily determinable.

Equation 5 may be solved as a quadratic in $(n' - n)$, the change in refractive index, in terms of the parameters n, d, d', and K. The result is

$$(n' - n) = -n \pm \sqrt{n^2 - \frac{(n^2+2)(n^2-1)(d'-d) - Kdd'(n^2+2)}{d'(n^2-1) - d(1+Kd')(n^2+2)}} \tag{6}$$

From equation 6 it is seen that the changes in density, concentration, and molecular refraction must be known in order to calculate the change of refractive index. It is also to be observed that there may be reaction systems wherein there will be a change in density but not in refractive index, and vice versa. Secondly, $(n' - n)$ is very nearly proportional to the change in density, $(d' - d)$, and to K, when these quantities do not exceed the magnitudes encountered in rate work, viz., when $|d' - d| < 0.01$, $|K| < 0.001$.[1] This is illustrated by table 1.

TABLE 1

Change of refractive index as a function of change of density and molar refraction

$(n' - n) = f[K, n, (d' - d), d]$

$K = 0, d = 1, n = 1.333$			$(d' - d) = 0, d = 1, n = 1.333$		
$d' - d$	$n' - n$	$\frac{n' - n}{d' - d}$	K	$(n' - n)$	$\frac{(n' - n)}{K}$
0.1	0.03844	0.3844	+0.01	−0.01773	−1.773
0.01	0.003685	0.3685	+0.001	0.001783	1.783
0.001	0.0003670	0.3670	+0.00001	0.00001784	1.784
0.0001	0.00003669	0.3669	0	0	
0.00001	0.00000366	0.366	−0.00001	+0.00001783	−1.783
0.0	0		−0.001	0.001785	1.785
			−0.01	0.01794	1.794

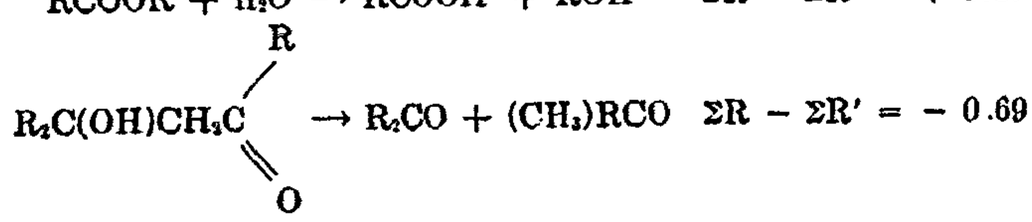
$d = 1, n = 1.333$

K	$d' - d$	$(n' - n)$	$(n' - n)$ obtained as sum of limiting values from columns 3 and 6 above
−0.01	0.01	0.02184	0.01784 + 0.00367 = 0.02151
−0.00001	0.01	0.003691	0.0000178 + 0.003669 = 0.003687
−0.01	0.00001	0.01786	0.01784 + 0.00000367 = 0.01784
−0.00001	0.00001	0.00002150	0.00001784 + 0.0000367 = 0.00002151

[1] To show that the limiting values for K are reasonable we have calculated the change in molecular refraction for the following reactions:

$$RCN + H_2O \rightarrow RCONH_2 \qquad \Sigma R - \Sigma R' = +0.39$$

$$RCOOR + H_2O \rightarrow RCOOH + ROH \qquad \Sigma R - \Sigma R' = +0.17$$



$$\Sigma R - \Sigma R' = -0.69$$

In dilute aqueous solutions, $(p - q)$/mol. wt. $= \Delta N \cdot 10^{-3}$, ΔN being the change in normality, and

$$K = N(\Sigma R - \Sigma R') \cdot 10^{-3}$$

If we take $N = 0.1$, then K falls between 10^{-4} and 10^{-5}.

In dilatometric investigations it has generally been assumed that the small changes occurring in the density are strictly proportional to the changes in concentration. We see from the above considerations that, if the assumption is valid for changes in density, it is also valid for changes in refractive index. However, with the interferometer it is not necessary, although it is convenient and generally satisfactory, to make this assumption, for usually a direct determination may be made of the relation between concentration and refractive index.

EXPERIMENTAL METHOD

The general methods for using the Rayleigh interferometer have been adequately described (1, 2, 4, 7, 10, 20). A very brief description of the instrument will be sufficient here. A beam of light is split into two portions, one of which passes through a length of a "reference" substance, then through a fixed glass compensator plate, the other through an equal length of an "unknown" substance and through an identical compensator plate; finally the beams are reunited through slits to form interference fringes. If the optical paths through the reference and unknown substances are not the same, i.e., if the refractive indices of the solutions are made different, there will result a shift of the fringe system. By adjusting one of the compensator plates by means of a micrometer screw this shift is overcome, and the fringes are brought back to the zero position. Differences of refractive index may be determined as a simple, almost linear, function, of micrometer readings. Two corrections must be applied to the readings to make them a true linear function of the differences in refractive index. These have been treated fully by Adams (1), Barth (2), and others. Crist, Murphy, and Urey (5) have noted recently that in some instruments errors may be introduced, owing to imperfections in the compensator plate mechanism. The substances (liquids or gases) to be compared are placed in the two troughs of a chamber fitted with glass endplates, and the chamber is then inserted in the instrument so that the two beams of light pass each through one of its troughs.

The instrument used in this investigation was a Zeiss portable liquid interferometer.

Ordinarily it is advisable that the reaction be allowed to proceed in the chamber rather than that the instrument be used for analysis of samples of the reaction solution at suitable times. This is largely a matter of convenience, but uncertainties, which are better avoided, are introduced by the large amount of manipulation required by the latter method.

PREPARATION OF SOLUTIONS

The following discussion is restricted to reactions in the liquid phase. In the simplest case the reaction mixture is obtained by mixing equal amounts of two solutions, A and B, each containing one of the reactants,

their concentrations being, of course, double those desired in the experiment. In addition a third solution, C, is prepared of some inert substance such as potassium chloride, which will not react with anything present in solution B. The concentration of C is such that when diluted by half it will give a zero reading in the interferometer when compared to solution A when the latter is diluted by half.[2] Then equal amounts of C and B, previously brought to thermostat temperature, are placed in one chamber; equal amounts of A and B are mixed, the time of mixing being taken as the zero time of the reaction, and are placed in the other chamber. As a consequence of the manner of preparation of the solutions, the readings at zero time should approximate the zero of the instrument. If the kinetic picture is simple, this may be shown to be true by extrapolating the readings to zero time. If, however, there is a rapid preceding reaction, the extrapolation to zero time will give a reading which differs from the zero of the instrument by the change in refractive index of that reaction. Using this method it is possible then to establish with a fairly high degree of certainty[3] the existence or non-existence of preceding reactions. In a similar manner, by using in the reference solution a substance thought to be a product of the reaction, the high probability that it is or is not a product may be established.

Szegö (19), in investigating the oxidation of nitric oxide to nitrogen dioxide, ingeniously took advantage of the fact that there is a change of refractive index in the oxidation, but none in the reaction of nitrogen dioxide to give nitrogen tetroxide. Consequently, with the interferometer he could follow the oxidation without regard for the existence of the following equilibrium. A few other applications will suggest themselves.

After such information on stoichiometry has been obtained, much less care need be taken with the reference solution; it is better, however, to have the readings during a run on the lower part of the scale, so that the corrections will be small and the high differences in dispersion accompanying high differences in refractive index will be minimized.

REDUCTION OF OBSERVATIONS

The problem of the reduction of observations for first-order reactions has been treated satisfactorily by Guggenheim (8). In the method described by him a series of readings $v_1 \ldots v_i \ldots v_n$ are made at

[2] The comparison of C and A must be made after dilution because of the shifting of the achromatic fringe, owing to the almost inevitable difference in dispersion of the two solutions. If the differences in dispersion are too large, the fringes will disappear (cf. Hirsch (9)).

[3] This degree of certainty is dependent upon the extent to which reactions are accompanied by changes of refractive index. We have experience only with nitrile, amide, ester, and diacetone alcohol hydrolysis, and with acid ionization (shift of equilibrium in buffers). The change of refractive index is of the same order of magnitude in each of these.

times $t_1 \ldots t_i \ldots t_n$ and another series $v_1' \ldots v_i' \ldots v_n'$ at times $t_{1+r} \ldots t_{i+r} \ldots t_{n+r}$. Then from the equation

$$kt_i = 2.303 \log_{10} (v_i' - v_i) + \text{constant} \tag{7}$$

the velocity constant may be obtained. Guggenheim obtained the constant by plotting $\log (v' - v)$ against t, but that is entirely incidental to the method. The constant may be obtained by any of four standard methods, viz., by plotting, by a method of averaging, by an unweighted least squares solution, or by a weighted least squares solution. The advantage of Guggenheim's method is that each reading is used once and once only; every point on a graph and every value in a calculation is independent of all other points or values. It is reasonable then to apply sophisticated methods of analysis to the data.

Reed and Theriault (13) have criticized Guggenheim's treatment on the grounds that, since the weights theoretically to be assigned to the points diminish as the reaction progresses, no treatment which neglects this factor can yield better than very approximate results. The statement implies that the graphical reduction of data is essential to the method, and that is not true.

Reed and Theriault (14) conclude a paper on the least squares treatment of first-order reactions with the rather extreme statement that, ". . . . the least squares treatment should be used whenever the velocity constant is to be determined within an allowable error of, say 5 per cent."

It is a fact not very generally recognized that whenever a very considerable body of data is at hand, almost any reasonable method of reducing that data to a final result will yield a result very close to the best value obtainable from a theoretically perfect least squares solution. A preliminary demonstration of the truth of this statement may be given by calculating velocity constants from the sample data given by Guggenheim. There are two sets of data taken during a single run, with twenty pairs of points in each. The constants are calculated by the four formulas given below, and the constants obtained are given in the right-hand columns:

	k ($\times 0.4342 \times 10^3$)	
(1) Graphically (by Guggenheim):	6.54	6.56

$$0.4342kt_i + \log (v_i' - v_i) = \text{Const.} \tag{8}$$

(2) Method of averages	6.558	6.566

$$0.4342k = -\frac{\sum_{1}^{n/2} \log (v_i' - v_i) - \sum_{n/2+1}^{n} \log (v_i' - v_i)}{\sum_{1}^{n/2} t_i - \sum_{n/2+1}^{n} t_i} \tag{9}$$

(3) Unweighted least squares: 6.565 6.568

$$0.4342k = -\frac{n\sum_1^n t_i \log(v_i' - v_i) - \sum_1^n t_i \sum_1^n \log(v_i' - v_i)}{n\sum_1^n t_i^2 - \left(\sum_1^n t_i\right)^2} \quad (10)$$

(4) Weighted least squares: 6.556 6.565

$$0.4342k = -\frac{\left[\sum_1^n (v_i' - v_i)^2\right]\left[\sum_1^n t_i (v_i' - v_i)^2 \log(v_i' - v_i)\right] - \left[\sum_1^n t_i (v_i' - v_i)^2\right]\left[\sum_1^n (v_i' - v_i)^2 \cdot \log(v_i' - v_i)\right]}{\sum_1^n (v_i' - v_i)^2 \sum_1^n (v_i' - v_i)^2 \cdot t_i^2 - \left[\sum_1^n (v_i' - v_i)^2 \cdot t_i\right]^2} \quad (11)$$

It is fairly obvious that the graphical method is not sensitive enough to do full justice to the data, but the uncertainty introduced by using any of the first three methods as alternatives for the weighted least squares is of an order of magnitude far less than 5 per cent.

While with accurate data it is thus apparent that the uncertainty introduced by using a less exact method of calculation may be reduced to a small quantity, there is yet no indication of the relationship between that uncertainty and the probable error which arises from accidental errors in the data. To shed light on this point four identical runs were made at low concentrations (0.005 N) to insure large probable errors in the results, which are given in table 2. The data are admittedly not sufficiently ample to be entirely convincing, but the indications are clear. The weighted least squares result is to be taken as the standard with which the other three are to be compared. The graphical method appears to be the least reliable, since it gives the largest deviations from the weighted least squares solutions. The solutions by averages and the unweighted least squares solutions give results which are of about the same reliability; since the latter method is somewhat more laborious, we shall discard it in favor of the method of averages. The differences between the constants obtained by averaging and those obtained by weighted least squares are all less than the probable error in the latter constants, averaging about two-thirds of the probable error.

The principle that the uncertainties introduced by calculations must be negligibly small in comparison with the experimental error, is indisputably sound in the common situation where the calculations form the lesser part of the investigation. There is, on the other hand, practical justification for using a less precise method of calculation in those situations where the time required for a least squares solution would be a major fraction of the

total time required for the work. In rate investigations there is a place for each of the methods with the exception of the third. The graphical method is the best when there are trends toward the end of the experiment due to complications such as often appear in organic reactions. These are usually of such an involved nature, or are so incompletely understood, that they may not be treated exactly, but the observer is, none the less, perfectly justified in giving less weight to points obtained after the appearance of the trend. On the other hand, if there are no systematic trends, if a fairly large amount of data can be obtained in each run, and if there are a large number of runs to be handled, then the method of averages is the most satisfactory solution. If the quantity of data is comparatively small and is characterized by a relatively high probable error, then the fourth method will give best results. Furthermore, if the data are known

TABLE 2

Rate constants for runs calculated by four methods

RUN NO.	RATE CONSTANTS			
	1 Graphical	2 Averages	3 Unweighted least squares	4 Weighted least squares
1	0.03823	0.03809	0.03805	0.03853
	±0.00057	±0.00059	±0.00066	±0.00056
2	0.03959	0.03973	0.04007	0.03982
3	0.04003	0.03924	0.03853	0.03878
4	0.03894	0.03779	0.03735	0.03802
Mean	0.03927	0.03868	0.03841	0.03885

Probable errors determined for each method by the external consistency of the four constants.

to be characterized by certain simple constant errors of known type, then the method described by Reed and Theriault finds its application.

In the interests of greater accuracy two cautions are to be observed. The time between the two readings of each pair should be equal to two or three half-times of the reaction. Roseveare (15) has shown that the rate constant is most accurately determined from two points, if the second occurs at two-thirds completion of the reaction. Accordingly, it is well to plan a concentration of points at the beginning of the reaction and another concentration near two-thirds completion.

Higher order reactions must still be treated by the methods developed for ordinary chemical analysis, which are apt to be, with this instrument and the dilatometer, incapable of yielding very reliable results. Roseveare has given an equation which eliminates the necessity of obtaining the infinite time reading directly for the bimolecular reaction, where $dx/dt = k(a - x)^2$.

RELIABILITY OF THE INTERFEROMETER

Returning to an examination of the data given in table 2, and adding the data from which the constants in run No. 1 (see table 3) were obtained, we find evidence that the systematic errors introduced by the interferometer are very small.

If a number of readings be made with the interferometer chambers empty, the probable error of a single reading, determined from the degree of consistency of the readings, is on our instrument about 0.2 division. In

TABLE 3

Results obtained in run No. 1

$k = 0.03809$

t	v	t'	v'	$v' - v$	$v' - v$ (calcd.)	RESIDUALS
minutes						
3	106.8	63	133.2	26.4	26.0	0.4
4	108.3	64	133.4	25.1	25.0	0.1
5	109.3	65	133.7	24.4	24.2	0.2
6	110.5	66	133.9	23.4	23.2	0.2
7	111.7	67	134.0	22.3	22.4	0.1
8	112.9	68	134.3	21.4	21.5	0.1
9	114.0	69	134.3	20.3	20.7	0.4
10	114.5	70	134.6	20.1	19.9	0.2
11	115.6	71	134.5	18.9	19.2	0.3
12	116.1	72	134.6	18.5	18.4	0.1
13	117.1	73	135.0	17.9	17.8	0.1
14	117.8	74	134.9	17.1	17.1	0
15	118.6	75	135.0	16.4	16.5	0.1
16	119.6	76	135.0	15.4	15.9	0.5
17	120.0	77	135.2	15.2	15.2	0
18	120.8	78	135.2	14.4	14.7	0.3
19	121.0	79	135.2	14.2	14.1	0.1
20	121.2	80	135.1	13.9	13.6	0.3
21	122.0	81	135.4	13.4	13.1	0.3
22	122.5	82	135.3	12.8	12.6	0.2

run No. 1 the probable error in $(v' - v)$ is 0.18 division as determined by the internal consistency of all the readings, that is, by the formula

$$r = 0.6745 \sqrt{\frac{\sum w_i^2}{n-2}} \tag{12}$$

where w_i is the residual $(v_i' - v_i)_{\text{obsd.}} - (v_i' - v_i)_{\text{calcd.}}$ The readings v_i' were each taken three times; assigning them a proper weight, the law of propagation of errors gives the probable error in v_i equal to 0.16. The agreement between this value and the one obtained from direct readings

indicates that the first-order rate equation is satisfactory. The probable error in the velocity constant, arising from this probable error in v, is found to be 0.00046. The probable error in the constant obtained from the external consistency of the four runs is 0.00059. Birge (3), in his treatment of the problem of internal and external consistencies, has shown for the case where there are four functions being compared, that owing to statistical fluctuations, the ratio of probable error from external consistency to that from internal consistency should be 1.24. It is in the case given above, fortuitously, 1.28. A much less close agreement would still be a strong indication that there are no systematic errors, which vary only from run to run.[4]

TEMPERATURE CONTROL

The commercial instrument is very inconveniently thermostated. Fairly satisfactory results were obtained within five or ten degrees of room temperature by pumping distilled water through 30 ft. of copper tubing in a thermostat, and then through the reservoir which surrounds the chamber containing the solutions. By making heavy brass cover plates for the chamber, of the type described by Cohen and Bruins, but hollow so that water could be drawn through them, the temperature regulation was made very satisfactory within ten degrees of room temperature and reasonably so within fifteen. The difficulties arising are due not to temperature variations which affect the rates of the reactions, but rather to much smaller inhomogeneities of temperatures, both in the reacting solution and in the surrounding bath, which affect the refractive indices enough to make the fringes very unsteady. A thermostat controlling the temperature to 0.01°C. should be satisfactory provided there are no sudden changes of

[4] Since the above was written it has been found that the instrumental defect described by Crist, Murphy, and Urey (5) is more common than might have been suspected. Results as consistent as those given above cannot be obtained from an instrument having an appreciable error of the type described. This error appears when the tip of the micrometer screw is not in the axis of the screw. A deviation of 0.05 mm. is sufficient to produce the results described by Crist, Murphy, and Urey. The error is periodic, going through a cycle in one complete turn of the micrometer screw. It disappears when the lever arm on which the screw acts is perpendicular to the screw. It was under these special conditions that the runs described above were made.

Crist, Murphy, and Urey calibrated their instrument by measuring each fringe throughout the whole scale. Adopting different tactics, we removed the micrometer screw from our instrument and reground the tip so as to center it. This can be done only on a very good lathe. After this treatment no regular periodicity could be found.

If this correction is not made, systematic errors as large as 2 per cent may appear in the rate constants when the concentrations are as low as those described above. At higher concentrations the errors become much less important.

temperature within it amounting to more than 0.002°C. It is not possible with the present design of the instrument to obtain temperature coefficients over a wide range of temperature.

If the heat of the reaction is large, the temperature of the reacting solution may rise slightly above that of the thermostat and the reference solution; this results in a very easily perceptible change of refractive index. From the nature of the relations involved it appears that the temperature difference reaches a maximum in a very few minutes, but is dissipated slowly, and exists as a potential source of error throughout three-quarters of the life of the reaction. For first-order reactions this potentiality disappears when we examine the situation more closely.

The temperature difference is given by the equation

$$(T - T_0) = \frac{\Delta H A_0 k}{1000(K - k)}\left[e^{-kt} - e^{-Kt}\right] \tag{13}$$

which is the solution of the differential equation,

$$\frac{dT}{dt} = -K(T - T_0) - \frac{\Delta H}{1000}\frac{dA}{dt} \tag{14}$$

k is the velocity constant, K the Newton's law of cooling constant, ΔH the heat of reaction in calories per mole, and A_0 the initial concentration of the reactant. We may set the observed reading at any time equal to the correct reading at that time plus the difference due to the temperature difference, so that

$$v_i = V_i + x_i \tag{15}$$

x_i is directly proportional to the change in refractive index due to the temperature disturbance and so is directly proportional to the temperature difference. Therefore we may say in any given case that

$$x_i = C_1\,(e^{-kt} - e^{-Kt_i}) \tag{16}$$

Now the exponential form of the first-order rate equation is

$$(V_i - V_\infty) = (V_0 - V_\infty)\,e^{-kt_i} \tag{17}$$

Eliminating x_i and v_i from equations 15, 16, and 17, we have, x being zero at both zero and infinite time,

$$(v_i - v_\infty) = (v_0 - v_\infty - C_1)\,e^{-kt_i} + C_1\,e^{-Kt_i} \tag{18}$$

As soon as the second exponential term becomes negligible with respect to the first, the temperature difference will have no influence on the rate constant. In a plot of log $(v_i - v_\infty)$ against time the observed result would be that the y-intercept would be log $(v_0 - v_\infty - C_1)$ rather than log

$(v_0 - v_\infty)$, while the slope would be unchanged. In a particular case at hand ΔH was about 18,000 cal., k was 0.0201 min.$^{-1}$, K for the interferometer chamber (all the metal chambers should give about the same value) was roughly 0.85 min.$^{-1}$, and A_0 was 0.05 N. The maximum temperature difference should be 0.019°C., occurring at 4.51 minutes. At that time the second exponential term is nearly negligible, and by eight minutes it is completely so. The temperature difference does not fall to the point where its effect on the refractive index is negligible for over two hours. In two runs where the first point was at fifteen minutes, there were no trends; in a third where the first point was at three minutes, there was a very definite trend, and the rate constant was two or three per cent lower.

For higher order reactions the same situation may be found; the matter has not been investigated, and there is no certainty that such is the case.

After several of the chambers had been used for some time, baffling irregularities began to appear in the results. It was finally found that the cement holding the end-plates in place had been partially dissolved away and the chambers had developed small leaks which resulted in a slow change of the refractive index of the solution. This is undoubtedly the source of the drift which was attributed by Stewart and Kung (18), in their use of the method, to unequal evaporation from the two chambers.

A COMPARISON OF THE MERITS OF THE DILATOMETER AND THE INTERFEROMETER

In its present design the interferometer is less flexible than the dilatometer; it can not be used over a wide range of temperatures; certain waxed joints must be protected if non-aqueous solvents are to be used; it is probably not applicable to reactions which are highly photosensitive throughout the range of visible light. Moreover the instrument is expensive. On the other hand the interferometer will normally handle faster reactions; it requires less care in thermostating; and when calibrated interferometers are available (in use for ordinary analytical work) results may be obtained with a minimum of effort. If only small amounts of reagents or solvents are available, experiments may be made in favorable cases with as little as 0.05 cc. of solution. It is difficult to compare the sensitivities of the two methods, since the practical consideration of temperature control constitutes the main restriction to the extension of the sensitivity of the dilatometer. Finally, as noted above, with the interferometer the presence or absence of rapid preceding reactions or of equilibria may be demonstrated with high probability.

SUMMARY

1. The quantitative relations between change of density and change of refractive index during reactions have been derived. It has been shown

that the change of refractive index is as reliable a measure of the progress of a reaction as is the change in density.

2. Practical methods for the application of the Rayleigh interferometer to rate measurements have been described.

3. It has been shown that the interferometer can be of value in the investigation of the stoichiometry of a reaction.

4. The reduction of observations has been discussed in some detail. Guggenheim's method is recommended for first-order reactions, and the method of averages is found to be the most convenient and, in general, a sound and thoroughly reasonable means of obtaining velocity constants.

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THE THIXOTROPY OF HEATHER HONEY

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Received May 2, 1934

The use of the viscometer for testing the purity of honey was introduced in 1911 by Fellenberg (4), who tested honeys mixed with water in an Ostwald viscometer. Eisenschitz (3) has shown that honey mixed with water behaves as a normal viscous liquid. It is known, however, that some undiluted honeys, even when not granulated, show abnormal viscous behavior (6), and de Boer and Kniphorst (1) have shown that stirred heather honey (from *Calluna vulgaris*) increases its viscosity gradually on standing. The rate at which this rise in viscosity takes place depends on the temperature, passing through a minimum at about 15°C., but even at this temperature, the viscosity (as measured by the time of outflow per gram from a Holde viscometer)[1] increases by many fold within twenty-four hours. On stirring, the viscosity returns to somewhere near its original value. This phenomenon is described by de Boer and Kniphorst as "thixotropy," but since it is not known how far this is really similar to the reversible sol-gel transformations to which the term thixotropy was originally applied, it is of interest to investigate further the viscous and rigid properties of the sol and gel forms. No information seems to be available, for example, as to whether the stirred honey is a true fluid, which on standing sets into a rigid gel; whether the setting is caused by a rise in viscosity only; or whether both sol and gel forms show rigid properties. Moreover, the phenomenon has a practical interest, since heather honey, by reason of its gelatinous character, holds its water in a different way from other honeys. Ordinary honey containing more than about 20 per cent of water (due to either immaturity or dilution) tends to ferment, whereas heather honey, since some of its water is held in an immobilized condition, does not do so until a considerably higher moisture content is reached. The term "heather honey" is used to describe any honey derived largely from the nectar of *Calluna vulgaris*, *Erica cinerea*,[2] and allied species. However, in many cases heather honeys are not obtained from a pure heather source,

[1] For a description of this instrument see Lunge-Berl Chemische Technologische Untersuchungen, 7th edition, Vol. III, p. 461.

[2] Added January, 1935: It now appears probable that honeys derived from *Erica* alone are not thixotropic.

samples showing a range of properties between those of a honey obtained entirely from heather on the one hand, and of an ordinary non-thixotropic honey on the other. A method of assessing the extent to which a given sample showed the gelatinous and thixotropic properties of a heather honey would be of value in deciding whether an apparently excessive moisture content would be likely to lead to subsequent spoiling due to fermentation.

THE GEL FORM

To investigate the properties of the gel form, a ball viscometer was used. As a preliminary experiment, in view of the fact that only comparatively small samples were available, and that viscometer vessels could not, therefore, be very large compared with the size of the balls, the effect of wall-correction on the viscosity measurements on a normal liquid (Lyle's Golden Syrup) was tested.

TABLE 1

Rate of fall of balls through Lyle's Golden Syrup

DIAMETER OF BALL	TIME	$\frac{\text{VELOCITY}}{\text{DIAMETER}^2}$
inches	*seconds*	*arbitrary units*
1/2	34.5	0.116
5/16	52.3	0.194
1/4	65.0	0.247
7/32	81.5	0.256
3/16	98.5	0.291
5/32	126.2	0.329
1/8	175.0	0.356

A Nessler tube of internal diameter 3.1 cm., having marks etched at a distance of 6 cm. apart, was filled with syrup, and left to stand overnight. On the following morning, a number of steel balls were dropped through the liquid, the time in seconds taken to fall between the marks being recorded.

The balls are not small compared with the size of the tube, and the results given in table 1 show that the rate of fall is by no means proportional to the square of the diameter of the ball.

Although various corrections have been proposed to allow for such errors (5), it seemed more satisfactory to eliminate differences in the error by using two balls of different size, falling in vessels whose diameters bear an approximately constant ratio to the diameters of the balls.[3]

For this purpose, two glass cylinders were chosen, A having a diameter of 3.4 cm., and B a diameter of 4.8 cm. Into A were dropped balls of

[3] I am indebted to Dr. R. K. Schofield for suggesting this arrangement.

diameter 0.80 cm.($\frac{5}{16}$ in.), and into B balls of diameter 1.11 cm. ($\frac{7}{16}$ in.). For a true fluid, in which the viscosity is independent of shearing stress, the times taken for the balls to fall between the marks (5 cm. apart in each case) should bear a ratio equal to the ratio of the squares of their diameters.[4] Moreover, for a true fluid, the rate of the fall should be unaffected by stirring.

As a first experiment, balls were timed to fall through a sample of Lyle's Golden Syrup (a different sample from that used in the earlier experiment). Immediately after the test, a perforated metal disk was forced twice up and down through the syrup so as to cause a thorough stirring, and the test was repeated.

The test was repeated exactly with a sample of heather honey which had been left in the viscometer vessels overnight. It is clear from table 2 that whereas syrup has a viscosity which is reasonably independent of

TABLE 2

Viscosity of Lyle's Golden Syrup and heather honey

FLUID	VELOCITY IN CM. PER SECOND		VELOCITY/D^2	
	A	B	A	B
Lyle's Golden Syrup				
Before stirring	0.108	0.217	0.171	0.176
After stirring	0.110	0.216	0.175	0.176
Heather honey				
Before stirring	0.0475	0.137	0.076	0.112
After stirring	0.395	0.770	0.625	0.625

Two heather honeys were used in these experiments, designated X and Y. The experiments were performed at room temperature, 15°C.

both stress and stirring, heather honey shows a variable viscosity in its unstirred state, and that its viscosity falls enormously after stirring.

[4] As a first approximation, to account for the effect of the walls of the containing tube (which is assumed to be infinitely long) Ladenburg (Ann. Physik **22**, 287 (1907)) has proposed the introduction of a term into the denominator of the Stokes equation, which then reads:

$$\eta = \frac{2r^2(\rho - \rho')g}{9v(1 + Ar/R)}$$

where r is the radius of the sphere
R is the radius of the tube
ρ is the density of the sphere
ρ' is the density of the medium
v is the velocity of the fall
η is the viscosity, and
A is a pure number.

Since the correction term $(1 + Ar/R)$ does not involve viscosity, the times of

To find whether this "gel" shows any marked yield value (i.e., whether the viscosity becomes practically infinite for very small stresses (cf. Scott Blair (9)), a very small ball (diameter $\frac{1}{8}$ in.) was placed just below the surface of a sample of heather honey (Y). After some hours, it was clear that the ball had fallen appreciably; thus, although the viscosity is very high for such small stresses, it is unlikely that there is any sharp yield value for the gel.

THE SOL FORM

To find out whether the thoroughly stirred honey (the sol) behaves as a true fluid,[5] a sample of Y was stirred in the manner described above, and tested in the Rothamsted plastometer. This instrument has already been described (2, 8), and it will suffice to say that in it the material is forced by compressed air through a capillary tube of known dimensions under varying pressures, the amount of flow per second being recorded for each pressure. The plastometer thermostat was set first at 15°C., and, for a second experiment at 30°C. At the latter temperature, two different capillary tubes having radii of 0.088 cm. (No. II) and 0.048 cm. (No. IV) were used. Both tubes were 12.25 cm. in length.

By plotting stress[6] ($PR/2L$) against velocity gradient ($4V/\pi R^3$), curves are obtained which should be independent of the capillary dimensions, provided that: (1) each element of the material moves in a straight line parallel to the tube walls; (2) the material in contact with the wall is at rest with respect to it; and (3) the velocity gradient has a unique value for each value of shearing stress (cf. Schofield (7)). For true fluids the curves are linear, and pass through the origin.

It has been shown (8) that for certain pastes, the second and third conditions above do not hold, owing to anomalous flow near the tube walls. Moreover many materials, although obeying these three conditions, show a decrease in viscosity as stress increases, giving either a curvilinear flow-

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fall for a given tube and sphere remain proportional to the viscosities. Moreover, since in the above experiment the ratio r/R is the same in both cases, it is true to say that in so far as Ladenburg's approximations are applicable, the times of fall for the two balls will bear a ratio equal to the ratios of the squares of their diameters. Corrections due to the effect of the end of the tube (which cannot be regarded as anything like infinitely long in practice) are not large, and may be neglected for the purpose of the above experiments.

For a further discussion on this subject see Hatschek's Viscosity of Liquids, p. 33 (G. Bell and Sons, Ltd., London, 1928), and Barr's Viscometry, p. 171 (Humphrey Milton, London, 1931).

[5] Paine, Gertler, and Lothrop have already shown that certain (non-thixotropic) honeys show a slight fall in viscosity with increasing stress. A Bingham-Green plastometer was used.

[6] P is the pressure, R is the tube radius, L is the tube length, and V is the flow in cubic centimeters per second.

curve, or a curve which, although straight at high stresses, does not extrapolate to the origin (6).

It is clear from figure 1 that the sample of stirred heather honey (sol) shows no appreciable anomaly of the first type, but that, although approximating closely to a true fluid (especially at 30°C.), there is a small but significant tendency for viscosity to rise at low stresses (though this is not great enough to be observed in the experiment shown in table 2).

There is no evidence of a sharp yield value.

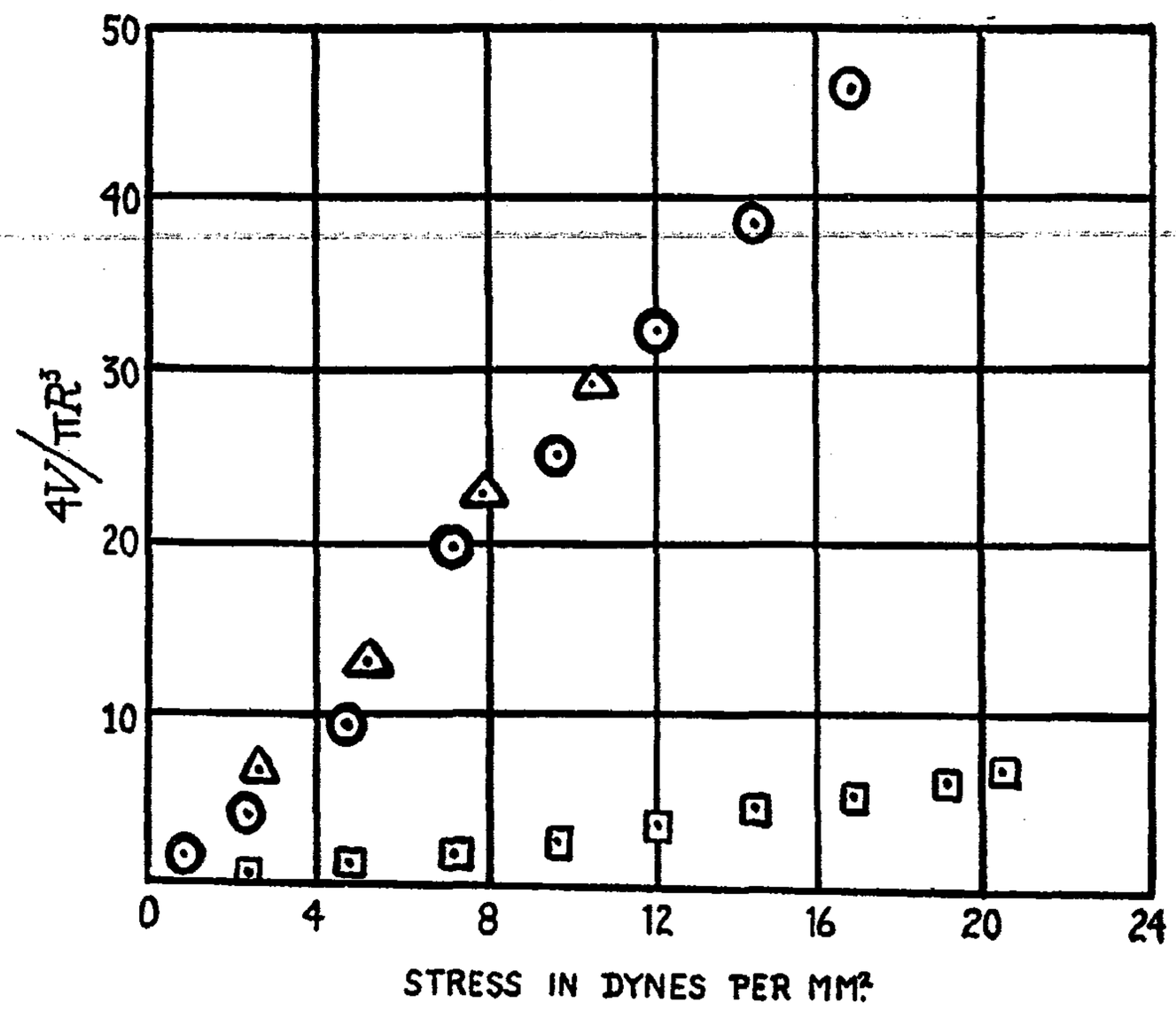

FIG. 1. FLOW CURVES FOR HEATHER HONEY

⊙ Capillary II, 30°C. △ Capillary IV, 30°C. ⊡ Capillary II, 15°C.

At 30°C. sample Y shows a viscosity at high stresses of about 37 C.G.S. units, and at 15°C. of approximately 300 C.G.S., though at 15°C. it is not certain that all thixotropic structure was really destroyed by shearing. Such a high viscosity brings the experiment rather near the limits of applicability of the plastometer.

DISCUSSION

Heather honey "gel" shows "rigid" properties in the sense that at low stresses, rapidly applied, the viscosity of the system is so high that it may

be said to behave as an elastic solid, but there is no marked yield value—i.e., the elastic limit is not sharp. The change which takes place when the gel is broken up by stirring is a continuous one, involving a fall in viscosity and an increasing approximation to a truly fluid condition, but even a vigorously stirred sample shows signs of viscosity increase at very small stresses. The data are not adequate to specify just how sharp this change in viscosity may be, but there is certainly no well-defined yield value. A semiquantitative measure of thixotropy may be obtained by timing the fall of a steel ball through a sample of honey which has been left to stand overnight, disintegrating the gel by stirring with a perforated metal disk, and then immediately timing a second ball of the same size. Under fixed conditions, the ratios of the times of fall for heather honey before and after stirring show values of from about 5 to 200,[7] as compared with unity for Golden Syrup, and approximately unity for ordinary clover honey. If standardized conditions of temperature, size of vessel and balls, etc., are used, this should prove a useful test for deciding whether a sample is to be rejected on account of high moisture content, which in a normal honey would be an indication of "unripeness" and might lead to its subsequent spoiling by fermentation, or whether it is to be excused on the ground of its heather origin.

SUMMARY

Experiments are described on the behavior of heather honey under shearing, both in its undisturbed ("gel") and stirred ("sol") forms. In both cases, the viscosity increased at low stresses, but in neither case was there found any sharp elastic limit (yield value). The sol form showed (considering its very high viscosity) only a very small deviation from truly fluid behavior.

A simple viscometric test is described to characterize honeys having thixotropic properties. This test should prove of use in deciding whether excess water in a honey is caused by unripeness, or is natural, owing to its heather origin.

The author is indebted to Mr. D. A. Morland of the Apiculture Section of the Entomology Department of the Rothamsted Experimental Station for bringing to his notice the need for this investigation, and for advising him in the selection and description of the honeys tested.

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[7] Not many samples have yet been tested, and it is possible that further tests will show a still larger range of values.

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THE PHYSICAL AND CHEMICAL RELATIONS IN FLUID PHASE HETEROGENEOUS REACTION[1]

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Received May 29, 1934

In reaction between two phases, two factors *a priori* determine the overall measured rate of reaction. The first is the rate of chemical reaction at the interface; the second is the rate of transport of reactant, or product of reaction, to or from the interface. For heterogeneous reaction in which one or both phases are fluid, the transport takes place between the interface and the point of measurement.

In the present work, dealing with the fluid–fluid or fluid–solid heterogeneous reaction, a quantitative relationship is derived for the measured rate as a function of the chemical reaction rate and rate of physical transport. No arbitrary postulates as to mechanism are made. The results follow in the first place from a solution of the diffusion equation with chemical reaction at the interface constituting one of the boundary conditions. In the second place, diffusion as a mode of transport is generalized to include transport due to stirring or other type of agitation.

THE NERNST THEORY

In 1904, Nernst (21, 2) proposed a theory of heterogeneous reaction which has been referred to widely. In this theory certain assumptions are made as to the chemical and physical factors of the liquid–solid heterogeneous reaction. On the chemical side, reaction is supposed to be infinitely rapid, owing to an "infinite force" at the boundary. On the physical side, a stationary liquid film is supposed to exist through which diffusion into the main body of the stirred liquid takes place. For the solution of a solid, or for reaction between a solid and a solution, the adhering film at moderate rates of stirring is calculated to be 20 to 50 microns thick (2, 29).

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Presented before the Division of Physical and Inorganic Chemistry at the Eighty-eighth Meeting of the American Chemical Society held at Cleveland, Ohio, September 10–14, 1934.

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Regarding the chemical aspect of the Nernst theory, there is no reason for supposing that the rate of heterogeneous chemical reaction is "infinite." In other words, not all collisions of the reacting molecules will be expected to be fruitful; rather, an activation energy should be required, as for homogeneous reaction. In many cases, no doubt the second phase will exert a catalytic effect on the rate, but our knowledge of heterogeneous catalysis leads us to expect that a catalytic effect of the second phase, if and when it exists, would hardly be complete.

Regarding the physical aspect of the Nernst theory, experimental evidence strongly contradicts the possible existence of a stationary film. Contrasted with the Nernst film of 20 to 50 microns thickness, microscopic observation indicates a thickness of any possible film of less than 0.4μ (26); solution of a fine sediment indicates the possibility as less than 0.2μ (23); flow through capillaries less than 0.03μ (3); reaction in the presence of a monomolecular fatty acid less than 0.0025μ, or 25A.U. (20); while ultramicroscopic examination of water flowing slowly in pipes shows that, though the flow is axial, motion in all three directions persists right up to the surface (10).

The evidence of sedimentation may be considered in some detail. It has been found (23) that the volume of a coarse sediment consisting of 100-micron particles is the same before as after centrifuging, and equal approximately to the value common to all particle sizes after centrifuging. The coarse particles in the normally settled state are therefore densely packed and touching. The force necessary to displace completely any possible aqueous film surrounding the particles is merely that of gravity acting on a 100-micron particle, or a compressive force of 20 dynes per square centimeter for a particle of density 3. However, with water stirred at the moderate linear rate of 50 cm. per second, the forces are much greater. The tangential shearing stress tending to displace any possible film of, say, 25 microns thickness, is ten times as great, or 200 dynes per square centimeter. If the flow is directed toward the surface of the solid, the compressive stress is two hundred and fifty times as great, or 5000 dynes per square centimeter. Therefore it is impossible that a stationary film could exist in the presence of the forces evoked by ordinary stirring, a result that agrees with the other evidence already cited.

In most liquid-phase heterogeneous reactions the chemical effect is obscured, though only superficially, by conditions of physical transport. However, in many cases the chemical effect predominates, as shown in the following results: (a) The non-dependence of rate of reaction on rate of stirring, as for rate of solution of glass in alkali (25), of metals in acid (5), of olefins in sulfuric acid (9), of mineral sulfides in dilute sulfuric acid (24), of crystallization from supersaturated solution (19), of hydrolysis and saponification (11); (b) the frequent wide difference in rate of solution

of certain of the crystalline faces of the self-same substance (22, 30); (c) a temperature coefficient appreciably greater than that for diffusion (1, 5, 18). The Nernst theory, which concentrates all attention on a hypothetical and apparently non-existent film, naturally has no explanation for these results.

On the contrary, these results and the more general facts of the heterogeneous reaction are accounted for in the relationships to be derived, which are founded simply on known physical and chemical laws.

RATE OF REACTION WITH TRANSPORT BY DIFFUSION

Let a plane solid of area F react with a prism of quiescent solution[3] of depth L, of area equal to that of the solid, and initial concentration c_0. In the body of the solution, the ordinary diffusion relation (equation 1), in which D is the diffusion coefficient, is obeyed.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{1}$$

Out of all the molecules in solution, only those in the immediate neighborhood of the solid–fluid interface are in a position to make impact with the solid surface. For a gas, for instance, by kinetic theory out of all molecules which are three mean free paths distant from the interface, less than 1 per cent will strike the surface on their next collision. For a solution, the reacting molecules probably will be confined to those within one or two molecular distances from the solid surface. For both gas and solution the number of impacts per second is proportional to concentration, c, in the neighborhood of the interface. The number of gram-moles, m, reacting per unit area per unit time is proportional to the number of impacts and is given by equation 2, in which k is the specific reaction velocity constant.

$$\frac{1}{F}\frac{\partial m}{\partial t} = kc \tag{2}$$

The rate at which dissolved molecules disappear by reaction at the solid surface equals the rate at which they diffuse from the neighborhood of the interface to the interface. Therefore, by definition of diffusion and by equation 2,

$$D \frac{\partial c}{\partial x} = -kc \tag{3}$$

at $x = L$.

[3] With partial pressure replacing concentration, the same derivation applies to reaction between a gas and solid, or gas and solution, provided it is of the first order.

At the surface of the solution,

$$\frac{\partial c}{\partial x} = 0 \tag{4}$$

at $x = 0$.

The solution of equation 1 with the boundary conditions imposed by equations 3 and 4 and the condition that $c = c_0$ when $t = 0$ is analogous to the solution of the equation for the radiating sphere in the theory of heat conduction (12). The concentration at point x and time t is found to be

$$c = c_0 \sum_1^\infty B_m e^{-\frac{D}{L^2}\beta_m^2 t} \cos \frac{\beta_m}{L} x \tag{5}$$

β_m is given by equation 6 and B_m by equation 7.

$$\beta_m \tan \beta_m = \frac{kL}{D} \tag{6}$$

$$B_m = \frac{4 \sin \beta_m}{2\beta_m + \sin 2\beta_m} \tag{7}$$

As a rule interest will be centered in the average concentration, $\bar{c}$, throughout the solution. $\bar{c}$ is obtained by integrating equation 5 between 0 and L, and dividing by L. There is thus obtained

$$\bar{c} = \bar{c}_0 \sum_1^\infty \bar{B}_m e^{-\frac{D}{L^2}\beta_m^2 t} \tag{8}$$

In equation 8 β_m is given by equation 6 as before. $\bar{B}_m$ is however now defined by equation 9 as follows:

$$\bar{B}_m = \frac{4 \sin^2 \beta_m}{(2\beta_m + \sin 2\beta_m)\beta_m} \tag{9}$$

Having determined $\bar{c}$ against t, β_m may be calculated by equations 8 and 9. Knowing β_m, the chemical reaction velocity constant k, which is the variable of interest, is then obtained from equation 6.

NUMERICAL SOLUTION OF EQUATION 8

To simplify the calculation by equations 8, 9, and 6 of the chemical velocity constant k, table 1 has been constructed. This gives the values of the first two terms in equation 8,

$$\bar{B}_1 e^{-\frac{D}{L^2}\beta_1^2 t} \quad \text{and} \quad \bar{B}_2 e^{-\frac{D}{L^2}\beta_2^2 t}$$

(also β_1 and β_2), for values of kL/D from 0 to ∞ and for Dt/L^2 up to 1.6.

It is seen from table 1 that for Dt/L^2 sufficiently great, the series of equation 8 converges very rapidly. For $Dt/L^2 = 0$, the second term is at the most 11 per cent of the first, while the sum of the second and all remaining terms is at the most 22 per cent of the first. For $Dt/L^2 = 0.1$, these figures become respectively 1.8 per cent and probably less than 3.6 per cent, while for $Dt/L^2 = 0.2$, they become 0.4 per cent and probably less than 0.8 per cent, respectively. For an error smaller than 1 per cent, all terms but the first may therefore be neglected, provided $Dt/L^2 \geqq 0.2$.

Table 1 is made use of as follows. At a given value of Dt/L^2, one proceeds down the column to a value of

$$\bar{B}_1 e^{-\frac{D}{L^2}\beta_1^2 t} \left(\text{or } \bar{B}_1 e^{-\frac{D}{L^2}\beta_1^2 t} + \bar{B}_2 e^{-\frac{D}{L^2}\beta_2^2 t}\right)$$

equal to the known value of $\bar{c}/\bar{c}_0$. The desired quantity kL/D is then obtained by reading across to the first column. For L one may substitute V/F, the ratio of volume of the vessel to surface area of the solid. In view of the fact that $\bar{c}$ is an average concentration, the same substitution appears possible when the vessel is non-prismatic. Knowing the diffusion coefficient and depth of the vessel, k is readily obtained from the known value of kL/D.

RELATION TO THE USUAL FIRST-ORDER EQUATION

The course of most fluid-phase heterogeneous reactions, it has been found, is represented by the usual first-order reaction velocity equation. The equation is, for the case of reaction between a solid and solution,

$$\frac{d\bar{c}}{dt} = -K\frac{F}{V}\bar{c} \tag{10}$$

On integration equation 10 gives

$$K = -\frac{2.303}{t}\frac{V}{F}\log\frac{\bar{c}}{\bar{c}_0} \tag{11}$$

In equation 11 K is the measured reaction velocity constant, V the volume of the vessel, and F the surface of the solid.

Under the condition that all terms but the first may be neglected, that is for $Dt/L^2 \geqq 0.2$ for an error smaller than 1 per cent, equation 8 assumes the form of a first-order reaction velocity equation, and, with V/F substituted for L, may be written

$$\frac{D}{L}\beta_1^2 = -\frac{2.303}{t}\frac{V}{F}\log\frac{\bar{c}}{\bar{B}_1\bar{c}_0} \qquad \frac{D}{L^2}t \geqq 0.2 \tag{12}$$

$\bar{B}_1$ in equation 12, as shown in the fourth column of table 1, is close to unity, especially for those values of kL/D that are themselves less than unity (which values it will be seen are of most interest).

TABLE 1

Numerical solution of equation 8

kL/D	β_1	β_2	$\frac{D}{L^2}t = 0.0$		$\frac{D}{L^2}t = 0.1$		$\frac{D}{L^2}t = 0.2$		$\frac{D}{L^2}t = 0.4$		$\frac{D}{L^2}t = 0.8$	$\frac{D}{L^2}t = 1.6$
			$B_{1c}e^{-\frac{D}{L^2}\beta_1^2 t}$	$B_{2c}e^{-\frac{D}{L^2}\beta_2^2 t}$	$B_{1c}e^{-\frac{D}{L^2}\beta_1^2 t}$	$B_{2c}e^{-\frac{D}{L^2}\beta_2^2 t}$	$B_{1c}e^{-\frac{D}{L^2}\beta_1^2 t}$	$B_{2c}e^{-\frac{D}{L^2}\beta_2^2 t}$	$B_{1c}e^{-\frac{D}{L^2}\beta_1^2 t}$	$B_{2c}e^{-\frac{D}{L^2}\beta_2^2 t}$	$B_{1c}e^{-\frac{D}{L^2}\beta_1^2 t}$	$B_{1c}e^{-\frac{D}{L^2}\beta_1^2 t}$
0.00	0.000	3.14	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.0000	1.000	1.000
0.25	0.480	3.22	0.999	0.001	0.976	0.000	0.954	0.000	0.911	0.0000	0.831	0.691
0.50	0.655	3.29	0.995	0.004	0.954	0.001	0.914	0.000	0.839	0.0001	0.708	0.502
1.00	0.860	3.43	0.990	0.013	0.918	0.004	0.854	0.001	0.736	0.0001	0.547	0.304
1.50	0.989	3.55	0.973	0.022	0.882	0.006	0.800	0.002	0.658	0.0001	0.445	0.204
2.00	1.079	3.65	0.956	0.032	0.852	0.008	0.758	0.002	0.600	0.0002	0.379	0.149
4.00	1.265	3.94	0.928	0.057	0.789	0.012	0.674	0.003	0.490	0.0001	0.259	0.072
8.00	1.398	4.22	0.885	0.080	0.728	0.013	0.600	0.002	0.406	0.0001	0.186	0.039
16.00	1.479	4.44	0.854	0.089	0.688	0.012	0.552	0.002	0.357	0.0000	0.150	0.026
32.00	1.522	4.57	0.834	0.091	0.661	0.011	0.524	0.001	0.330	0.0000	0.131	0.021
∞	1.562	4.70	0.819	0.090	0.642	0.010	0.503	0.001	0.309	0.0000	0.117	0.016

With $\bar{B}_1$ assumed nearly equal to unity and $Dt/L^2 \geqq 0.2$, the right-hand sides of equations 11 and 12 are substantially equal. Therefore

$$K = \frac{D}{L}\beta_1^2 \qquad \begin{matrix} \bar{B}_1 \doteq 1 \\ \frac{Dt}{L^2} \geqq 0.2 \end{matrix} \tag{13}$$

Equation 13 is exact, subject to the stipulated conditions, which are easily satisfied. In this equation K, the measured velocity constant, is given indirectly as a function of k, the true chemical rate constant, D, the diffusion coefficient, and L (or V/F), the depth of the vessel.

EXPLICIT SOLUTION FOR MEASURED VELOCITY CONSTANT

β_1^2 in equation 13 is determined by equation 6. The latter is a transcendental expression which does not allow of explicit solution for β_1^2. In table 1 are given the indirectly solved values of β_1, which are seen to extend over a narrow range, for kL/D from 0 to ∞.

It will be highly desirable (especially for the purpose of later generalization) that β_1^2 be expressed explicitly if possible, even though an approximation be introduced thereby. From equation 6 it is seen that β_1^2 is a function of kL/D. In any substitution for β_1^2, it is necessary that β_1^2 be zero for kL/D zero, finite for kL/D infinite, and that there be numerical agreement at least over a certain range. It is proposed as meeting these conditions that β_1^2 be set equal to $(1 - e^{-kL/D})$. When the substitution is made, equation 13 becomes

$$K = D/L\,(1 - e^{-kL/D}) \tag{14}$$

Equation 14 is readily solved for the chemical rate constant k, giving

$$k = -2.303\, D/L \log (1 - KL/D) \tag{14'}$$

According to equation 14, when $k \geqslant D/L$, the measured rate constant K is determined by D/L. On the other hand when $k \leqslant D/L$, $K \doteq k$, or the measured rate constant is closely equal to the true chemical velocity constant.

To test the validity of the functional substitution for β_1^2, table 2 has been constructed comparing kL/D calculated from equation 14′ with the correct value of kL/D obtained from table 1, for different assumed values of KL/D, i.e. β_1^2 by equation 13. It is seen that kL/D varies over an infinite range, while the variation of KL/D is restricted to the narrow range 0.0 to 2.44. Agreement in the exact values of kL/D and values calculated from equation 14′ are within 10 per cent for KL/D less than 0.4, and within 35 per cent for KL/D less than 0.75. KL/D between 0 and

0.75 covers about one-third the total range in values of KL/D. However KL/D lying in the low range of values is most significant, because it is in the low range that k plays an important rôle in determining the magnitude of K. With increase in KL/D, the effect of k in determining the value of K becomes smaller and smaller compared to that of diffusion. Bearing this consideration in mind, the explicit approximation represented by equation 14 may be considered as fairly satisfactory. In the end, the approximation represented by equation 14 is intended not so much for pure diffusion as a mode of transport as for other modes of transport for which the validity appears to be more extended, as will shortly be discussed.

TABLE 2

kL/D, exact and as determined by equation 14′, against KL/D

KL/D	kL/D	
	Exact	Equation 14′
0.00	0.00	0.00
0.23	0.25	0.26
0.43	0.50	0.55
0.74	1.00	1.35
1.00	1.5	∞
2.44	∞	

RATE OF SOLUTION AND CRYSTALLIZATION

Solution or crystallization differs from simple chemical reaction just considered in that molecules simultaneously condense at and are liberated from the solid surface. The mole rate of condensation at the interface is given by equation 2. The mole rate of liberation of molecules from the surface is determined by the equilibrium condition that it equal the rate of condensation from the saturated solution, or kc_s. The rate of solution or of crystallization at the interface is the difference between the rate of condensation and of liberation, and is given by

$$1/F\frac{\partial m}{\partial t} = k(c_s - c) \tag{2'}$$

at $x = L$.

From this point the derivation is exactly analogous to that already considered ($c_s - c$ merely replacing c as variable), and the same final expression for K is obtained (equation 14).

GENERALIZED EQUATION FOR MEASURED VELOCITY CONSTANT

Transport of reactant or product of reaction will usually occur by modes independent of and in addition to diffusion. Concentration and convection currents are frequent natural accompaniments of the diffusion process. Artificial transport is secured by mechanical stirring, agitation, etc. These various modes of transport usually are much more effective than is diffusion itself. Unless they are taken into account, any relationship between the measured and the true chemical velocity constant can be only of very limited scope.

It is observed that D/L in equation 14 has the dimensions of a velocity. It may be defined therefore as the rate of group molecule transport by molecular diffusion, i.e., as the coefficient of transport by diffusion. An obvious extension of equation 14 is to replace the diffusion coefficient of transport, D/L, as simply a special case, by a general coefficient of transport, S. Equation 14 for the measured rate constant then becomes

$$K = S(1 - e^{-k/S}) \tag{15}$$

By analogy with equation 14 it may be expected that the limit of validity of equation 15 will be determined by the value of K/S. How close K/S may approach to unity before the equation palpably fails can not be told beforehand, and is to be answered only by experiment.

It may be noted at this point that with transport by mechanical stirring, the generalized equation held, within limit of error as seen below, practically for all values of K/S that were encountered. While an exact limit for K/S can not now be given, it appears that with transport by mechanical stirring the equation holds for K/S equal to 0.9 at least, and probably also for greater values.

TRANSPORT BY MECHANICAL STIRRING

In the measurement of liquid-phase heterogeneous reaction rate, the most common method of inducing molecule transport in the liquid is by mechanical stirring. The coefficient of transport obviously will increase with the rate of stirring. For fast reactions, which are determined by transport, Jablczynski (13) found that the rate varied approximately with the 0.85th power of the rate of stirring, while Van Name and Edgar (27) found the power to be 0.80. For the intermediate rates of solution and reaction considered below, the transport likewise is found to be proportional to the 0.8th power of the rate of stirring. Therefore, transport by diffusion being neglected against that effected by the stirring, the coefficient of transport S is given by

$$S = As^{0.8} \tag{16}$$

where s is the rate of stirring in R.P.M., and A a constant which depends on experimental conditions and on the physical properties of the fluid, namely the viscosity and the density.

The result for the exponent of s in equation 16 agrees with that found in heat transfer with fluid flow in pipes, where the transfer coefficient, as summarized by McAdams (17), varies with the 0.8th power of the rate of flow of fluid.[4]

It has been held (15, 16) that the rate of reaction varies with the first power of the rate of mechanical stirring. Although this result might obtain under exceptional stirring conditions, as in the combined gas-feed and mechanical stirring of Huber and Reid (11), it is contrary to the generally recognized result of an exponent less than unity. The occasional apparent linear dependence probably arises from the combination of inaccurate, insufficient, or non-uniform data with the fact that a plot of $y = x^{0.8}$ shows but small curvature.

King and Braverman (16), for instance, find that the rate of solution of a zinc specimen rotating axially in acetic acid becomes linear above a certain speed and up to 5500 R.P.M. Nevertheless their plot for zinc and hydrochloric acid shows continuous curvature throughout, and incidentally, as far as can be estimated from the plotted points, the plot for hydrochloric acid appears to be fitted tolerably well by equation 17 below. If any linearity existed it should have applied to the faster reaction with hydrochloric acid, rather than to the reaction with acetic acid. It is to be concluded that the apparent linear result with acetic acid is due probably to the entrance of some secondary effect with increased high-speed stirring, such as heating, vibration, vortices, or some other disturbing factor not present under uniform conditions.

Substituting, then, from equation 16 into equation 15, the following relationship connecting K and k with the rate of mechanical stirring is obtained:

$$K = As^{0.8}(1 - e^{-k/As^{0.8}}) \tag{17}$$

An apparent exponent of less than 0.8, in accordance with equation 17, is due to the progressive influence of the chemical reaction velocity on the measured rate constant. For instance, Brunner (2) considered that the rate of solution of benzoic acid in water was proportional to the two-thirds

[4] The film theory has also been widely carried over to heterogeneous heat transfer. Recently Kennard (14) has examined the atmosphere adjacent to a hot solid surface and found no evidence of any film. The case of heterogeneous heat transfer is analogous to that of heterogeneous chemical reaction, and the results obtained here apply also to heat transfer, K being redefined as the measured coefficient of heat transfer and k as the velocity constant of heat transfer at the interface. In view of an exponent of 0.8 for the fluid velocity, k would appear to be large against the coefficient of physical transport.

power of the rate of stirring. However, it will be seen below that the exponent for Brunner's data is 0.8 as usual, but the rate of solution is slow enough to affect measurably the value of K and thus to result in an apparent exponent of less than 0.8.

APPLICATION

In heterogeneous as in homogeneous chemical reaction one is interested in the value of the chemical reaction velocity constant, k. Separation of the physical and chemical factors that determine the measured constant K is secured in general by equation 15.

When the transport is effected by mechanical stirring, equation 17 applies. To determine k, it merely is necessary to evaluate A by measurement of K at different stirring speeds.

For the calculated value of k to be accurate, its contribution to the value of the measured constant K must be sufficiently great. In other words, K must be measured at sufficiently high stirring speeds. A criterion as to whether one is in a range of stirring speeds in which k exerts an appreciable influence on the magnitude of K is found in the ratio $K/s^{0.8}$. If this ratio decreases sufficiently with increase in stirring speed, the range of speeds is then proper to an accurate determination of k.

EXAMPLES

The oxidation of mercury by iodine in potassium iodide solution, measured by Van Name and Edgar (27) at different stirring speeds up to 300 R.P.M., is a reaction in which the decrease in the ratio $K_{obsd.}/s^{0.8}$ is so small that accurate determination of the true reaction constant k is not possible. The data for this reaction are given in table 3.[5] It is seen from column 3 that the decrease in the ratio with decrease in stirring speed is less than 2 per cent over the whole range of stirring speeds from 170 to 300 R.P.M.

However, a large proportion of the reactions that have been reported in the literature show a sufficiently rapid decrease of $K_{obsd.}/s^{0.8}$ with increase in stirring speed to permit application of equation 17. Reactions for which accurate data are available are the following: (a) Benzoic acid in water (30), (b) oxygen in water (4), (c) magnesium in 1/8 M hydrochloric acid (6), (d) thallium in 1/2 M nitric acid (8), (e) zinc in 0.02 M copper sulfate (7). These typical reactions are considered in tables 4 to 8 inclusive. In column 2 of these tables is shown the decrease in $K_{obsd.}/s^{0.8}$ with increase in s. In the third and fourth columns are shown $K_{obsd.}$ and the value of K calculated by equation 17 for assigned values of k and A.

[5] In all examples, the author's value of the measured rate is recalculated where necessary so as to conform to the precise equation (11), or to its analogue, for $K_{obsd.}$. K and k are expressed in centimeters per minute.

For benzoic acid in water (table 4), the same value of k satisfies excellently the results of three different observers, though naturally the values of A differ for the different experimental conditions. The fifth column shows that there is no systematic deviation in the percentage difference between the calculated and observed values of K, the differences being positive and negative at random.

TABLE 3

Rate of oxidation of mercury by iodine in potassium iodide (97)

s IN R.P.M.	$K_{obsd.}$	$\frac{K_{obsd.}}{s^{0.8}} \times 10^3$
170	0.574	9.45
210	0.679	9.45
240	0.759	9.45
300	0.885	9.30

TABLE 4

Rate of solution of benzoic acid in water

$k = 0.157$

s IN R.P.M.	$\frac{K_{obsd.} \times 10^3}{s^{0.8}}$	$K_{obsd.}$	$K_{calcd.}$	PERCENTAGE DIFFERENCE
		$A = 0.00147(30)$		
3	2.18	0.0052	0.0035	+32
53	1.13	0.0270	0.0348	−29
122	1.10	0.0513	0.0618	−20
204	1.34	0.0943	0.0810	+14
365	1.00	0.1120	0.1015	+9
470	0.75	0.1030	0.1090	−6
		$A = 0.0011(1)$		
100	1.16	0.046	0.042	+8
450	0.67	0.088	0.096	−9
		$A = 0.0055(2)$		
144	2.20	0.118	0.121	−2.5
202	1.85	0.131	0.129	+1.5

The least accurate data are those for benzoic acid; this is reflected in the irregular decrease in $K/s^{0.8}$ for this reaction (table 4), contrary to that for the other reactions. The percentage difference averaged for all the experimental points for benzoic acid is ±13 per cent. The most accurate measurements appear to be those on the solution of zinc in copper sulfate (table 8). The average percentage difference is only ±1.2 per cent. For all the reactions the average difference is ±6.2 per cent.

Table 9 summarizes the values of k and A for the reactions considered. It is seen that k varies between 0.078 and 2.80, or over a thirty-five-fold range. The variation of A, from 1.1 to 12.0×10^{-3}, is more restricted.

TABLE 5

Rate of solution of oxygen in water (4)

$k = 2.06; A = 0.00177$

s IN R.P.M.	$\frac{K_{obsd.}}{s^{0.6}} \times 10^3$	$K_{obsd.}$	$K_{calcd.}$	PERCENTAGE DIFFERENCE
60	1.82	0.0480	0.0462	+3.7
93	1.64	0.0621	0.0639	−2.9
120	1.63	0.0749	0.0749	0
145	1.55	0.0835	0.0844	−1.1
180	1.54	0.0977	0.0942	+3.6

TABLE 6

Rate of solution of magnesium in 1/8 M hydrochloric acid (6)

$k = 2.80; A = 0.010$

s IN R.P.M.	$\frac{K_{obsd.}}{s^{0.6}} \times 10^3$	$K_{obsd.}$	$K_{calcd.}$	PERCENTAGE DIFFERENCE
50	15.7	0.36	0.23	+33
100	10.5	0.41	0.40	+3
200	9.7	0.67	0.68	−1
400	7.9	0.95	1.08	−14
750	7.2	1.43	1.50	−5
855	7.7	1.72	1.59	+8

TABLE 7

Rate of solution of thallium in 1/2 M nitric acid (8)

$k = 0.078; A = 0.0044$

s IN R.P.M.	$\frac{K_{obsd.}}{s^{0.6}} \times 10^3$	$K_{obsd.}$	$K_{calcd.}$	PERCENTAGE DIFFERENCE
32	2.96	0.0474	0.0472	+0.4
74	1.84	0.0578	0.0596	−3.1
120	1.42	0.0654	0.0649	+0.8
193	1.00	0.0678	0.0688	−1.5
454	0.55	0.0733	0.0731	+0.3

THE FORM OF THE CURVE

In figure 1, $K_{calcd.}$ is plotted against R.P.M. for reactions a to e. The experimental points fall irregularly on either side of the curves. The curves all are concave downward. The degree of curvature shows con-

siderable variation. For reaction b it is slight, the curve appearing almost as a straight line; for reaction d it is very pronounced up to 150 R.P.M., after which the curve becomes asymptotic. For the other reactions the curvature is intermediate.

In the same range of stirring speeds, the form of the curve is determined by the ratio k/A shown in table 9. For reaction d the ratio is only 0.02 $\times 10^3$, and the curvature is high; for reaction b the ratio is 1.16 $\times 10^3$, and the curvature is very small. Reactions a and e have about the same intermediate ratio and curvature.

TABLE 8

Rate of solution of zinc in 0.02 M copper sulfate (7)

$k = 1.50; A = 0.012$

s IN R.P.M.	$\frac{K_{obsd.}}{s^{0.8}} \times 10^3$	$K_{obsd.}$	$K_{calcd.}$	PERCENTAGE DIFFERENCE
54	13.8	0.336	0.292	+13.0
94	11.5	0.436	0.440	−0.9
295	8.8	0.836	0.834	+0.2
500	7.0	1.007	1.005	+0.2
600	6.4	1.061	1.055	+0.6
680	5.6	1.028	1.088	−5.8

TABLE 9

Summary of values of chemical reaction velocity constant, k, and of A

REACTION	k	$A \times 10^3$	$\frac{k}{A} \times 10^{-3}$
	cm. per min.		
(a) Benzoic acid in water (30)	0.157	1.47	0.11
Benzoic acid in water (1)	0.157	1.10	0.14
Benzoic acid in water (2)	0.157	5.50	0.03
(b) Oxygen in water (4)	2.06	1.77	1.16
(c) Magnesium in 1/8 *M* hydrochloric acid (6)	2.80	10.0	0.28
(d) Thallium in 1/2 *M* nitric acid (8)	0.078	4.4	0.02
(e) Zinc in 0.02 *M* copper sulfate (7)	1.50	12.0	0.12

TEMPERATURE COEFFICIENT

By equation 17 the temperature coefficient of K is determined by that of k and of A. A varies with temperature chiefly through its dependence on the viscosity. By analogy with the heat transfer coefficient (based simply on the Reynold's number and considered as a coefficient of transport), A should be equal to $A'\phi^{0.8}$, where ϕ is the fluidity. This result accords with the measurements of the temperature coefficient of zinc in 0.02 M copper

sulfate at 100 R.P.M. (reaction e) by Centnerszwer and Heller (7). These authors find $K_{25}/K_0 = 1.83$, while $\phi_{25}/\phi_0 = 1.97$ and $\phi_{25}^{0.8}/\phi_0^{0.8} = 1.72$; also $K_{50}/K_{25} = 1.47$, while $\phi_{50}/\phi_{25} = 1.64$ and $\phi_{50}^{0.8}/\phi_{25}^{0.8} = 1.48$.

On the other hand, the results of King and Braverman (16) and Van Name and Hill (28) for rapid reactions in which alcohol and cane sugar have been added to the solutions, indicate that the measured constant

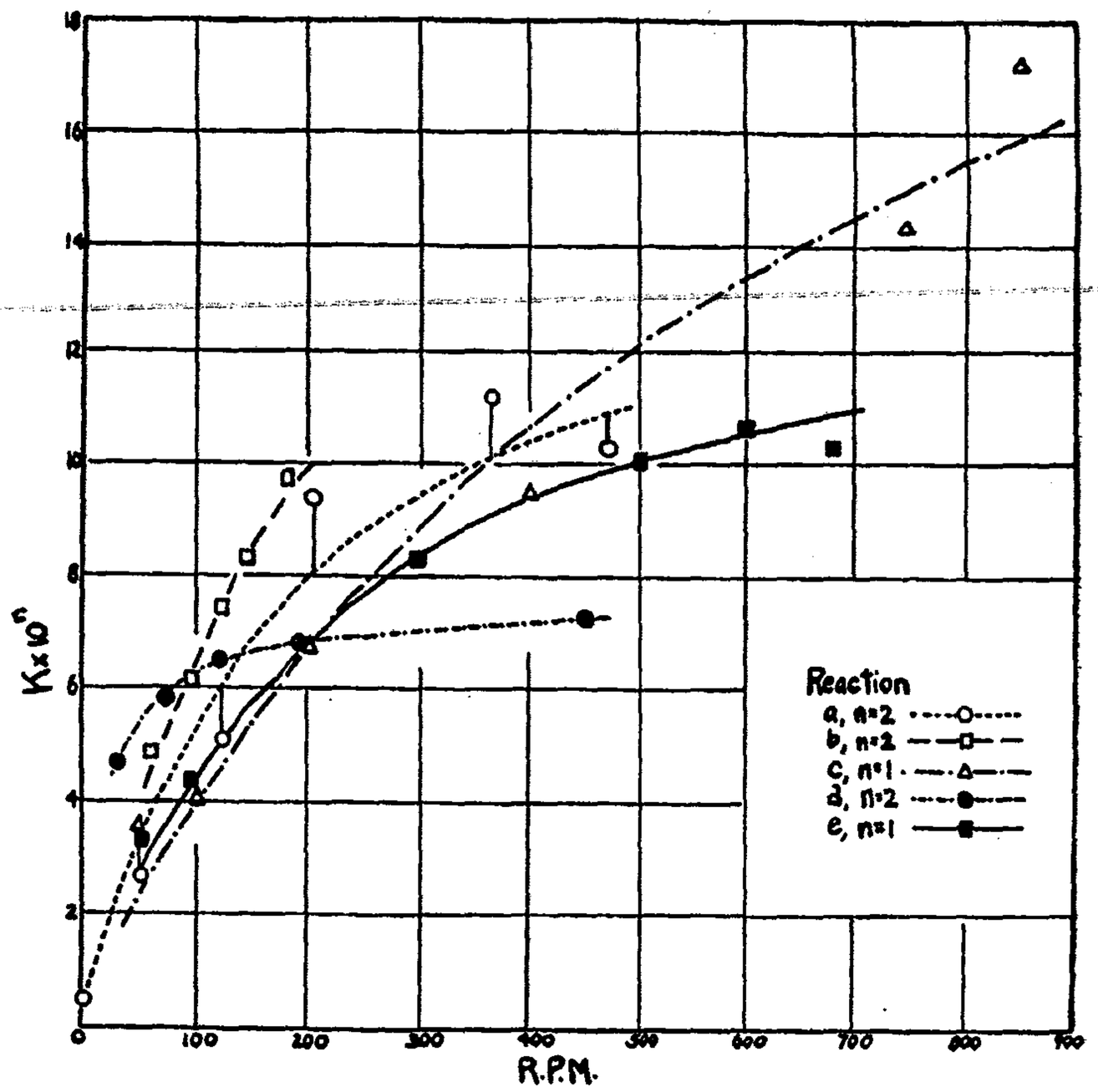

FIG. 1. RELATION OF MEASURED RATE CONSTANT TO SPEED OF STIRRING

varies as the first power of the fluidity. If these measurements are accurate, and if a possible effect of added reagent on the chemical velocity constant is neglected, then $A = A'\phi$.

In any case

$$k_{t+10}/k_t > \varphi_{t+10}^{0.8\ (\text{or}\ 1)}/\varphi_t^{0.8\ (\text{or}\ 1)}.$$

Applying this inequality to equation 17, and remembering that in the limit $K = k$, the following relation is found to hold

$$k_{t+10}/k_t > K_{t+10}/K_t > \varphi_{t+10}^{0.8\,(\text{or}\,1)}/\varphi_t^{0.8\,(\text{or}\,1)} \tag{18}$$

The inequality 18 states that the measured temperature coefficient will lie between the coefficient of viscosity and of true chemical reaction. This is the result that has been found generally, with leanings toward viscosity coefficient or chemical coefficient depending on the ratio $k/As^{0.8}$.

SUMMARY

1. The postulates of the Nernst theory of fluid-phase heterogeneous reaction are criticized. In particular, independent experimental evidence is brought forward against the assumed existence of a stationary film.

2. In this paper, the measured rate of fluid-phase heterogeneous reaction is considered to be simply the resultant of two simultaneous processes —of chemical reaction at the interface and of physical transport to or from the interface—with no arbitrary assumptions as to mechanism.

3. To determine the functional relationship between the chemical and physical factors, the ordinary diffusion equation has been solved with one of the boundary conditions that of first-order reaction at the interface. The solution permits accurate calculation of the true chemical rate constant, knowing the value of the diffusion coefficient and the dimensions of the vessel.

The solved equation is brought into relation to the first-order rate equation that is usually found to apply. An implicit, and finally an explicit equation, connecting the usual measured rate constant, true chemical velocity constant, and diffusion coefficient are deduced, and the range of validity indicated.

4. By regarding diffusion as a special mode of molecule transport, the explicit equation is generalized to the following expression for the measured rate constant K,

$$K = S(1 - e^{-k/S})$$

where k is the chemical reaction velocity constant, and S the coefficient of physical transport of reactant or product of reaction to or from the interface.

5. For transport by mechanical stirring of the liquid phase, it is found that $S = As^{0.8}$, where A is a constant and s is the stirring speed. Exponent 0.8 agrees with that commonly found for the fluid velocity in the expression for the coefficient of heat transfer.

6. The values of K, measured as a function of the stirring speed for five typical reactions, are compared with the calculated values, and excellent

agreement obtained. k varies thirty-five-fold between 0.078 and 2.80 for the different reactions, while A lies between 1.1 and 12×10^{-3}.

7. The form of the curve of K against R.P.M. is considered in terms of the ratio k/A.

8. It is shown that the temperature coefficient of K must lie between the chemical coefficient and the viscosity coefficient, depending on the ratio $k/As^{0.8}$.

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SOLUBILITIES OF SOME STRYCHNINE BENZOATES

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AS B - 656 *Received May 2, 1934*

During the use of some strychnine benzoates in a series of toxicological and pharmacological experiments (1), it became necessary to determine their solubilities in water at 20°C. It was decided to make like determinations at other temperatures, and the results of this investigation are reported in the present communication.

For the determination of the solubilities up to 60°C., a constant temperature bath, capable of being regulated to ±0.05°, was used. The strychnine salt was placed in a Pyrex test tube with about 30 cc. of water, and the tube was sealed. For the lower temperatures the mouth of the test tube was closed by sealing in the flame; for the higher temperatures pure gum rubber stoppers were used. A number of tubes were fastened to a frame, which in turn was connected to a mechanical shaker. The tubes were allowed to remain in the bath for from thirty-six to forty-eight hours.

For the determination of solubilities at the higher temperatures, an excess of the strychnine salt in distilled water was brought to the boiling point and then allowed to cool to the desired temperature. The tube containing the solution was allowed to remain in a constant temperature bath at this temperature for at least thirty minutes. In order to obtain a temperature of 95°C., since water at this altitude boils below this temperature, a small amount of sodium chloride was added to the water in the water bath. The tubes containing the strychnine salts in water were placed in this boiling solution. The bath used was a large Erlenmeyer flask. Most of the water which evaporated condensed and ran back in the flask. If the thermometer kept in the salt solution indicated that the temperature was greater than 95°C., a new salt solution was used. In every case the tubes were frequently agitated.

After the salts had remained in contact with the water at the desired temperature for the required length of time, the tubes were removed to a constant temperature air oven regulated to the same temperature. With pipettes heated to this same temperature, 25 cc. of the solution was removed from each tube, placed in a weighed platinum dish, and evaporated to dryness on the water bath. The dish was then placed in an air oven and

dried to constant weight at 100°C. The grams of the strychnine compound present in 100 cc. of solution were calculated. The results showing the different solubilities are presented in table 1. From the data in this table it may be noted that a number of the compounds gave rather high solubility values in water. As a rule the ortho compounds gave the highest

TABLE 1

Solubilities of some strychnine benzoates

STRYCHNINE SALT	GRAMS OF SALT PER 100 CC. OF SOLUTION AT THE GIVEN TEMPERATURES						
	T = 20°C.	T = 30°C.	T = 40°C.	T = 50°C.	T = 60°C.	T = 75°C.	T = 95°C.
Benzoate	0.433	0.578	0.784	1.156	1.607	2.311	3.460
o-Chlorobenzoate	1.783	1.995	2.211	2.770	3.410	4.798	10.725
m-Chlorobenzoate	0.176	0.229	0.344	0.509	0.669	0.944	1.376
p-Chlorobenzoate	0.264	0.302	0.330	0.425	0.551	0.688	1.158
o-Bromobenzoate	1.063	1.204	1.410	1.846	2.470	3.818	6.571
m-Bromobenzoate	0.092	0.115	0.141	0.201	0.402	0.576	0.835
p-Bromobenzoate	0.211	0.244	0.299	0.351	0.528	0.744	0.915
o-Iodobenzoate	0.526	0.582	0.653	0.768	1.122	1.514	2.116
p-Iodobenzoate	0.167	0.195	0.229	0.341	0.475	0.606	0.840
o-Nitrobenzoate	0.521	0.621	0.724	0.928	1.320	1.970	3.140
m-Nitrobenzoate	0.447	0.565	0.706	0.896	1.359	2.452	4.138
p-Nitrobenzoate	0.183	0.222	0.266	0.328	0.467	0.698	0.970
o-Hydroxybenzoate	0.250	0.297	0.402	0.606	0.964	1.470	2.500
m-Hydroxybenzoate	0.179	0.185	0.335	0.432	0.562	0.872	1.517
p-Hydroxybenzoate	0.149	0.188	0.241	0.339	0.517	0.875	1.432
o-Methylbenzoate	0.519	0.634	0.984	1.331	1.958	2.807	4.142
m-Methylbenzoate	0.869	0.992	1.181	1.688	2.350	3.856	7.765
p-Methylbenzoate	0.560	0.578	0.625	0.828	0.931	1.250	1.808
o-Aminobenzoate	0.297	0.378	0.462	0.710	0.984	1.590	2.602
m-Aminobenzoate	1.092	1.204	1.437	2.107	2.971	4.786	7.963
p-Aminobenzoate	0.371	0.652	0.986	1.324	2.046	3.586	7.136
3,5-Dinitrobenzoate	0.136	0.163	0.197	0.271	0.384	0.599	0.951
2,4-Dinitrobenzoate	0.249	0.298	0.389	0.557	0.821	1.230	1.610
2,4,6-Trinitrobenzoate	0.075	0.098	0.116	0.165	0.273	0.450	0.717
5-Iodosalicylate	0.037	0.045	0.057	0.079	0.126	0.215	0.374
3,5-Dinitrosalicylate	0.025	0.041	0.063	0.088	0.116	0.422	1.064
Diiodosalicylate	0.020	0.023	0.031	0.032	0.046	0.071	0.127

values, but this was not true for the nitro, methyl, and amino compounds. In these three compounds the meta form showed the greatest solubility. The compounds with the benzoic acids having more than one substituted group gave, as a rule, very low solubility values. The strychnine diiodosalicylate was almost insoluble in water at all temperatures.

SUMMARY

The solubilities in water at different temperatures have been determined for twenty-seven strychnine benzoates.

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THE CONCENTRATION CHANGES AT MEMBRANES AND THE ELECTROÖSMOTIC MEMBRANE POTENTIALS

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Received February 5, 1934

In a previous paper (2) I have derived from Gouy's theory of a "diffuse" double layer, formulas for the transport numbers of ions in electroösmotic systems. They permit us to calculate both the concentration changes and the potential difference at diaphragms through which an electroösmotic current is driven.

At first, however, we will deduce the expressions for the transport numbers and bring these to a more convenient form. For a capillary slit, h cm. high and l cm. wide, we have for the fraction of the current carried by the anion

$$\begin{aligned} i_a &= \nu FCv_a hlX + 2\nu FChX \int_0^{l/2} v_a(N_a - 1)\,dx - 2\nu FCh \int_0^{l/2} uN_a\,dx \\ &= \nu FCv_a hlX + 2\nu FChX \int_0^{l/2} v_a(N_a - 1)\,dx - 2\nu FCh \int_0^{l/2} u\,dx \\ &\quad - 2\nu FCh \int_0^{l/2} u(N_a - 1)\,dx \end{aligned} \tag{1}$$

where X is the field strength in the capillary, ν valency of both ions, F the Faraday constant, C the concentration of anion (in gram-ions per cubic centimeter) in the middle of the slit, N_aC this concentration at the distance x from the slit wall, v_a the mobility of the anion (centimeters per second per 300 volts per centimeter), u the electroösmotic velocity. A proof of this equation is to be found in my previously mentioned paper. In the same paper expressions were given for u and N_a; after integrating and with regard to the relation $2h\int_0^{l/2} u\,dx = V$, where V is the total liquid flow through the slit, we have, if the capillary is not too narrow,[2]

$$i_a = \nu FChX \left\{ v_a l - \frac{8v_a}{\alpha(A+1)} - \frac{V}{hX} - \frac{32\nu FC}{\eta\alpha^2}\left[\frac{1}{A+1} - \frac{1}{2}\ln\frac{A+1}{A-1}\right]\right\} \tag{2}$$

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[2] In this case we can write (see equation 11 of reference 2)

$$u = X\frac{4\nu FC}{\eta\alpha^2}\left(\ln\frac{A+1}{A-1} - \ln\frac{Ae^{\alpha x}+1}{Ae^{\alpha x}-1}\right)$$

where η is the viscosity,

$$\alpha = \frac{2\nu F\sqrt{2\pi C}}{\sqrt{DRT}} \tag{3}$$

D the specific inductive capacity,

$$A = \frac{e^{-\frac{\nu F}{2RT}\zeta} + 1}{e^{-\frac{\nu F}{2RT}\zeta} - 1} \tag{4}$$

ζ being the electrokinetic potential difference.

The expression for the fraction of the current carried by the cation is like equation 2,

$$i_c = \nu FChX\left\{v_c l + \frac{8v_c}{\alpha(A-1)} + \frac{V}{hX} + \frac{32\nu FC}{\eta\alpha^3}\left[\frac{1}{A-1} - \frac{1}{2}\ln\frac{A+1}{A-1}\right]\right\} \tag{5}$$

The transport numbers are evidently $\frac{i_c}{i_c + i_a}$ and $\frac{i_a}{i_c + i_a}$, as we suppose that the solution contains two kinds of ions only.

We consider now (the "pinch effect" (3, 4) being neglected) the cross section of the slit at the flow entrance. Suppose that the liquid is positive relative to the negatively charged slit wall and moves to the cathode. If the field strength outside the slit be X_0, the amount of electricity brought by the cations per second to the slit entrance will be

$$i_c^0 = \nu FCv_c hlX_0$$

The amount of electricity going away with the cation is i_c. The accumulation of cation charge per second is therefore

$$i_c^0 - i_c = \nu FC\,v_c hl(X_0 - X) - \nu FChX \left\{\frac{8v_c}{\alpha(A-1)} + \frac{V}{hX} + \frac{32\nu FC}{\eta\alpha^3}\left[\frac{1}{A-1} - \frac{1}{2}\ln\frac{A+1}{A-1}\right]\right\} \tag{6}$$

In an analogous manner we find for the accumulation of the anion charge

$$i_a - i_a^0 = -\nu FCv_a hl(X_0 - X) - \nu FChX \left\{\frac{8v_a}{\alpha(A+1)} + \frac{V}{hX} + \frac{32\nu FC}{\eta\alpha^3}\left[\frac{1}{A+1} - \frac{1}{2}\ln\frac{A+1}{A-1}\right]\right\} \tag{7}$$

In the stationary state these two expressions must be equal, because otherwise a continual increase of free electric charge should take place. From the equation $i_c^0 - i_c = i_a - i_a^0$ we obtain

$$(v_c + v_a)l(X_0 - X) = X\cdot\frac{8}{\alpha}\left[\frac{v_c}{A-1} - \frac{v_a}{A+1} + \frac{8\nu FC}{\eta\alpha^2}\cdot\frac{1}{A^2-1}\right] \tag{8}$$

whence

$$X_0 - X = X \cdot \frac{8}{\alpha l(v_c + v_a)} \left[\frac{v_c}{A - 1} - \frac{v_a}{A + 1} + \frac{8\nu FC}{\eta \alpha^2} \cdot \frac{1}{A^2 - 1} \right] \tag{9}$$

Now the right-hand fraction, according to equation 27 (see reference 2), equals $\frac{\kappa_\omega}{\kappa}$, where κ_ω and κ are the surface conductivity (not related to unit area!) and the volume conductivity, respectively; it follows that

$$X_0 - X = X \cdot \frac{\kappa_\omega}{\kappa} \tag{10}$$

That the field strength in the capillary, X, has another value than that outside, X_0, is a consequence of the *membrane potential*, Π. The latter is equal to $(X - X_0)L$, where L is the length of the slit, hence

$$\Pi = -\frac{\kappa_\omega}{\kappa} \cdot XL \tag{11}$$

or, inserting the value of X from equation 10,

$$\Pi = -\frac{\kappa_\omega}{\kappa + \kappa_\omega} \cdot X_0 L \tag{12}$$

The direction of this membrane potential difference is such that the additional field is opposite to the impressed electric field for positive as well as for negative membranes; X is always lower than X_0.

After the switching-off of the external field the membrane potential will vanish with a very great velocity; we can calculate that ca. 10^{-6} or 10^{-7} second is sufficient to reduce it to 0.01 of the original magnitude. But during the current's flow a measurement of Π must be practicable and perhaps will not be more difficult than the measurement of the surface conductance. A determination of both Π and κ_ω on the same capillary system would make it possible to verify the relation 12.

If the expression $X_0 - X$ from equation 9 is put into equation 6 or 7 we find the decrease of the salt amount before the slit, this decrease per second, ΔS, being equal to

$$\frac{1}{\nu F}(i_c^0 - i_c) = \frac{1}{\nu F}(i_a - i_a^0)$$

The equation thus obtained can, however, be very much simplified, if the slit is wide enough. Then the surface conductance is very small compared to the bulk conductance and we can put $X_0 - X = 0$; moreover all the other terms in the bracket of equation 6 or 7 will be negligible[3] except for the

[3] A discussion of these terms will be found in the previous paper (reference 2).

term $\frac{V}{hX}$. To the order of approximation of the Helmholtz theory, therefore,

$$\Delta S = -CV \tag{13}$$

The current $I = i_c^0 + i_a^0$ moves and decomposes $\frac{I}{\nu F}$ gram-equivalents per second. We may compare this amount to the loss of solute ΔS and we write the dimensionless relation

$$\frac{\nu F}{I} \cdot \Delta S = -\frac{CV}{ChlX_0(v_c + v_a)} = -\frac{u_0}{v_c + v_a} \tag{14}$$

where

$$u_0 = \frac{V}{hlX_0} = \frac{D\zeta}{4\pi\eta} \tag{15}$$

is the velocity of the electroösmotic flow in unit field, according to Helmholtz.

At the other side of the slit we have evidently a *gain* of the salt of the same magnitude ΔS.

Both the relations 12 and 13 are, as far as I can see, independent of the particular distribution of the electric charge across the electric double layer.

The value Π is one of the second order of magnitude like the surface conductivity, but ΔS is one of the first order like the electric endosmose, the stream potential, etc. Thus the concentration change at diaphragms was discovered at the same time as the laws of electroösmotic phenomena. Its extensive exploration has, however, been hardly undertaken.

Particularly A. Bethe and Th. Toropoff (1) have investigated the connection between ΔS and the electroösmotic behavior (at diaphragms of chromated gelatin chiefly).

The most important results of their experiments are as follows: (1) If in a $0.01N$ solution of sodium chloride we gradually replace the sodium chloride by hydrochloric acid, both the transported liquid volume V and the transported electrolyte amount ΔS change their magnitude and even their direction, but an approximate proportionality between ΔS and V subsists always (see figure 3 of the paper of Bethe and Toropoff). It seems to be a verification of our equation 13, since this can be applied also to a mixture of binary electrolytes of the same valence; C will be in this case the total concentration (in Bethe and Toropoff's experiments $= 0.01N$). Unfortunately the flow V is given by Bethe and Toropoff in conventional units only, so that it is not possible to show that the proportionality factor $\Delta S : V$ is really equal to C.

(2) In a $0.01N$ sodium chloride solution 1 coulomb has transported nearly 1.6×10^{-6} moles of sodium chloride to the cathode side of the diaphragm. Since 1 coulomb corresponds to 10^{-5} moles nearly, we obtain

$$\frac{\nu F}{I} \cdot \Delta S = \frac{1.6 \times 10^{-6}}{10^{-5}}$$

hence, according to equation 14,

$$-u_0 = 0.16\,(v_e + v_a)$$

The mobilities of Na^+ and Cl^- being 4.8×10^{-4} and 7.2×10^{-4} cm. per second per volt per centimeter, respectively (at 20°C.), we find $u_0 = -1.9 \times 10^{-4}$ and, according to equation 15, $\zeta = -0.027$ volt, a probable figure for the system $0.01N$ sodium chloride–chromated gelatin.

In a $0.01N$ hydrochloric acid solution 1 coulomb has transported nearly 1.5×10^{-6} moles of hydrogen chloride in the opposite direction; whence $\zeta = 0.087$ volt.

(3) Besides Bethe and Toropoff have observed and measured a "neutrality trouble," i.e., an appearance of alkaline reaction in the anode compartment and of acid reaction in the cathode compartment after the electroösmose in a $0.01N$ sodium chloride solution. But the "trouble" is so small (after the passage of 4 coulombs the pH has risen from 7.00 to 7.2–7.3 and fallen from 7.00 to 6.8–6.9, respectively) that it need not be taken into account.

SUMMARY

From the theory of the diffuse double layer expressions are derived for both the electrolyte transport and the potential differences at membranes through which an electroösmotic current is driven. These expressions are discussed and compared with the experimental evidence.

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ELECTROKINETIC PROPERTIES OF PROTEINS. III

The Rôle of Electrical Forces in the Adsorption of Gliadin at a Glass-Liquid Interface[1]

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Received April 26, 1934

INTRODUCTION

Streaming potential data presented in the preceding paper (13) of this series indicated that the rate of adsorption of gliadin at a glass-liquid interface was determined primarily by the sign and the magnitude of the electric charge of the protein micelles in relation to that of the glass, adsorption apparently being a mutual precipitation of the oppositely charged bodies. The rôle of electrical forces of attraction and repulsion in adsorption, and the reversibility of the process have been further investigated in the present work.

EXPERIMENTAL

Apparatus

The apparatus used in the preceding investigation (13) was modified to facilitate changing from one solution to another without interrupting the streaming potential measurements. This was accomplished by connecting the streaming cell through a three-way stopcock to two solution reservoirs, each of which was equipped with a mechanical stirrer. The apparatus was otherwise identical with that described in the above paper, and therefore needs no further description.

Materials

The gliadin preparation described in the previous paper (13) was used in these studies. All solutions were prepared from chemically pure sodium hydroxide, acetic acid, and conductivity water. The gliadin was dispersed in a 70 per cent ethanol solution and sufficient of the resulting sol added to the aqueous solutions to give a concentration of 0.002 g. of gliadin per liter.

[1] Paper no. 43, Journal Series, from the Agricultural Experiment Station, Montana State College, Bozeman, Montana.

Calculation of the electric moment of the double layer at the solid–liquid interface

The values for the electric moment of the double layer at the solid–liquid interface were calculated from the streaming potential data by the formula of Bull and Gortner (6)

$$qd = \frac{\eta \kappa_s H}{P}$$

in which the c.g.s. constants are evaluated, as previously explained (13), to give

$$qd = 224755.22 \times \eta \times \frac{\kappa_s H}{P}$$

where q is the charge per unit area of the double layer in electrostatic units, d the thickness of the double layer in centimeters, η the viscosity of the streaming liquid in poises, κ_s the electrical conductance across the diaphragm in reciprocal ohms, H the streaming potential in volts and P the hydrostatic pressure in centimeters of mercury. The values for κ_s, H, and P were determined experimentally, and the values for η, the viscosity of the solutions, were assumed to be the same as that of water (9) at the temperatures at which the streaming potential measurements were made. Although the viscosity of aqueous solutions varies with composition and concentration, as shown by the work of Jones and Talley (10), the differences in the extremely dilute solutions used in these studies were not sufficient to be measured by the usual methods. The viscosity values for pure water were therefore used in the calculations.

ADSORPTION OF GLIADIN ON GLASS AS INFLUENCED BY ELECTRICAL FORCES OF ATTRACTION AND REPULSION

When a protein is dispersed in an aqueous solution it may ionize amphoterically to form electropositive, electroneutral, or electronegative micelles, the degree of ionization of its acidic or basic groups being influenced by the common-ion effect of the hydrogen and hydroxyl ions of the solution. Protein micelles are thus positively charged in acidic solutions, negatively charged in alkaline, and electrically neutral in isoelectric solutions. Glass, however, is electronegative in both acidic and alkaline solutions. It follows, therefore, that in an alkaline solution both the protein micelles and the glass are negatively charged, and consequently are repelled from each other. If, however, the hydrogen-ion concentration of the solution is progressively increased by adding increments of acid, the charge of the protein micelles will reverse when the isoelectric point is passed, and they will be precipitated on to the glass by the forces of attraction between the electric charges of opposite sign. The system will thus change from a

glass-liquid to a glass-protein-liquid system, resulting in a reversal of the potential across the interface.

The foregoing was demonstrated experimentally by streaming a dilute sodium hydroxide solution containing 0.002 g. of gliadin per liter through the fritted glass diaphragm and measuring simultaneously the change in the streaming potential as the hydrogen-ion concentration of the solution was progressively increased by adding increments of dilute acetic acid.

The potential across the diaphragm quickly attained a constant value following addition of acid until it reversed in sign, after which it decreased gradually with time. All measurements were therefore made exactly 10

TABLE 1

Effect of hydrogen-ion concentration on the adsorption of gliadin at a glass-liquid interface

HYDROGEN-ION CONCENTRATION	ELECTRICAL CONDUCTANCE ACROSS DIAPHRAGM κ_s	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	H/P	ELECTRIC MOMENT OF DOUBLE LAYER μ
pH	$\kappa_s \times 10^{-4}$	cm.Hg	millivolts		e.s.u. $\times 10^{-4}$
9.98	30.24	12.5	−279	−22.32	−13.35
9.79	25.26	12.3	−322	−26.18	−13.08
9.56	20.61	12.3	−390	−31.71	−12.92
9.07	16.98	12.2	−434	−35.57	−11.95
8.36	14.19	12.2	−469	−38.44	−10.79
7.41	12.22	12.1	−494	−40.83	−9.87
6.89	11.48	12.1	−501	−41.40	−9.40
6.29	11.02	12.0	+11	+0.92	+0.20
6.01	10.84	11.9	+53	+4.45	+0.95
5.55	11.14	11.9	+172	+14.45	+3.18
5.32	12.52	11.8	+185	+15.68	+3.88
5.10	14.19	11.6	+213	+18.36	+5.15
4.80	16.71	11.4	+223	+19.56	+6.46
4.48	23.95	11.2	+182	+16.25	+7.70

Viscosity of above solutions, η, is 0.0088.

minutes after adding each increment of acid in order to obtain comparable results. Although the applied hydrostatic pressure was automatically maintained constant, the effective hydrostatic pressure decreased slightly during the progress of the measurements, owing to a lowering of the solution in the reservoir. Since the streaming potential is directly proportional to the hydrostatic pressure, the values for the ratio $H:P$, given in table 1, and represented by the curve in figure 1, show the influence of the hydrogen-ion concentration on the streaming potential.

To determine whether the gliadin was adsorbed from an alkaline solution in which its charge was the same as that of the fritted glass diaphragm, the charge of the latter was determined before and after streaming through it

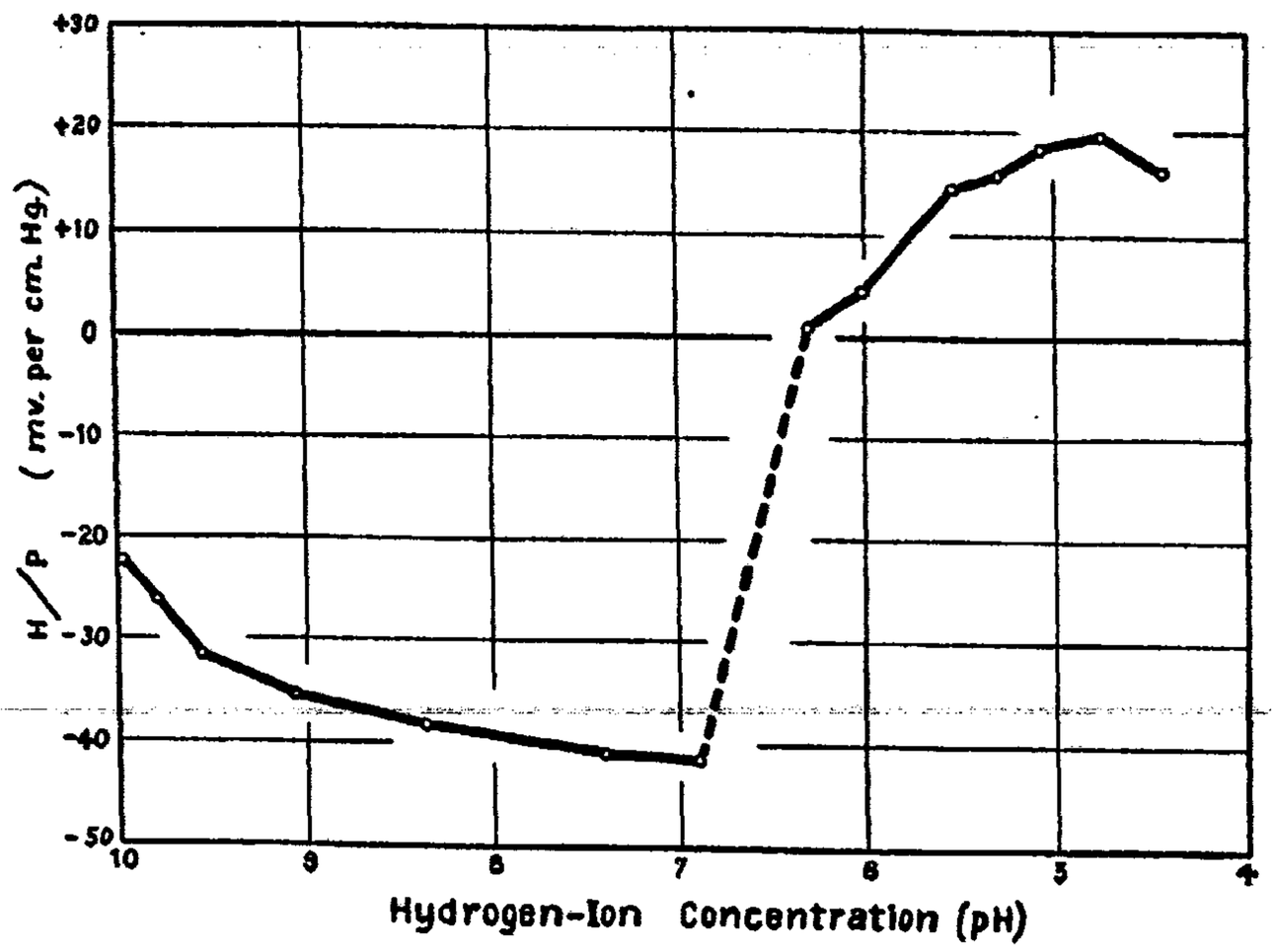

FIG. 1. THE REVERSAL OF THE STREAMING POTENTIAL BY THE ADSORPTION OF GLIADIN

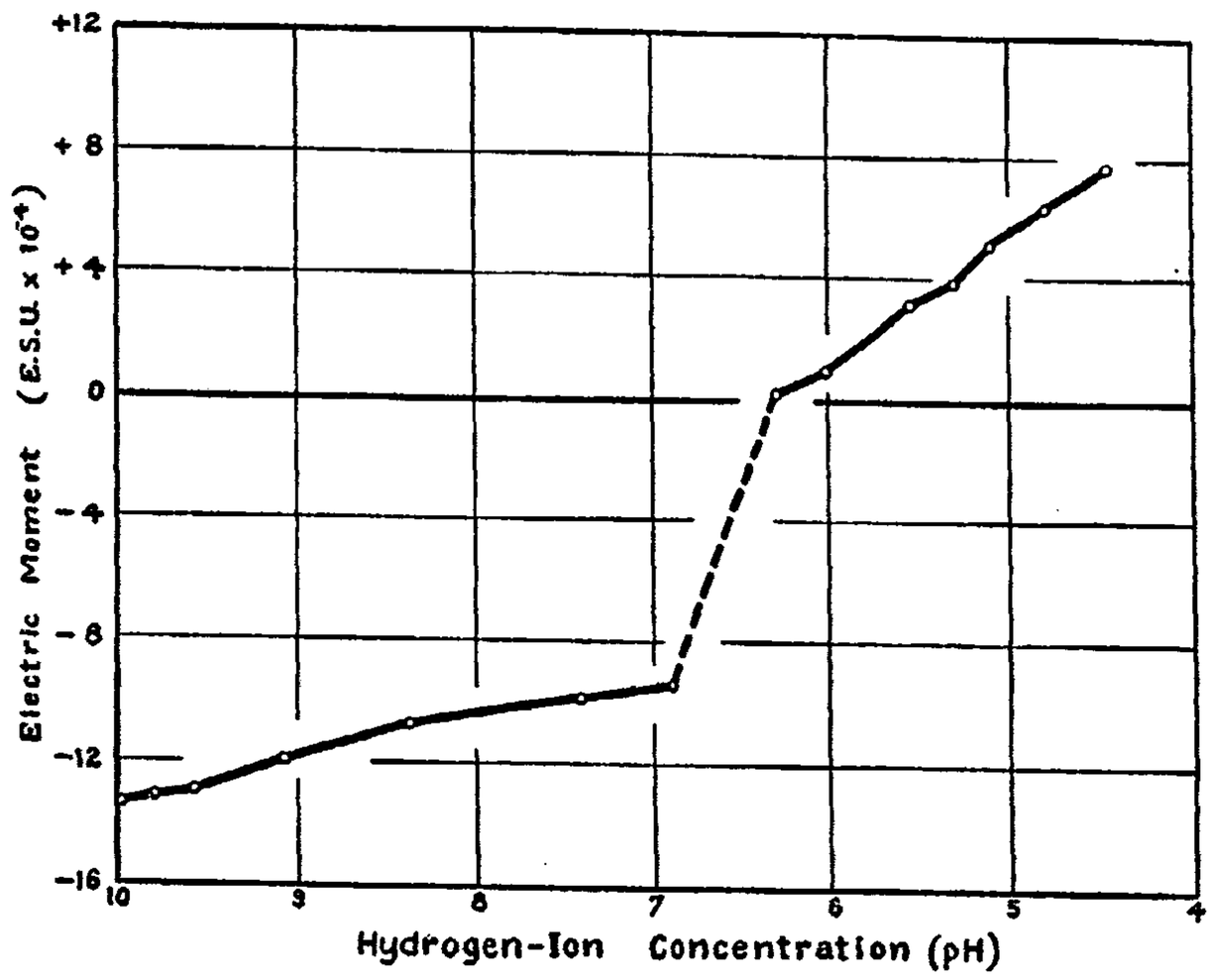

FIG. 2. THE REVERSAL OF THE ELECTRIC MOMENT OF THE DOUBLE LAYER AT THE GLASS-LIQUID INTERFACE BY THE ADSORPTION OF GLIADIN

TABLE 2

Adsorption of gliadin on glass in alkaline and acidic solutions

TIME	HYDROGEN-ION CONCENTRATION	ELECTRICAL CONDUCTANCE ACROSS DIAPHRAGM κ_s	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	ELECTRIC MOMENT OF DOUBLE LAYER μ
		Acetic acid solution			
minutes	pH	$\kappa_s \times 10^{-4}$	*cm.Hg*	*millivolts*	*e.s.u.* $\times 10^{-4}$
0	4.46	15.44	11.8	−451	−12.86
5	4.46	15.44	11.7	−448	−12.89
10	4.46	15.44	11.6	−443	−12.85
		Changed to sodium hydroxide solution			
12	10.10	29.12	11.7	−201	−10.91
15	10.10	29.12	11.7	−194	−10.53
20	10.10	29.12	11.6	−189	−10.34
25	10.10	29.12	11.6	−187	−10.23
30	10.10	29.12	11.5	−184	−10.18
		0.002 g. gliadin per liter added			
32	9.80	30.65	11.6	−154	−8.87
35	9.80	30.65	11.6	−146	−8.41
40	9.80	30.65	11.5	−141	−8.19
45	9.80	30.65	11.5	−138	−8.02
50	9.80	30.65	11.4	−136	−7.97
55	9.80	30.65	11.3	−134	−7.92
60	9.80	30.65	11.2	−131	−7.82
		Changed to sodium hydroxide solution			
62	10.08	28.91	11.9	−162	−8.58
65	10.08	28.91	11.8	−171	−9.13
70	10.08	28.91	11.8	−175	−9.35
75	10.08	28.91	11.7	−177	−9.53
80	10.08	28.91	11.7	−178	−9.59
85	10.08	28.91	11.6	−178	−9.67
90	10.08	28.91	11.5	−178	−9.75
		Changed to acetic acid solution			
92	4.37	15.44	11.8	+13	+0.37
95	4.37	15.44	11.8	−6	−0.17
100	4.37	15.44	11.7	−14	−0.40
105	4.37	15.44	11.7	−15	−0.43
110	4.37	15.44	11.6	−16	−0.46
115	4.37	15.44	11.6	−18	−0.52
120	4.37	15.44	11.5	−19	−0.56
		0.002 g. gliadin per liter added			
121	4.83	16.18	11.5	+72	+2.21
122	4.83	16.18	11.5	+105	+3.22
125	4.83	16.18	11.4	+134	+4.15
130	4.83	16.18	11.4	+149	+4.61
135	4.83	16.18	11.3	+154	+4.81
140	4.83	16.18	11.2	+159	+5.01
150	4.83	16.18	11.2	+166	+5.23
160	4.83	16.18	11.1	+169	+5.37

Viscosity of above solutions, η, is 0.0097.

an alkaline solution of the gliadin. The data from these measurements are presented in table 2 and figure 3. The charge of the diaphragm in an acetic acid solution of pH 4.46 and in a sodium hydroxide solution of pH 10.10 is shown by curves *AB* and *BC*, respectively, in the figure. At *C* 2 mg. of gliadin per liter was added to the alkaline solution and the resulting sol streamed through the fritted glass diaphragm for 30 minutes. The

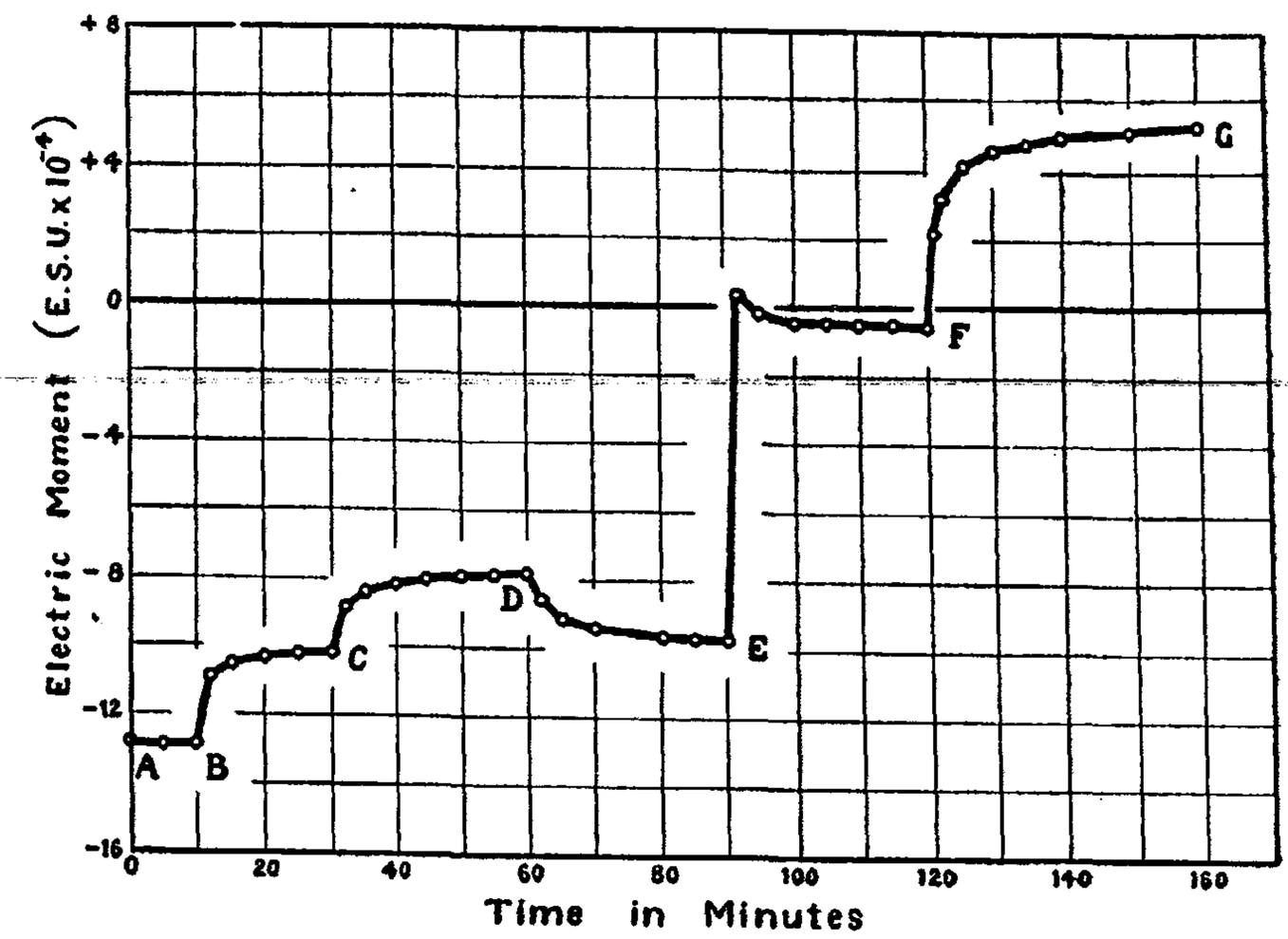

FIG. 3. STUDIES ON THE ADSORPTION OF NEGATIVELY CHARGED GLIADIN ON GLASS

AB, electric charge of fritted glass diaphragm in a protein-free acetic acid solution of pH 4.46.
B, changed to protein-free sodium hydroxide solution of pH 10.10.
C, added 0.002 g. gliadin per liter of streaming solution.
D, changed to protein-free sodium hydroxide solution of pH 10.08.
E, changed to protein-free acetic acid solution of pH 4.37.
F, added 0.002 g. gliadin per liter of streaming solution.
FG, electric charge of diaphragm in gliadin sol of pH 4.83.

alkaline sol was then displaced from the diaphragm at *D* by a protein-free sodium hydroxide solution, which was streamed through the system for 30 minutes to remove any unadsorbed protein. Following this treatment the diaphragm was tested for adsorbed protein by determining the sign of its charge in a protein-free acid solution. As shown by curve *EF*, its charge reversed momentarily and then attained a constant negative value, which indicated that the surface of the glass had not been completely

TABLE 3

Effect of hydrogen-ion concentration on the desorption of gliadin from a glass-liquid interface

TIME	HYDROGEN-ION CONCENTRATION	ELECTRICAL CONDUCTANCE ACROSS DIAPHRAGM κ_s	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL Π	ELECTRIC MOMENT OF DOUBLE LAYER μ
		Dilute acetic acid solution			
minutes	pH	$\kappa_s \times 10^{-4}$	*cm.Hg*	*millivolts*	*e.s.u.* $\times 10^{-4}$
0	4.72	11.83	12.4	−314	−6.40
5	4.72	11.83	12.3	−312	−6.41
10	4.72	11.83	12.2	−309	−6.40
		0.002 g. gliadin per liter added			
11	5.15	12.48	12.2	−187	−4.08
12	5.15	12.48	12.2	−66	−1.44
14	5.15	12.48	12.2	+50	+1.09
16	5.15	12.48	12.2	+91	+1.99
18	5.15	12.48	12.2	+112	+2.45
20	5.15	12.48	12.2	+124	+2.71
25	5.15	12.48	12.1	+137	+3.02
30	5.15	12.48	12.1	+142	+3.13
35	5.15	12.48	12.0	+145	+3.22
40	5.15	12.48	12.0	+147	+3.26
45	5.15	12.48	12.0	+148	+3.29
50	5.15	12.48	12.0	+147	+3.26
		Changed to dilute sodium hydroxide solution			
51	8.37	13.76	12.6	−462	−10.77
52	8.37	13.76	12.6	−440	−10.26
54	8.37	13.76	12.5	−426	−10.01
56	8.37	13.76	12.5	−427	−10.04
58	8.37	13.76	12.4	−432	−10.24
60	8.37	13.76	12.4	−439	−10.40
65	8.37	13.76	12.3	−445	−10.63
70	8.37	13.76	12.3	−448	−10.70
75	8.37	13.76	12.2	−451	−10.86
80	8.37	13.76	12.2	−448	−10.79
90	8.37	13.76	12.1	−444	−10.78
100	8.37	13.76	12.0	−438	−10.72
		Changed to dilute acetic acid solution			
101	4.72	11.69	12.0	+141	+2.93
102	4.72	11.69	12.0	+134	+2.79
104	4.72	11.69	12.0	+129	+2.68
106	4.72	11.69	12.0	+117	+2.43
108	4.72	11.69	12.0	+107	+2.22
110	4.72	11.69	12.0	+99	+2.06
115	4.72	11.69	11.9	+90	+1.89
120	4.72	11.69	11.9	+80	+1.68
125	4.72	11.69	11.8	+72	+1.52
130	4.72	11.69	11.8	+67	+1.42

Viscosity of above solutions, η, is 0.0095.

covered with the protein, otherwise it would have been positively charged in the acid solution. This was demonstrated by adding 0.002 g. of gliadin per liter to the streaming solution at *F*, which immediately reversed the charge of the glass as shown by the adsorption curve *FG*.

REVERSIBILITY OF THE ADSORPTION PROCESS

An attempt was made in the following experiments, the results of which are presented in table 3 and figure 4, to reverse the adsorption process by

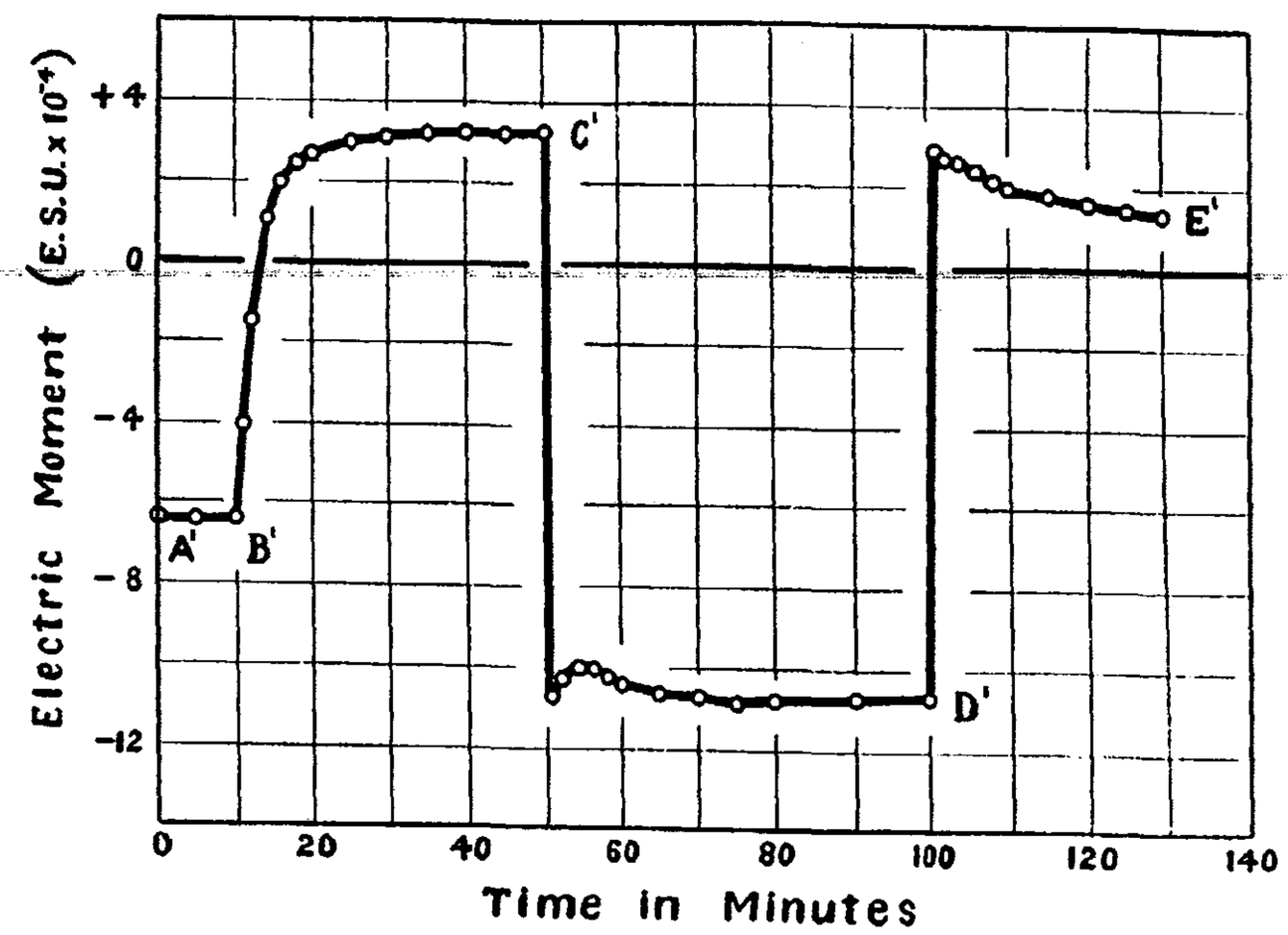

FIG. 4. IRREVERSIBILITY OF THE ADSORPTION PROCESS

A'B', electric charge of fritted glass diaphragm in a protein-free acetic acid solution of pH 4.72.
B', added 0.002 g. gliadin per liter of streaming solution.
C', changed to protein-free sodium hydroxide solution of pH 8.37. Solution was streamed through diaphragm for fifty minutes to remove any gliadin desorbed from the glass.
D', changed to protein-free acetic acid solution of pH 4.72.
D'E', electric charge of diaphragm in protein-free acetic acid solution of pH 4.72.

reversing the charge of the protein to the same sign as that of the glass on which it was adsorbed and thus to cause it to be desorbed by the electrical forces of repulsion.

The charge of the protein-free diaphragm (glass) shown by curve *A'B'* in figure 4 was first determined by streaming through it an acetic acid solution of pH 4.72. At *B'* 2 mg. of gliadin per liter was added to the

TABLE 4

Influence of changes in hydrogen-ion concentration on the electrical properties of gliadin adsorbed at a glass-liquid interface

TIME	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	ELECTRIC MOMENT OF DOUBLE LAYER μ
Distilled water containing 0.002 g. gliadin per liter; $\kappa_s = 1.44 \times 10^{-6}$; pH = 6.29			
minutes	*cm. Hg*	*millivolts*	*e.s.u.* $\times 10^{-4}$
2	11.8	+1610	+4.42
4	11.8	+1609	+4.42
7	11.8	+1606	+4.41
12	11.7	+1598	+4.42
Sodium hydroxide added; $\kappa_s = 1.48 \times 10^{-6}$; pH = 6.67			
2	12.6	−98	−0.26
4	12.6	−48	−0.13
6	12.6	−9	−0.02
8	12.5	+26	+0.07
10	12.5	+64	+0.17
12	12.5	+103	+0.27
14	12.5	+146	+0.39
16	12.4	+189	+0.51
18	12.4	+227	+0.61
20	12.4	+267	+0.72
22	12.4	+295	+0.79
Sodium hydroxide added; $\kappa_s = 1.55 \times 10^{-6}$; pH = 7.10			
2	12.4	−1469	−4.13
4	12.4	−1408	−3.96
6	12.4	−1344	−3.78
8	12.4	−1278	−3.59
10	12.4	−1215	−3.42
12	12.4	−1164	−3.27
14	12.4	−1103	−3.10
16	12.4	−1049	−2.95
18	12.4	−1002	−2.82
20	12.3	−955	−2.71
22	12.3	−917	−2.60
Sodium hydroxide added; $\kappa_s = 3.53 \times 10^{-6}$; pH = 8.07			
2	12.1	−1259	−8.26
4	12.1	−1245	−8.17
6	12.1	−1231	−8.08
Sodium hydroxide added; $\kappa_s = 3.53 \times 10^{-6}$; pH =8.07—*Cont'd*			
minutes	*cm. Hg*	*millivolts*	*e.s.u.* $\times 10^{-4}$
8	12.1	−1220	−8.01
10	12.0	−1210	−8.01
12	12.0	−1202	−7.95
14	12.0	−1192	−7.89
16	12.0	−1181	−7.81
18	12.0	−1171	−7.75
20	12.0	−1161	−7.68
22	12.0	−1152	−7.62
Sodium hydroxide added; $\kappa_s = 8.08 \times 10^{-6}$; pH = 8.83			
2	12.0	−583	−8.83
4	12.0	−583	−8.83
7	12.0	−582	−8.81
12	11.9	−574	−8.77
Sodium hydroxide solution containing 0.002 g. gliadin per liter; $\kappa_s = 13.77 \times 10^{-6}$; pH = 9.49			
2	12.6	−414	−10.18
4	12.6	−413	−10.15
7	12.5	−412	−10.21
12	12.5	−411	−10.18
Acetic acid added; $\kappa_s = 5.67 \times 10^{-6}$; pH = 8.45			
2	12.2	−496	−5.18
4	12.2	−503	−5.26
6	12.2	−522	−5.46
8	12.2	−532	−5.56
10	12.2	−540	−5.64
12	12.2	−549	−5.74
14	12.2	−557	−5.82
16	12.2	−562	−5.87
18	12.2	−569	−5.95
20	12.2	−572	−5.98
22	12.2	−574	−6.00

TABLE 4—*Concluded*

TIME	HYDROSTATIC PRESSURE P	STREAMING POTENTIAL H	ELECTRIC MOMENT OF DOUBLE LAYER μ
Acetic acid added; $\kappa_s = 4.52 \times 10^{-6}$; pH = 7.41			
minutes	*cm. Hg*	*millivolts*	*e.s.u.* $\times 10^{-4}$
2	12.2	−273	−2.43
4	12.1	−281	−2.52
6	12.1	−294	−2.63
8	12.1	−303	−2.71
10	12.1	−308	−2.76
12	12.1	−311	−2.79
14	12.1	−315	−2.82
16	12.1	−318	−2.85
18	12.1	−320	−2.87
20	12.1	−322	−2.88
22	12.1	−324	−2.90
Acetic acid added; $\kappa_s = 4.63 \times 10^{-6}$; pH = 6.63			
2	12.0	0	0
4	11.9	−7	−0.06
6	11.9	−14	−0.12
8	11.9	−20	−0.17
10	11.9	−27	−0.24
12	11.9	−33	−0.29
14	11.9	−39	−0.34
16	11.9	−45	−0.39
18	11.9	−50	−0.44
20	11.9	−54	−0.47
22	11.9	−59	−0.52
Acetic acid added; $\kappa_s = 5.49 \times 10^{-6}$; pH = 5.38			
2	11.8	+363	+3.80
4	11.8	+356	+3.73
6	11.8	+347	+3.63
Acetic acid added; $\kappa_s = 5.49 \times 10^{-6}$; pH = 5.38—*Cont'd*			
minutes	*cm. Hg*	*millivolts*	*e.s.u.* $\times 10^{-4}$
8	11.8	+340	+3.56
10	11.8	+334	+3.50
12	11.8	+329	+3.44
14	11.8	+325	+3.40
16	11.7	+321	+3.39
18	11.7	+317	+3.35
20	11.7	+314	+3.31
22	11.7	+312	+3.29
Acetic acid added; $\kappa_s = 6.91 \times 10^{-6}$; pH = 4.88			
2	11.7	+438	+5.82
4	11.7	+433	+5.75
6	11.7	+430	+5.71
8	11.6	+428	+5.73
10	11.6	+427	+5.72
12	11.6	+425	+5.69
14	11.6	+424	+5.68
16	11.6	+422	+5.65
18	11.6	+421	+5.64
20	11.5	+419	+5.66
22	11.5	+418	+5.65
Acetic acid added; $\kappa_s = 10.39 \times 10^{-6}$; pH = 4.49			
2	11.5	+338	+6.87
4	11.4	+332	+6.81
7	11.3	+331	+6.85
12	11.2	+327	+6.82

Viscosity of above solutions, η, is 0.0100.

solution, which resulted in completely covering the glass with protein in 40 minutes, as indicated by the adsorption curve $B'C'$. The charge of the adsorbed protein was then reversed at C' by replacing the acid sol with a protein-free sodium hydroxide solution. The latter was streamed through the diaphragm for 50 minutes to remove any protein desorbed from the glass. Upon testing the diaphragm for adsorbed protein by again streaming through it a protein-free acetic acid solution of pH 4.72, it was found

to be positively charged as shown by curve $D'E'$, which indicated that it was still covered with a layer of protein.

INFLUENCE OF CHANGES IN HYDROGEN-ION CONCENTRATION ON THE ADSORPTION EQUILIBRIUM AT THE GLASS–LIQUID INTERFACE

In measuring the charge of proteins adsorbed on porous diaphragms by the streaming potential method, it was observed in this and in the preced-

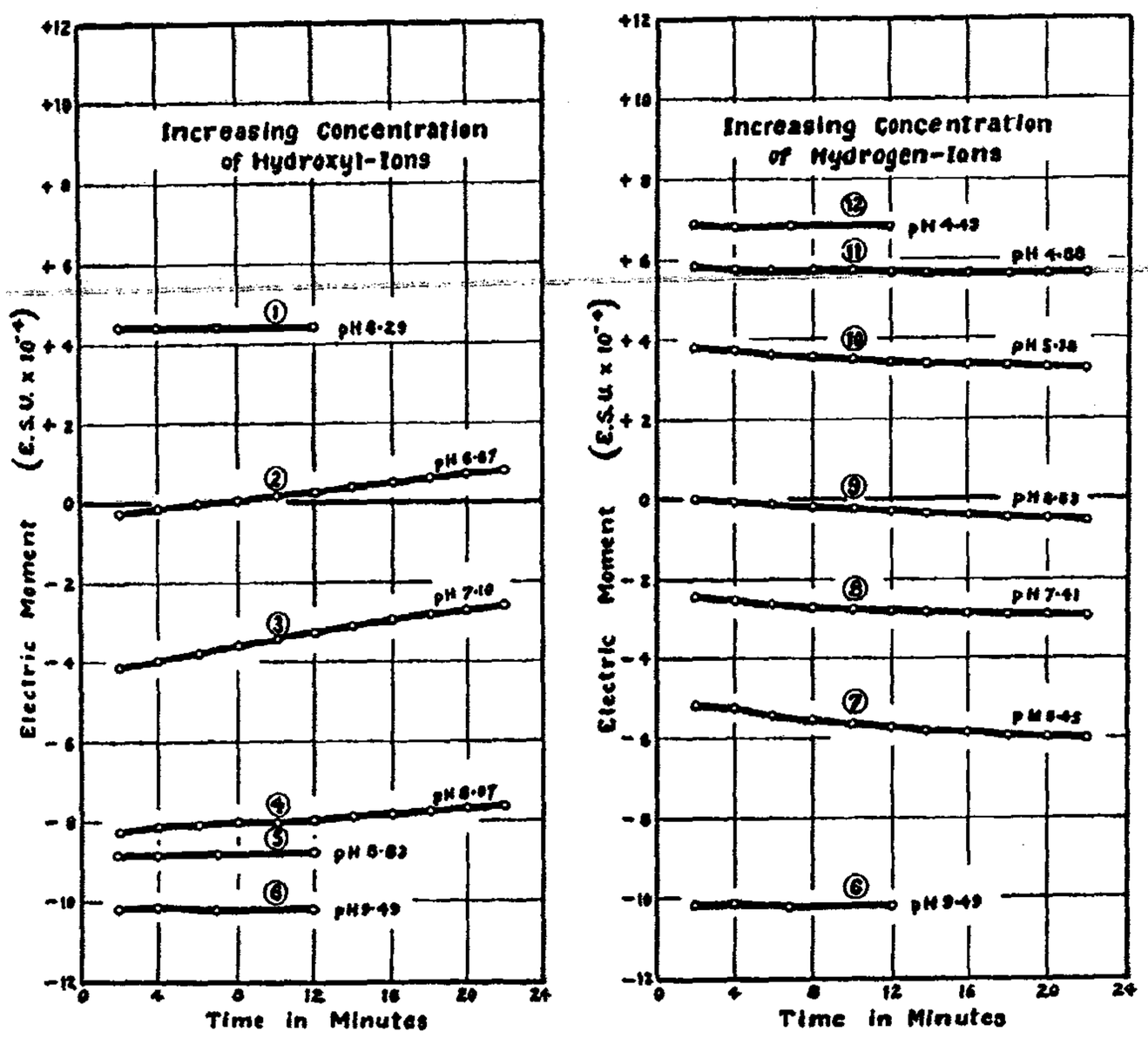

FIG. 5. INFLUENCE OF CHANGES IN HYDROGEN-ION CONCENTRATION ON THE ADSORPTION EQUILIBRIUM AT THE GLASS–LIQUID INTERFACE

Curve 1 represents the charge of the fritted glass diaphragm in equilibrium with distilled water containing 0.002 g. of gliadin per liter. Curves 2 to 6, inclusive, show the changes in the charge following successive additions of sodium hydroxide to the streaming solution, and curves 6 to 12 show the changes following the addition of acetic acid.

ing investigations (12, 13) that the streaming potential did not attain a constant value immediately following the addition of acid or alkali to the solution streamed through the diaphragm, but that the potential increased positively following the addition of alkali and negatively following the addition of acid.

This effect is shown by the data in table 4 and by the electric moment-time curves in figure 5. Curve 1 in the figure shows the charge of the diaphragm which had come to equilibrium in conductivity water containing 0.002 g. of gliadin per liter; curves 2, 3, and 4 show the change in the charge following successive additions of sodium hydroxide to the solution. The charge of the diaphragm increased positively following each increase in the concentration of hydroxyl ions up to pH 8.83, after which equilibrium was quickly attained as indicated by curves 5 and 6. Upon reversing the foregoing procedure, however, by adding successive increments of acid to an alkaline sol, the charge of the diaphragm increased negatively following each addition of acid until the hydrogen-ion concentration reached pH 4.88, after which it became constant, as shown by curves 7 to 10 inclusive.

DISCUSSION

The streaming potential curve in figure 1 indicates that the fritted glass diaphragm adsorbed gliadin only from solutions in which its charge was opposite in sign to that of the glass. The abrupt reversal of the potential between pH 6.89 and pH 6.29, shown by the break in the curve, thus represents the transition from a glass–liquid to a glass–protein–liquid system, the change in potential being caused by the precipitation of the positively charged protein on the negatively charged glass. Although the streaming potential increased with increasing hydrogen-ion concentration from pH 9.98 up to the isoelectric region, the electric moment of the double layer at the solid–liquid interface decreased as shown by the curve in figure 2. This may have been due to the decrease in the total ionic concentration of the liquid phase, similar to that observed in the previous investigation (13), or it may have been caused by the adsorption of a positively charged protein fraction from the alkaline solution. The decrease in the charge of the diaphragm from that represented by curve *AB* to that of *EF* in figure 3 indicates that at least a trace of protein was adsorbed from the alkaline sol during the interval *CD*. The reversal of the potential following the addition of gliadin to the acetic acid solution at *F* indicates, however, that the glass had not adsorbed a complete covering of protein from the alkaline solution.

The curves in figure 4 show that the reversal of the charge of the protein to the same sign as that of the glass on which it was adsorbed did not result in its desorption. This is shown by the fact that the diaphragm was still positively charged in an acid solution after streaming through it for 50 minutes a protein-free alkaline solution. Obviously, if the protein had been desorbed from the glass it would have been removed by the liquid streamed through the diaphragm during the interval *C′D′*, and the potential across the interface would have been the same at *E′* as at *B′*.

When the drift or change in potential shown by the data in table 4 and

by the electric moment-time curves in figure 5 was first observed in the earlier investigations (11, 12), it appeared to be caused by a decrease in the size of the pores of the diaphragm due to the adsorption of protein on their walls, the change in potential apparently being caused by the "back-pressure" effect of the small capillaries, similar to that observed by Bull (5), Abramson (2), and White, Urban, and Krick (18). However, the change in the positive direction following the addition of alkali, and in the negative direction following the addition of acid, as shown by the slope of the curves, indicates that the effect was due to a change in the equilibrium of the forces acting across the solid-liquid interface rather than to "back-pressure." This effect may have been caused by a disturbance of the adsorption equilibrium or by a change in the polarity of the adsorbed protein molecules through chemical reaction with the acid or alkali added to the streaming solutions. Abramson (3) has presented experimental evidence showing that proteins are adsorbed at a solid-liquid interface with the non-polar part of the molecule toward the solid phase and the polar groups toward the liquid phase. Daniel (7) has likewise shown that gelatin is adsorbed on quartz particles with the active groups oriented toward the liquid phase. It follows, therefore, that the change in potential represented by curves 2, 3, and 4 in figure 5 may have been caused by the reaction of the carboxyl groups of the adsorbed protein with the alkali added to the streaming solution, and that represented by curves 7, 8, 9, and 10 by the reaction of the amino groups with the acid, the rate of reaction being determined by the rate at which the acid or alkali ions were brought in contact with the adsorbed layer of protein by the solution streamed through the diaphragm. Curves 1, 5, 6, 11, and 12, however, show that a constant potential was quickly attained following the addition of acid or alkali to solutions more alkaline than pH 8.83 or more acidic than pH 4.88. This apparently indicates that all of the free amino and carboxyl groups of the adsorbed protein had combined with the acid and alkali, respectively, within the hydrogen-ion range pH 4.88 to pH 8.83. The change in potential across the solid-liquid interface observed in these studies may therefore have been caused, not only by an interchange between the proteins of the adsorbed layer and those dispersed in the liquid phase, but also by a change in the polarity of the adsorbed proteins due to salt formation.

It is evident from the data presented that the adsorption of gliadin on glass is an electrical precipitation process. The mechanism of adsorption of gliadin on glass is thus similar to that observed by Weinland and France (17), whose experiments showed that the adsorption of dyes by a growing crystal of sodium nitrate is dependent on the residual valency force fields of the crystal face, and on the distribution of the polar groups of the adsorbed dye molecules. That the mechanism of adsorption is the same

for matter-in-mass as for molecules or micelles in the ionic state is indicated by the experiments of Northrop (14), which showed that the charge of glass was reversed by the adsorption of a layer of bacteria on its surface. Moreover, these data, as well as the observations reported in the previous paper (13), indicate that proteins prepared by the usual empirical methods are composed of two or more species of molecules having different isoelectric points, and that within the hydrogen-ion limits of the latter, part of the molecules are positively charged and part negatively charged, the proportion of each being determined by the common-ion effect of the hydrogen and hydroxyl ions. This accounts for the fact that protein preparations generally show an isoelectric *range* and not an isoelectric *point*, the latter usually being an interpolated value and not an experimentally determined point. It follows therefore that within the isoelectric range, the oppositely charged protein ions aggregate to form micelles, whereas outside this range their charges are of the same sign, and in consequence they are dispersed by the electrical forces of repulsion. The *true* isoelectric range thus appears to be the same as the "pH stability region" observed by Svedberg (16) and his coworkers.

The foregoing hypothesis not only accounts for the fact that the proteins show an isoelectric range rather than an isoelectric point, but it also explains why the experimental studies of a number of investigators, notably Abramson (1), Briggs (4), Daniel (7), Hitchcock (8), Loeb (11), Palmer (15), and Wintersteiner and Abramson (19), led to the general assumption that the adsorption of proteins on such inert substances as quartz, glass, and collodion was independent of the sign of the electric charge of the adsorbent and adsorbate. For example, the data of Hitchcock and Palmer show that collodion, which is negatively charged in dilute aqueous solutions, adsorbed a maximum amount of protein in the region of its isoelectric point, while those of Wintersteiner and Abramson show that quartz, which is likewise negatively charged in aqueous solutions, adsorbed insulin as readily from solutions on the alkaline side of its isoelectric point as from solutions on the acidic side. Granting that within the isoelectric range (pH stability region) the micelles are composed of both positively and negatively charged protein ions, it follows that the negatively charged adsorbents would selectively adsorb the positively charged protein ions from the micelles. Moreover, the magnitude of the charge of the individual protein ions associated as micelles would be lower in the isoelectric region and in consequence more of them would be required to neutralize the charge of the adsorbent. This explains why a maximum amount of protein is adsorbed in the isoelectric region.

SUMMARY

The rôle of electrical forces of attraction and repulsion in the adsorption of gliadin on glass has been studied by the streaming potential method. The results obtained support the following conclusions.

1. The adsorption of gliadin on glass from dilute aqueous solutions is an electrical precipitation process.

2. The adsorption process is not completely reversible.

3. A highly purified gliadin preparation is not chemically homogeneous, but contains within the isoelectric range both positively and negatively charged fractions.

4. Gliadin is adsorbed on glass with its free amino and carboxyl groups toward the liquid phase.

5. The free amino and carboxyl groups of the adsorbed gliadin react with acids and alkalis, respectively, within the hydrogen-ion range pH 4.88 to pH 8.83.

6. The *true* isoelectric range of a protein is probably identical with the "pH stability region."

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SUPERHEATING AND FOAMING PHENOMENA IN DEHYDRATING EMULSIFIED OILS[1]

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Received July 9, 1934

Crude petroleum oil, whether obtained from a level of a few hundred feet in the earth's crust or from a level of more than nine thousand feet, usually contains water. When oil and water pass through pipes to the earth's surface, or when pressure is released, an emulsion forms. As a matter of fact, over 200,000,000 barrels (42 gallons each) of emulsified crude oil are dehydrated yearly by means of heat, heat and pressure, chemicals, electrical energy, or combinations thereof.

Crude oil emulsions are usually of the water-in-oil type, while a few show the oil dispersed in water. Some manifest a double type emulsion of water-in-oil and oil-in-water, while others are of the water-in-oil type with oil also dispersed in the water drop. The water content of emulsified crude oils may vary from 0 per cent to over 90 per cent as produced. Emulsified crude oils are, in general, of a highly complex character; this study is directed toward their superheating and foaming characteristics.

The dehydration of emulsified oil by heat is based primarily upon lowering the viscosity and surface tension and changing the colloidal properties of the emulsifier. It is difficult to generalize on the specific effect of heat in the sense of changing the properties of the emulsifier, because the effect produced depends more upon the individual case to be treated, i.e., the nature of the components involved and the physical conditions of the system. A suitable increase in temperature is combined with a change in the state of aggregation, and the steam and oil vapor formed cause breaks in the surrounding protective films. Heat does not effect the separation of water and oil directly, but rather accelerates it. The accelerated precipitation of water does not occur solely on account of the increase in the difference in the specific gravity of the components due to heating. A more rapid precipitation of water on heating may be attributed rather to a decrease in the viscosity of the oil. The temperature to which an emulsion must be heated for complete dehydration depends to a certain extent upon the nature of the crude oil emulsion and may vary widely. When

[1] Presented at the Eighty-fifth Meeting of the American Chemical Society, held in Washington, D. C., March 30, 1933.

the temperature is increased, the density of the hydrocarbon oils decreases more rapidly than the density of water. In heating an oil from 15.55–65.5°C., the decrease in density amounts to about 7 per cent, whereas in heating water from 15.55–65.5°C., the decrease in density amounts to 1.1 per cent. For this reason it is possible to obtain a more rapid separation of oil and water at higher temperatures than at lower temperatures. At a given temperature and with oils of equal specific gravity, the one having the lower viscosity will separate more readily from water. This effect is pronounced when the amount of oil is large as compared with the amount of water. Increasing the temperature of an emulsified oil from 15.55–65.5°C. reduces its viscosity at times as much as 55 per cent. The rate of separation varies with the amount of material charged to the still, the size of the still, the amount and degree of dispersion of the water present in the oil, and the stage of the process.

Two phenomena, well known to the industrial chemist, accompany heat dehydration: first, a priming or puking of the oil to be dehydrated, a kind of explosion caused by a superheating effect; second, foaming of the emulsion. Observations reveal that there is a certain relationship between these two phenomena. Some form of heat treatment is generally used for the removal of water from oil emulsions, therefore it is of interest to discuss both these phenomena.

If an emulsified oil is heated too rapidly, it usually causes the still to puke. Sometimes puking of the oil is effected by irregularities occurring in heating. Occasionally, when the same amount of the same oil is charged to three stills of the same size, one pukes more readily than the others.

Marcet (14) was the first to note that the temperature at which water and certain other liquids begin to boil varies with the nature and the state of the surface of the container in which the boiling takes place. These differences were attributed to a molecular change produced by the surface of the container, or by the presence of certain substances. It has been suggested that the part these substances play is to produce a more or a less perfect contact, or a more or a less close adhesion between the molecules of the liquid and the walls of the container. Whether the conversion of the liquid into vapor is made more difficult or, on the contrary, facilitated, is determined by the action of these substances.

Evaporation and ebullition are both molecular phenomena. Both, depending upon the action of heat, differ in the degree of vapor tension produced, as well as in the rapidity with which the change of the liquid into a vapor takes place. While in ebullition the change of the phase is sudden and visible, occurring simultaneously throughout the liquid, the change of the phase in evaporation is slow and always progressive, restricted to conversion into molecular vapor situated at the surface, or very close to it. Any factor increasing the cohesion of the molecules to each other, or their

adhesion to the walls of the container in which they are enclosed, would have a tendency to slow down the evaporation of this liquid or delay its ebullition.

Donny (4), Dufour (5), and Faraday (6) found that water freed from air does not boil until it reaches a temperature of 132°C. and then it explodes. Water raised to a temperature of 132°C. under ordinary atmospheric pressure remains as water, but the introduction of the smallest amount of air or steam induces it to vaporize immediately and, at the same time, its temperature decreases. Donny assumed that the superheating phenomenon was due to a rupture either in the cohesion of the heated liquid, or in its adhesion to the container. Under ordinary conditions, liquids begin to boil approximately at a temperature required by their vapors so as to establish equilibrium with atmospheric pressure. By the effect of ebullition, liquids lose the greater part of the air held in solution, the boiling of the liquid being influenced principally by cohesion and adhesion. The liquid, free from air and heated beyond its boiling point, finally releases vapor explosively when a lowering of the temperature brings back a momentary quietness to the liquid. Cohesion is the force preventing, or at least delaying considerably, ebullition of liquids free from air. The phenomenon of priming or puking once started continues to reproduce the effect with an increasing violence. If the principle that the liquid has to be freed from air in order to produce the above phenomenon holds true then, by passing a gas through a liquid, the disturbing phenomenon may be avoided. Donny's experiments revealed that this holds true only for certain cases. De la Rive (3) and Dufour (5) studied the change of phases under the influence of temperature. They pointed out that the presence of a foreign substance in a liquid may hasten the evaporation, assuming that the change in phase does not necessarily occur when by heating the liquid a tension equal to the outside pressure is produced, but it may occur partially, owing to certain molecular conditions of the contact to which the liquid is subjected.

The molecular influences of contacts tend to promote vaporization at a minimum temperature. Owing to this fact, noticeable differences in boiling point are observed when water, alcohol, or sulfuric acid is heated in a glass or in a porcelain container (experiments by Donny (4), Marcet (14), and Magnus (12)), or when they are heated away from contact with solid particles. In some cases it appears that the contact of solid particles is a determining cause of the change of phase for fluids. If a globule of liquid comes in contact with a solid particle entrained by currents induced by heat, or with the walls of the container, a sudden production of a vapor bubble takes place. If water is mixed with sand (3) with a liquid layer of a few millimeters thickness, the water evaporates more rapidly in air than the same quantity of water alone. Thus the temperature of a water-sand

mixture evaporating in air is lower than that of water exposed alone under the same conditions. Water containing sea salt also evaporates less rapidly, producing a smaller degree of cooling by its evaporation than water under the same conditions.

Kenrick (10) and his coworkers studied the superheating phenomenon of liquids. A study was made of the extent to which liquids may be superheated and the physical conditions under which superheating is possible, i.e., where temperatures are equal to or higher than those where the elastic force of the liquid produces equilibrium to the external pressure. The question regarding the location of the ebullating and superheating influences also appeared of interest to these investigators. They assumed that ebullition takes place locally, either at a few fixed points on the walls of the

TABLE 1

Association coefficient of liquids as determined by Gilbert

LIQUID	HIGHEST TEMPERATURE	PRESSURE	BOILING POINT	ASSOCIATION COEFFICIENT
	degrees C.	*mm.*	*degrees C.*	
Ethyl ether	143	11,500	35	1.0
Ethyl alcohol	201	22,700	78	2.7
Methyl alcohol	180	20,100	63	3.4
Chloroform	173	11,000	61	1.0
Acetone	174	14,400	56	1.3
Carbon bisulfide	168	11,700	46	1.0
Water	270	41,200	100	2.3–3.8
Sulfur dioxide	50	6,300	−10	1.0
Benzene	203	11,200	79	1.0
Chlorobenzene	250	8,300	132	
Bromobenzene	261	6,100	156	
Aniline	262		183	
m-Xylene	235		137	

vessel, or from particles suspended in the liquid from which actually streams of bubbles rise. If this be true, then the superheating effect should depend on the ability of the liquid to wet the material which serves as a nucleus.

Kenrick found a gradation in the effectiveness of the nuclei present. Some of them caused ebullition when the liquid was slightly superheated; others were effective only when it was heated to a higher temperature. Experimentally, it was not clear whether there was a real temperature limit or merely a rapid shortening of the time interval with increase in temperature. He also found that the smaller the vessel in which the liquid is heated, the higher the temperature to which it could be heated without boiling. Wismer (19) calculated the diameter of a spherical particle act-

ing as a nucleus enclosed by bubbles and found that it was equal to 5×10^{-7} cm. Calculation of the pressure in the bubbles gave a value of about 12.5 atmospheres, corresponding to a temperature of about 130°C. (extrapolated). Gilbert (7) calculated the amount of vapor in a bubble whose pressure, caused by surface tension, balances the outside vapor pressure. Quantities about one hundred times greater than those corresponding to the ordinarily accepted molecular dimensions were determined. This led Gilbert to the conclusion that liquids which can be heated to temperatures corresponding to abnormally high vapor pressures are those which are abnormal in possessing high association coefficients as shown in table 1.

Wismer (18) determined the pressure–volume relations for ether at 121°, 128°, and 134°C. and at corresponding pressures above 30 atmospheres to as low as 1 atmosphere. He made similar measurements with ethyl chloride at 99°, 110°, and 117°C. The P–V curve in both cases appeared to be almost a straight line, and showed no sign of more rapid curving as the limit of superheating was reached, although in both cases the temperatures reached at atmospheric pressure were above the maximum calculated from van der Waals equation.

The most characteristic points in the superheating effect are the extent to which superheating of a given liquid is carried out and the time during which a liquid is kept under these conditions. It was observed that these characteristics vary from one experiment to another. Kenrick, Gilbert, and Wismer (9) attempted to work out these questions concerning superheating phenomenon. Previous work (1, 20) indicated that the superheating of liquids is closely allied to the "stretching" phenomena of liquids (15), as well as to the supersaturation of gases (19).

Supersaturation is favored by long heating of a solution at high temperature. Liquids saturated with gases at concentrations corresponding to a pressure over 100 atmospheres showed that when the pressure was reduced to 1 atmosphere, no bubbles were formed in the liquid. In the case of superheating of liquids, Kenrick, Wismer, and Wyatt observed that with a rise in temperature there is a very rapid shortening of the time interval between the lowering of the pressure and the formation of bubbles, in spite of the fact that the adsorption coefficient of the gas decreased but little with rise in temperature. There is definite evidence in favor of the old theories on the superheating phenomenon, namely, that liquids must be free from gases and air in order to undergo superheating effects.

Krebs (11) removed air from water by mixing it with alcohol (about three times the volume of water) and boiling down the mixture to a small volume (the boiling point rose steadily to 107°C.). When a very large flask was used and the mixture evaporated to a small volume, the boiling point could be increased still more. In the boiling of this water–alcohol mixture, Krebs observed for the first time the coëxistence of superheating and foaming.

There is a certain analogy between the superheating phenomenon in liquids and in emulsion systems. But in the latter, the superheating effect finds its explanation rather in the behavior of the interfacial phase. As early as 1836, Magnus (13) showed that water with oil poured over it presents a considerably delayed ebullition. If oil is poured upon water, the explosive boiling is much more violent. Rideal (16) proved that evaporation of water from a surface is considerably diminished in the presence of fatty acids, such as stearic and oleic, as compared with evaporation from a free surface (8). An increase in the concentration, or in the pressure, upon the surface may also delay evaporation. It is to be expected that surface layers in a condensed or a vapor state primarily influence evaporation. When an oil–water emulsion is heated, the continuous phase, which is covered with a thin layer of oil, must be heated to a higher temperature, to start boiling, than that required to start the boiling of pure water. A sudden decrease from a higher boiling temperature to a lower may be attributed to a change in the Brownian movement during the heating, causing a cessation in the continuity in the interface oil skin and a decrease in temperature.

Taylor (17) in his article "The Structure and Decomposition of Liquid Skins" states that monomolecular layers actually have thick spots which interfere with their stability. It is possible that the problem of whether skins in the interface play a part in the explanation of the superheating phenomenon in emulsion systems may be solved experimentally, using dyestuffs. Frumkin, in a work on spreading dye substances on a water surface, proved that a competition of two substances over the same water surface can be demonstrated. When a drop of oleic acid is placed on a water–crystal violet (dye) surface, then the oleic acid molecules displace the dyestuff molecules and the dyed layer sinks to the bottom in streams. On a water surface previously covered with an oleic acid film, the crystal violet particles of dye remain colorless upon the surface. Tetraiodofluorescein may be used similarly. Perhaps, by means of such a dyestuff, it will be possible to prove whether superheated water in an oil–water emulsion is actually covered with a thin layer of oil, causing a decrease in evaporation, depressing ebullition and, consequently, producing the superheating effect during dehydration of crude oil emulsions.

Foaming is a phenomenon intimately connected with heat dehydration of emulsified oils. Emulsions, in their original form, often cannot be subjected to distillation without high danger of foaming over. The foaming is, of course, undesirable, not only because distillation must be repeated, but also because of the ever-present danger of fire. A belief is entertained that incipient foam formation with a rapid breaking down of the foam may play a large part in the mechanism of dehydration itself. Pressure and high temperature are two factors which favor the dehydration process, reducing

at the same time the foaming tendency of the emulsion system. Pressure weakens the foam film structure; at higher temperatures the ability of oil to make and to maintain individual foam laminae is decreased. In petroleum emulsions the emulsifying agent is usually asphalt, "soaps," or mineral matter, and the decreased foaming with increase in temperature is due less to change in composition at the temperature at which foaming ceases than to a decreased protective action.

A number of experiments were carried out in connection with foam formation in heat dehydration of emulsified crude oils. The first question arising in connection with the problem concerns itself with the conditions under which foam originates in crude oil emulsions.

1. It was found that for the same temperature more water may be separated from an emulsion where a vapor space is present, than where no vapor space exists.

When one-quarter, one-half, or three-quarters of the still capacity was charged with a crude oil emulsion having 36 per cent of water and heated to 121.1°C. under a pressure of 2.74 kg. per square centimeter, 10 to 12 per cent of water was separated. When a full charge was maintained at the same temperature, 121.1°C., although using a pressure of 3.31 kg. per square centimeter only 6 per cent of water separated out.

The lack of vapor space prevents substantial foam formation which, in all probability, accounts for the difference in the dehydration effect.

2. A series of tests was made with sixteen samples of California emulsified oils to determine their foaming properties. The emulsified oils to be investigated were charged in beakers, immersed in a glycerol heating bath, and the foaming properties and height of the foam noted. The California emulsified oils which were experimented with had a water content ranging from 6 per cent to 69 per cent. The temperature of the glycerol bath in these comparative tests was maintained constant at 177°C. It was found that under the temperature conditions prevailing the foam column in the emulsified crude oil varied from 1½ in. to over 5 in. in height. It is interesting to note that a mixture of California oils No. N6 and N2 taken in equal portions showed a foam column height which was higher than when the oils were subjected singly to the same heating. California oil No. N6 with 6 per cent water: foam height, 3.8 cm. California oil No. N2 with 30 per cent water: foam height, 10.5 cm. A mixture of the two oils in equal proportions: foam height, 11.8 cm.

This brings out, as far as these tests are concerned, that the properties of emulsified crude oils as to foaming are not additive when mixed. One would expect that the foam column of California oil No. N2 would be reduced, owing to the addition of an oil having a low water content. However, this is not the case. As a matter of fact, the diluted oil No. N6 did not decrease the foam column, but actually increased it.

3. Distilling of crude oils of different origin revealed that foam formation in emulsified oils depends greatly upon the nature of the crude oil. The crude oils compared were derived from Casmalia, Santa Maria, Lompoc, and Efson oil wells. Casmalia oil is very persistent in foaming; Santa Maria oil foams slightly; Lompoc oil foams strongly; Efson oil foams, showing explosive characteristics.

Some emulsified oils distill quickly and then begin to foam after distillation has proceeded for a while, whereas other oils foam violently from the beginning of heat application.

Lompoc emulsified oil from Efson well No. N10 produced more foam at 149°C. than any Santa Maria crude oil tested, but Casmalia crude oil was the most persistent foam producer of all those experimented with. It was found further that the Lompoc oil acted in an explosive manner when heated. To overcome the violent bumping of this oil, gasoline was added to it and the foaming test conducted. The oil evaporated in a much less violent manner, but spattered and spat during the heating, and the foam was not persistent. This indicates that the gasoline added to the Lompoc emulsified oil has a marked influence upon its foaming and evaporating properties.

Some emulsified oils, upon application of heat, form relatively small foam bubbles, while others produce large bubbles.

4. The effect of temperature on the foaming properties of the emulsified oil was studied as a function of the depth of the liquid placed in the tubes. The oil investigated was Santa Maria crude oil containing 29 per cent of water. The procedure was to charge glass test tubes 2.24 cm. in diameter and 20.3 cm. long filled with 1, 2, and 3 cc. of Santa Maria emulsified oil which were immersed to 17.8 cm. of their length in a heated glycerol bath. After the glycerol bath reached the desired temperature, the tube containing the emulsified oil was placed therein. At the beginning of the test, the emulsified oil distilled quietly, with little foaming. As vapors passed from the top of the tube, a time was reached when the foam which started in a fine dispersion became coarse and persistent. The foam rising in the tube became at times somewhat irregular, seeming to give a breathing action, but finally attained a maximum and then gradually subsided. The maximum height which the foam column reached was recorded and all comparisons made in a similar manner.

It was found that the foam column of the Santa Maria emulsified oil increased as a function of the depth of the oil in the tube, and also increased as a function of the temperature employed, to a maximum which was attained at a glycerol bath temperature of 140°C., the foam column decreasing as the temperature of the bath reached 176°C.

Table 2 gives the order of the foam formation, as a function of the temperature variation, and depth of liquid employed during this set of experiments.

5. Finally, from a series of tests in which California emulsified crude oils were dehydrated, it was ascertained (a fact already indicated by Krebs (11), that foaming in heat dehydration was combined with the superheating effect discussed previously, as well as with self-cooling. Usually, during the heating of California emulsified oils, the temperature rose quite rapidly to a little above the boiling point of water, where it remained relatively

TABLE 2

Order of foam formation

TEMPERATURE OF BATH	VOLUME OF EMULSIFIED OIL USED		
	1 cc.	2 cc.	3 cc.
degrees C.			
125	16	19	32
140	32	52	80
150	34	49	70
160	26	42	50
176	23	33	44

TABLE 3

Foam in heat dehydration combined with superheating effect and self-cooling

PHASES IN HEATING PROCESS	TEMPERATURE IN DEGREES C.	CHARACTERISTICS OF FOAMING
	Oil sample No. 1	
I Phase	Up to 111.1	Little foaming
II Phase	Drop in temperature to 102.2 constant for a time	Foam column rising
III Phase	Rise in temperature from 102.7 to 104.4	Foam column starting to collapse
	Oil Sample No. 2	
I Phase	Up to 107.2	Slight foaming
II Phase	From 107.2 to 102.2	Foaming increases
III Phase	From 101.6 to 111.1	Foaming rapidly recedes
	At 150.0	Foaming almost zero

constant for a time until a portion of the water was distilled from the oil, the temperature rising until a maximum was reached where the oil was dehydrated with a few fine drops of water still dispersed in the tar residue. With several of the emulsified crude oils, a marked departure from the behavior just described was noted.

Santa Maria crude oil from Rice Ranch well No. N2 showed a distinct superheating effect with rise in temperature followed by more or less foam-

ing, a drop in the temperature of the oil taking place despite the fact that the oil was still being heated. In other words, water was apparently held in the oil above its boiling point, and by this superheating suddenly formed steam, with cooling taking place in the liquid. The mechanism would, therefore, be either that the oil system during this period absorbed heat from the oil faster than from an external source to an extent of producing a cooling effect (manifested by an actual drop in the temperature of the oil), or, under critical temperature conditions, the protective films were ruptured, or else chemical changes occurred in the emulsifying agent (a dissociation of the hydrates of the hydrocarbons present in the emulsified crude oil system), which took heat from the system, thereby cooling it.

In table 3 are illustrated (on two samples) the three phases in heat conditions of a Rice Ranch Santa Maria crude oil emulsion accompanied by foaming.

SUMMARY

Two phenomena accompany heat dehydration of emulsified oils: priming or puking, and foaming, resulting from superheating water.

Superheating of various liquids may be compared with superheating of emulsified oils. The conversion of a liquid into its vapor state is influenced by the character of the surface of the container in which the boiling occurs, or by the presence of solid particles in the liquid. Cohesion of molecules of the liquid or their adhesion to the walls of the container or suspended solids slows down evaporation and delays ebullition. Liquids freed from air are apparently a critical condition for the delay in ebullition. The extent of superheating is determined by the temperature necessary for sustaining equilibrium of the liquid against external pressure. Ebullition is restricted to certain localities in the liquid. A gradation in the effectiveness of the material serving as a nucleus for the superheating phenomenon is observed. The extent to which superheating of a liquid is carried out, and the time during which it is held under a superheated condition are the characteristics and the variables in the process.

An analogy between superheating and foaming effects in liquids and emulsions may be postulated, considering the significance of the interfacial phase in the case of emulsions. A thin layer of oil spread upon superheated water in an oil–water emulsion is responsible for the decrease in the evaporation of the system, depressing ebullition.

The mechanism of dehydration includes, in addition to the prevention of the superheating influences, the break-down of foam formed during the process. Pressure and high temperature favoring dehydration likewise reduce the tendency of the emulsion system to foam. At the same temperature, more water may be separated from an emulsion where a vapor space is present than where no vapor space exists. The lack of vapor

space substantially prevents foam formation, thus accounting for changes in the dehydration effect. The properties of emulsified crude oils with respect to foaming are not additive. The intensity and persistence in foaming of emulsified oils which are to be dehydrated is decided by the nature of the oil. Foaming and evaporation of water from the emulsified oil are markedly influenced by certain substances, for example, gasoline. The foaming of emulsified oil increases as a function of the depth of the oil in the container, reaching its maximum at a definite temperature.

Superheating and foaming observed in the dehydration of emulsified oils produce evidence for the existence of a self-cooling effect. The latter may be interpreted as a result of superheating when the heat from the oil is adsorbed faster than from an external source. It may also be due to a rupture of protective films or else to chemical changes occurring in the system, requiring heat to be taken from the system itself and thereby cooling it.

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A SOURCE OF ERROR IN THERMOCHEMICAL MEASUREMENTS MAKING USE OF COMMERCIAL OXYGEN

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Received November 30, 1933

In a previous paper (1) it has been shown that the apparent value obtained for the water equivalent of a calorimeter is dependent not only upon the small amounts of combustible impurities usually present in commercial oxygen, but also upon the pressure in the cylinder at the time of delivery of its contents into the bomb. With the particular samples of oxygen (denoted G and K) by means of which this phenomenon was first brought to light, there was a gradual decrease in the apparent value for the water equivalent; this decrease ultimately reached seven and five parts per ten thousand for G and K, respectively, after the pressure in the cylinder had dropped from about 125 to 35 atmospheres. It will be the object of the present paper to investigate whether compressed oxygen does always show the same behavior under the particular conditions prevailing in bomb calorimetry.

I. THERMOCHEMICAL DATA IN SUPPORT OF THE CONTENTION THAT THE PURITY OF THE OXYGEN DELIVERED INTO A BOMB IS DEPENDENT UPON THE PRESSURE IN THE OXYGEN CYLINDER AT THE TIME OF DELIVERY

Two series of combustions were carried out with a constant amount of standard benzoic acid in the bomb and at a fixed initial temperature; for the first series, oxygen (sample J) from unknown origin was used throughout, while for the second series, the oxygen (sample M) had been obtained from liquid air by fractionation. In both cases the oxygen was delivered into the bomb to a constant pressure of 35 atmospheres.

A. Data relative to oxygen J

In order to estimate from the figures in table 1 the amounts of the combustible impurities present in the oxygen delivered at the various pressures, it is necessary to compare them with those obtained from the head portions of four different cylinders of oxygen, namely, L, K, G, and E (see table 2), by means of which the value of a constant heat capacity had been determined in an earlier series of combustions with the same preparation of standard benzoic acid and under exactly the same conditions as in

the case of oxygen J (or later on oxygen M). In the case of oxygen E, all traces of combustible impurities had been removed by a previous purification.

It is difficult to suppose that such a remarkable agreement between so many individual values and especially between the means, which are identical for all practical purposes, is entirely due to chance. When it is further taken into account that there is a similar kind of agreement between the heats of combustion found at various periods with several different cylinders of oxygen, when the precaution was taken to determine the water equivalent with the same oxygen as for those heats of combustion and as simultaneously as possible with the latter, it must be concluded that the influence of chance must obviously be ruled out altogether.

TABLE 1

Apparent variation of the water equivalent for decreasing pressures of the oxygen in cylinder J

PRESSURE	WATER EQUIVALENT	MEAN WATER EQUIVALENT
atmospheres	*cal.$_{15}$ per degree*	*cal.$_{15}$ per degree*
122 ± 1	4274.7 4273.3 4272.8	4273.6
90 ± 1	4273.6	4273.6
71 ± 1	4275.5 4276.3	4275.9
38 ± 3	4275.4 4274.8	4275.1

B. Data relative to oxygen M

The results obtained for the apparent value of the water equivalent with some new oxygen (M) were found to be strikingly similar to those just recorded for oxygen J, as will appear from an examination of tables 3 and 4. The similarity is so complete, indeed, that the values obtained with sample J may be used for sample M as well for all pressures recorded, at least within the very small margin of a few tenths of 1 calorie for the experimental error.

In order to simplify the problem raised by the above data, it was felt advisable to arrange the experimental conditions so as to obtain results which could correspond only to one impurity at a time. Such a result was not impossible to attain by purely thermochemical means, namely, by preparing or purifying some oxygen and then adulterating it with a known

amount of one single and well-defined impurity. But as it meant purifying compressed oxygen at a temperature of about 800°C. in order to free it from any combustible impurity possibly contained in it, or alternately purifying oxygen at ordinary pressure and afterwards compressing it to at least 100 atmospheres, it introduced considerable technical difficulties. Such a solution will be tried in the future, as soon as some conditions required for its successful fulfillment will have been realized. For the present a

TABLE 2

Values obtained for the water equivalent for pressures above 100 atmospheres in the cylinder and 35 atmospheres in the bomb, with oxygen from the cylinders L, K, G, and E

OXYGEN	PRESSURE IN CYLINDER	BENZOIC ACID USED NO.	WATER EQUIVALENT	MEAN WATER EQUIVALENT
			cal.₁₅ per degree	*cal.₁₅ per degree*
L	121/102	48a	4277.6 4276.9	4277.2
K	116/113	48a	4276.3 4276.5 4277.8 4277.4	4277.0
K	112/109	39b	4276.8 4277.0 4276.5 4278.7	4277.2
G	123/121	39b	4277.7 4277.0 4276.6	4277.1
E	Preheated	39c	4277.4 4278.0 4276.3 4275.6 4278.0	4277.1

simpler, though quite efficient, procedure has been devised, which is based upon the fact that in the combustion inside the bomb, under well-defined conditions, of a constant amount of a definite substance in the presence of oxygen containing a small amount of nitrogen as impurity, a constant proportion of the latter is converted to nitric acid; by means of a simple titration of the acid with standard alkali the percentage of nitrogen impurity present in any one bomb filling may thus be determined.

II. PREPARATION AND ANALYSIS OF A MIXTURE OF OXYGEN AND NITROGEN IN SUITABLE PROPORTIONS AND UNDER A TOTAL PRESSURE OF ABOUT 100 ATMOSPHERES

A mixture of oxygen and nitrogen containing approximately 0.1 per cent of nitrogen was first prepared. This mixture was then used for combustions of a fixed amount of 1.72 g. of pure salicylic acid, under a constant

TABLE 3

Apparent variation of the water equivalent for decreasing pressures of the oxygen in cylinder M

PRESSURE IN CYLINDER	WATER EQUIVALENT	MEAN WATER EQUIVALENT	MEAN ERROR FOR MEAN IN PARTS PER THOUSAND
atmospheres	*cal.15 per degree*	*cal.15 per degree*	
135/132	4273.3 4273.1 4275.2	4274.0	0.05
80/77	4275.6 4275.7 4275.6	4275.6	0.00
47/44	4274.2 4275.7 4275.5	4275.1	0.03

TABLE 4

Comparison between the variations in the water equivalent when determined with oxygen J and oxygen M, respectively

PRESSURE IN CYLINDER	MEAN WATER EQUIVALENT		NUMBER OF COMBUSTIONS
	Oxygen J	Oxygen M	
atmospheres	*cal.15 per degree*	*cal.15 per degree*	
135		4274.0	3
120	4273.6		3
80		4275.6	3
70	4275.9		3
40	4275.1	4275.1	3 + 3

pressure of 35 atmospheres in the bomb and with a calorimeter at a constant initial temperature of 20.5°C. The successive amounts of nitric acid found as the pressure in the cylinder decreased from 110 to 15 atmospheres have been collected in table 5. The results recorded for pressures in the cylinder which were lower than the final pressure in the bomb have been obtained by means of the following artifice: the bomb was first filled to a pressure of

15 atmospheres with the oxygen–nitrogen mixture; it was then connected with the particular cylinder of nitrogen-free oxygen already used for making up the oxygen–nitrogen mixture, until the pressure had risen to the usual mark of 35 atmospheres, in order to allow for the lesser amount of nitrogen impurity introduced in the bomb as the result of this procedure. Three blank combustions were also carried out with the nitrogen-free oxygen.

A consideration of table 5 shows that there is first an unmistakable increase in the amount of nitric acid formed during the successive combustions, as the pressure in the cylinder decreased from 110 to 55 atmospheres; indeed, for a pressure of 81 to 74 atmospheres, the amount of nitrogen converted to nitric acid was found to be just double of that obtained at the

TABLE 5

Mean correction to be applied to the water equivalent for different ranges of pressure in the cylinder in order to allow for the formation of nitric acid

PRESSURE IN CYLINDER	NITRIC ACID CORRECTION	MEAN NITRIC ACID CORRECTION
atmospheres	*calories*	*calories*
106/98	0.3 0.8 0.7	0.6
81/74	0.5 1.3 2.1	1.3
61/55	1.9 2.6 2.7	2.4
20/18	0.0 0.5 0.1	0.2

higher pressure; and for a further drop of pressure down to 61 to 55 atmospheres, the amount of nitric acid formed was four times as large as the original amount found. When, however, the pressure in the cylinder had fallen to about 20 atmospheres, the results obtained for the nitric acid were just below those found at the very start (after the difference between the mean for these results and the mean for the blanks had been multiplied by the factor 15/35 in order to allow for the lesser concentration of the nitrogen impurity in the three final bomb fillings made with the nitrogen mixture and thus to render the final data entirely comparable with the original ones).

CONCLUSIONS

Whatever the true cause of the phenomenon recorded in the preceding pages, the following conclusions will apply:

(1) The statement made in a previous paper that the concentration of a combustible impurity eventually present in compressed oxygen may vary appreciably with the pressure in the cylinder at the time of delivery into the bomb, has been confirmed with three more cylinders of oxygen, one of unknown source and the other two derived from liquid air.

(2) The apparent value for the water equivalent of a calorimetric system, when determined by means of oxygen from any of these cylinders, all received from the British Oxygen Company, showed a total variation of the order of five to seven parts in ten thousand, which therefore cannot be ignored if a precision of the order of one or two parts per ten thousand is to be secured.

(3) The character of the curve, water equivalent against pressure in the cylinder, as revealed by the investigation of four different cylinders, may take one or other of two different forms, presumably depending upon the nature of the combustible impurity causing the contamination.

In conclusion, the author wishes to tender his thanks to Prof. E. C. C. Baly, Head of the Inorganic Department, for the facilities provided for this research.

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CHROMIUM HYDROXIDE HYDROSOLS AND THE BURTON-BISHOP RULE

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Received May 7, 1934

INTRODUCTION

Burton and Bishop (3), working with copper, gum mastic, and arsenious sulfide hydrosols, concluded that the flocculation values increase with decreasing concentration of sol for monovalent ions, remain about the same for divalent ions, and decrease for trivalent ions. This conclusion is referred to as the Burton-Bishop rule (4). It has been demonstrated that, whereas moderately purified ferric oxide and chromic oxide sols do not follow the above rule for monovalent ions (2, 5, 6), highly purified ferric oxide sols do (4). The experimental results presented in this paper show that highly purified chromic hydroxide hydrosols, like ferric oxide hydrosols, follow the Burton-Bishop rule.

PREPARATION OF SOLS

Normal ammonium hydroxide was slowly dropped into a normal chromium chloride solution at 60–70°C. with constant shaking until six-tenths of the stoichiometric amount had been added. Two purified sols were prepared from the stock sample by dialysis in collodion bags. Table 1 gives data on the preparation and some of the properties of the two sols.

RESULTS

Flocculation values were determined in the usual standard manner (4) and are reported as millimoles of electrolyte per liter of solution. With all sols flocculation values were determined with the original sol, referred to as 100 per cent, and concentrations of 80, 60, and 40 per cent of the original, dilution being made with water and, in some instances, with ethyl alcohol. The data that follow are typical of the results obtained.

Table 2 shows the flocculation values for different electrolytes with sol No. 1, dilutions being made with water. Table 3 shows the flocculation values for the same sol, dilutions being made with 95 per cent ethyl alcohol.

Table 4 and figure 1 show flocculation values for sol No. 2, dilutions being

TABLE 1

Data on preparation and properties of the two sols

SOL NO.	TIME OF DIALYSIS	TEMPERATURE OF DIALYSIS	CONCENTRATION OF CHROMIUM	RELATIVE VISCOSITY	pH	PURITY
	hours	*degrees C.*	*grams per liter*			
1	48 48	80 60	0.814	1.580	3.7	Slight precipitate with $AgNO_3$
2	96	85	0.769	Too viscous to measure	6.1	No precipitate with $AgNO_3$

TABLE 2

Flocculation values for different electrolytes with sol No. 1

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	1.4	1.8	2.2	2.7
KCl	1.5	1.7	2.3	2.7
$BaCl_2$	0.9	1.3	1.6	1.9
Na_2SO_4	0.05	0.06	0.05	0.06
Na_3PO_4	0.03	0.03	0.03	0.02

TABLE 3

Flocculation values for different electrolytes with sol No. 1

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	1.4	1.7	1.9	2.3
Na_2SO_4	0.05	0.05	0.05	0.04
Na_3PO_4	0.03	0.03	0.03	0.03

TABLE 4

Flocculation values for different electrolytes with sol No. 2

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	0.3	0.9	1.5	2.2
KCl	0.4	0.9	1.4	2.3
$BaCl_2$	0.3	0.8	1.0	1.2
Na_2SO_4	0.04	0.04	0.04	0.04
Na_3PO_4	0.032	0.03	0.024	0.02

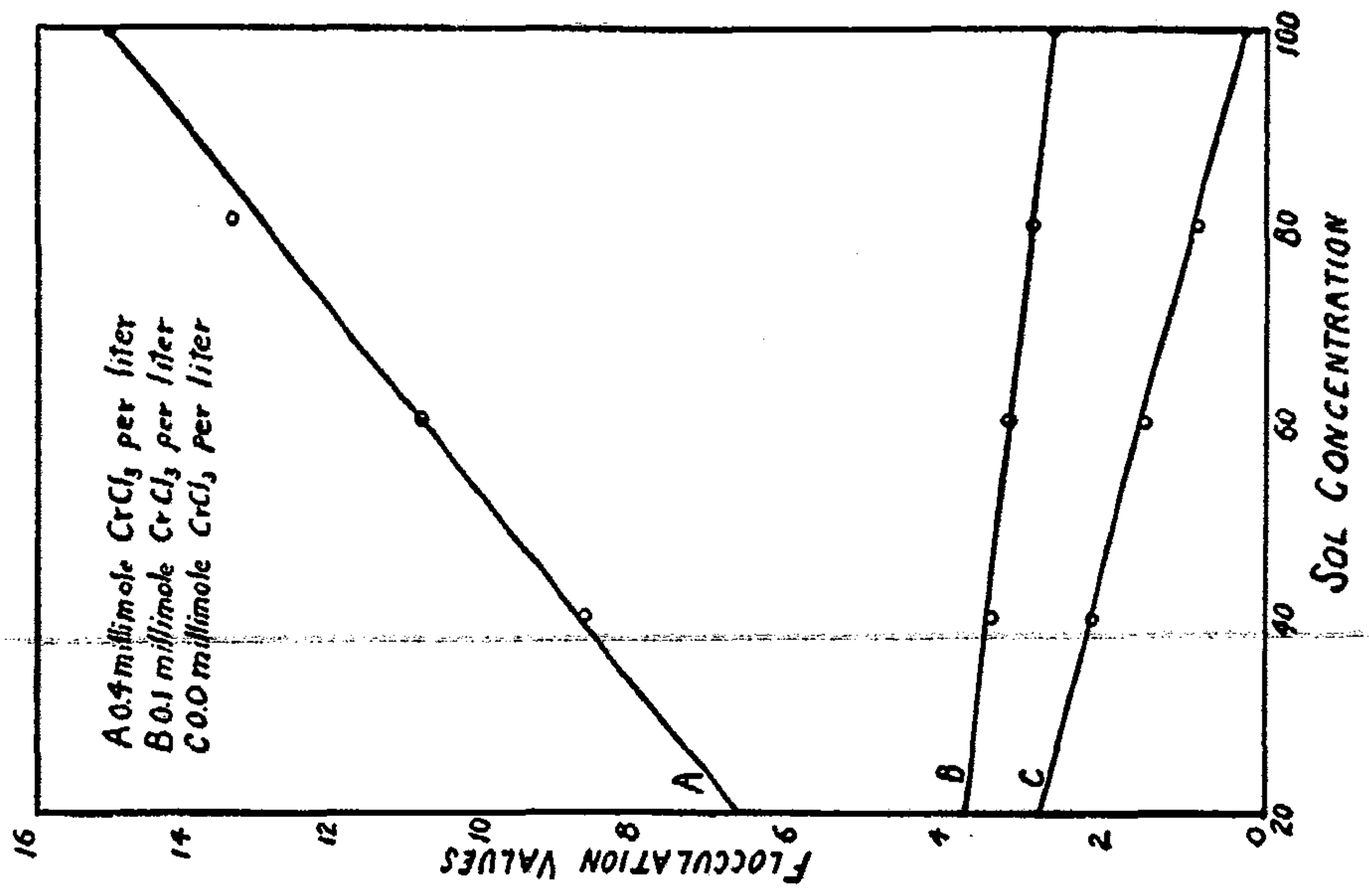

Fig. 2

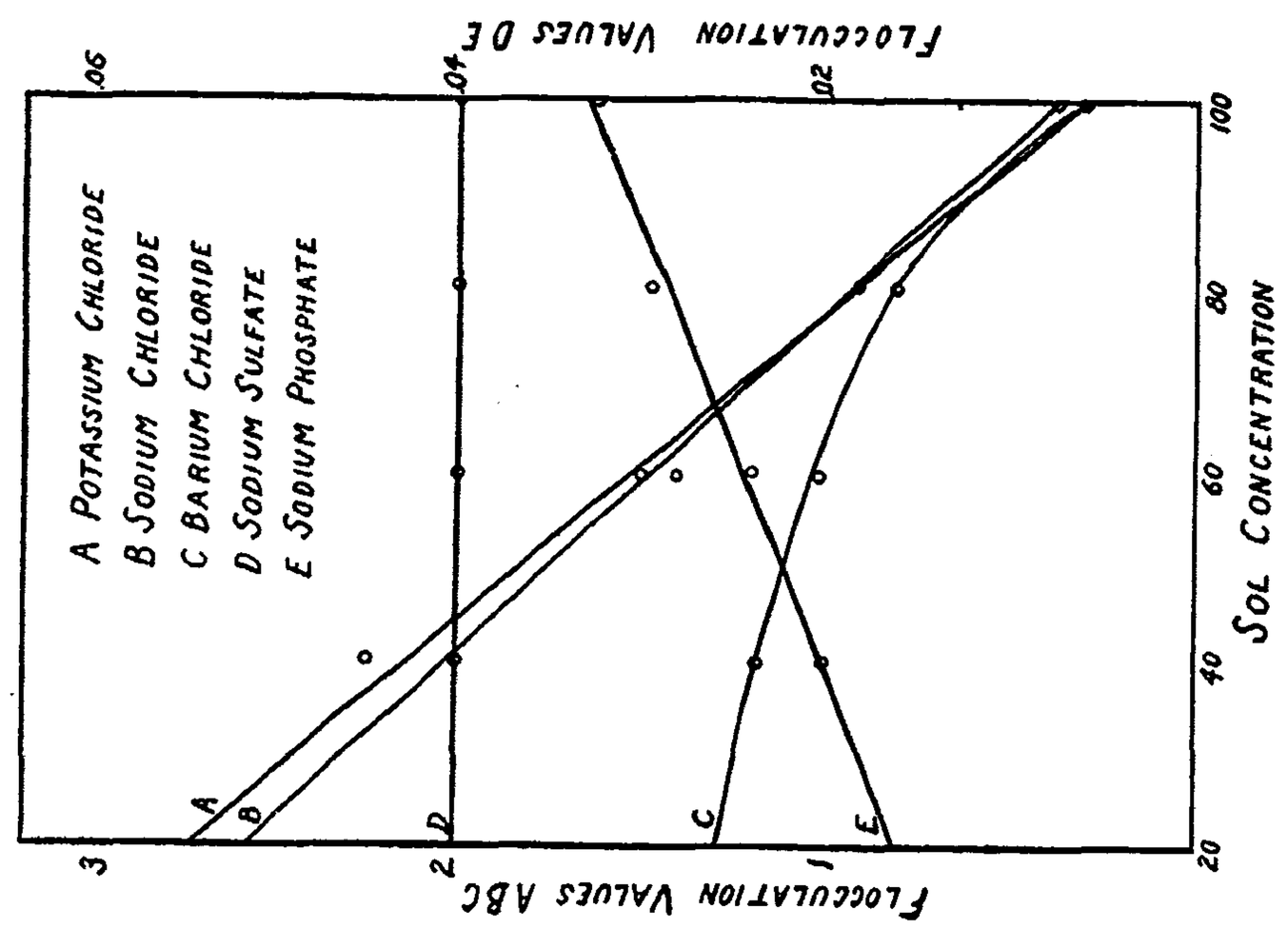

Fig. 1

Fig. 1. Change of Flocculation Value with Sol Concentration

Fig. 2. Sol Purity and Change of Flocculation Value

made with water. Table 5 shows flocculation values for the same sol, dilutions being made with 95 per cent ethyl alcohol.

Stock samples of sol No. 2 were made impure by adding respectively 0.1 and 0.4 millimoles of chromium chloride per liter. Dilutions were made with water and flocculation values for sodium chloride determined as above. The results are given in table 6 and figure 2.

TABLE 5

Flocculation values for different electrolytes with sol No. 2

ELECTROLYTE	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
NaCl	0.3	0.7	0.5	0.04
Na_2SO_4	0.04	0.06	0.03	<0.001
Na_3PO_4	0.032	0.04	0.02	<0.001

TABLE 6

Flocculation values obtained with sol No. 2 and sodium chloride in the presence of chromium chloride

CHROMIUM CHLORIDE ADDED	FLOCCULATION VALUES WHEN SOL CONCENTRATION IS			
	100 per cent	80 per cent	60 per cent	40 per cent
millimoles				
0	0.3	0.9	1.5	2.2
0.1	2.7	3.0	3.2	3.4
0.4	15.0	13.4	10.5	8.8

DISCUSSION OF RESULTS

The purified sols follow the Burton-Bishop rule for all ions (tables 2 and 4, figure 1). When sufficient chromium chloride is added to the purified sols they fail to follow the rule for monovalent ions (table 6, figure 2). This fact, combined with the fact that the slope of the curve obtained when flocculation values are plotted against sol concentration (figure 2) varies with the purity of the sol, strengthens the conclusion (4) that the applicability of the Burton-Bishop rule is a function of sol purity.

When dilutions are made with alcohol the very highly purified sols (table 4) do not follow the Burton-Bishop rule for monovalent ions, but the less highly purified sols (table 2) do. The stability of chromic hydroxide hydrosols is due to hydration as well as ion adsorption. In the very highly purified sol the rôle of hydration is probably relatively great; in the less highly purified sol it is relatively small. Alcohol is a dehydrating agent; accordingly it will sensitize and even coagulate a hydrated sol (1). When a very highly purified sol is diluted with alcohol, the relative dehy-

drating effect may be so great and the sensitization so acute that the Burton-Bishop rule does not function. When a less highly purified sol which owes less of its stability to hydration is diluted with alcohol, the sensitization produced by dehydration is so slight compared to the initial stability due to ion adsorption that the dilution effect still follows the Burton-Bishop rule.

SUMMARY

The applicability of the Burton-Bishop rule to chromium hydroxide hydrosols is a function of the purity of the sol; highly purified sols follow the rule, impure sols do not.

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THE DIFFUSION COEFFICIENTS OF MOLECULES AND IONS FROM MEASUREMENTS OF UNDISTURBED DIFFUSION IN A STATIONARY MEDIUM

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Received May 10, 1934

Numerous measurements of the rate of penetration of dissolved substances into diffusion media have been made. The work of Stiles (2), who used an indicator for determining the rate of penetration of electrolytes into gels, illustrates a simple and direct type of experimental method for such measurements. However, the results of many such measurements have been expressed by means of empirical equations which do not permit the calculation of diffusion coefficients. The various equations which have been derived for the calculation of diffusion coefficients appear either to be inapplicable to this particular type of experimental method, or to involve a complicated and sometimes questionable method of calculation. This is particularly true of the calculation of the diffusion coefficient of an individual ion of an electrolyte in solution.

The purpose of the present paper is to present a simple mathematical basis for such methods, and to point out a relationship between the distance of penetration and the diffusion coefficient which should be useful for measurements with solutions.

DIFFUSION OF UNCHARGED PARTICLES

If a diffusing particle is placed in the center of a tube of motionless diffusion medium of indefinite length at zero time, then the probability curves for the position of the particle at later times are shown in figure 1a. These probability curves are expressed by the well-known Gaussian equation,

$$y = \frac{1}{q(2\pi)^{\frac{1}{2}}} e^{-\frac{X^2}{2q^2}} \tag{1}$$

where $y\mathrm{d}X$ is the probability of the particle being in any given section, $X - X + \mathrm{d}X$, in the diffusion medium and q is a function of the diffusion coefficient D and the time t.

This family of curves represents also a family of concentration curves if a large number of diffusing particles are placed in the central section at

zero time. Under such conditions the number of particles in any given section, $X - X + dX$, is given at any time by

$$ny\,dX = \frac{n}{q(2\pi)^{\frac{1}{2}}} e^{-\frac{X^2}{2q^2}} dX. \tag{2}$$

Thus the concentration in this section is $ny = m$, and

$$m = \frac{n}{q(2\pi)^{\frac{1}{2}}} e^{-\frac{X^2}{2q^2}} \tag{3}$$

But q^2, the mean square deviation from the mean, is given by

$$q^2 = \frac{1}{n} \sum_{i=1}^{i=n} (X_i - \bar{X})^2 \tag{4}$$

where $\bar{X}$ is the mean distance traveled by the particles in time t. For uniform diffusion in both directions

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{i=n} X_i = 0 \tag{5}$$

and therefore

$$q^2 = \frac{1}{n} \sum_{i=1}^{i=n} X_i^2 \tag{6}$$

But this is the value of $\overline{\Delta x^2}$ in the equation of Einstein (1)

$$\overline{\Delta x^2} = \frac{1}{n} \sum_{i=1}^{i=n} X_i^2 = 2Dt \tag{7}$$

Substituting $2Dt$ for q^2 in equation 3,

$$m = \frac{n}{(4\pi Dt)^{\frac{1}{2}}} e^{-\frac{X^2}{4Dt}} \tag{8}$$

In this equation, m is the concentration of diffusing particles at any distance X from the central section at any time t, $\frac{n}{(4\pi Dt)^{\frac{1}{2}}}$ representing the concentration in the central section at that time.

If the concentration in the central section is kept constant at m_0, each ordinate in figure 1a will in effect be multiplied by a constant times $(4\pi Dt)^{\frac{1}{2}}$ and as a result a family of concentration distance curves as in figure 1b and equation 9 will be obtained.

$$m = m_0 e^{-\frac{X^2}{4Dt}} \tag{9}$$

or

$$\frac{X^2}{4Dt} = \ln m_0 - \ln m \tag{10}$$

or for any given constant value of m ($= m'$)

$$D = \frac{X^2}{4t} \frac{1}{\ln m_0 - \ln m'} \tag{11}$$

Thus the value of the diffusion coefficient may be determined, m_0 being the concentration in the central section and X being the distance from the central section at which the concentration is m' at time t.

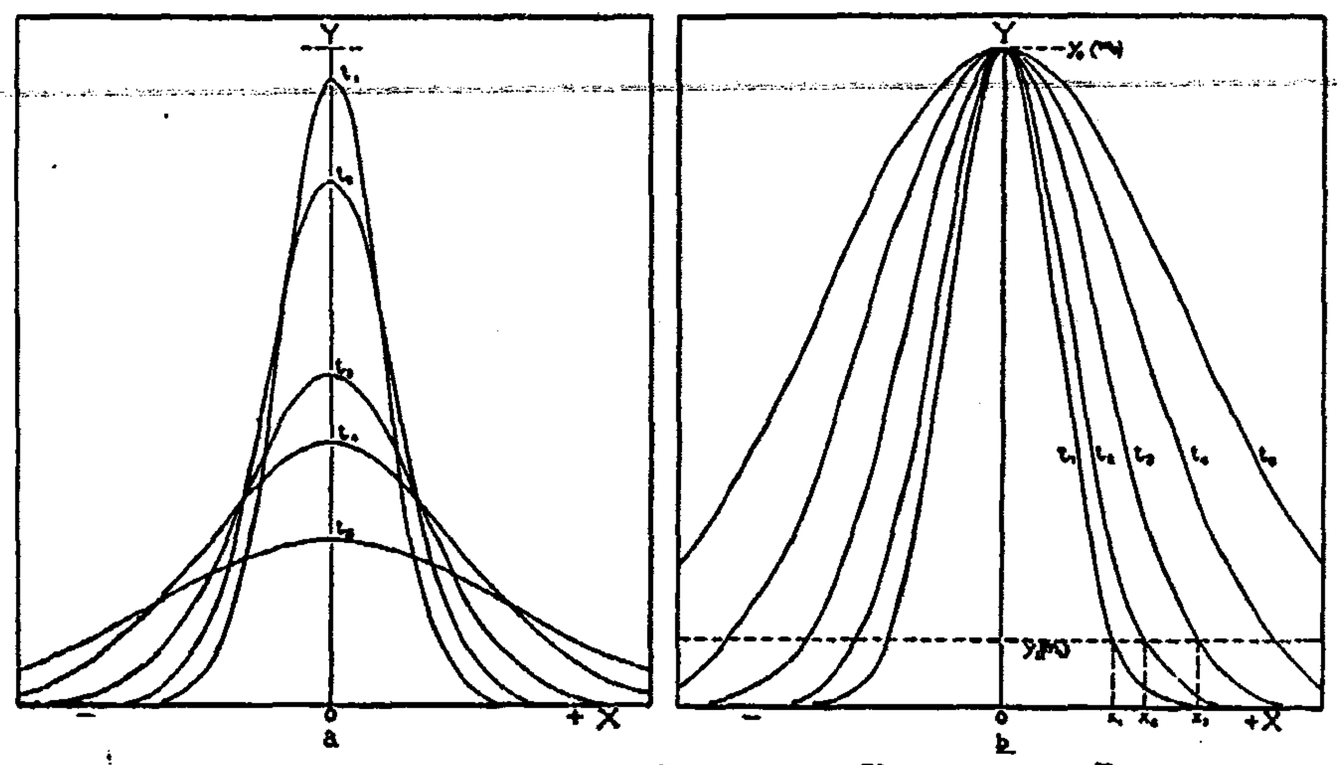

FIG. 1. CONCENTRATION–DISTANCE CURVES FOR UNDISTURBED DIFFUSION

DIFFUSION OF CHARGED PARTICLES

If the diffusing particles are ions, the distance of penetration due to normal diffusion X will differ from the experimentally determined distance X_a by the amount X_e, where X_e is the distance migrated by the ions due to the potential gradient resulting from the diffusion potential E. For very small values of m', we may assume that the diffusion potential in the system is distributed uniformly over the distance X_a, and the velocity of migration is therefore

$$\frac{dX_e}{dt} = U\frac{E}{X_a} \tag{12}$$

where U is the mobility of the diffusing ion. Since both this velocity and the velocity due to normal diffusion are inversely proportional to the distance of the concentration m' from the central section, the sum of the

two velocities $\left(\frac{dX_a}{dt}\right)$ must also be inversely proportional to this distance and therefore

$$\frac{X_a^2}{t} = k \qquad (13)$$

Thus X_a^2 is proportional to the time, as has been observed by many investigators (2, 3, 4).

The value of X_e is given by

$$X_e = \int_0^t U \frac{E}{X_a} dt = \frac{2UE}{k^{\frac{1}{2}}} t^{\frac{1}{2}} \qquad (14)$$

Therefore

$$X = X_a - \frac{2UE}{k^{\frac{1}{2}}} t^{\frac{1}{2}} = \left(1 - \frac{2UE}{k}\right) X_a \qquad (15)$$

Substituting the values of X and k into equation 11

$$D = \frac{X_a^2}{4t}\left(1 - \frac{2UE}{\frac{X_a^2}{t}}\right)^2 \frac{1}{\ln m_0 - \ln m'} \qquad (16)$$

Equation 16 reduces to equation 11 if the diffusing particles are uncharged or if the diffusion potential is zero.

Preliminary results of colorimetric measurements of the penetration of cupric chloride into gels indicate that the equations suggested are useful and accurate.

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THE HEATS OF ADSORPTION OF CERTAIN ORGANIC VAPORS ON ACTIVATED CHARCOAL AT 25°C. AND 50°C.[1]

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Received January 12, 1934

The heat evolved on contact of a vapor with an adsorbent is one of the most important and characteristic quantities associated with the adsorption phenomenon. It has been calculated most generally from the slopes of the isosteres. McBain (12), however, claims that this method is physically impossible when the saturation values are different at different temperatures and an amount of sorption within the range of saturation values is under consideration. The basis of this claim is the fact that the equation involved,

$$\frac{d \ln p}{dT} = -\frac{q}{RT^2}, \quad \text{or} \quad \frac{d \ln p}{d(1/T)} = \frac{q}{R}$$

applies quite strictly also when the saturation pressure is just exceeded and liquid is being condensed. In general (6), it has been found that the heats of adsorption thus calculated are usually lower than those experimentally determined.

The refinements in the use of the ice calorimeter first made by Lamb and Coolidge (6), and later by Marshall and Bramston-Cook (11), have made this instrument a means of precise measurement of the heat of adsorption. Gregg (4) has employed both the ice calorimeter and the phenol calorimeter at 40.36°C. Employing a copper calorimeter similar to that used in measuring heat capacities at low temperatures, Magnus and his coworkers (9, 10) have measured the heat of adsorption of carbon dioxide on charcoal at 0°C. and 25°C.

In spite of the accuracy attainable, the use of the ice calorimeter involves one serious disadvantage in that most ordinary vapors may exist as liquids at 0°C., and hence the heat liberated may be in part a heat of condensation. These condensation effects may be entirely eliminated at high temperatures by the use of the apparatus designed by Pearce and McKinley (14) and later used by the present authors (15). Temperature changes are measured

[1] This paper is a brief extract of a dissertation presented to the Graduate Faculty of the State University of Iowa by George H. Reed in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

by a 24-junction thermoelement, and the apparatus is suitable for any temperature for which satisfactory calorimeter liquids are available.

TABLE 1

The heats of adsorption of methyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.433	11.17	4.95	4.95	0.423	0.322	9.24	4.08	4.08	0.442
1.021	21.01	3.95	8.91	0.401	0.932	18.58	4.04	8.12	0.433
1.748	29.11	3.10	12.01	0.383	1.695	25.39	2.59	10.71	0.380
3.202	41.34	4.69	16.70	0.384	2.612	32.88	3.16	13.87	0.422
1.120	8.57	3.94	3.94	0.460	3.781	39.95	3.12	16.99	0.441
2.475	15.79	2.86	6.80	0.396	0.401	10.60	4.80	4.80	0.453
3.864	21.79	2.57	9.37	0.428	1.254	20.40	3.96	8.76	0.404
5.955	29.66	3.32	12.69	0.422	2.111	27.86	3.21	11.79	0.430
9.312	39.08	3.65	16.34	0.388	3.102	34.35	2.46	14.43	0.379
					4.960	43.63	3.65	18.08	0.393
$h = 0.4887X^{0.9545}$; $\Delta = 0.15$					$h = 0.4820X^{0.9600}$; $\Delta = 0.13$				

TABLE 2

The heats of adsorption of ethyl and n-propyl chloride vapors at 50°C.

ETHYL CHLORIDE					n-PROPYL CHLORIDE				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.040	7.85	5.06	5.06	0.645	1.903	1.28	1.10	1.10	0.859
0.144	15.73	4.65	9.71	0.590	4.614	3.15	1.54	2.64	0.824
0.273	22.83	3.53	13.24	0.497	8.310	5.54	1.68	4.32	0.703
0.441	30.03	3.71	16.95	0.515	14.644	8.23	1.41	5.73	0.524
0.709	37.43	3.62	20.57	0.490	1.328	1.43	1.19	1.19	0.832
1.090	44.32	3.18	23.75	0.462	2.914	3.36	1.45	2.64	0.751
0.347	8.21	4.45	4.45	0.542	5.367	5.95	1.88	4.52	0.726
0.808	15.38	4.36	8.81	0.608	7.914	7.79	1.37	5.89	0.745
1.283	22.02	4.42	13.23	0.666	10.991	10.39	1.70	7.59	0.654
1.873	28.20	2.87	16.10	0.464	13.692	12.69	1.55	9.14	0.674
2.750	35.40	4.05	20.15	0.362					
$h = 0.7534X^{0.9150}$; $\Delta = 0.30$					$h = 0.8790X^{0.9220}$; $\Delta = 0.07$				

Garner and his coworkers (1, 3, 13) have devised an adiabatic calorimeter employing two thermoelements. With this they have measured the heat of adsorption of oxygen on coals and charcoals at temperatures between

TABLE 3

The heat of adsorption of isopropyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.000	9.02	4.80	4.80	0.532	0.000	7.74	4.58	4.58	0.592
0.040	17.07	4.93	9.73	0.612	0.079	16.98	5.74	10.32	0.621
0.055	24.85	4.80	14.53	0.617	0.233	25.22	4.82	15.14	0.585
0.070	31.96	3.95	18.48	0.556	0.317	32.14	4.34	19.48	0.627
0.075	40.25	4.90	23.38	0.591	0.491	39.99	4.65	24.13	0.592
0.100	48.14	4.57	27.95	0.579	0.045	5.44	3.35	3.35	0.616
0.000	7.09	3.91	3.91	0.552	0.050	12.56	3.89	7.24	0.546
0.060	15.76	5.61	9.52	0.647	0.055	19.48	4.44	11.68	0.642
0.065	22.20	3.75	13.27	0.582	0.094	27.24	4.81	16.49	0.621
0.075	30.60	4.63	17.90	0.551	0.159	34.28	4.10	20.59	0.582
0.095	39.08	4.53	22.43	0.534	0.248	43.05	4.95	25.54	0.564
0.124	46.96	4.01	26.44	0.509					
$h = 0.6412X^{0.9720}$; $\Delta = 0.26$					$h = 0.6398X^{0.9850}$; $\Delta = 0.14$				

TABLE 4

The heat of adsorption of n-butyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.000	6.98	5.03	5.03	0.721	0.000	4.27	3.49	3.49	0.817
0.000	12.06	3.61	8.64	0.711	0.000	10.02	3.56	7.05	0.619
0.000	21.38	6.52	15.16	0.700	0.025	15.42	4.14	11.19	0.767
0.000	26.56	3.58	18.74	0.691	0.030	22.87	5.22	16.41	0.701
0.000	31.72	3.58	22.32	0.694	0.069	30.17	4.79	21.20	0.656
0.000	40.63	6.05	28.37	0.679	0.114	37.71	5.26	26.46	0.698
0.000	5.13	3.59	3.59	0.700	0.203	45.09	5.07	31.53	0.687
0.000	10.52	3.86	7.45	0.716	0.773	62.10	12.06	43.59	0.709
0.000	15.80	3.74	11.19	0.708	0.000	5.95	4.55	4.55	0.765
0.000	29.07	9.34	20.53	0.704	0.000	13.49	5.26	9.81	0.698
0.000	34.32	4.06	24.59	0.773	0.000	23.77	7.36	17.17	0.716
0.000	39.16	2.62	27.21	0.541	0.070	29.12	3.18	20.35	0.594
0.025	50.70	7.66	34.87	0.664	0.075	35.38	4.39	24.74	0.701
					0.110	43.19	4.98	29.72	0.638
$h = 0.7925X^{0.9640}$; $\Delta = 0.15$					$h = 0.7905X^{0.9690}$; $\Delta = 0.23$				

18°C. and 450°C. Observations made in their experiments have shown that on admission the oxygen is first adsorbed on the outside layers of the

TABLE 5

The heats of adsorption of secondary-butyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.635	2.04	1.35	1.35	0.662	0.728	2.84	1.89	1.89	0.666
1.758	4.88	1.91	3.26	0.673	1.378	5.11	1.10	2.99	0.485
2.719	6.93	1.35	4.61	0.659	1.977	6.73	1.13	4.12	0.698
3.745	9.03	1.35	5.96	0.643	3.147	9.96	2.23	6.35	0.690
4.875	11.20	1.41	7.37	0.650	4.772	13.26	2.41	8.76	0.730
1.265	1.71	1.16	1.16	0.678	6.388	16.26	1.86	10.62	0.620
2.211	2.86	0.74	1.90	0.644	0.803	2.68	1.88	1.88	0.702
3.610	4.10	0.86	2.76	0.694	1.467	4.44	1.14	3.02	0.648
5.174	5.41	0.83	3.59	0.634	2.250	6.38	1.02	4.04	0.526
8.176	7.78	1.42	5.01	0.599	3.097	8.42	1.36	5.40	0.667
$h = 0.6775X^{0.9890}$; $\Delta = 0.03$					$h = 0.6699X^{0.9890}$; $\Delta = 0.14$				

TABLE 6

The heats of adsorption of tertiary-butyl chloride vapor on charcoal at 25°C. and 50°C.

AT 25°C.					AT 50°C.				
P	X	dh	h	dh/dX	P	X	dh	h	dh/dX
cm.	*cc. per gram*	*cal. per gram*	*cal. per gram*		*cm.*	*cc. per gram*	*cal. per gram*	*cal. per gram*	
0.000	5.20	3.50	3.50	0.673	1.715	1.83	1.23	1.23	0.671
0.000	11.56	4.01	7.51	0.631	3.105	3.11	0.77	2.00	0.602
0.070	17.87	3.80	11.31	0.602	5.129	5.01	1.29	3.29	0.679
0.110	24.30	4.01	15.32	0.624	9.515	7.21	1.51	4.80	0.686
0.179	29.37	3.03	18.35	0.598	12.944	10.10	1.72	6.52	0.595
0.000	5.68	3.80	3.80	0.669	17.731	13.32	2.21	8.73	0.686
0.065	11.51	3.44	7.24	0.590	1.219	1.65	1.14	1.14	0.691
0.139	17.11	3.47	10.71	0.620	1.977	2.77	0.74	1.88	0.661
0.214	22.10	2.83	13.54	0.567	2.701	3.53	0.55	2.43	0.724
0.433	29.46	4.33	17.87	0.588	4.034	5.18	1.05	3.48	0.636
0.483	35.24	3.92	21.79	0.678	5.629	6.73	1.08	4.56	0.697
$h = 0.7096X^{0.9610}$; $\Delta = 0.13$					$h = 0.7064X^{0.9650}$; $\Delta = 0.06$				

charcoal. The rate of adsorption is so rapid that with small volumes of gas no oxygen penetrates the interstices between the grains to the charcoal around the thermoelement. For this reason the surfaces of capillaries

lying nearest to the surface are the first to be saturated with oxygen. The very small, not easily accessible capillaries are not reached by the first admissions of gas. To meet these difficulties the original apparatus has since been modified (2) in such a way that the gas must first pass directly to the center of the charcoal and then diffuse through it to the outer wall of the gauze cylinder. The intimate contact between the fine grains of charcoal and the wire spirals of our adsorption bulbs justifies us in believing that the same conditions are equally met in the method that we have used.

We now present a brief report of the results obtained in a study of the heats of adsorption of a number of alkyl chloride vapors on activated charcoal at 25°C. and 50°C. The complete apparatus, its capabilities and technique, as well as the charcoal used are described in the previous paper (15).

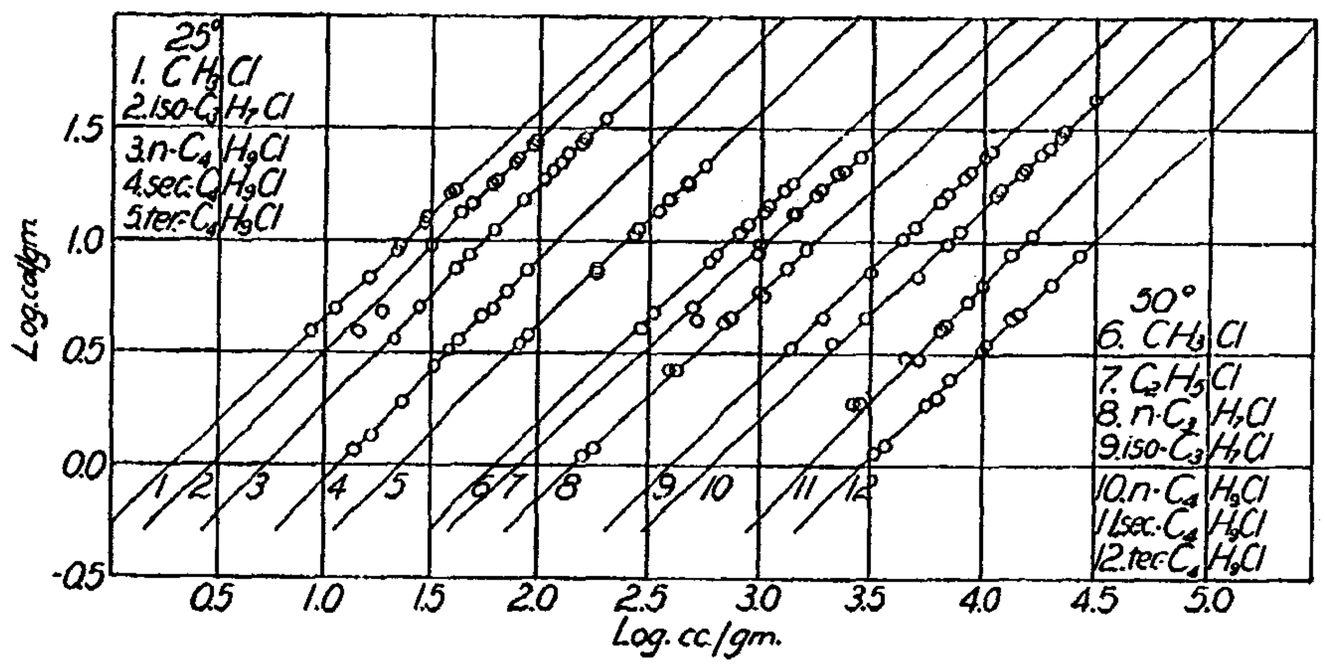

FIG. 1

The liquids whose vapors were studied were purified by the generally accepted methods. Only the constant-boiling middle fractions were used.

The results of the experimental work are collected in tables 1 to 6. The second column of each table contains the number of cubic centimeters (N. T. P.) of vapor adsorbed by 1 g. of charcoal under the equilibrium pressure given in column one. The third column contains the observed heat effects, dh; the total heats of adsorption, h, are given in column four. In the last column are the differential heats of adsorption in calories per cubic centimeter of gas per 1 g. of charcoal. The data given in these tables represent two or more series; they have been obtained with various weights of charcoal, some fresh and others previously used, and with variation in the rate of admission to the charcoal.

Lamb and Coolidge (6) have found that chlorine-containing vapors poison charcoal in such a way that the heat of adsorption decreases in

successive runs on the same sample of charcoal. This poisoning effect did not appear in our work. The heat of adsorption has been found to be independent of previous use, if the used sample is outgassed at 550°C. to a pressure of 0.0001 mm.

The data are represented in the curves of figure 1. These have been successively displaced to the right by definite intervals to avoid superposition. The curves are rectilinear and are represented by the relation

$$\log h = \log m + n \log X$$

where h is the number of calories liberated when X cc. of vapor are adsorbed by 1 g. of charcoal, n is the slope, and $\log m$ is the value of the intercept at unit concentration. The constants are indicated in the empirical equations to be found at the bottom of the different tables. It is interesting to note that the values of m and n for any one vapor are very nearly identical at the two temperatures. The values for the total heats of adsorption calculated with the aid of these equations are in good agreement with the values found experimentally. The average deviation, Δ, between the observed and calculated values, is for the most part within the limits of accuracy of the experiment.

It appears to have been definitely proved to many interested in adsorption that the heat of adsorption of a gas or vapor by charcoal does vary considerably with the temperature. This view is fully supported by researches upon the heat of adsorption of oxygen and carbon dioxide by charcoal at different temperatures.

Garner and his coworkers (1, 3, 13) have found that for an oxygen concentration of 1.5×10^{-4} moles per gram of charcoal the heat of adsorption increases from 70,000 cals. at 18°C. to somewhat more than 115,000 cals. at 200°C., and it finally attains a value of 224,000 cals. at 450°C. Thus, we find the heat of adsorption of oxygen on charcoal to be approximately equal to the heat of formation of carbon dioxide at a temperature not far above 100°C. That they are not dealing with a case of simple reversible adsorption, but rather, possibly, with an activated adsorption or with a chemical surface reaction, is shown in part by their observation that when oxygen is heated in contact with charcoal to 100°C. only traces of carbon dioxide are evolved. With further increase in temperature carbon dioxide is formed in increasing quantity.

Long ago, Rhead and Wheeler (16) came to the conclusion that oxygen combines directly with charcoal to form a physicochemical complex, C_xO_y, which decomposes on heating to carbon dioxide and carbon monoxide. Their conclusion is completely confirmed by the work of Hulett and Lowry (7). The latter thoroughly outgassed their charcoal at 900°C. to 1000°C., allowed it to cool to room temperature in a vacuum, and then admitted various gases. They found it possible to recover 90 per cent of the carbon

dioxide and a smaller percentage of water at room temperature, but both were completely recovered at 184°C. Gases like hydrogen, nitrogen, and carbon monoxide were completely recovered at room temperature. Oxygen, however, behaved very differently. After being admitted to the charcoal and allowed to come to equilibrium, only about one-half of the oxygen was recovered by evacuating at room temperature, and only traces of oxygen were obtained by heating the charcoal to 184°C. Upon increasing the temperature still further the oxides of carbon began to appear, but not until a temperature of 900°C. to 1000°C. was reached did they recover all of the oxygen admitted. And then it was not oxygen, but a mixture of the oxides of carbon.

Magnus and Braner (8) have studied the heat of adsorption of carbon dioxide on charcoal at 17°, 27°, and 37°C. They have found that at constant temperature the heat of adsorption decreases with increase in pressure; furthermore, it decreases with rise in temperature at constant pressure.

In spite of the fact that Lowry and Hulett found it possible to remove only 90 per cent of their carbon dioxide, Shah (17) states that there is no indication of a chemical interaction between charcoal and oxygen at ordinary temperatures. He did find, however, that not until the temperature is raised to 200°C. does carbon dioxide begin to be slowly reduced.

Keyes and Marshall (5) have studied the adsorption of oxygen, chlorine, carbon dioxide, ammonia, and ether by charcoal at 0°C. Of these the behavior of oxygen was peculiarly striking. The log q–log c curve is not only not rectilinear, but it actually shows an inflexion. Only for the very low, and possibly for high oxygen concentrations, is there any direct proportionality between log q and log c. Although linear equations of these two variables represent the data of carbon dioxide fairly well, the curve shows a trend which is slightly convex to the log c axis. Chlorine and ammonia show a similar behavior. The curves for oxygen and ether, on the other hand, are concave to the log c axis. The log h–log c curves for the vapors studied in this work are rectilinear throughout.

It is evident from the work cited that oxygen and carbon dioxide do show very pronounced heats of adsorption on charcoal, and these vary markedly with increase in temperature. That these heat effects are modified in no uncertain degree by heat effects due to some kind of chemical interaction between the gas and the charcoal at the gas-solid interface appears most probable. The heats of adsorption should be expected, therefore, to be considerably different from those which would be obtained if the adsorption forces were of the van der Waals type only. It is the latter forces which appear to be involved in the adsorption of the vapors employed in this work.

The molecular heats of adsorption, h_m, calculated by the method employed in the previous paper (14), are collected in table 7. It will be observed

that the heats of adsorption increase with increase in the length of the hydrocarbon chain. Also, that these heats are greater than those obtained for the branched chain compounds. Further, the difference between the molecular heats of adsorption for each vapor at the two temperatures is very small. This would indicate that the forces involved are those of van der Waals. The number of vapors studied is too small to make any general deductions regarding the effect of molecular complexity upon the heat of adsorption.

TABLE 7

The molecular heats of adsorption of alkyl chlorides at 25°C. and 50°C.

ALKYL CHLORIDE	MOLECULAR HEATS OF ADSORPTION		ISOSTERES
	At 25°C.	At 50°C.	
	kg-cals.	*kg-cals.*	*kg-cals.*
CH_3Cl	9.2	9.2	8.3
C_2H_5Cl	11.6*	12.2	10.6
n-C_3H_7Cl	15.0*	14.6	12.3
iso C_3H_7Cl	12.9	13.3	12.3
n-C_4H_9Cl	15.4	15.7	13.4
secondary C_4H_9Cl	14.5	14.4	
tertiary C_4H_9Cl	13.7	13.6	11.6

* From Pearce and McKinley (14).

SUMMARY

1. The heats of adsorption of certain alkyl chloride vapors on charcoal have been measured at 25°C. and 50°C. The heats of adsorption of ethyl chloride and *n*-propyl chloride have been determined at 50°C.

2. The molecular heats of adsorption at the two temperatures are of approximately the same magnitude. The temperature coefficient of adsorption between these temperatures is very small, if there is one at all.

3. The total heat of adsorption of any vapor increases apparently rectilinearly with the total amount adsorbed.

4. The molecular heat of adsorption of vapors with branched chains is always less than that of the vapors of the normal compounds at the same temperature. That of the normal compounds increases with increase in the length of the hydrocarbon chain.

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COMMUNICATION TO THE EDITOR

DENSITY OF WATER FROM VARIOUS SOURCES AND ISOTOPIC RATIO IN HYDROGEN

H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell, and H. V. A. Briscoe (J. Chem. Soc. **1934**, 1207) have determined the density of water with unquestionable accuracy. They have ascribed microchemical variation in the density of water from animal, vegetable, and mineral sources to the isotopic ratio in hydrogen in water.

W. D. Bancroft and L. P. Gould (J. Phys. Chem. **38**, 209 (1934)), as well as many others, have concluded that liquid water is a mixture of polymerized molecules coëxisting in reversible equilibrium. Emeléus and his coworkers made no mention of such a phenomenon. It seems worth while paying attention to the variation in polymerization of water molecules with rise of temperature in connection with so delicate a study of the isotopic ratio in hydrogen by means of the determination of the density of water. The question is to what extent the observed variation in density is influenced by polymerization and depolymerization with fall and rise in the temperature of water samples under the conditions of the experiment.

JITENDRA NATH RAKSHIT.

Ghazipur, U. P.,
India.

NEW BOOKS

Electrolytes. By HANS FALKENHAGEN. Translated by R. P. Bell. xvi + 348 pp. Oxford: Clarendon Press, 1934. Price: $9.50.

This book can be cordially recommended to the attention of physical chemists.

After a short discussion of ideal dilute solutions, the author gives a sketch of the "classical" theory of electrolytes as developed by Arrhenius. The anomalies in the thermodynamic properties and in the electrical conductance of strong electrolytes are pointed out. This is followed by a section devoted to the early theories proposed to account for the observed anomalies. The theory of Debye is then given in considerable detail in its application both to the thermodynamic properties of solutions and to their electrical conductance. The last three chapters are devoted to the modern theory of the viscosity of strong electrolytes, more concentrated solutions, and the statistical foundations of Debye's theory. The appendix contains a short paper, by R. H. Fowler, on recent applications of quantum mechanics to the theory of electrolytes.

The book contains numerous references to original sources. The index is entirely inadequate, but this defect is partly counterbalanced by an unusually detailed table of contents.

Students who desire to become acquainted with recent developments in the theory of electrolytes will find this book of great value.

F. H. MACDOUGALL.

Inorganic Colloid Chemistry. By H. B. WEISER. 15.5 x 23.5 cm.; xi + 389 pp. New York: John Wiley and Sons, Inc., 1933. Price: $4.50.

Professor Weiser has done chemistry a great service by bringing together, for the first time in a critical survey, the colloidal behavior of the elements. Up to the present time many sources had to be consulted in order to assemble the material presented in this single volume. Not only does the author give the latest accepted methods for preparing the elements in the colloidal form, but he thoroughly discusses their properties as well as theories concerning their behavior in this state. General principles of colloid theory are sufficiently treated, together with biological and industrial applications, so that the book is useful both as a text and as a source book of information.

Following a chapter on the formation of the colloidal elements, the book is naturally divided into a section on the metallic elements and one on the non-metallic elements. As far as possible the elements are taken up in the order in which they appear in the periodic table. The section devoted to the metallic elements is completed by chapters on the adsorption of gases by metals and colloidal metals as contact catalysts. Covering about sixty pages these two chapters give the reader a remarkably complete picture of the present status of these important and expanding fields of investigation. In the section devoted to the non-metals the chapter on colloidal carbon appeared to the reviewer to be especially complete and well written.

The book is well illustrated and a very complete list of references to original work is given. An author as well as a subject index appears at the end of the book. Workers in the field will welcome this important addition to the growing list of publica-

tions, while graduate students will find that the book is very useful in giving them a reasonably complete survey of the subject.

L. H. REYERSON.

Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikatforschung in Berlin-Dahlem. Edited by WILHELM EITEL. Vol. VI. 21 x 29 cm.; 234 pp. Brunswick: Fried. Vieweg und Sohn, 1934. Price: 28 RM.

The Institute, under the direction of Dr. Wilhelm Eitel, continues to be very active in research, and the sixth volume of its collected papers contains much that is of scientific interest. Several investigations by H. E. Schwiete and H. Elsner von Gronow and colleagues deal with calcareous cements. Crystals from a Portland cement kiln in which small additions of fluorspar were made to the charge, and identified as alite, proved on analysis to consist of tricalcium silicate holding 4.5 per cent of tricalcium aluminate in solid solution; the fact that such solubility occurs was confirmed by x-ray examination, the lines of the compound being clearly discernible, but disappearing on heating the clinker. The specific heats of the principal compounds present in Portland cement have been determined from 20°C. to 1500°C., these data being required for the calculation of the heats of reaction in the kiln. Several other thermochemical investigations in this field have been completed, covering both the compounds present in clinker and those formed by hydration. A study of the development of heat during the setting of aluminous cement leads to the conclusion that the process is purely colloidal and is governed by the pH value, an increase in this value accelerating setting, whilst a diminution retards it. This conclusion requires to be controlled by other methods, such as microscopical and x-ray examination. A similar study of the setting of Portland cement also lays stress on gel formation as an essential part of the process.

The papers on glass include a long review of the constitution of glass by W. Weyl, in which the subject is reviewed as a whole, as well as an experimental investigation in which glasses were prepared under high oxygen pressure, with the object of retaining in solution the higher oxides which ordinarily dissociate. Alkali lead glass in this way forms plumbates, which evolve oxygen when the glass is fused under reduced pressure. Manganese may also be retained as the higher oxide, so that under pressure a deep violet glass has been prepared, containing only 0.1 per cent MnO. A series of studies of the flow of glass in various machine processes for the production of bottles and other objects is remarkable for the very beautiful series of photographs taken by the Schlieren method.

As usual, the volume contains accounts of several improvements in technique, which may be of interest to workers in other fields than that of the silicates.

C. H. DESCH.

The Design and Use of Instruments and Accurate Mechanism (Underlying Principles). By T. N. WHITEHEAD. 279 pp.; 85 figs. New York: The Macmillan Co., 1934.

The book is written for the designers of accurate scientific instruments such as, for example, comparators. But the discussion covers much more than this field. The author deals with the fundamental principles covering design and the use of the resulting devices. He therefore deals with the theory of errors of observation from the standpoint of the instrument and from the standpoint of the human nature of the observer. He admits the utility of mathematics in the expression of physical phenomena, but warns that the use of mathematics must be tempered by independent check of the physical facts. The aim in writing the book has been "to concentrate on those parts of the subject which seem to call for revision and with which me-

chanical designers are less likely to be acquainted." Anyone interested in the building of scientific instruments and of precision machines should read this volume.

GEORGE GLOCKLER.

The Kinetic Theory of Gases. Some Modern Aspects. By MARTIN KNUDSEN. Methuen's Monographs on Physical Subjects. 17 x 11 cm.; 64 pp. London: Methuen and Co., Ltd., 1934. Price: 2s. 6d.

This book embodies the material of three lectures given in 1933 in the University of London by its distinguished author. It is less a treatise on the kinetic theory than a summary of Professor Knudsen's own researches, but since these are concerned with several fundamental parts of the kinetic theory, the author has been able to make a connected story of the material. The simpler formulas are deduced, whilst the complicated are merely quoted. The apparatus is described and illustrated. The sections deal with the vapor pressure of mercury, evaporation and condensation, molecular flow through tubes, the cosine law, resistance to motion in gases, thermal molecular pressure, molecular heat conduction and coefficient of accommodation, and the absolute manometer. The treatment is clear and attractive, and the book is one which will be read with interest and profit by many kinds of readers.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 59: Eisen, Teil A, Lieferung 6. 26 x 18 cm.; xxi + 1167-1420 pp. Berlin: Verlag Chemie, 1934. Price: 41.50 Marks. Subscription price: 36 Marks.

This volume contains a description of the systems composed of iron and the nonmetallic elements sulfur, selenium, tellurium, boron, and carbon. The treatment is on the lines of the phase rule, although in many cases the chemical properties of the compounds are dealt with in full. The section on the iron-carbon system, in view of its great technical importance, is very detailed, and the volume is essentially a monograph on carbon steels. Nitriding of iron is included. The technical and patent literature is exhaustively covered. The volume is one of exceptional interest and is a valuable summary of a very extensive literature.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 59: Eisen, Teil A, Lieferung 7. 26 x 18 cm.; xxvi + 1421-1634 pp. Berlin: Verlag Chemie, 1934. Price: 36 Marks. Subscription price: 31.5 Marks.

This volume is concerned solely with the magnetic and electrical properties of iron and steel. The magnetic properties, which are of great technical importance, are very fully described, the section being introduced by a clear account of the general theory of ferromagnetism, including a discussion of the units, the names of which have recently been altered. The text is illustrated by a large number of diagrams and contains much numerical data. The electrical properties include conductivity, thermoelectric properties, contact potentials, discharges between electrodes, and electron emission. The volume is essentially of physical interest and constitutes a valuable monograph on the subjects with which it deals. The brief accounts of the various phenomena dealt with from the general point of view, and the definitions of the various magnitudes concerned in the effects, will be found very useful for reference by chemists, and the inclusion of x-ray data and lattice constants is a valuable feature.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium, Teil A, Lieferung 1. 26 x 18 cm.; iv + 284 pp. Berlin: Verlag Chemie, 1934. Price: 42 Marks. Subscription price: 38 Marks.

This volume deals with the occurrence, production, and physical properties of metallic aluminum. The section on its occurrence includes an account of the aluminum minerals, including silicates, and contains a long section on bauxite and laterite, which are used in the technical production of the metal. The section on the production of the metal deals briefly with the older chemical methods and in detail with the electrolytic processes now in use, and with refining processes. The forms of commercial aluminum are described. The physical properties are classified under the headings atomic, crystallographic, mechanical, thermal, optical, magnetic and electrical, and in the descriptions a large amount of numerical data is collected. The volume provides a very exhaustive and authoritative account of aluminum metal both from the physical and chemical aspects, although the description of the purely chemical properties belongs to a later issue. The references are very complete and the literature, which is brought well up to date, is international.

J. R. PARTINGTON.

The Adsorption of Gases by Solids. By S. J. GREGG. 17 x 11 cm.; viii + 120 pp. London: Methuen and Co., Ltd., 1934. Price: 2s. 6d.

The subject of adsorption of gases by solids is one of great complexity and interest, and some reasoned survey of the present state of affairs was much in need. A recent volume published by the Faraday Society indicated that the interest was there, and Mr. Gregg has in small compass given us a detached survey of the subject, admirable in its grasp of essentials and breadth of scope. It is a pity therefore that the series of monographs to which the book belongs has made it necessary to deal with many aspects in only a very brief way. Perhaps when agreement has been reached on some of the more controversial items, Mr. Gregg will undertake a larger survey. In the meantime he has managed to pack into one hundred and twenty small pages nine chapters on general characteristics, experimental methods, heats of adsorption, theories, adsorption forces, adsorption layers, surface structure, activated adsorption and, finally, chemisorption. In addition each chapter has its own bibliography, guiding readers to the original papers of importance. The author's interest has perhaps centred on the explanations of the many results obtained rather than on experimental method, to which only a little over two pages have been devoted. In common with other writers on adsorption, Mr. Gregg has failed to make reference to the practically important process of clean-up, whereby gases are retained at the gettered glass surfaces of vacuum lamps and wireless valves. In spite of this blemish Mr. Gregg's book is a well thought out little volume and is worth a good deal more than the very reasonable price the publishers ask for it.

J. T. RANDALL.

Oberflächenspannung in der Biologie und Medizin. By FERDINAND HERCIK. 15 x 22 cm.; xii + 220 pp. Dresden and Berlin: Steinkopff, 1934. Price: unbound, 14 M; bound, 15 M.

This small volume deals essentially with the changes in surface tension caused by the solution of materials mainly of biological processes. Great emphasis is laid upon the utility of the ring method for determining these changes, a view with which many investigators would in all probability not agree. The data of Du Noüy are cited in extenso. These data on the surface tensions of dilute solutions present the

interesting feature of exhibiting a series of minima at what are believed to be critical concentrations. From these minima Du Noüy and his coworkers have computed molecular dimensions which in some cases are in fair agreement with those obtained by other methods. It is somewhat remarkable that no such peculiarities are observed in the Langmuir trough, and it would seem eminently desirable for a series of parallel experiments to be carried out under identical conditions. A brief account is given of the relationships suggested between capillary activity and various other properties, such as enhancement of membrane permeability, increased sensitivity in the precipitin reaction, and the rates of sedimentation of red blood cells and erythrocytes. It is clear both from the divergencies in views expressed by various workers in these fields, as well as the lack of uniformity in the experimental results, that this is a fertile field ready to be cultivated by those who possess both the requisite physicochemical and biological experience.

ERIC K. RIDEAL.

German-English Chemical Terminology. An Introduction to Chemistry in English and German. By A. KING and H. FROMBERG. 21 x 13 cm.; xvii + 324 pp. London: Thomas Murby and Co., 1934. Leipzig: Max Weg, 1934. Price: 12s. 6d.

The method of this book is the use of English on each left-hand page with German on the right. The subject matter has been selected, from well-known textbooks of both languages, so as to be representative of chemistry as a whole. Original and translation can be compared paragraph by paragraph, and the general accuracy can be relied on, since the book is the joint work of an English and a German chemist. The other feature of this book is the printing in italics of corresponding terms of both languages on their first appearance in the text, with also an index of these at the end.

The series has been started with geology; under the general editorship of Dr. W. R. Jones, other sciences are to follow.

The claim made that such books may be equally useful to both English and German students and that the use of dictionaries is avoided is probably true, provided that each knows something of the other language. It must be remembered that exact translation is not always possible, and that it is often an equivalent which is rendered in the other language. With this in mind such books should prove very useful.

W. H. PATTERSON.

Bilder zur qualitativen Mikroanalyse anorganischer Stoffe. By W. GEILMANN. 23 x 16 cm.; xii + 80 pp. Leipzig: Leopold Voss, 1934. Price: 8 RM.

In view of the increasing employment of microchemical tests in qualitative analysis, the present small atlas of photomicrographs comes as a useful addition to the analyst's library. The work contains close on two hundred and fifty illustrations, reproduced from actual photomicrographs obtained by the author, showing the characteristic forms of the crystals and crystalline precipitates resulting from the various microchemical tests, details of which are briefly given.

The difficulty that in the case of many reactions the appearance of the precipitate formed is liable to vary considerably with the concentration of the interacting solutions, etc., has been met by including in such cases two or more separate illustrations of the precipitates in question, showing their appearance when formed under differing conditions, and thus facilitating their identification.

A number of illustrations are also given of certain precipitates, such as zinc ammonium phosphate, which although not in themselves of value as a means of identification, are liable to be formed during the testing of mixtures, and may easily be misinterpreted.

A full index is provided, and the book is well printed, with clear and good illustrations.

H. F. HARWOOD.

Ergebnisse der exakten Naturwissenschaften. Sonderabdruck aus Bd XIII. Über den ausseren Photoeffekt an adsorbierten Schichten. By R. SUHRMANN. 23 x 16 cm.; 74 pp. Berlin: J. Springer, 1934. Obtainable only in complete issue. Price: unbound, 28 RM; bound, 29.40 RM.

In this section of the *Ergebnisse* Dr. Suhrmann has given a survey of work on measurements of the external photoeffect for adsorbed layers. The outlook of the survey is for the most part experimental, and apparatus and results are illustrated in sixty-four diagrams. Until very recently the necessity for a really first class vacuum technique in work of this kind was not universally appreciated. As a result much of the older work is of little value. Dr. Suhrmann, however, steers a careful course through the maze of results available. After a preliminary historical survey he deals very briefly with the fundamental photoelectric laws. Many aspects of adsorbed layer problems are dealt with in the main section of the report, and of these we may mention the influence of gases and of outgassing technique on the photoelectric properties of the layers, the properties of adsorbed metal films, such as cesium on tungsten, the effects of temperature and of the electric field. Over two hundred references to original papers are appended.

J. T. RANDALL.

Ergebnisse der exakten Naturwissenschaften. Sonderabdruck aus Bd XIII. Elektrische Leitfähigkeit elektronischer Halbleiter. By B. GUDDEN. 23 x 16 cm.; 33 pp. Berlin: J. Springer, 1934. Obtainable only in complete issue. Price: unbound, 28 RM; bound, 29.40 RM.

Semiconductors have long been one of the mysteries of physics, but during the last year or two the general advances of quantum mechanics have gone far towards sketching in the main outlines of the fundamental conducting mechanism in these bodies. These theoretical advances are for the most part due to A. H. Wilson and R. H. Fowler, but a great deal of fundamental experimental work has been done by Gudden and Pohl from 1920 onwards. The work of greatest importance has been done on single crystals, such as zinc blende, while much of practical import has been carried out on copper oxide, selenium, and the associated rectifying contacts. The general division of work falls naturally into two classes. On the one hand there are single crystals, on the other powdered crystals, and both these types have been investigated with and without the stimulation of incident light. In the present reprint Professor Gudden has not attempted an exhaustive survey of the subject, but all who wish to obtain a good idea of the experimental results and their interpretation will do well to consult it, for it is written in a clear and simple way and is confined to main issues. The main items dealt with in the survey are: the existence of ionic or electronic conduction in semiconductors; the validity of Ohm's Law and the question of specific conductivity; the effect of temperature on the conductivity; photoelectric effects; and an outline of modern theory. A point of interest to chemists is the fact that the physical properties of semiconductors are largely dependent on impurities which may frequently be difficult or impossible to detect by ordinary chemical means.

J. T. RANDALL.

CONTRIBUTION TO THE THEORY OF SURFACE CONDUCTIVITY AT SOLID-LIQUID INTERFACES[1,2]

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Received June 14, 1934

The double layer theory of Otto Stern may be briefly summarized as follows (7, 12, 14). The theory of Helmholtz gives values for the capacity of the double layer which agree approximately with those obtained from electrocapillary experiments. However, owing to kinetic heat motion, the double layer ions facing the liquid cannot have the distribution postulated by Helmholtz. On the other hand, Gouy's (6) theory, which is based on the existence of a diffuse double layer, gives values for the capacity which are far too great. Stern develops his concept of the double layer in this manner: under the influence of the electrostatic forces of the wall, one type of ion forms a sheet of charges of constant density ($-\sigma_0$) directly on the surface of the solid phase (inner Helmholtz layer). A sheet of positive charges ($+\sigma_0$) (outer Helmholtz layer) would be located at a distance δ from the negative layer providing the kinetic heat motion did not exist, say at a temperature of zero degrees absolute. At room temperature this charge will acquire a certain depth. A fraction, $+\sigma_1$, of the positive charges will face the sheet of negative ions, the rest ($+\rho$, in a column of liquid of 1 cm.^{2} cross section) extends into the interior of the solution with an asymptotically decreasing charge density (diffuse layer).

$$\sigma_0 = \sigma_1 + \rho$$

The electrokinetic potential, ζ, is the potential drop across the mobile component of the positive layer. According to Gouy all of the double layer ions, except those on the wall, are mobile with respect to hydrostatic forces, while according to Stern both sheets of ions comprising the Helmholtz layer are immobile with respect to hydrostatic forces.

In the present communication the equation for surface conductivity is developed, based on the layer of Stern, so as to include not only the diffuse

[1] Presented before the Eleventh Colloid Symposium held at Madison, Wisconsin, June 14-16, 1934.

[2] The work reported in this paper has been aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

layer ions, but also those of the outer Helmholtz layer.[3] The equation thus becomes applicable to concentrated solutions, in which the surface conductivities predicted by the double layer theories of Stern, on the one hand, and of Gouy, on the other, would be expected to show a more marked disagreement. By comparison with experimental surface conductivity values, it should then be possible to choose between the theories.

The following cases are theoretically possible: (A) The ions attached to the wall possess no electrical mobility. The surface conductivity is due to those components of the double layer which lie in the liquid phase. Electrosmose, by increasing the velocity of double layer ions, these being carried along by the moving column of liquid, will increase surface conductivity. Case A would be expected to occur when the conductivity is determined with D. C. (B) The same as case A, except that no electrosmose occurs.[4] (C) All double layer ions, including those on the wall, conduct;

[3] The simplified equation proposed last year (J. Phys. Chem. **36**, 3157 (1932)) did not include the Helmholtz layer ions, nor an electrosmotic correction. It agrees with equation 20, independently derived by Bikerman (Z. physik. Chem. **163A**, 378 (1933)), except for the mobility factor. Bikerman's equation 20 is as follows:

$$\text{(a) Surface conductivity per 2 cm}^2. = \Delta_c l_c + \Delta_a l_a$$

l_a and l_c are the ionic mobilities of cation and anion, while

$$\text{(b) } \Delta_c = \sqrt{\frac{2DRTc}{\pi F^2}} \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\}$$

$$\text{(c) } \Delta_a = \sqrt{\frac{2DRTc}{\pi F^2}} \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\}$$

For potassium chloride, since $l_a = l_c$

$$\text{(d) Surface conductivity per 1 cm}^2. = \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{2RT}} + e^{\frac{-F\zeta}{2RT}} - 2 \right\} l_c$$

$$\text{(e) Surface conductivity per 1 cm}^2. = \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{4RT}} - e^{\frac{-F\zeta}{4RT}} \right\}^2 l_c$$

If $e^{\frac{-F\zeta}{4RT}}$ can be neglected—large ζ —

$$\text{(f) Surface conductivity per 1 cm}^2. = \sqrt{\frac{DRT}{2\pi F^2}}\, c\, e^{\frac{F\zeta}{2RT}} \cdot l_c$$

[4] The surface conductivity measurements reported below were carried out with 1000-cycle A.C. From The Svedberg and Hugo Anderson's paper on electrophoresis (Kolloid-Z. **24**, 156 (1919)), we have drawn the conclusion that no significant electrosmose is likely to occur at this frequency. If this conclusion is correct the attempt made by some authors to explain A.C. surface conductivity data by the von Smoluchowski equation—which is equivalent to the electrosmotic component of surface conductivity—is meaningless.

there is electrosmose. (D) All double layer ions conduct; there is no electrosmose.

The experimental data do not permit a clean-cut choice between A–C, B–D to be made. Since A and B are the more conventional assumptions, the surface conductivity equations for these cases will be developed.

The equation for the Stern layer is:[5]

$$K_0(\epsilon - \zeta) = FZ\left\{\frac{1}{1 + \frac{1}{18c}e^{\frac{\Phi_+ - F\zeta}{RT}}} - \frac{1}{1 + \frac{1}{18c}e^{\frac{\Phi_- + F\zeta}{RT}}}\right\} + \sqrt{\frac{DRT}{2\pi}}\,c\left\{e^{\frac{F\zeta}{2RT}} - e^{\frac{-F\zeta}{2RT}}\right\} \quad (1)$$

[5] Symbols used:

a = area of glass particles enclosing 1 cm³. of 5×10^{-4} M potassium chloride.

$A = \dfrac{e^{\frac{F\zeta}{2RT}} + 1}{e^{\frac{F\zeta}{2RT}} - 1}$.

c = concentration in moles per cm³.

c_{I} = 5×10^{-7} moles per cm³.

c_{II} = 3×10^{-6} moles per cm³.

c_{III} = 1×10^{-5} moles per cm³.

D = dielectric constant.

D^* = dielectric constant in Helmholtz layer.

F = Faraday (96,500 coulombs).

K_0 = capacity of Helmholtz layer.

l_a = mobility of anion.

l_c = mobility of cation.

R = gas constant (8.324×10^7 ergs).

T = absolute temperature.

u = electrosmotic velocity (cm. per second).

u_0 = electrosmotic velocity between Helmholtz and diffuse layer.

u_m = electrosmotic velocity in center of slit of thickness l.

u_h = electrosmotic velocity of outer Helmholtz layer.

u_h^* = $u_h F$, when E (electrical field) = 1.

z = number of ions per cm². of outer Helmholtz layer.

Z = moles of ions per cm². of outer Helmholtz layer.

$\alpha = \dfrac{2F\sqrt{2\pi c}}{\sqrt{DRT}}$.

δ = thickness of Helmholtz layer (5×10^{-8} cm. assumed).

ϵ = potential drop across entire double layer.

ζ = potential drop across diffuse layer.

η = viscosity coefficient.

Φ_+ = adsorption potential of cation.

Φ_- = adsorption potential of anion.

It follows from the equation that the outer Helmholtz layer contains

$$\frac{Z}{1 + \frac{1}{18c} e^{\frac{\Phi_+ - F\zeta}{RT}}} = \text{moles of cations per cm.}^2 \text{ of surface} \qquad (2)$$

and

$$\frac{Z}{1 + \frac{1}{18c} e^{\frac{\Phi_- + F\zeta}{RT}}} = \text{moles of anions per cm.}^2 \text{ of surface} \qquad (3)$$

Equations 2 and 3 may be simplified; the wall is assumed to be negatively charged.

$$18cZe^{\frac{-\Phi_+ + F\zeta}{RT}} = \text{moles of cations per cm.}^2 \text{ of surface} \qquad (2a)$$

and

$$18cZe^{\frac{-\Phi_- - F\zeta}{RT}} = \text{moles of anions per cm.}^2 \text{ of surface} \qquad (3a)$$

The concentration of cations and anions in the diffuse layer is:

$$\sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} \text{ moles of cations per cm.}^2 \text{ in excess of those normally present.} \qquad (4)$$

$$\sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} \text{ moles of anions per cm.}^2 \text{ in excess of those normally present.} \qquad (5)$$

Since the Stern layer consists of a diffuse (Gouy) layer and a Helmholtz layer, we can use, for the value of the conductivity of the former (uni-univalent salts), the sum of Bikerman's (1) equations 19 and 23. It is:

Specific surface conductivity of diffuse layer (with electrosmose) =

$$\sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} \left\{ l_c + \frac{DRT}{2\pi\eta} \right\} + \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} \left\{ l_a + \frac{DRT}{2\pi\eta} \right\} \qquad (6)$$

The specific surface conductivity expressed in equation 6 is based on the assumption that, at the boundary of the diffuse layer near the wall ($x = 0$), the electrosmotic velocity $u = 0$. This is not the case for the Stern layer, for we have, at the boundary of the diffuse layer ($x = 0$):

$$u = u_h = \frac{E \cdot D^* \cdot (\epsilon - \zeta)}{4\pi\eta} \qquad (7)$$

This is the velocity of the outer Helmholtz layer. This means that integration of Bikerman's[6] equation 10 now involves the boundary conditions

$$\frac{du}{dx} = 0 \tag{8}$$

when $x = \frac{l}{2}$, where the thickness of the Helmholtz layer is neglected;

$$u_h = \frac{E \cdot D^* \cdot (\epsilon - \zeta)}{4\pi\eta} \tag{9}$$

when $x = 0$. Performing the integration, Bikerman's equation 12 now becomes (see footnote 7)

$$u_m = \frac{E \cdot D \cdot \zeta}{4\pi\eta} + \frac{E \cdot D^* \cdot (\epsilon - \zeta)}{4\pi\eta} \tag{9}$$

The increase in conductivity (Δ_h) of the diffuse layer, caused by the movement of the outer Helmholtz layer, is

$$\Delta_h = \sqrt{\frac{DRT}{2\pi}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} u_h - \sqrt{\frac{DRT}{2\pi}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} u_h \tag{10}$$

When the potential $(\epsilon - \zeta)$ in equation 7 is expressed in terms of charge (equations 2a and 3a, multiplied by F) and capacity of the Helmholtz condenser, we get

$$u_h = \frac{E \cdot \delta \cdot 18cZF \left\{ e^{\frac{-\Phi_+ + F\zeta}{RT}} - e^{\frac{-\Phi_- - F\zeta}{RT}} \right\}}{\eta} \tag{11}$$

The conductivity of the diffuse (Gouy) layer is the sum of equations 6 and 10; or, substituting equation 11 in equation 10,

$$^{6}E \cdot 8Fc \frac{Ae^{\alpha z}\,(A^2e^{2\alpha z} + 1)\,dx}{(A^2e^{2\alpha z} - 1)^2} = \eta \frac{d^2u}{dx^2}\,dx\,.$$

The left-hand side represents the electrical force causing osmosis which is exerted on a volume of solution of $1 \times 1 \times dx$ cm³. The right-hand side is the frictional force counterbalancing the electrical force.

[7] From equation 9 the important conclusion follows that electrosmose may still occur when $\zeta = 0$, since the Helmholtz layer still exists. See Monaghan, White, and Urban: J. Phys. Chem., May, 1935.

Specific surface conductivity of diffuse (Gouy) part of Stern layer (with electrosmose)

$$= \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{F\zeta}{2RT}} - 1 \right\} \left\{ l_c + \frac{DRT}{2\pi\eta} + \frac{F^2 \cdot \delta \cdot 18cZ \left(e^{\frac{-\Phi_+ + F\zeta}{RT}} - e^{\frac{-\Phi_- - F\zeta}{RT}} \right)}{\eta} \right\}$$

$$+ \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ e^{\frac{-F\zeta}{2RT}} - 1 \right\} \left\{ l_a + \frac{DRT}{2\pi\eta} - \frac{F^2 \cdot \delta \cdot 18cZ \left(e^{\frac{-\Phi_+ + F\zeta}{RT}} - e^{\frac{-\Phi_- - F\zeta}{RT}} \right)}{\eta} \right\} \quad (12)$$

The conductivity of the outer Helmholtz layer has to be added to the diffuse layer conductivity expressed in equation 12. The former is composed of two parts: the conductivity of the outer Helmholtz layer ions; the excess conductivity shown by these ions because the liquid moves. The total conductivity will be equal to:

$$\left\{ \begin{matrix} \text{Moles of cations in outer} \\ \text{Helmholtz layer} \end{matrix} \right\} \times l_c + \left\{ \begin{matrix} \text{Moles of anions in outer} \\ \text{Helmholtz layer} \end{matrix} \right\} \times l_a$$

$$+ \left\{ \begin{matrix} \text{Moles of cations in outer} \\ \text{Helmholtz layer} \end{matrix} - \begin{matrix} \text{Moles of anions in outer} \\ \text{Helmholtz layer} \end{matrix} \right\} u_h^* \quad (13)$$

$u_h^* = \frac{u_h F}{E}$, where E is the applied potential.

Substituting from equations 2a, 3a, and 11:

Specific surface conductivity of outer Helmholtz layer (with electrosmose) =

$$18cZe^{\frac{-\Phi_+ + F\zeta}{RT}} \cdot l_c + 18cZe^{\frac{-\Phi_- - F\zeta}{RT}}\, l_a + \frac{F^2\delta}{\eta} \left\{ 18cZe^{\frac{-\Phi_+ + F\zeta}{RT}} - 18cZe^{\frac{-\Phi_- - F\zeta}{RT}} \right\}^2 \quad (14)$$

The specific surface conductivity of the entire (Stern) double layer is the sum of equations 12 and 14.

When no electrosmose occurs (high frequency A.C.), the specific surface conductivity becomes:

Specific surface conductivity (no electrosmose)

$$= \sqrt{\frac{DRT}{2\pi F^2}}\, c \left\{ \left(e^{\frac{F\zeta}{2RT}} - 1 \right) l_c + \left(e^{\frac{-F\zeta}{2RT}} - 1 \right) l_a \right\}$$

$$+ 18cZ \left\{ e^{\frac{-\Phi_+ + F\zeta}{RT}}\, l_c + e^{\frac{-\Phi_- - F\zeta}{RT}}\, l_a \right\} \quad (15)$$

EXPERIMENTAL

The surface conductivity was determined in the following manner. Pyrex glass particles were equilibrated with potassium chloride and sodium

chloride solutions (1.25×10^{-4} *M* to 1×10^{-1} *M*), transferred to a conductivity cell, and the conductivity as well as the *volume* of the particles carefully determined. After deducting bulk from observed conductivity, the difference represented the total surface conductivity. The surface area of the glass particles being known,[8] the specific surface conductivity (conductivity per cm.^{2}) is also known.

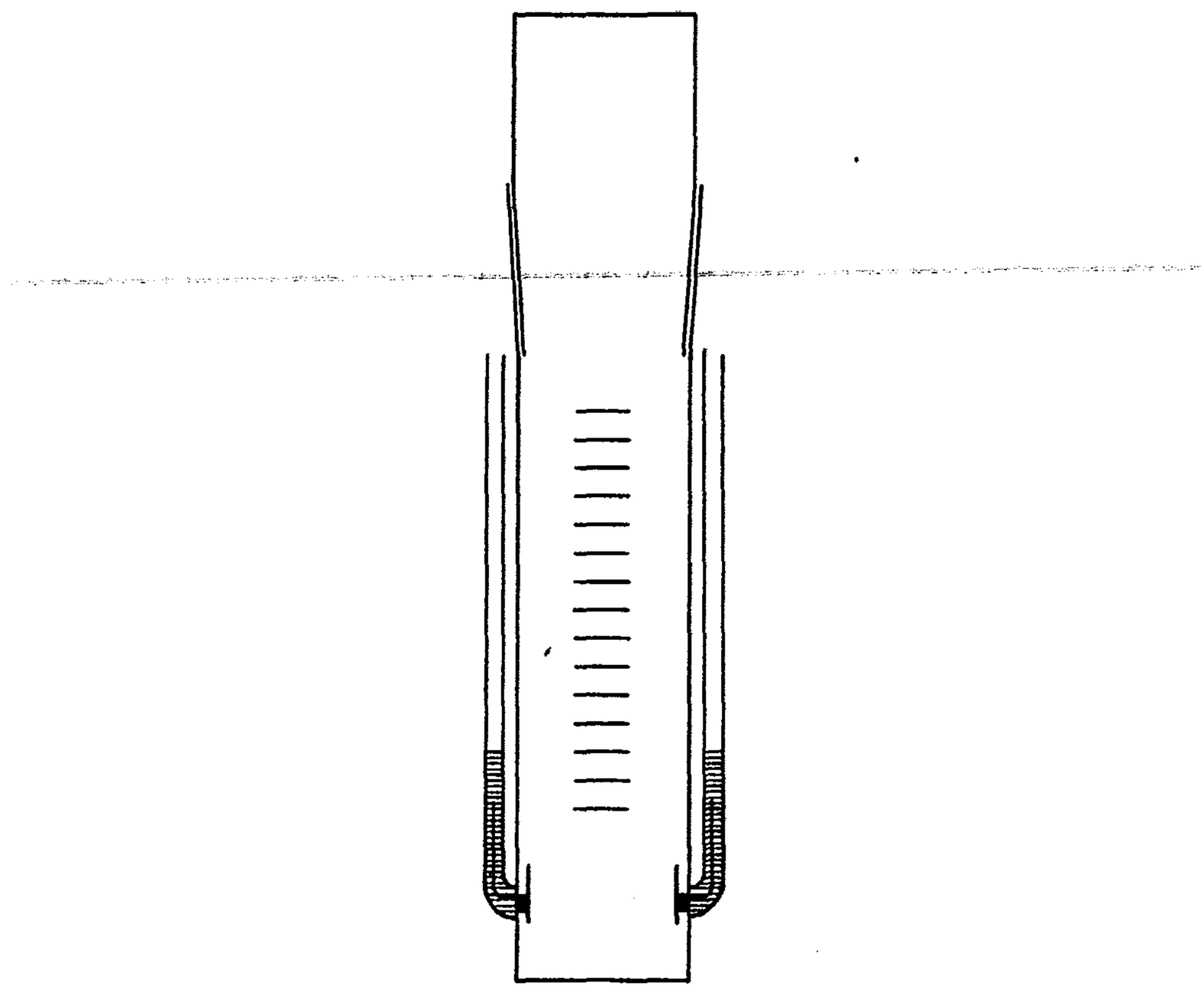

FIG. 1

The experimental determination of specific surface conductivities will now be discussed.

1. Apparatus

The measurements were carried out in a kerosene bath (9) at 25.000° ± 0.002°C. The conductivity cell was constructed of Pyrex glass and had a ground glass joint stopper (figure 1). It was graduated and carefully

[8] See section 10, below.

calibrated. The Wheatstone bridge was a 5-dial Gray instrument, coils accurate to 0.025 per cent. The current was supplied by a Leeds and Northrup 1000-cycle motor generator. The cathetometer used read to 0.02 mm.; 0.01 mm. could be estimated.[9] This permitted the volume of the Pyrex glass particles (52–55 cc.) to be read to ± 0.005 cc. The volume readings were taken with the conductivity cell in the constant temperature bath. The salts used were Kahlbaum's "Zur Analyse" grade. The interferometer was a Zeiss instrument.

The need for careful measurements is obvious, as surface conductivity is obtained by subtracting bulk conductivity from observed conductivity. Dividing total surface conductivity by the area of the glass particles gives the conductivity per cm.^{2} of surface. As was pointed out previously, the micro surface structure should not affect this calculation.

2. *Volume occupied by constant amount of Pyrex glass particles as a function of electrolyte concentration*

We early noticed that a given amount of Pyrex glass particles does not occupy the same volume in solutions of different electrolyte concentration.[10] This phenomenon had already been observed by Wo. Ostwald and von Buzagh (5, 11, 16). The latter observed a volume change of as high as 55 per cent, when quartz particles were transferred from water to benzene. Neglect of this factor may lead to serious errors in surface conductivity measurements.[11]

3. *Effect of the amount of Pyrex glass particles in the cell on the cell constant*

When a small amount of Pyrex glass particles is used, such that the electrodes are just covered by the particles, a value for the cell constant is obtained which is less than the one found when more particles are placed in the cell. In both cases the remainder of the cell volume is filled with solution to the same mark. As more and more particles are added, the differences in cell constant grow less. Finally a region is reached where the cell constant is unaffected by further addition of glass particles. The measurements must be performed with amounts of glass particles which lie in this region. Otherwise the volume changes discussed in section 2 will bring about unknown changes in the cell constant.

[9] We are indebted to Prof. A. L. Hughes for the loan of this instrument.

[10] The effect of vibration on sedimentation volume must not be confused with the above effect.

[11] Fairbrother and Balkin (J. Chem. Soc. 1931, Part I, 1564–78) obtained their cell constant in aqueous 0.1 *M* potassium chloride and applied this value to measurements in benzene solutions. They make no mention of a volume correction.

4. The size of the Pyrex glass particles and its influence on the reliability of the measurements

The particles were obtained by grinding Pyrex chemical glassware in a mortar and sieving. The fraction between 100 and 200 mesh was retained, weighed, washed one hundred times with boiling distilled water, equilibrated with potassium chloride solution, and transferred to the conductivity cell.

Under these conditions it was difficult to duplicate our readings. Some improvement was noted after the cell and contents had been shaken vigorously and after the powder had settled spontaneously in the thermostat. But as the powder surface was still cloudy and uneven, the volume measurements were of doubtful value. Finally the difficulty was overcome by using only the particles which settled within 1 minute. This powder gave sharply defined horizontal surfaces and reproducible volume and conductivity measurements, as shown by a representative experiment (table 1). The estimate of the area of all the glass powder, based on microscopic observation of about two hundred particles, is 20,000 cm². This value is probably too low, as no correction for surface curvature was applied. The area determined by surface conductance is 27,000 cm².

TABLE 1

Constancy of sedimentation volumes and resistance

SOLUTION	VOLUME	RESISTANCE
	cc.	*ohms*
1.25×10^{-4} *M* KCl	52.06_7	8.975×10^4
	51.97_7	9.055×10^4
	51.92_3	9.075×10^4
	51.92_8	9.044×10^4
	52.09_4	9.024×10^4
1×10^{-3} *M* KCl	51.82_0	1408.9
	51.85_3	1406.5
	51.84_8	1409.8
	51.94_1	1406.4
	51.89_3	1405.0
	51.81_0	1409.2
	51.80_9	1409.0

5. Change in cell constant (Parker effect)[12]

The Parker effect of a conductivity cell comprises a set of factors, such as construction of the cell, bridge set-up, etc., which result in a variation

[12] G. Jones and G. M. Bollinger (J. Am. Chem. Soc. **53**, 411 (1931) made a careful study of this effect. All references will be found in their paper.

of cell constant with concentration. The effect was evaluated from conductivity measurements in 2.5×10^{-4}, 1×10^{-3}, 3×10^{-3}, 3×10^{-2}, 7×10^{-2}, 9×10^{-2}, 1×10^{-1}, and 2.5×10^{-1} M potassium chloride. The values for the specific conductivity of these solutions were taken from a paper by Shedlovsky (13).[13] The observed resistances of these solutions in our cell covered the range 56–44,000 ohms. The cell constant is expressed by the empirical equation

$$\text{Cell constant} = 0.6970 - 0.00265 \log R$$

from which the percentage change of the cell constant at two different resistances can be calculated. The equation holds to about 60 ohms. Below this value, polarization of the electrodes begins to exert an influence on cell constants.

It should be shown next that the percentage change of the constant with resistance is uninfluenced by the presence of glass particles between the electrodes. On account of surface conductivity, cell constants cannot be calculated from conductivity measurements, except in concentrated solutions.

Hence the following procedure was adopted. The glass particles and solution were placed inside of a sealed, flat-bottomed glass tube which was coaxially cemented inside the conductivity cell. The annular space between the conductivity cell wall and the glass tube was then filled with a series of known solutions and their conductivities determined. The percentage variation of the cell constant was found to be the same as before.

6. *Equilibration of electrodes*

It is known that platinized platinum electrodes may retain adsorbed electrolyte with great tenacity (2). The effect is particularly noticeable when dilute solutions are placed in cells previously containing concentrated solutions. The electrodes were carefully equilibrated with the solution before conductivity measurements were taken.

7. *Equilibration of Pyrex glass particles*

The particles were freed from electrolyte by repeated washing with boiling distilled water each time, before being equilibrated with a given electrolyte solution. The latter was decanted and renewed until the conductivity of the supernatant liquid or its refractive index (interferometer) was the same as that of the solution taken from the volumetric glass-stoppered Pyrex flask. A rubber bulb was used for operating a wash bottle, thus preventing contamination by exhaled carbon dioxide.

[13] For a discussion of Shedlovsky's values see G. Jones and B. C. Bradshaw (J. Am. Chem. Soc. **55**, 1780 (1933)). We are indebted to Prof. Grinnell Jones for a résumé of specific conductivity measurements (private communication).

8. Conductivity of the water

The latter was always determined and the surface conductivity measurements of the powder were corrected accordingly. This is important in dilute solutions, such as 1.25×10^{-4} *M* potassium chloride, where the specific conductivity of the water amounted to 8 per cent of the specific conductivity of the solution.

9. Determination of the density of the Pyrex glass particles

The density was calculated from the volume increase in our cell, when a known weight of powder was added to a known volume of water. We found $d_{4^\circ}^{25^\circ} = 2.225 \pm 0.005$.

10. Determination of effective surface area of Pyrex particles

The effective surface area of the particles which are *in contact with 1 cm.³ of solution* was calculated according to the expression:

$$\frac{\text{Cell constant}}{\text{Observed resistance}} = \text{bulk specific conductivity} + \text{effective surface area (cm.}^2) \times \text{specific surface conductivity} \quad (16)$$

In this equation all quantities, except the area, are known for 5×10^{-4} *M* potassium chloride, the specific surface conductivity being 4.3×10^{-9} mho, which is the value obtained with slits of known dimensions using A.C.[14] The effective surface area may be defined as the area of that portion of the surface in contact with 1 cm.³ of solution (interstitial liquid) which contributes to conductance.

11. Change of cell constant with concentration

The cell constant of the conductivity cell containing the glass powder is calculated from the observed conductivity in 1×10^{-1} *M* potassium chloride. The bulk conductance is so great in this solution that the contribution of the surface may be neglected. At all other concentrations, the cell constant is found by applying the percentage correction outlined under section 5.

12. Correction of cell constant when the glass powder volume changes

It has been tacitly assumed so far that a given quantity of glass powder, when settling spontaneously, will always occupy the same volume, irrespec-

[14] See Urban, Feldman, and White (J. Phys. Chem., April, 1935). The older figure of 2.24×10^{-9} mho, obtained by White, Urban, and Van Atta (J. Phys. Chem. **36**, 1371 (1932)) does not apply in this calculation, owing to the operation of Bikerman's membrane potential factor, discussed by Urban, Feldman, and White, and of electrosmose.

tive of the nature and concentration of the solution in which the powder is suspended. This is not the case (see section 2).

For instance, the volume of glass powder + solution was 51.759 cc. in 5×10^{-4} M potassium chloride, but 53.482 cc. in 1×10^{-1} M potassium chloride (see column 2, table 3a).

In order to carry out the calculations outlined under sections 10 and 11, it is necessary to determine what the cell resistance in 1×10^{-1} M potassium chloride would have been if the volumes of the glass particles + solution had been 51.759 cc. (instead of the observed 53.482).

The correction has been made by equation 17

$$\frac{R}{r} = \frac{(V_r - g)}{(V - g)} \tag{17}$$

where R = calculated resistance at volume V (glass powder + interstitial liquid),

r = observed resistance at volume V_r,

g = volume of glass particles (weight ÷ density).

Equation 17 can be tested. Thus we found that 24.79 cc. of particles suspended in 0.1 M potassium chloride solution gave a V_r reading of 54.28 cc. in one determination, and 53.48 in another, probably due to vibration. The corresponding (observed) resistances were 146.44 and 150.49, respectively. The resistance at the larger volume, calculated from the resistance at the smaller volume, is 146.48 ohms (observed 146.44 ohms).

The factor of non-homogeneous packing does not enter into the surface conductivity measurements, because the particles were always allowed to settle spontaneously. After one determination, the cells were shaken and both volume and resistance were redetermined. This was repeated from five to ten times. The volume and resistance measurements agreed closely, indicating that the same kind of packing always occurred under our experimental conditions.

DISCUSSION

Calculations

The observed specific surface conductivities (tables 3a, 3b, column 14) were next compared with the ones calculated according to equations 12 + 14, and 15, respectively, after appropriate values for ζ and the constants had been substituted.

The ζ-potentials were those of Lachs and Biczyk (10), calculated from their experimentally determined stream potentials. The following values were obtained (table 2). Since Lachs and Biczyk gave the stream potentials only for 1×10^{-4}, 1×10^{-3}, and 1×10^{-2} M potassium chloride, it was necessary to interpolate. When the log of the potassium chloride

concentration is plotted against the log of the stream potential, a nearly straight line is obtained. The interpolated ζ-potentials may, therefore, be considered as reasonably accurate. The interpolated Lachs and Biczyk ζ value for 5×10^{-4} M potassium chloride is 0.1209 volt; our (experimental) value is 0.1214 volt (17). The adsorption potentials, Φ_+ and Φ_-,[15] have also been treated as constant and independent of the concentration. This seems permissible in the present concentration range.

The values for $Ze^{\frac{-\Phi_+}{RT}}$ and $Ze^{\frac{-\Phi_-}{RT}}$ were determined by solving two simultaneous equations, obtained by substituting ζ and specific surface conductivity (the experimental value) for the two concentrations 3×10^{-3} M and 1×10^{-2} M potassium chloride, in equations 12 + 14 (assumption A, electrosmose), and in equation 15 (assumption B, no electrosmose). These two solutions possess a Helmholtz layer conductance which is high com-

TABLE 2

Values of ζ-potential at various concentrations

CONCENTRATION OF POTASSIUM CHLORIDE SOLUTION	ζ-POTENTIAL
M	*volts*
1.25×10^{-4}	0.1100
2.5×10^{-4}	0.1160
5×10^{-4}	0.1209
1×10^{-3}	0.1226
3×10^{-3}	0.1113
1×10^{-2}	0.0816

pared with that of the diffuse layer. For this reason the uncertainty in the value of the (calculated) diffuse layer conductivity cannot greatly affect the fraction of the observed surface conductivity which is assigned to the Helmholtz layer.[10] A tentative value ($\eta \times 1.2$) was used for the vis-

[15] Φ_+ and Φ_- signify adsorption "potentials" in the outer Helmholtz layer. They are of the same kind as those encountered near crystal surfaces. W. H. Zachariasen (J. Am. Chem. Soc. **54**, 3841–51 (1932)) has recently developed a picture of the atomic arrangement in oxide glasses. He finds that atoms in glasses are linked together by forces essentially as in crystals. There are extended three-dimensional networks. The principal difference between crystal and glass networks is symmetry and periodicity in the crystal and their absence in the glass network. In this connection, the discussion of surface forces by Irving Langmuir (J. Am. Chem. Soc. **40**, 1361 (1918)) is of interest. It may be further pointed out that the ζ-potential at fused and unfused glass surfaces is the same. See Monaghan and White (J. Phys. Chem., in press).

[16] Solution of these simultaneous equations (KCl):

	$z = 1 \times 10^{15}$	$z = 1.27 \times 10^{15}$
A (electrosmose)	$\Phi_- = -2.5 \times 10^{11}$	-2.4×10^{11}
	$\Phi_+ = -8.0 \times 10^{10}$	-6.1×10^{10}
B (no electrosmose)	$\Phi_- = -2.5 \times 10^{11}$	-2.5×10^{11}
	$\Phi_+ = -6.9 \times 10^{10}$	-7.4×10^{10}

Solution of the two simultaneous equations (NaCl):

cosity coefficient of the Helmholtz double layer. The correction was made according to the H. A. Lorentz equation, cited by Bikerman. A similar correction has been developed by The Svedberg and Hugo Anderson (15).

Sedimentation volume

The regular decrease of the values for the interstitial solution (table 3a, column 4) indicates a closer approach of the particles with increasing electrolyte concentration. The interpretation of this phenomenon by Zocher (18) is this: "Beim Entladen durch Elektrolyte nimmt der Abstand zwischen den Schichten ab. . . . ." We do not believe that this shrinkage depends on ζ-potential changes alone. If the volume decrease effect were associated only with ζ-potentials, the two should run parallel, which is not the case.[17] The effective particle volume falls progressively beginning with 1.25×10^{-4} M potassium chloride, until a second effect appears which again causes a rise in sedimentation volume. The ζ-potentials, however, do not decrease progressively, but go through a maximum.

The sharp rise in sedimentation volume beginning between 3×10^{-3} M and 1×10^{-2} M potassium chloride is probably not due to a "Haftefekt" (4), since the glass particles were far from dehydrated, as evidenced by the fact that in 4.5×10^{-4} M thorium chloride solution the volume of interstitial solution is about 2 cc. less than in 3×10^{-3} M potassium chlo-

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(no electrosmose)	$\Phi_- = -2.6 \times 10^{11}$	-2.5×10^{11}
	$\Phi_+ = -8.1 \times 10^{10}$	-7.5×10^{10}

Solving for $Ze^{\frac{-\Phi_+}{RT}}$ and $Ze^{\frac{-\Phi_-}{RT}}$, instead of for Φ_+ and Φ_-, offers the advantage that Z does not have to be evaluated separately.

The ratio $Ze^{\frac{-\Phi^+}{RT}} \Big/ Ze^{\frac{-\Phi_-}{RT}}$ corresponds to the ratio of anions to cations in the outer Helmholtz layer, *in the absence* of a double layer electrical field, i.e., if van der Waals forces alone were operative (E. Hueckel, reference 8, p. 57). For potassium chloride, it is 0.001, i.e., for 10,000 Cl^- there are 10 K^+ in the outer Helmholtz layer.

For the time being only approximate values can be assigned to Z. Stern uses the value $\frac{1 \times 10^{15}}{6.06 \times 10^{23}}$. Since the glass particles are hydrated, Z can be approximately calculated by using Tammann's (Z. anorg. Chem. **158**, 1 (1926)) value of 0.992 for the specific volume of depolymerized water. The number of water molecules per cm^3. is $\frac{6.06 \times 10^{23}}{0.992 \times 18} = 3.4 \times 10^{22}$. The approximate number of lattice points z is $\sqrt[3]{3.4 \times 10^{22}} = 1 \times 10^{15}$, compared with a value of 1.27×10^{15} for the number of lattice points per cm^2. in a potassium chloride crystal.

[17] It may be concluded that the electroviscous effect must be due to more than one factor, in agreement with Bungenberg de Jong, Kruyt and Lens (Kolloidchem. Beihefte **37**, 395 (1933)).

TABLE 3a

(1) KCl MOLES PER LITER OF SOLUTION	(2) TOTAL VOLUME GLASS + SOLUTION	(3) VOLUME OF GLASS PARTICLES	(4) VOLUME OF SOLUTION (INTERSTITIAL)	(5) OBSERVED RESISTANCE	(6) CALCULATED RESISTANCE OF 0.1 *M* KCl	(7) CELL CONSTANT (THEORETICAL)	(8) CELL CONSTANT CORRECTED FOR PARKER EFFECT (ACTUAL)	(9) CONDUCTIVITY PER CM.³ OF SOLUTION	(10) SPECIFIC CONDUCTIVITY OF KCl (SHEDLOVSKY)	(11) SPECIFIC CONDUCTIVITY OF H_2O	(12) SURFACE CONDUCTIVITY PER CM.³	(13) EFFECTIVE SURFACE AREA IN CM.² PER CM.³ OF SOLUTION	(14) SURFACE CONDUCTIVITY PER CM.²	(15) $l_c = l_a$
moles	*cc.*	*cc.*	*cc.*	*ohms*	*ohms*			*mhos* $\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-4}$		$\times 10^{-9}$	
1.25×10^{-4}	52.00_0	24.79	27.21	90350	158.68	2.045_6	2.024_0	2.24_{02}	1.860	0.151	2.29	1058	2.17	74.40
2.5×10^{-4}	51.87_3	24.79	27.08	47840	159.44	2.055_4	2.036_0	4.25_{19}	3.709	0.151	3.96	1063	3.73	74.20
5×10^{-4}	51.75_0	24.79	26.97	25575	160.09	2.063_7	2.046_0	8.00_{02}	7.390	0.151	4.59	1067	4.30	73.90
1×10^{-3}	51.67_3	24.79	26.88	13147	160.62	2.070_6	2.055_6	15.6_{35}	14.693	0.151	7.91	1071	7.39	73.47
3×10^{-3}	51.54_6	24.79	26.76	4558	161.34	2.079_8	2.068_4	45.3_{51}	43.485	0.151	17.45	1075	16.23	72.48
1×10^{-2}	51.85_4	24.79	27.06	1407	159.55	2.056_9	2.047_4	145.43	141.32	0.151	39.6	1063	37.20	70.66
1×10^{-1}	53.48_2	24.79	28.69	150.4_9		1.940_0	1.940_5	1289	1289	0.151				

TABLE 3b

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
NaCl MOLES PER LITER OF SOLUTION	TOTAL VOLUME GLASS + SOLUTION	VOLUME OF GLASS PARTICLES	VOLUME OF SOLUTION (INTERSTITIAL)	OBSERVED RESISTANCE	CALCULATED RESISTANCE OF 0.1 M NaCl	CELL CONSTANT (THEORETICAL)	CELL CONSTANT CORRECTED FOR PARKER EFFECT (ACTUAL)	CONDUCTIVITY PER CM.³ OF SOLUTION	SPECIFIC CONDUCTIVITY OF NaCl (SHEDLOVSKY)	SPECIFIC CONDUCTIVITY OF H_2O	SURFACE CONDUCTIVITY PER CM.³	EFFECTIVE SURFACE AREA IN CM.² PER CM.³ OF SOLUTION	SURFACE CONDUCTIVITY PER CM.²	l_a	l_a
moles	*cc.*	*cc.*	*cc.*	*ohms*	*ohms*			*mhos* $\times 10^{-5}$	$\times 10^{-3}$	$\times 10^{-5}$	$\times 10^{-6}$		$\times 10^{-9}$		
1.25×10^{-4}	52.35_8	24.79	27.57	99850	189.25	2.018_9	1.997_0	2.00_0	1.569	0.191	2.24	1044	2.15	50.21	75.31
2.5×10^{-4}	52.28_0	24.79	27.49	55470	189.80	2.024_8	2.004_9	3.61_4	3.127	0.191	2.96	1047	2.83	50.03	75.05
5×10^{-4}	52.06_7	24.79	27.28	29900	191.27	2.040_5	2.022_5	6.76_4	6.225	0.191	3.48	1055	3.30	49.80	74.70
1×10^{-3}	51.81_3	24.79	27.02	15504	193.10	2.060_0	2.044_2	13.18_5	12.372	0.191	6.22	1065	5.84	49.49	74.23
3×10^{-3}	51.66_5	24.79	26.88	5389	194.11	2.070_8	2.058_8	38.20_4	36.558	0.191	15.55	1071	14.53	48.74	73.12
1×10^{-2}	51.61_6	24.79	26.83	1686	194.47	2.074_6	2.066_8	122.5_6	118.43	0.191	39.4	1073	36.74	47.37	71.06
1×10^{-1}	53.02_0	24.79	28.23	184.8_3	184.83	1.971_7	1.971_7	$1067._0$	1066.8	0.191					

ride. The cause for this rise demands further investigation. It may possibly be connected with a rigidity change of the lyosphere which accompanies the increase in double layer field strength. This has shrunk to a thickness of 2×10^{-7} cm. in 1×10^{-4} M potassium chloride, compared with a thickness of 55×10^{-7} in 1.25×10^{-4} M potassium chloride (see below). For purposes of the work presented here, an exact knowledge of the mechanism producing these changes is not necessary.

The conductivity of the diffuse layer (for potassium chloride $l_a = l_c$) without electrosmose is, per cm.^{2} of surface,

$$\sqrt{\frac{DRTc}{2\pi F^2}}\left\{e^{\frac{F\zeta}{2RT}} + e^{\frac{-F\zeta}{2RT}} - 2\right\}l_c$$

This is the difference between total diffuse layer ions, and the ions normally present. The latter quantity is

$$\sqrt{\frac{DRTc}{2\pi F^2}} \cdot \text{moles of solute}$$

Inasmuch as 1 cm.^{3} contains normally c moles, the thickness of the diffuse double layer must be

$$\sqrt{\frac{DRTc}{2\pi F^2}} \Big/ c = \sqrt{\frac{DRT}{2\pi F^2 c}} \text{ cm.}$$

The following thicknesses have been calculated (table 4).

Accuracy of measurements

The observed specific surface conductivities in 3.0×10^{-3} M potassium chloride and 1.0×10^{-2} M potassium chloride are believed accurate to ± 10 per cent. This percentage error is deduced as follows. The accuracy of the values in table 3a, column 9, is ± 0.2 per cent; in column 10, ± 0.02 per cent. The error in column 12 (total observed surface conductivity in 1 cm.^{3} of solution) depends on how small a fraction of column 9 it is. If total surface conductivity is one-tenth of total specific conductivity, the error is ± 2 per cent; if it is one one-hundredth, the error is ± 20 per cent. In calculating specific surface conductivity, column 14, the effective surface area of the powder must be known. It is obtained by dividing total surface conductivity in 5.0×10^{-4} M potassium chloride by 4.3×10^{-9}. If $\pm a$ is the error in total surface conductivity A, and $\pm b$ the error in the specific surface conductivity B, then the error in the area will be

$$\pm \frac{\sqrt{B^2a^2 + A^2b^2}}{B^2} \tag{18}$$

On the basis of an error of ±3.5 per cent in total surface conductivity and ±7.5 per cent in the specific surface conductivity in 5.0×10^{-4} *M* potassium chloride, the error in the area is ± 8 per cent. The percentage error for all values in table 3, column 14, has been estimated by the above equation of Fenner (3). It is about ±10 per cent. It follows that the accuracy of the calculated $Ze^{\frac{-\Phi}{RT}}$ values, allowing furthermore for the uncertainty in δ, the thickness of the Helmholtz layer, l = ionic mobility (assumed to be normal), and the value of ζ, must be of the order of ±20 per cent.

TABLE 4

Thickness of diffuse double layer in various potassium chloride solutions

MOLES KCl PER LITER	THICKNESS OF DIFFUSE LAYER
moles	*cm.*
1.25×10^{-4}	5.5×10^{-6}
2.5×10^{-4}	3.9×10^{-6}
5×10^{-4}	2.7×10^{-6}
1×10^{-3}	1.9×10^{-6}
3×10^{-3}	1.1×10^{-6}
1×10^{-2}	0.6×10^{-6}
1×10^{-1}	0.2×10^{-6}

TABLE 5

MOLES OF SALT PER LITER	OBSERVED SPECIFIC SURFACE CONDUCTIVITY	CALCULATED ACCORDING TO 12 + 14 (ELECTROSMOSE)	CALCULATED ACCORDING TO GOUY'S DOUBLE LAYER (1)	CALCULATED ACCORDING TO 15 (NO ELECTROSMOSE)	CALCULATED ACCORDING TO GOUY'S DOUBLE LAYER (1)
	mhos $\times 10^{-9}$	*mhos* $\times 10^{-9}$	*mhos* $\times 10^{-9}$	*mhos* $\times 10^{-9}$	*mhos* $\times 10^{-9}$
KCl					
1.25×10^{-4}	2.17	0.93	0.51	0.94	0.34
2.5×10^{-4}	3.73	1.85	0.84	1.97	0.56
5.0×10^{-4}	4.30	4.18	1.36	4.36	0.91
1.0×10^{-3}	7.39	8.52	2.03	8.61	1.35
3.0×10^{-3}	16.23	(16.23)	2.58	(16.23)	1.72
1.0×10^{-2}	37.20	(37.20)	2.13	(37.20)	1.42
NaCl					
1.25×10^{-4}	2.15			0.80	0.27
2.5×10^{-4}	2.83			1.72	0.44
5.0×10^{-4}	3.30			3.89	0.72
1.0×10^{-3}	5.84			7.77	1.06
3.0×10^{-3}	14.53			(14.53)	1.36
1.0×10^{-2}	36.74			(36.74)	1.13

The error in the volume occupied by the glass particles practically cancels out in the division described in section 12.

RESULTS

The experimental data have been summarized in tables 3a and 3b, which are self-explanatory.

In table 5 observed and calculated specific surface conductivities have been tabulated for potassium chloride and sodium chloride.[18] The agreement between observed and calculated values is good, when the sources of error and the experimental difficulties are kept in mind.

The values calculated according to Bikerman's equations 19 and 26 have also been included. It is seen that they are far too low.

We interpret these results as confirming the essential accuracy of the Stern double layer theory which has been tested here for the first time.

SUMMARY

1. Specific surface conductivities of Pyrex glass particles in potassium chloride and sodium chloride solutions of concentration 1.25×10^{-4} M to 1×10^{-2} M were determined.

2. The surface conductivities represent the same fraction of total conductivity as in a glass capillary of about 10μ diameter.

3. An equation, based on the Stern double layer, for calculating specific surface conductivities was developed.

4. The calculated values are in agreement with experiment; values calculated according to Gouy's theory are not.

5. Evidence is adduced to show that (a) electrosmose may occur when $\zeta = 0$; (b) a sudden increase in sedimentation volume need not be due to "Hafteffekt"; (c) the electroviscous factor contains more than one component.

6. The thickness of the diffuse layer has been calculated.

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THE MAGNITUDE OF SURFACE CONDUCTIVITY[1]

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Received June 14, 1934

The only measurements of surface conductivity on surfaces of approximately known area measured with alternating current are those carried out during a period of ten years at Bristol and Stanford Universities and finally published in 1929 (8, 9). They comprise measurements made with optically polished glass and with ordinary Pyrex tubing in contact with aqueous solutions of potassium chloride and, in addition, measurements of the surface conductivity of an insoluble film of stearic acid on water. All yielded results of the same magnitude, namely, several mhos $\times 10^{-8}$ when referred to 1 square centimeter of surface. Nevertheless, many writers have decided to reject these results for two reasons. In the first place, the conductivity is far larger than can be accounted for by current theories in which the phenomena are referred wholly to the outer portion of the diffuse part of the double layer. In the second place, the only other measurements from another laboratory (11) with approximately known area of surfaces in contact with solutions of potassium chloride have yielded little or no surface conductivity.

These other measurements by White, Urban, and collaborators are characterized by three important features. First, the measurements are made with direct current. Next, the liquid was kept in motion by applied hydrostatic pressure, streaming through the capillary. Lastly, almost alone amongst those who have measured the conductivity of salt solutions since the time of Kohlrausch, these authors have not seen fit to correct the observed conductivity of potassium chloride solutions for the conductivity of the solvent. This correction nullifies the very slight surface conductance which they report, rendering it zero or negative.

We have now repeated with every precaution measurements with alternating current on systems consisting of tubing in contact with solutions of potassium chloride, and we have also extended and developed the measurements of surface conductivity of films of stearic acid, oleic acid, and palmitic acid on water. The results substantially confirm the previous measurements with alternating current, which would now appear to be

[1] Presented before the Eleventh Colloid Symposium held at Madison, Wisconsin, June 14–16, 1934

fully established and to require modification of any theory with which they are not in accord.

We also emphasize what has been implicitly known but not fully realized or explicitly expressed except in papers from this laboratory (1, 6, 7), namely, the free mobility of the mobile ions of the double layer. In other words we stress the importance of the recognition of the fragility of the double layer. Attempts to measure electrokinetic properties of the double layer easily tend profoundly to modify or to destroy the object of measurement.

Mobile ions lie passive in the liquid which surrounds them and in the absence of an applied force have neither any definite tendency towards directed movement nor, apart from discontinuities in the nature of the surface, any tendency to resist being carried along when the liquid in which they are embedded is moved parallel to the double layer. Any streaming of the liquid therefore, whether produced by applied hydrostatic pressure or induced by the application of direct current as in electrosmosis, sweeps along with it the mobile ions of the double layer. These would have to be replaced if the double layer is not to remain depleted.

Surface conductance as measured can only be due to the physical presence of bodily carriers or ions free to move under the conditions of the experiment and in numbers greater than that corresponding to the ordinary bulk conductivity of the unchanged liquid or solution. If the mobile ions are being ejected from the outlet of the capillary system, the surface conductivity will disappear unless they are replaced. Only immobile ions are left upon the surface. The replacement has to occur in the stream of liquid at the inlet. Ordinary electrolysis cannot accomplish this, because it merely discharges a space charge without in any way altering the concentration of the intermediate liquid through which the current is carried, as is well known in the field of transport or migration measurements. Especially is this evident with potassium chloride where both ions move with equal velocity in opposite directions, so that electrolysis through the entering stream of liquid cannot affect the total number of ions present, since a gain of one ion is exactly compensated with a loss of another of opposite charge and equal conductivity. Hence any loss of ions in the effluent cannot be replenished by ordinary electrolysis in the inflowing liquid. The depletion must be made good by diffusion, which requires time. The time required may be too great when the liquid is moving with appreciable velocity.

Electrokinetic phenomena need not by any means disappear when, through streaming, the surface conductivity is thus partially or largely eliminated. Redistribution of the available charges within the capillary system in a direction perpendicular to the double layer will be almost instantaneous, and streaming potential or electrosmosis will remain

prominent. Thus, even surface conductivity will be actually present, although practically masked by the corresponding depletion of the bulk solution available within the capillary.

An especially illuminating case for consideration is where there are no electrokinetic phenomena, either because the number of positive and negative points on the surface is equal, or because the surface is not charged anywhere but there is a general accumulation of ions in the neighborhood. In both cases there would be observable surface conductivity as long as the total number of ions in the solution exceeded that in the same volume of liquid outside the capillary system. Rapid flushing out with that liquid would sweep away the excess carriers and with it the observable surface conductivity.

It follows from the considerations outlined above that one should not expect exact concordance between electrokinetic effects measured by different procedures which directly modify the preëxisting double layer. The most striking instance of this is that observed by DuBois and Roberts (private communication) in one and the same system in which a ζ-potential was positive and equal to +32 millivolts as measured by streaming potential, but negative and equal to −47 millivolts as measured by electrosmosis. The measurements were made in immediate alternation without any other interference with the system.

Finally, it is possible that certain ions in the double layer may be capable of a restricted excursion and so may contribute to conductance as measured with alternating current, whilst not being measured by direct current. A careful examination of Ohm's law and comparison of the two kinds of current should determine this point.

EXPERIMENTAL METHODS[2]

Three experimental methods were employed, and in each case a whole series of cells was designed successively to eliminate difficulties of measurement or interpretation. The last cells actually used in each series were of Pyrex glass and are illustrated in figures 1, 2, and 3. Figure 1 represents a cell containing seven concentric tubes between platinum electrodes which fill the cross section of the cell and are plane polished on the surfaces facing the concentric tubes. They are sufficiently far apart to permit of the tubes being slid in and out of each other without quite coming apart.[3] The distance between electrodes was checked by measurement with a travelling microscope in each experiment. The tubes were settled by gravity on the plane surface; in every case a measurement was made before

[2] Experiments by J. F. F.

[3] The electrodes should not be much further apart than their own diameter, and the inner tubes replaced by a single solid cylinder. Then each would rest firmly upon its base without danger of tilting.

and after agitation, tapping, standing undisturbed, sliding the tubes in and out, etc. The tubes were originally cleaned with chromic acid solution,

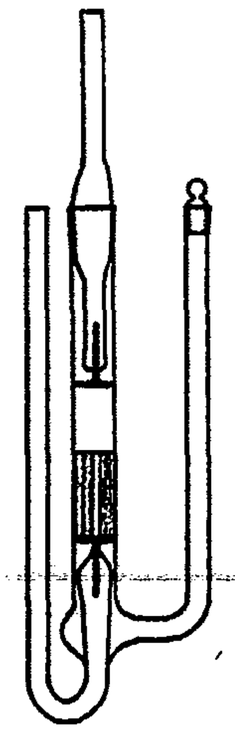

FIG. 1. CELL WITH CAPILLARY SPACES BETWEEN CONCENTRIC TUBES

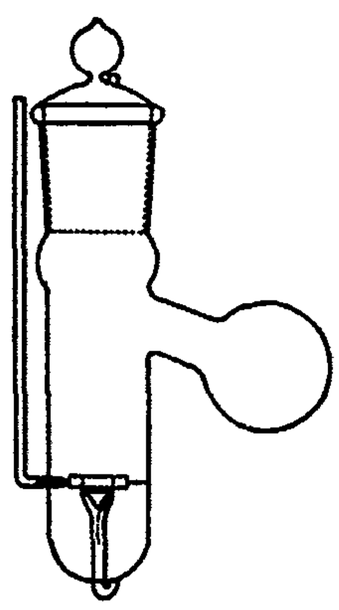

FIG. 2

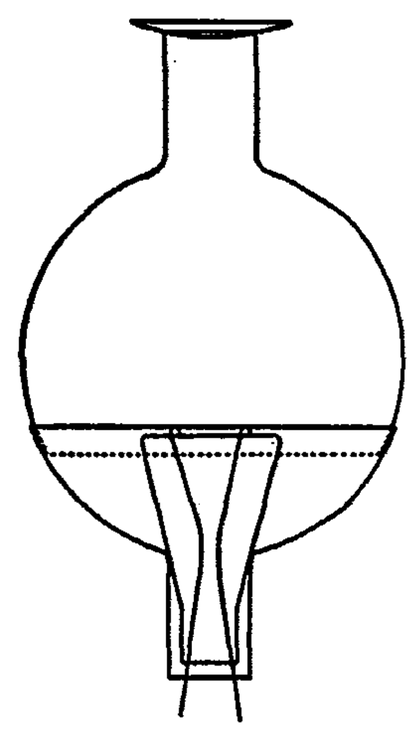

FIG. 3

FIG. 2. CELL FOR DETERMINING SURFACE CONDUCTIVITY OF THE AIR-WATER INTERFACE BY ELIMINATING THE EFFECT OF BULK CONDUCTIVITY

FIG. 3. CIRCULAR TROUGH FOR MEASURING INSTANTANEOUS PRODUCTION OF SURFACE CONDUCTIVITY

The cell is shown empty

but were kept under constant changes of water or solution for periods of months. The final measurements were taken after a year of continuous

use since the last cleaning with chromic acid solution.[4] Recleaning was effected by heating to 400–500°C. The cell in figure 2 was heated in a blast flame. That in figure 3 was likewise heated in a free flame and in a muffle furnace.

Figure 2 for insoluble or slightly soluble films on water is a modification of that used by Peaker. The cell is first measured full of conductivity water; then again, without opening, with the meniscus immediately above the electrodes but not touching them. The ratio gives the ratio of bulk conductivities for the two positions. Without moving the meniscus, the film is placed upon the surface and ample time is allowed for equilibrium. The additional conductivity consists of surface conductivity and additional bulk conductivity. The latter is determined by raising the meniscus to the top position, applying the ratio previously determined. The cell is opened only to introduce the surface film. Excess liquid is stored in the side arm. The two essential points are that neither the electrodes nor their supports should come into contact with the surface, which might cover them with an insulating film. This requires correct adjustment of the size and position of the side arm.

Figure 3 is for nearly instantaneous observations of the production of surface conductivity. Here again neither the electrodes nor their supports touch the surface. The diameter is at least 12 cm. to avoid alterations in level at the electrodes due to surface tension changes at the walls.

Measurements were in all cases made by the latest Leeds and Northrup equipment, the Grinnell Jones bridge. Any supplementary resistances used were Curtis wound coils. The oil thermostat was adjusted to 25.00° ± 0.005°C. Potassium chloride solutions were made up by weight by the method of Parker and Parker. The specific conductivity of the water was $0.4–0.5 \times 10^{-6}$ mho. Kahlbaum's best stearic and palmitic acids were used, together with some specially pure fatty acids made by Dr. Lepovsky of the University of California. In all cases they were repeatedly extracted with conductivity water before use.

EXPERIMENTAL DATA WITH CONCENTRIC TUBES (FIGURE 1)

The value of observed resistance represents in the case of each concentration a mean of many separate determinations which agree very closely among themselves. The cell was emptied and refilled with fresh solution several times, and the tubes were slid back and forth between individual measurements. The cell was always placed accurately vertical in the oil thermostat. At the end of measurements on one concentration the tubes were removed and the cell constant measured or remeasured before proceeding to the next higher concentration. In each instance the measured

[4] Compare the similar prolonged treatment described on p. 3299 of a previous communication (9).

resistance without tubes agreed with the resistance calculated from the dimensions of the cell within 0.1 per cent. Dimensions of cell and tubes were as follows: cross section of tubes, 0.959 sq. cm.; length of tubes, 2.94 cm.; cross section of cell, 1.246 sq. cm.; distance between electrodes, 5.450 cm.; "surface cross section," 18.50 cm. (sum of circumferences). Observed values of specific surface conductivities are high because the microscopic surface of the tubes is much larger than the apparent area. These results were confirmed with a complete series of measurements with the same set of tubes in an earlier design of cell which, however, did not allow as exact an evaluation of k, because it was not truly cylindrical.

Rapid streaming of the liquid through the tubes always caused a rise in resistance which continued usually to a point at which there was no surface conductivity, thus demonstrating the fragility of the double layer.

EXPERIMENTAL DATA ON INSOLUBLE FILMS IN CLOSED CELL (FIGURE 2)

This cell gives consistently reproducible results for surface conductivity of acid films on water. It was cleaned by heating in an oven at 450–500°C., then filled with conductivity water to the proper level, closed and placed in a thermostat at 25°C. to come to equilibrium. The cell was carefully levelled so that the tops of the electrodes were horizontal. In general the contents of the cell reached equilibrium with the enclosed atmosphere in about twenty-four hours, at which time it was possible to pour the water back and forth without changing the resistance of the cell by as much as 0.1 per cent. Two resistances were measured: (I) resistance of the cell with all the water in the main cell and the meniscus far above the tops of the electrodes, and (II) resistance of the cell with part of the water poured into the side bulb so that the surface of the liquid was just above the upper edges of the electrodes.[5] Care was taken so that no part of the electrodes or supports broke the surface.

After completion of the first two measurements, the cell was opened and the surface of the liquid in both the main cell and side bulb coated with the acid film. Again the cell was closed and allowed to stand for twenty-four hours to come into equilibrium with the surface film. Extreme precautions were observed to change neither the position of the cell nor the height of the meniscus during contamination.

With equilibrium reëstablished, two more resistances were measured: III, resistance of the cell with the meniscus unchanged since measurement II, but with the addition of the surface conductivity of the film and a certain bulk conductivity due to a slight solubility of the fatty acid, and IV, resistance of the cell with the meniscus again raised above the edges of the electrodes as in position I. Resistance IV is lower than resistance I

[5] No difference was observed in the ratio of resistances I and II using conductivity water and using $N/1000$ potassium chloride.

because of the conductivity of the small amount of dissolved fatty acid, and also probably because of a certain amount of contamination from the atmosphere when the cell was opened.

The total surface conductivity is deduced from resistance III by calculating from resistance IV and the ratio between II and I the value for bulk conductance only, and hence necessarily taking the difference as surface conductivity. This is then corrected to specific surface conductivity from the dimensions of the electrodes. For example, in the first experiment in the table, calculated resistance = (46,970 × 72,450)/59,350 = 57,340; observed (III), 56,140. Difference in conductivity = 1/56,140 − 1/57,340 = 37.3×10^{-8} mho. Hence specific surface conductivity = 3.73×10^{-8} mho.

EXPERIMENTAL DATA ON INSOLUBLE FILMS IN CIRCULAR TROUGH (FIGURE 3)

The experiments of this section are presented in the form of three graphs, representing the effect of a film of oleic acid upon the time–resistance curves of conductivity water in the cell. After long investigation it was discovered that it is necessary to stir the surface thoroughly before the film is placed thereon; otherwise the mechanical disturbance accompanying the spreading of the film affects the resistance so seriously as to mask any surface conductivity which may be produced.

When the uncontaminated surface is stirred vigorously with a clean glass rod, the resistance *rises* immediately to a maximum and falls rapidly again after agitation ceases. The reason for this is either that atmospheric impurities are absorbed to form at the surface a thin conducting layer of solution which is replaced by pure water from the lower part of the cell during stirring, or that the highly cleaned surfaces of glass and platinum adsorb the impurities from the liquid in contact with them.

After the cell had been heated in a free flame, allowed to cool, and filled with conductivity water, tests with flowers of sulfur showed repeatedly that the surface of the liquid was clean and free from any premature contamination; the small particles could be blown about freely and without hindrance. Consequently the prior technique of brushing the surface with a paraffined rod was discontinued in the final experiments as probably superfluous.

Upon contamination with the oleic acid there is a rapid drop in resistance which is partly or wholly due to the surface conductance of the film. It has often been observed that a surface film tends to prevent contamination from the atmosphere, so that the total drop may be caused by surface conductance and not partially by solution of carbon dioxide or other contaminants from the enclosed atmosphere. When the acid film is disturbed by further stirring after contamination, a momentary rise in resistance takes place, which is attributed to a partial destruction of surface con-

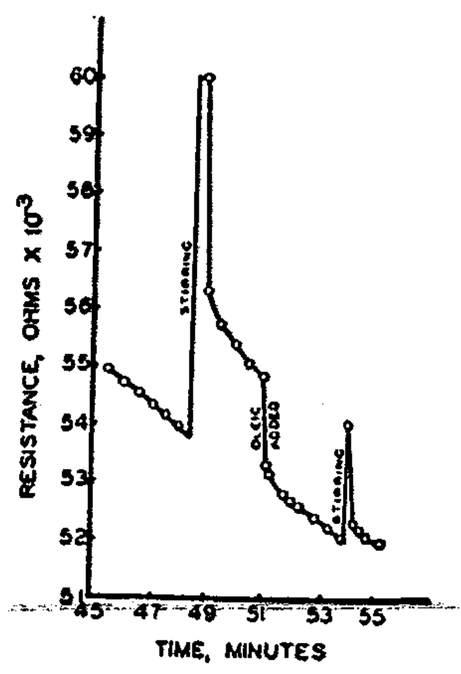

FIG. 4

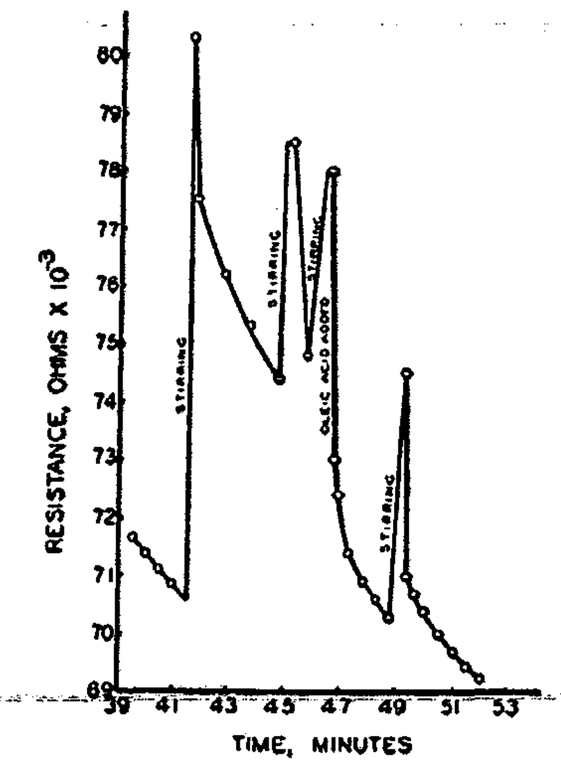

FIG. 5

FIG. 4. CHANGE IN RESISTANCE WITH TIME IN CELL (FIGURE 3)
Showing effects of stirring and instantaneous production of surface conductivity upon adding insoluble fatty acid.

FIG. 5. CHANGE IN RESISTANCE WITH TIME IN CELL (FIGURE 3)
Showing effects of stirring and instantaneous production of surface conductivity upon adding insoluble fatty acid.

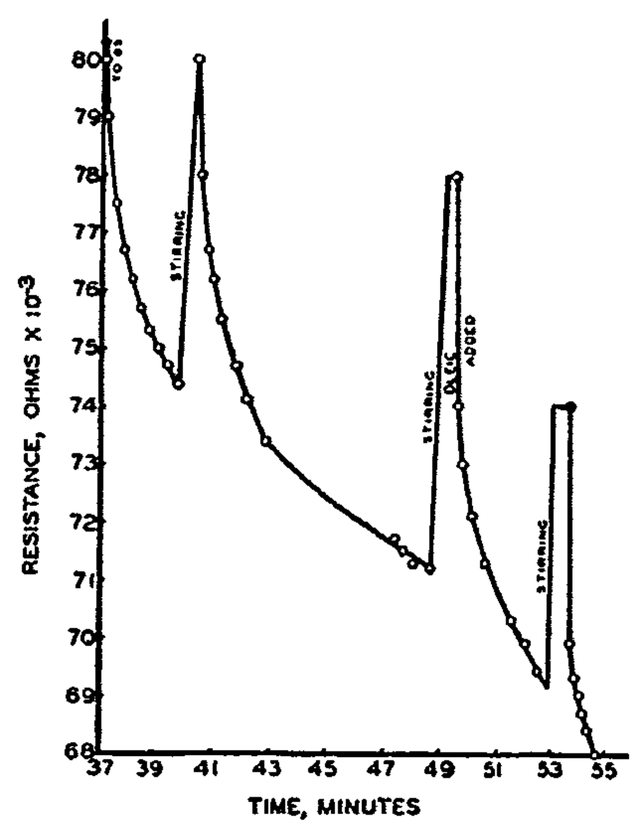

FIG. 6. CHANGE IN RESISTANCE WITH TIME IN CELL (FIGURE 3)
Showing effects of stirring and instantaneous production of surface conductivity upon adding insoluble fatty acid.

ductivity by disturbance of the double layer of ions at the interface, which is of course immediately restored.

Calculation of specific surface conductivity involves a selection of values of resistance which represent (I) resistance of the cell without surface conductivity, and (II) resistance of the cell in the same condition as in (I) except for the addition of a surface film imparting a certain amount of surface conductivity. Such a selection is obviously somewhat arbitrary, although the order of magnitude of the surface conductivity thus calculated is unaffected by any reasonable choice. The experiment is too rapid for appreciable diffusion or alteration of bulk conductance, more especially as the oleic acid is practically insoluble.

It should again be emphasized that surface conductance so measured is merely the amount by which the surface conductance of the oleic film exceeds that of the uncontaminated air–water interface.

DISCUSSION

The outstanding result is the magnitude of the surface conductivity which uniformly exceeds 10^{-8} mho per square centimeter, sometimes by a very large factor, as in the last line of table 1, p. 7. This fully confirms the previous findings of McBain, Peaker, King, and collaborators. The results with glass tubing are very high on account of the microscopically visible irregularities of the surface.

The previously reported results for optically polished glass did not exceed 10×10^{-8} mho. Of course all glass which has ever been exposed to water or even water vapor is superficially decomposed and corroded chemically upon a molecular scale. This would tend to increase the effective above the apparent area, although, as has been pointed out (6), it is essentially only the projection of the molecular discontinuities in the direction of the current that is effective, and for the most part continuous passages of adequate cross section will be lacking. Hence this would not appear materially to affect the magnitude of the results. Another communication by DuBois and Roberts will present comprehensive electrokinetic studies with these same optical surfaces.

The ζ-potential found by DuBois and Roberts with 0.001 N potassium chloride by measurements of electrosmosis in the optically polished glass slit is -50 millivolts; DuBois (1) had used the value -78 millivolts derived from the data of Powis (10).

No uncertainty attaches to the similar results with the air–water interface, which is ideally plane. The surface conductivity therefore exceeds in order of magnitude that currently calculated[6] for the mobile ions of the diffuse part of the double layer.

[6] For example, Bikermann (Z. Elektrochem. 38, 763 (1932)) and Cole (Cold Spring Harbor Symposia on Quantitative Biology 1, 27 (1933)). Bikermann in attempting

It is now well known (5) that the so-called double layer in its classical continuous form cannot exist, but that charges on any surface are far apart and often of different sign. Hence the continuous distribution postulated in the cloud of ions in the diffuse double layer, based upon Poisson continuity of electrical charge in the surface, does not in general occur in the neighborhood of the surface where strictly localized conditions prevail, although it may be built up at relatively remote distances. This is one more reason for disbelieving the real occurrence of the ζ-potentials classically or currently calculated.

TABLE 1

Deduction of surface conductivity in mhos × 10^8 of solutions of potassium chloride in contact with glass, assuming that the conductivity of 1 N potassium chloride is not appreciably influenced by surface conductivity

	CONCENTRATION				REMARKS
	N/1000	*N*/100	*N*/10	*N*/1	
Observed *R*	83,825	8,850	980.4	114.24	Measured on bridge
Conductivity of solvent (× 10^6)	0.5	0.4	0.7	0.7	Measured in another cell
Observed *R* corrected	84,110	8,850	980.4	114.24	Corrected for conductivity of solvent
Calculated *R* in tubes	69,878	7,263	795.5	91.72	Calculated from cross section, length, specific conductivity
R outside tubes	17,160	1,783	195.3	22.52	22.52 × ratios of specific conductivities
Observed *R* tubes	66,950	7,067	785.1	91.72	(Total observed *R*) − (*R* outside tubes)
Surface conductivity, K_s	62.6	382	1,660		$\frac{1}{R_{obsd.}} - \frac{1}{R_{calcd.}}$
Specific surface conductivity, k_s	9.96	60.8	264		$K_s \times 0.159 = k_s$

Surface conductivity is undoubtedly exhibited by all mobile ions whether in the diffuse part of the double layer or not, and also (Laing paradox) by all unbalanced ions attached to or within the surface. DuBois (1) has

to defend the classical theory made the very serious error of abandonning in his calculation the well-known distinction between the Nernst potential ϵ and the electrokinetic potential ζ, taking the ζ-potential as 1 volt. His conclusions are therefore fallacious. A ζ-potential of 50 millivolts in his calculation would lead to the requirement that a film of water 0.4 A. U. thick had the viscosity and dielectric constant of water, although such a conclusion can carry but little weight if molecular dimensions retain any physical significance.

calculated from the data of McBain, Peaker, and King the individual surface conductances and mobilities which appear in the systems here considered.

TABLE 2

Surface conductivity of acid films on conductivity water (figure 2)

Cell constant (for surface conductivity): 1/10. Dimensions of electrodes (measured by Cambridge cathetometer): outer electrode (inside diameter), 1.932 cm.; inner electrode (outside diameter), 1.037 cm.

POSITION	RESISTANCE	POSITION	RESISTANCE	POSITION	RESISTANCE
Stearic acid		Stearic acid		Palmitic acid	
I	59,350	I	107,330	I	43,720*
II	72,450	II	150,360	II	48,610*
III	56,140	III	138,260	III	45,320*
IV	46,970	IV	104,450	IV	41,490*
$k_s = 3.73 \times 10^{-8}$		$k_s = 3.98 \times 10^{-8}$		$k_s = 3.87 \times 10^{-8}$	
Palmitic acid		Oleic acid		Oleic acid	
I	51,174*	I	49,785	I	44,546*
II	57,003*	II	64,150	II	50,110*
III	48,642*	III	55,640	III	43,757*
IV	44,574*	IV	45,270	IV	40,400*
$k_s = 4.18 \times 10^{-8}$		$k_s = 8.30 \times 10^{-8}$		$k_s = 8.48 \times 10^{-8}$	

* Cell + 100,000 ohm shunt.

TABLE 3

Surface conductivity of a film of oleic acid in a circular trough

Cell constant: 1/27. Resistance for continuous overflow, 170,000. Surface conductivity of oleic acid in closed cell (figure 2) was 8.4×10^{-8}

FIGURE NO.	R DURING STIRRING OF CONTAMINATED SURFACE (I)	R BEFORE DISTURBING ACID FILM (II)	$k_s \times 10^8$	R BEFORE CONTAMINATION (I)	R AFTER CONTAMINATION (II)	$k_s \times 10^8$
4	54,000	52,000	2.6	60,000	53,700	7.2
5	74,500	70,100	3.1	78,000	71,100	4.6
6	74,000	69,100	3.5	78,000	70,600	5.0

If this surface conductance is not sufficient there remain but two alternatives. The first is that which was suggested as reasonable by Horace Lamb (4), namely, that slip or sliding occurs between the two parts of the double layer, or between ions and the surface with which they are in

contact, making all such ions mobile. Later authors have not endorsed this point of view, although some, like Smoluchowski, suspended judgment.

The other alternative, to adopt the terminology of Frenkel (2, 3) who has used it for explaining conductivity of dielectrics and supraconductivity of metals is "polarization current" carried by discontinuous jumps of otherwise sessile ions, the charge being thus transmitted from place to place. In the introduction we mentioned that a variety of polarization current might be exhibited with alternating current when it could not be produced by low voltages of direct current.

SUMMARY

Measurements extending over the past two years demonstrate the large surface conductivity per square centimeter exhibited by potassium chloride solutions in contact with glass surfaces, and likewise by films of fatty acid at the air-water interface. The specific surface conductivity of close packed films of stearic acid is 3.8×10^{-8} mho, that for palmitic acid 4.0×10^{-8} mho, and that for oleic acid 8.4×10^{-8} mho.

New designs of cells have been developed which permit a ready demonstration of these results.

These results are much too high to be attributable solely to the mobile ions in the outer portion of the diffuse double layer.

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CARBON DIOXIDE CLEAVAGE FROM DIBROMOMALONIC ACID

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Received June 19, 1934

The kinetics of the decomposition of carboxylic acids according to the scheme:

$$RCOOH \rightarrow RH + CO_2$$

has been studied several times. The type of acid which has been most thoroughly investigated is that of the β-ketocarboxylic acids. N. O. Engfeldt (6), E. Widmark (14), H. von Euler (7) and Ljunggren (10) have studied the decomposition of acetoacetic acid. Both the acid and the ion are unstable in aqueous solution. Amines catalyze the reaction. The decomposition of camphorcarboxylic acid and that of α-bromocamphorcarboxylic acid in water and in various organic solvents were studied by Bredig and his coworkers (2, 8, 11). These reactions were also catalyzed by amines.

β-Ketocarboxylic acids with a hydrogen atom in the α-position exist in two different forms, an enol and a keto form. The fact that both α- and γ-ketocarboxylic acids are stable has led to the hypothesis that the unstable form is the enol. K. J. Pedersen (13) has shown that α,α'-dimethylacetoacetic acid decomposes with even greater velocity than acetoacetic acid. The α,α'-dimethylacetoacetic acid cannot exist in the enol form, therefore in all probability the keto form is the unstable form.

Nitroacetic acid was studied by K. J. Pedersen (12) and J. F. Heuberger (9). The monovalent ion decomposes unimolecularly, while the undissociated acid is stable.

The acid used for the present investigation was dibromomalonic acid. The decomposition of this acid

$$Br_2C(COOH)_2 \rightarrow Br_2HCCOOH + CO_2$$

proceeds in aqueous solution even at room temperature with measurable velocity. The reaction velocity was studied at different hydrogen-ion concentrations and different salt concentrations. Dibromoacetic acid, which is a product of the reaction, was stable under these conditions. Most of the experiments were carried out at 25°C., a few at 35°C.

EXPERIMENTAL

Preparation of dibromomalonic acid

Dibromomalonic acid was prepared by the method of Conrad and Reinbach (5). The crude product was purified by dissolving it in ether, adding toluene, and concentrating the mixture *in vacuo* at room temperature until crystallization took place. Dibromomalonic acid is very soluble in ether and only slightly soluble in toluene, but addition of toluene to the ethereal solution in amount sufficient to precipitate the dibromomalonic acid does not yield the acid in the form of crystals, but gives rise to the formation of an oil or a mixture of oil and crystals. Also the addition of petroleum ether to the ethereal solution gave a mixture of crystals and oil. The product recrystallized from the ether–toluene mixture was pure, except for a small amount of dibromoacetic acid (about 1 per cent).

Experimental procedure

The velocity of the decomposition was determined by measuring the pressure of the evolved carbon dioxide during the reaction by means of an apparatus described by J. N. Brønsted (4). The concentration of dibromomalonic acid at the time t is proportional to $p_\infty - p$, where p_∞ is the pressure when the reaction is complete and p is the pressure at the time t. The reaction was studied in solutions containing hydrochloric acid and in buffer solutions. The initial concentration of dibromomalonic acid was in most experiments about 0.01 M; the concentration of the hydrochloric acid varied from 0.05 M to 1 M; the buffer concentration was usually about 0.1 M.

As dibromomalonic acid is a fairly strong acid and the concentration is not negligible compared with the buffer concentration used, it is necessary to know the dissociation constants in order to calculate the hydrogen-ion concentration of the mixtures.

Dissociation constants of dibromomalonic acid

The hydrogen-ion concentration in mixtures of the acid and its salts was measured electrometrically by means of a quinhydrone electrode. Three series of mixtures with different salt concentrations were made. To a weighed amount of dibromomalonic acid was added a known volume of a solution of sodium hydroxide and potassium chloride in such concentrations that the total salt concentration in the mixture after dissolution of the dibromomalonic acid was 0.1 N, 0.2 N, and 1 N, respectively. The solution was transferred into an electrode vessel fitted with a bright platinum electrode and quinhydrone. The potential of this electrode compared with a 0.1 N calomel electrode (connected through a saturated potassium chloride bridge) was read off as quickly as possible, and readings

were continued every minute for ten minutes. Owing to the decomposition of dibromomalonic acid the potential falls off continually, but since the fall is practically linear in the first minutes, the initial value of the potential can be found by extrapolating to zero time. The potential was then determined, compared with the same calomel electrode, of an electrode with 0.01 N hydrochloric acid and potassium chloride to the same total salt concentration as that of the dibromomalonic acid solution.

The hydrogen-ion concentration was calculated by means of the formula

$$\mathrm{pH} = 2.000 + \frac{\pi_{\text{hydrochloric acid}} \div \pi_{\text{dibromomalonic acid}}}{0.0001984 \cdot 298}$$

where pH stands for the logarithm of the reciprocal of the hydrogen-ion concentration. $\pi_{\text{hydrochloric acid}}$ and $\pi_{\text{dibromomalonic acid}}$ are the potentials of the

TABLE 1

Concentration dissociation constants of dibromomalonic acid at different salt concentrations

Temperature, 25°C.

EQUIVALENT CONCENTRATION OF SALT	K_1	K_2
N		
0.1	1	9.0×10^{-3}
0.2	1	1.25×10^{-2}
1	1	1.70×10^{-2}

cells with hydrochloric acid and with dibromomalonic acid, respectively, at the same salt concentration. π is considered positive when the calomel electrode is the negative pole of the element.

The two "concentration" dissociation constants can be calculated from the expressions

$$K_1 = C_{\mathrm{H}} \frac{C_{\mathrm{Br_2C(COOH)COO^-}}}{C_{\mathrm{Br_2C(COOH)_2}}} \quad \text{and} \quad K_2 = C_{\mathrm{H}} \frac{C_{\mathrm{Br_2C(COO^-)_2}}}{C_{\mathrm{Br_2C(COOH)COO^-}}}$$

or, if C_{acid} be the total concentration of dibromomalonic acid and C_{base} the initial concentration of sodium hydroxide:

$$K_1K_2(2C_{\text{acid}} - (C_{\text{base}} + C_{\mathrm{H}})) + K_1C_{\mathrm{H}}\,(C_{\text{acid}} - (C_{\text{base}} + C_{\mathrm{H}})) = C_{\mathrm{H}}^2(C_{\text{base}} + \rho_{\mathrm{H}})$$

The average values from several series of determinations are collected in table 1. These values (especially those of K_1) are only to be looked upon as approximate, owing to the magnitude of K_1 and K_2.

The dissociation constant of dibromoacetic acid at 0.1 N salt concentration was determined in a similar way and found to be $K = 6.9 \times 10^{-2}$.

Experiments in solutions of hydrochloric acid

The solutions were of three types: (1) x M hydrochloric acid, (1 − x) M potassium chloride; (2) x M hydrochloric acid, (0.2 − x) M potassium chloride; (3) x M hydrochloric acid, (0.1 − x) M potassium chloride. The reaction followed the first-order law

$$-kt = \log c + \text{const.} = \log (p_\infty - p) + \text{const.} \qquad (1)$$

The velocity constant was calculated by means of decadic logarithms, t being the time in minutes.

The results of the experiments are given in tables 2a, 3a, and 4a.

Experiments in buffer solutions

The solutions were of the following types: (1) x M hydrochloric acid, (0.1 − x) M glycine, (0.1 − x) M sodium chloride; (2) x M hydrochloric acid, (0.1 − x) M secondary sodium citrate; (3) x M hydrochloric acid, (0.2 − x) M glycine, (0.2 − x) M sodium chloride; (4) x M sodium hydroxide, 0.1 M citric acid + potassium chloride to a total salt concentration of 1 N; (5) x M acetic acid, (0.1 − x) M sodium acetate to a total salt concentration of 1 N; (6) x M hydrochloric acid, (0.2 − x) M glycine + potassium chloride to a total salt concentration of 1 N; (7) A few experiments were performed in solutions with double buffer concentration but with the same total salt concentration as in Nos. 4 and 5. M is the number of moles dissolved in 1 liter, neglecting reactions which may have taken place after mixing.

While the reaction in solutions of hydrochloric acid strictly follows the first-order law, k calculated from equation 1 in the experiments in buffer solutions falls off during the reaction. This is due to a decrease in the hydrogen-ion concentration accompanying the decomposition of dibromomalonic acid, and will be further discussed later on. The falling-off of k is not very marked, and the initial value of k can be determined with sufficient accuracy by extrapolating graphically to zero time. The values of k computed in this way are given in tables 2b, 2c, 2d, 3b, 4b, and 4c.

The hydrogen-ion concentration of the different buffer solutions can be calculated if the dissociation constants of the acids are known. At 0.1 N salt the following values found by Bjerrum (1) were used:

Glycine	$pK = 2.359 - 0.041 \sqrt[3]{c} + 0.18c$
Citric acid	$pK = 3.080 - 0.46 \sqrt[3]{c} + 0.18c$
Citric acid	$pK = 4.799 - 1.04 \sqrt[3]{c} + 0.18c$
Citric acid	$pK = 6.443 - 1.71 \sqrt[3]{c} + 0.18c$

TABLE 2

Decomposition of dibromomalonic acid at 25°C.

Total salt concentration, 1 *N*

(a) HCl + KCl

HCl	DIBROMOMALONIC ACID	C_{H^+}	pH	k	$\frac{k}{\alpha}$
M	*M*				
1.00			0	2.83×10^{-3}	5.7×10^{-3}
0.75	0.00924	0.755	0.122	3.25×10^{-3}	5.9×10^{-3}
0.50	0.01023	0.507	0.295	4.04×10^{-3}	6.2×10^{-3}
0.25	0.00977	0.258	0.588	4.53×10^{-3}	6.0×10^{-3}
0.20	0.00936	0.209	0.680	4.56×10^{-3}	5.9×10^{-3}
0.10	0.00853	0.109	0.963	4.48×10^{-3}	5.7×10^{-3}
0.08	0.00961	0.0907	1.042	4.22×10^{-3}	5.4×10^{-3}
0.05	0.00929	0.0612	1.213	4.10×10^{-3}	5.6×10^{-3}
0	0.0215	0.0290	1.54	3.31×10^{-3}	5.4×10^{-3}

(b) Glycine buffer + KCl

HCl	GLYCINE	DIBROMOMALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.16	0.04	0.00962	0.90	4.58×10^{-3}	5.8×10^{-3}

(c) Citric acid buffer + KCl

CITRIC ACID	PRIMARY CITRATE	DIBROMOMALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.18	0.02	0.00960	1.84	2.55×10^{-3}	5.5×10^{-3}
0.07	0.03	0.00912	2.18	1.49×10^{-3}	5.4×10^{-3}
0.05	0.05	0.00866	2.51	8.27×10^{-4}	5.5×10^{-3}
PRIMARY CITRATE	SECONDARY CITRATE				
M	*M*				
0.10	0	0.00861	3.20	1.92×10^{-4}	5.4×10^{-3}
0.08	0.02	0.00930	3.44	1.08×10^{-4}	5.2×10^{-3}
0.06	0.04	0.00970	3.70	6.90×10^{-5}	5.9×10^{-3}

(d) Acetic acid buffer + KCl

ACETIC ACID	ACETATE	DIBROMOMALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.10	0.10	0.0211	4.14	2.01×10^{-5}	4.8×10^{-3}
0.04	0.06	0.0100	4.35	1.26×10^{-5}	4.8×10^{-3}
0.02	0.08	0.0100	4.71	5.1×10^{-6}	4.5×10^{-3}

TABLE 3

Decomposition of dibromomalonic acid at 25°C.

Total salt concentration, 0.2 *N*

(a) HCl + KCl

HCl	DIBROMO-MALONIC ACID	C_H	pH	k	$\frac{k}{\alpha}$
M	*M*				
0.20	0.00935	0.208	0.68	4.07×10^{-3}	5.1×10^{-3}
0.10	0.00934	0.1095	0.96	4.26×10^{-3}	5.2×10^{-3}
0.08	0.00936	0.0899	1.05	4.40×10^{-3}	5.4×10^{-3}
0.05	0.00907	0.0605	1.22	4.12×10^{-3}	5.1×10^{-3}

(b) Glycine buffer

HCl	GLYCINE	DIBROMO-MALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.16	0.04	0.00939	0.89	4.37×10^{-3}	5.4×10^{-3}
0.14	0.06	0.00946	1.04	3.98×10^{-3}	4.9×10^{-3}
0.12	0.08	0.00930	1.24	3.85×10^{-3}	4.9×10^{-3}
0.10	0.10	0.00972	1.55	3.66×10^{-3}	5.4×10^{-3}
0.08	0.12	0.00920	1.97	2.54×10^{-3}	5.5×10^{-3}
0.06	0.14	0.00940	2.31	1.44×10^{-3}	5.1×10^{-3}
0.04	0.16	0.00928	2.62	7.72×10^{-4}	4.9×10^{-3}

TABLE 4

Decomposition of dibromomalonic acid at 25°C.

Total salt concentration, 0.1 *N*

(a) HCl + KCl

HCl	DIBROMO-MALONIC ACID	C_H	pH	k	$\frac{k}{\alpha}$
M	*M*				
0.10	0.00970	0.110	0.96	4.31×10^{-3}	5.0×10^{-3}
0.08	0.00932	0.0896	1.05	4.25×10^{-3}	5.0×10^{-3}
0.05	0.00959	0.0605	1.22	4.24×10^{-3}	5.1×10^{-3}

(b) Glycine buffer

HCl	GLYCINE	DIBROMO-MALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.08	0.02	0.00952	1.20	4.18×10^{-3}	5.0×10^{-3}
0.07	0.03	0.00946	1.29	4.06×10^{-3}	5.0×10^{-3}
0.06	0.04	0.00921	1.46	3.76×10^{-3}	4.9×10^{-3}
0.05	0.05	0.00950	1.68	3.29×10^{-3}	4.9×10^{-3}
0.04	0.06	0.00979	1.96	2.78×10^{-3}	5.0×10^{-3}
0.03	0.07	0.00966	2.22	1.84×10^{-3}	4.6×10^{-3}
0.02	0.08	0.00938	2.50	1.20×10^{-3}	4.7×10^{-3}

TABLE 4—*Concluded*

(c) Citric acid buffer

HCl	SECONDARY CITRATE	DIBROMO-MALONIC ACID	pH	k	$\frac{k}{\alpha}$
M	*M*	*M*			
0.08	0.02	0.00937	1.29	4.25×10^{-3}	5.3×10^{-3}
0.07	0.03	0.00962	1.62	3.68×10^{-3}	5.3×10^{-3}
0.06	0.04	0.00947	2.34	1.58×10^{-3}	4.8×10^{-3}
0.05	0.05	0.00935	3.08	4.20×10^{-4}	4.9×10^{-3}
0.04	0.06	0.00955	3.64	9.97×10^{-5}	4.5×10^{-3}
0.03	0.07	0.00939	4.06	5.40×10^{-5}	5.6×10^{-3}
0.02	0.08	0.01013	4.30	2.3×10^{-5}	4.1×10^{-3}
0.01	0.09	0.00975	4.55	1.5×10^{-5}	4.9×10^{-3}

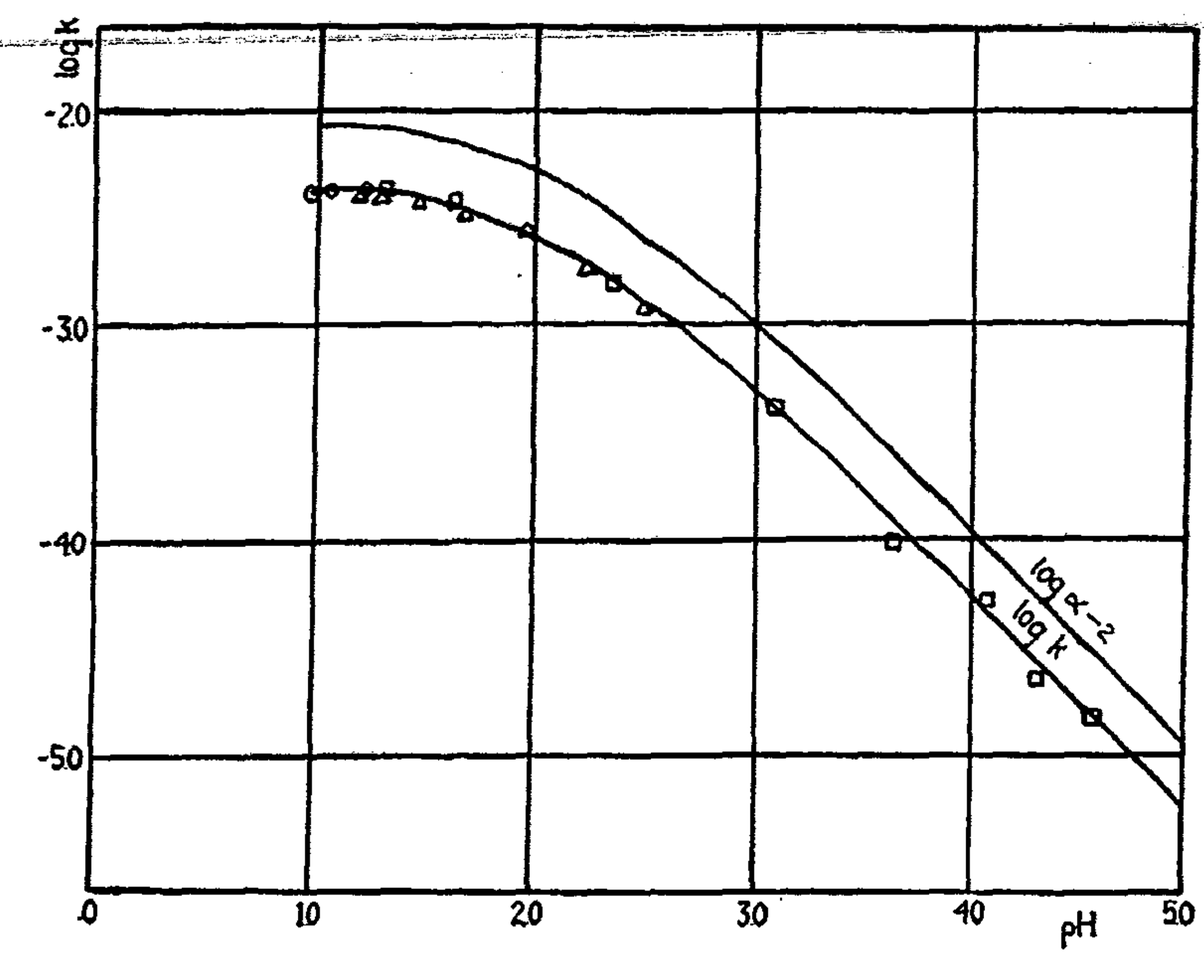

FIG. 1. EXPERIMENTS IN 1 *N* SALT SOLUTIONS

k, velocity constant of the decomposition of dibromomalonic acid.
α, fraction of dibromomalonic acid present as $Br_2C(COOH)COO^-$.
○, experiments in solutions of hydrochloric acid and potassium chloride.
△, experiments in solutions of glycine buffer and potassium chloride.
□, experiments in solutions of citric acid buffer and potassium chloride.
▽, experiments in solutions of acetic acid buffer and potassium chloride.

pK is the logarithm of the reciprocal of the concentration dissociation constant; c is the equivalent salt concentration. These formulas are valid up to 0.1 *N* salt concentration.

At 0.2 N and 1 N salt concentration no such values could be found in the literature, and it was necessary to determine the dissociation constants of glycine at 0.2 N salt concentration and of citric acid and acetic acid at 1 N salt concentration. This was carried out in a manner similar to that described for dibromomalonic acid. The results of the measurements were:

Glycine	$K = 4.68 \times 10^{-3}$	0.2 N salt at 25°C.
Citric acid	$K_1 = 1.71 \times 10^{-3}$	1 N salt at 25°C.
Citric acid	$K_2 = 8.05 \times 10^{-5}$	
Acetic acid	$K = 2.95 \times 10^{-5}$	

By means of these constants and those found for dibromomalonic acid the initial hydrogen-ion concentration in each experiment was calculated. In column 4 of tables 2, 3, and 4 the pH of the solutions is given. In figure 1 log k is plotted against pH. The curve shows a maximum at about pH 0.9; from pH ca. 2.5 it approaches a straight line.

Influence of temperature

A few experiments were carried out at 35°C. to determine the influence of temperature on the reaction velocity.

DISCUSSION

In solution dibromomalonic acid is present partly as the undissociated acid, partly as the ions $Br_2C(COOH)COO^-$ and $Br_2C(COO^-)_2$. On figure 1 log k and (log α − 2), where α is the fraction of dibromomalonic acid present as the univalent ion, are plotted against pH. The two curves seem to be very nearly parallel. This leads to the conclusion that the unstable compound is the univalent ion.

In the last column of tables 2, 3, and 4, k/α is given. This quantity is fairly constant over a wide range of pH, i.e.,

$$\frac{d \log c}{dt} = k = Q \cdot \alpha$$

where Q is a constant and c the total concentration of dibromomalonic acid, or

$$\frac{dc}{dt} = Q \cdot \alpha \cdot c$$

the rate of decomposition is proportional to the concentration of the univalent ion.[1]

[1] According to the mass action law we have

$$K_1 = \frac{C_H \cdot \alpha}{(1 - \alpha - \beta)} = \frac{k_w \cdot \alpha}{C_{OH}(1 - \alpha - \beta)} \text{ and } K_2 = \frac{C_H \cdot \beta}{\alpha}$$

α is proportional to $C_H \cdot \beta$ and to C_{OH} $(1 - \alpha - \beta)$, and the constancy of k/α might just as well be explained by assuming hydrogen-ion catalysis on the divalent ion or hydroxyl-ion catalysis on the undissociated acid.

The $Br_2C(COO^-)_2$ ion seems to be stable. After two months at pH 10, no detectable amounts of carbonate were formed.

Whether or not the undissociated acid is stable cannot be demonstrated in aqueous solution, as the univalent ion even at pH 0 is present in an amount sufficient to conceal a possible decomposition of the undissociated acid. The decomposition of the acid might be shown by experiments in non-ionizing solvents. Such experiments are now in progress.

k/α is constant not only in the experiments in solutions of hydrochloric acid, but also in the buffer solutions. This indicates that there is no general acid or base catalysis.

According to Brønsted (3) the kinetic salt effect can be divided into two groups: (1) a primary salt effect, which consists in a direct influence on the reaction velocity of a reacting molecule, and (2) a secondary salt effect which is the influence on the reaction velocity caused by a change in the concentration of the reacting molecules. A thorough investigation of the

TABLE 5

Experiments in 1 N salt solutions at 35°C.

HCl	DIBROMOMALONIC ACID	k	$k_{35°}/k_{25°}$	$k_{35°}/k_{25°}$ MEAN VALUE
M	*M*			
1.0	0.01	1.13×10^{-2}	4.08	4.01
0.5	0.01	1.58×10^{-2}	4.08	
0.2	0.01	1.86×10^{-2}	3.91	
0.1	0.01	1.83×10^{-2}	3.99	

salt effect requires experiments in very dilute solutions, but as the dibromomalonic acid is a fairly strong acid, this would involve great changes in the hydrogen-ion concentration and the salt concentration during the reaction, thus complicating the theoretical treatment of the experimental material.

In the present investigation experiments have been carried out at 0.1 *N*, 0.2 *N*, and 1 *N* salt concentrations. From the experimental data it will be seen that there is a marked secondary salt effect consisting in a change in the concentration of $Br_2C(COOH)COO^-$, while the primary salt effect is very small or zero. As already pointed out, there is a decrease in k during the reaction in the experiments in buffer solution. This may be due to a decrease in the hydrogen-ion concentration owing to the disappearance of the dibromomalonic acid.

Example 1. 0.05 *M* hydrochloric acid, 0.05 *M* glycine, 0.00930 *M* dibromomalonic acid:

At $t = 0$, pH = 1.68 — $k_{calcd.} = 3.31 \times 10^{-3}$; $k_{found} = 3.29 \times 10^{-3}$

After 75 per cent decomposition, pH = 1.74 — $k_{calcd.} = 3.17 \times 10^{-3}$; $k_{found} = 2.91 \times 10^{-3}$

Example 2. 0.06 *M* hydrochloric acid, 0.04 *M* secondary citrate, 0.00947 *M* malonic acid:

At $t = 0$, pH = 2.34	$k_{calcd.} = 1.62 \times 10^{-3}$; $k_{found} = 1.58 \times 10^{-3}$
After 75 per cent decomposition, pH = 2.51	$k_{calcd.} = 1.26 \times 10^{-3}$; $k_{found} = 1.40 \times 10^{-3}$

Since the determination of k is very inaccurate when the reaction is so far advanced, no better agreement with the calculated values could be expected.

At 35°C. the decomposition of dibromomalonic acid is too rapid to allow an electrometrical determination of the dissociation constants, but as the maximum velocity is found to be at about the same hydrogen-ion concentration as at 25°C., there seems to be no great change in these constants. Hence the results can be directly compared. The energy of activation calculated from the equation

$$E = R \frac{d \log (k_2/k_1)}{d (T^{-1})}$$

is found to be $E = 25{,}000$ calories per gram-molecule.

SUMMARY

The velocity of decomposition of dibromomalonic acid

$$Br_2C(COOH)_2 \rightarrow Br_2HCCOOH + CO_2$$

in aqueous solution at 25°C. has been studied at various hydrogen-ion concentrations and various salt concentrations.

At constant hydrogen-ion concentration the reaction follows the first-order law. The velocity is dependent upon the hydrogen-ion concentration.

The concentration dissociation constants were determined electrometrically at various salt concentrations.

The velocity was found to be proportional to the concentration of the $Br_2C(COOH)COO^-$ ion, i.e., the reaction can be described as a spontaneous decomposition of this ion. The velocity constant of the decomposition of the univalent ion in solutions containing 0.1 *N* salt was found to be 4.9×10^{-3} (min.$^{-1}$, decadic log.).

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THE INFLUENCE OF DEPOLARIZERS UPON THE PHOTOVOLTAIC EFFECT IN CELLS CONTAINING GRIGNARD REAGENTS[1]

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Received March 2, 1934

More than two hundred papers have appeared on the photovoltaic effect since Becquerel (1) reported his discovery of the effect in 1839. A review of the work that has been done, together with a summary of the theories that have been advanced, may be found in papers by Lifschitz and Hooghoudt (16) and by Dufford (7). A brief discussion is given by Hughes and DuBridge in their recent book (15).

An extensive study of the effect in Grignard compounds has been in progress at the Physical Laboratories of the University of Missouri for many years. Numerous compounds have been studied in connection with many different metals as electrodes. Measurable effects were observed in practically every case (2–6, 8–14, 17, 18).

All Grignard compound cells are easily polarized. In general the response to light is changed by electrical polarization. The polarization is probably produced by affecting the adsorbed layers on the electrodes. By observing the effect, if any, which depolarizers would produce, it was believed that additional light could be thrown upon the nature of these adsorbed layers. Hence this study was undertaken.

APPARATUS AND MATERIALS

The apparatus and experimental arrangements were essentially those used by Hammond (14) with only minor changes and improvements. The cells were made up in 1 in. by 8 in. test tubes which were covered with black friction tape except for 1½ in. at the bottom. One electrode was exposed below the friction-tape screen, and the other was above the lower edge of the screen, thus keeping it in darkness except for light diffused by the liquid or reflected from the exposed electrode.

Electrodes of copper, zinc, aluminum, iron, lead, and platinum were used

[1] Abstracted from a thesis submitted to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics, August, 1932.

in combination with two electrolytes and two depolarizers. The electrolytes were ethylmagnesium bromide and phenylmagnesium bromide solutions in ether. The depolarizers were ethyl bromide and ethyl iodide.

EXPERIMENTAL PROCEDURE

In making Grignard compounds, especial precaution was observed in keeping all glassware clean and dry. Every piece was washed thoroughly, allowed to stand in cleaning solution for at least twenty-four hours, again washed, rinsed with distilled water, and allowed to dry. The ether, which was kept over sodium in the storeroom, was distilled over sodium at least once, sometimes twice, before using. Molar solutions of the Grignard compounds in ether were made in the usual manner and diluted, in most cases, to 0.5 molar solution.

With only a few exceptions, all electrodes except platinum were brightly polished with steel wool just before inserting into the test tubes. In a few cases the oxides were left on the metals, and in a few other cases copper electrodes were coated with oxide by heating in an oxygen flame. Platinum electrodes were cleaned with nitric acid, washed thoroughly in distilled water, dried, and flamed.

The cells were allowed to stand in the dark, or in a relatively dark place, for at least thirty hours after being made up, before being put into the bath. There were a few exceptions to this practice when an attempt was made to determine the effect of standing. After being put into the bath, they were allowed to stand until the voltage became fairly constant, the time required varying from a few minutes to an hour.

A long series of observations was made on each cell before the depolarizer was added. After adding the depolarizer and thoroughly mixing, the cell was again allowed to stand in the dark for at least thirty hours. The same series of observations was made after depolarizing as before. Studies were made of (1) the dark voltage, (2) the voltage response to light, (3) current strength and current response to light when the cell was connected directly to the galvanometer with no external voltage in the circuit, (4) current strength and current response to light when an external voltage in series with the cell was applied from the potentiometer, causing a current to flow in such a direction as to make the illuminated electrode the anode, (5) current strength and current response to light when an external voltage made the illuminated electrode the cathode, (6) resistance and resistance response to light, taken after each of the observations 1 to 5 above, and (7) capacitance and capacitance response to light, taken simultaneously with the resistance readings. This was the general plan of study, and was carried out quite completely except for the resistance and capacitance. They were omitted from the study of many cells and were observed for some cells after only a part of the series of readings. In many other cases

the resistance was measured without attempting to get the response to light.

In making these observations, it was the practice to continue taking readings at intervals of one minute or less until the quantity (voltage, current, or resistance) being measured changed relatively little or not at all during an interval. Usually this required from four to fifteen minutes.

A series of tests was made to determine the most effective quantity of depolarizer to add. The effect was studied for amounts varying from one drop to 10 cc. It was found that the effect on voltage and current responses to light increased with increasing amounts of depolarizer; but after 1 cc. was added the increase in the effect of the depolarizer was small. In the cases of resistance and capacitance the depolarizer seemed to produce no increased effect by adding more than 1 cc. Consequently, in most cases 1 cc. was used. The cells contained about 40 cc. of the Grignard solutions.

A cell was regarded as a resistance and capacitance in series, and the bridge equations used by Hammond (14) were employed with only slight simplifications.

As will be seen in the next section, voltage–time curves, current–time curves, resistance–time curves, and capacitance–time curves have been made showing responses to light in all the variations of the study. More than seven hundred curves were made, but only a few are included in this paper. The data when assembled consisted of five hundred seventy-six tables. Space does not, of course, permit the showing of more than a small fraction of this material, but an attempt has been made to select typical curves and data.

RESULTS

The writer believes that the curves and tables are, for the most part, self-explanatory. The notations concerning the curves and the headings of the tables were purposely made full and explicit. There are, nevertheless, a few cases where the notations are not entirely clear without explanation.

The curves are exhibited in pairs. The first curve shows the conditions before a depolarizer was added; the second, the conditions after the depolarizer was added. Arrows pointing upward indicate the time at which the light was turned on the cell, while arrows pointing downward indicate the time at which the light was turned off. The coördinates are the same for both curves; consequently they are omitted from the second curve of each pair. "No external voltage," as it occurs in the tables and with the curves, refers to the case where a cell has been short-circuited through the galvanometer for several minutes, thus allowing a current to flow, due alone to the E.M.F. of the cell. By "anode illuminated" is meant that a current has been sent through the cell from an external voltage for some time in

TAB

Typical

KIND OF CELL	DEPOLARIZER	DARK VOLTAGE, MILLIVOLTS		VOLTAGE RESPONSE, MILLIVOLTS		CURRENT, μμ A. PER. M.V., NO EXTERNAL VOLTAGE		CURRENT, μμ A. PER MV., ANODE ILLUMINATED		CURRENT, μμ A. PER MV., CATHODE ILLUMINATED	
		No D	With D	No D	With D	No D	With D	No D	With D	No D	With D
Pt/E_1/Pt	D_1	(2) 31.5	51.0	(3) − 27.0	12.6	(12) 61.5	250	(6) 181.0	684.0	(5) 166	683.5
Pt/E_1/Pt	D_2	(5) 4.5	2.8	(5) − 15.7	+ 3.2	(5) 388	1,040	(5) 458	1,500	(5) 453	1,040
Pt/E_2/Pt	D_1	(6) 46.7	62.1	(6) − 59.2	− 45.4	(3) 327	313	(2) 398	450	(3) 444	463
Pt/E_2/Pt	D_2	(13) 18.2	33.0	(3) − 48.3	− 21.4	(2) 80.2	101.8	(1) 126.2	135.0	(1) 130.8	137.5
Cu/E_1/Cu	D_1	(3) 165.9	63.5	(3) + 100.1	+ 20.8	(3) 307	385	(3) 304	279.5	(3) 398	394
Cu/E_1/Cu	D_2	(3) 6.6	20.5	(3) − 50.0	− 4.9	(3) 323.5	744.1	(2) 315	712	(2) 817	727
Cu/E_2/Cu	D_1	(3) 1.6	12.5	(3) + 30.0	+ 4.4	(2) 1,580	6,350	(2) 1,990	7,300	(2) 2,122	8,340
Cu/E_2/Cu	D_2	(3) 1.6	6.2	(3) + 1.4	+ 5.2	(3) 4,230	6,760	(1) 664	234	(1) 285	231
Al/E_1/Al	D_1	(4) 27.2	4.9	(4) + 4.7	+ 0.7	(4) 18,186	372,054	(4) 24,017	647,725	(4) 2,091	662,790
Al/E_1/Al	D_2	(2) 11.4	1.0	(2) + 6.3	+ 0.7	(2) 1,360	11,550	(1) 676	1,169	(4) 679	1,074
Al/E_2/Al	D_1	(2) 4.0	2.9	(2) + 53.7	+ 11.6	(2) 3,722	46,800			(2) 79.2	382
Al/E_2/Al	D_2	(2) 11.6	16.2	(2) + 68.8	+ 92.3	(2) 6.3	254,000	(2) 70.2	274,000	(2) 73.0	271,000
Fe/E_1/Fe	D_1	(3) 3607	1.2	(2) − 8.0	− 3.5	(3) 58.8	1466	(3) 138	199	(3) 126.6	16.4
Fe/E_1/Fe	D_2	(2) 150.6	102.0	(2) + 65.9	+ 2.0	(3) 271	396	(2) 281	423	(1) 619	448
Fe/E_2/Fe	D_1	(2) 5.1	5.6	(2) + 8.7	+ 0.4	(2) 255	692	(2) 328	547	(2) 258	622
Fe/E_2/Fe	D_2	(2) 8.0	7.0	(2) + 7.9	+ 12.3	(2) 202	275	(2) 142.5	143.5	(2) 172	195.2
Zn/E_1/Zn	D_1	(4) 20.9	5.0	(4) + 6.2	+ 1.1	(4) 17,050	23,301	(4) 28,952	31,900	(3) 28,900	34,950
Zn/E_1/Zn	D_2	(3) 10.0	19.0	(2) + 8.1	+ 3.5	(2) 378	1,530	(2) 1,060	1,620	(2) 1,073	1,595
Zn/E_2/Zn	D_1	(3) 7.5	13.7	(3) + 23.6	+ 28.2	(3) 302	183.5	(1) 2,920	28.9	(1) 2,880	310
Zn/E_2/Zn	D_2	(2) 1.5	0.6	(2) + 20	+ 1	(2) 167	12,100	(1) 11,700	178,000	(1) 11,700	39,300
Pb/E_1/Pb	D_1	(2) 16.4	4.0	(2) + 7.3	+ 6.4	(2) 572	1,030	(2) 436	1,135	(2) 412	1,135
Pb/E_1/Pb	D_2	(2) 9.5	14.5	(2) + 0.7	+ 2.4	(2) 16,500	162,450	(2) 27,500	142,500	(2) 27,500	142,500
Pb/E_2/Pb	D_1	(8) 11.0	10.1	(8) + 7.1	+ 4.7	(2) 879	1,168	(2) 1,222	1,780	(2) 932	1,525
Pb/E_2/Pb	D_2	(2) 1.6	1.7	(2) + 0 7	+ 3.2	(2) 20,200	23,000	(2) 22,000	11,450	(2) 21,100	18,050

LE 1

results

CURRENT RESPONSE, μμ A., NO EXTERNAL VOLTAGE		CURRENT RESPONSE, μμ A., ANODE ILLUMINATED		CURRENT RESPONSE, μμ A., CATHODE ILLUMINATED		RESISTANCE WITHOUT FORMING		RESISTANCE AFTER FORMING, NO EXTERNAL VOLTAGE		RESISTANCE AFTER FORMING, ANODE ILLUMINATED		RESISTANCE AFTER FORMING, CATHODE ILLUMINATED	
No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D
(9) − 3,080	− 1,760	(6) − 6,160	− 3,300	(5) − 5,940	− 1,760	(6) 33,370	44,890						
(5) − 3,300	+ 1,650	(5) − 6,270	+ 1,430	(5) − 1,100	+ 2,530	(1) 20,770	25,040	(1) 20,870	34,340	(1) 21,940	34,890	(1) 21,730	34,620
(2) − 21,850	− 9,790	(2) − 39,700	− 15,300	(1) − 12,420	− 4,510	(1) 303,000	281,000	(1) 303,000	281,000				
(1) − 5,835	990	(1) − 13,200	− 1,320	(1) − 220	− 770								
(3) + 4,070	+ 1,650	(3) + 35,700	+ 19,250	(3) + 41,700	+ 24,400	(1) 4,590	21,540	(1) 4,612	21,740	(1) 4,634	22,310	(1) 4,060	22,130
		(1) − 2,090	+ 18,700	(1) + 4,400	− 16,500	(1) 5,480	12,050	(1) 5,543	12,110				
(2) 57,100	+ 27,700	(3) + 34,100	+ 17,600	(2) + 73,700	+ 12,200	(2) 78,190	51,100	(2) 78,180	51,950	(2) 78,790	51,750	(2) 78,300	52,400
(3) + 14,520	+ 27,300	(2) + 26,700	+ 37,600	(2) + 16,500	+ 21,900	(2) 16,940	15,500	(2) 17,220	15,670	(2) 17,460	15,750	(2) 17,920	15,920
(4) + 4,950	+ 467,000	(4) + 3,300	+ 1,622,000	(4) + 4,290	+ 1,765,000	(1) 5,077	1,670	(1) 5,154	1,570	(1) 5,867	1,050	(1) 5,339	1,030
(2) + 7,150	+ 36,800	(1) + 4,400	+ 3,960	(1) + 15,400	+ 2,860	(1) 8,413	3,880	(1) 8,553	3,764				
(2) + 3,410	+ 43,500	(2) − 1,100	− 26,400	(2) + 41,300	+ 6,600	(2) 43,000	6,020	(2) 43,300	6,060	(2) 43,000	6,088	43,150	6,054
(2) + 2,090	279,000	(2) + 6,050	+ 43,300	(2) + 41,150	+ 118,900	(2) 48,200	22,960	(2) 48,800	23,470	(2) 50,880	23,340	49,600	23,810
(2) − 2,970	− 13,640	(3) − 7,810	+ 4,510	(3) − 1,210	+ 550	(1) 4,990	27,180	(1) 5,185	27,490	(1) 22,800	28,440	(1) 5,314	28,160
(2) + 4,400	+ 3,400	(2) − 4,400	− 1,100	(2) + 8,800	+ 4,400	(2) 40,600	35,050	41,540	35,160	43,690	35,750	43,090	35,450
(3) + 1,540	+ 1,760	(3) − 4,950	− 880	(3) + 11,000	+ 15,400	(2) 67,500	24,500	(2) 67,400	24,400	(2) 61,800	22,600	(2) 66,200	24,280
(4) + 1,650	+ 550	(4) + 4,950	+ 4,560	(3) + 4,730	+ 771	(1) 40,090	36,940	(1) 40,400	37,100	(1) 39,340	37,500	(1) 39,070	37,400
(2) + 6,160	+ 5,830	(1) − 6,490	+ 5,610	(1) + 12,870	+ 7,260	(1) 48,800	736,600	(1) 113,200	708,700				
(2) + 6,940	+ 15,500	(3) + 12,100	+ 3,300	(3) + 2,200	31,900	(3) 85,990	60,590	(3) 87,300	61,400	(3) 389,500	57,700	(3) 88,400	57,700
(2) + 1,210	+ 222,000	(2) − 9,900	+ 285,000	(2) + 15,720	+ 282,000	(2) 19,300	3,270	(2) 19,470	3,176	(2) 19,910	3,198	(2) 20,000	3,193
(2) + 7,360	+ 4,285	(2) + 2,200	+ 3,300	(1) + 32,000	+ 4,285	(1) 5,710	16,800	(1) 5,931	16,300	(1) 5,996	16,890	(1) 5,975	16,590
(2) + 17,600	4,428,000	(2) − 96,800	− 279,300	(2) − 17,600	+ 3,351,600	(1) 26,310	2,726	(1) 26,670	2,720	(1) 28,130	2,960	(1) 27,730	2,920
(2) + 8,360	+ 4,180	(1) − 9,900	− 5,500	(1) + 33,200	+ 15,400	(1) 132,860	84,370	(1) 135,800	86,130	(1) 135,800	87,810	(1) 112,070	87,810
(2) + 2,310	+ 16,200	(2) 3,570	+ 59,400	(2) + 3,520	+ 35,400	(2) 26,150	13,120	(2) 26,760	13,110	(2) 27,460	13,350	(2) 27,030	13,210

TAB

Typical results

KIND OF CELL	DEPOLARIZER	RESISTANCE RESPONSE, WITHOUT FORMING		RESISTANCE RESPONSE AFTER FORMING, NO EXTERNAL VOLTAGE		RESISTANCE RESPONSE AFTER FORMING, ANODE ILLUMINATED		RESISTANCE RESPONSE AFTER FORMING, CATHODE ILLUMINATED		CAPACITANCE, M.F., WITHOUT FORMING		CAPACITANCE, M.F., AFTER FORMING, NO EXTERNAL VOLTAGE	
		No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D
$Pt/E_1/Pt$	D_1	(1) + 210	+ 510	(1) + 270	+ 30					(1) 0.23296	0.10364	(1) 0.21857	0.8530
$Pt/E_1/Pt$	D_2									(1) 4.65	2.23	(1) 4.49	0.437
$Pt/E_2/Pt$	D_1												
$Pt/E_2/Pt$	D_2												
$Cu/E_1/Cu$	D_1			(1) − 15	+ 50					(1) 7.7005	1.9900	(1) 7.3742	1.9150
$Cu/E_1/Cu$	D_2	(1) + 8	+ 70	(1) + 6	+ 57					(1) 7.225	3.55	(1) 7.186	3.4898
$Cu/E_2/Cu$	D_1							(2) + 430	+ 300	(2) 0.1475	0.198	(2) 0.159	0.191
$Cu/E_2/Cu$	D_2	(1) + 90	+ 55	(1) + 53	+ 50	(1) + 90	+ 60	(1) + 70	+ 60	(2) 0.559	0.132	(2) 0.511	0.130
$Al/E_1/Al$	D_1									(1) 2.57		(1) 2.40	
$Al/E_1/Al$	D_2	(1) + 32	+ 9	(1) + 19	+ 10					(1) 2.6959	2.75	(1) 2.49	2.745
$Al/E_2/Al$	D_1	(1) + 85	+ 50	(1) + 115	+ 57	(2) + 90	+ 70	(1) + 120	+ 50	(1) 0.462	7.08	(1) 0.491	6.74
$Al/E_2/Al$	D_2	(1) + 200		(1) + 150				(2) + 380	+ 200	(2) 0.243	0.1885	(2) 0.223	0.178
$Fe/E_1/Fe$	D_1	(1) 0.00	+ 230	(1) 0.00		(1) + 250	+ 120	(1) 0.00		(1) 1.3392	0.54709	(1) 1.518	0.56685
$Fe/E_1/Fe$	D_2												
$Fe/E_2/Fe$	D_1	(1) + 130	+ 137	(1) + 460	+ 210	(1) + 200	+ 145	(1) + 220	+ 166	(2) 0.534	0.781	(2) 0.50377	0.74175
$Fe/E_2/Fe$	D_2	(1) + 360		(1) + 340	+ 190	(1) + 440		(1) + 500	+ 280	(2) 0.249	0.422	(2) 0.2492	0.426
$Zn/E_1/Zn$	D_1			(1) + 290	+ 130					(1) 0.45506	1.1377	(1) 0.68022	0.86006
$Zn/E_1/Zn$	D_2												
$Zn/E_2/Zn$	D_1			(1) + 200	+ 200					(2) 0.219	0.0301	(2) 0.0219	0.0312
$Zn/E_2/Zn$	D_2	(2) + 250	+ 20	(2) + 350	+ 9	(2) + 140	+ 6	(2) + 150	− 6	(2) 1.491		(2) 1.451	
$Pb/E_1/Pb$	D_1			(1)	+ 130					(1) 7.8536	2.4415	(1) 5.6049	1.9479
$Pb/E_1/Pb$	D_2	(1) + 120	+ 8.0	(1) 110	10					(1) 1.001		(1) 0.94505	1.889
$Pb/E_2/Pb$	D_1												
$Pb/E_2/Pb$	D_2	(1) + 390	+ 350			(1) + 230	+ 150			(2) 1.495	2.76	(2) 1.125	2.86

LE 2
—Continued

CAPACITANCE, M.F., AFTER FORMING, ANODE ILLUMINATED		CAPACITANCE, M.F., AFTER FORMING, CATHODE ILLUMINATED		CAPACITANCE RESPONSE WITHOUT FORMING		CAPACITANCE RESPONSE AFTER FORMING, NO EXTERNAL VOLTAGE		CAPACITANCE RESPONSE AFTER FORMING, ANODE ILLUMINATED		CAPACITANCE RESPONSE AFTER FORMING, CATHODE ILLUMINATED	
No D	With D	No D	With D	No D	With D	No D	With D	No D	With D	No D	With D
				(1) 0.00244	− 0.00122						
(1) 1.29	0.153	(1) 2.14	0.425								
(1) 7.09	1.697	(1) 6.73	(1) 1.869			(1) 0.1163	− 0.014				
				(1) + 0.607	− 0.0919	(1) − 0.060	− 0.0844				
(2) 0.156	0.187	(2) 0.1585	0.1868							(1) 0.0019	0.0019
(2) 0.457	0.114	(2) 1.005	2.090	(1) − 0.053	− 0.06	(1) − 0.027	− 0.056	(1) − 0.04	− 0.04	(1) − 0.015	− 0.02
(1) 2.62		(1) 2.62									
				(1) − 0.0425	− 0.03	(1) − 0.02	+ 0.03				
(1) 0.3983	6.243	(2) 1.3758	1.4933	(1) − 0.00499	− 0.2331	(1) − 0.0383	− 0.0223				
(2) 0.216	0.182	(2) 0.2258	0.1758	(1) − 0.035		(1) − 0.027				(1) − 0.00380	− 0.00312
(1) 0.80128	0.53481	(1) 1.5313	0.53354	(1) 0.00	+ 0.02914			(1) − 0.0233	− 0.00595		
(2) 0.446	0.691	(2) 0.462	0.703	(1) − 0.0704	− 0.1216	(1) − 0.01348	− 0.01180				
(2) 0.2655	0.474	(2) 0.2592	0.1535			(1) − 0.02612	− 0.0189			(1) − 0.00434	− 0.0037
(1) 1.8109	0.8345	(1) 0.74857	0.8409			(1) − 0.01066	− 0.00842				
(3) 0.02195	0.0288	(3) 0.0216	0.0298								
(2) 1.3468		(2) 1.698		(2) − 0.031		(2) − 0.043		(2) − 0.0121		− 0.046	
(1) 5.6035	1.736	(1) 5.748	1.823			(1)	− 0.0586				
(1) 0.79433	1.6111	(1) 0.86002	0.9236	(1) − 0.115				(1) − 0.01676	− 0.0498		
(2) 0.91532	2.6538	(2) 1.097	2.675	(1) − 0.00541	− 0.02837			(1) − 0.02142	− 0.1288		

such a direction that the electrode exposed for illumination was the anode. It does not mean that the anode was always illuminated at the time the measurement was made.

When the light causes the voltage of the irradiated electrode to become more positive, or less negative, with respect to the dark electrode, the change is called a "positive response." If the light produces the reverse effect, the change is called a "negative response." A positive resistance response or a positive capacitance response is a change in which the resistance or capacitance of the cell is increased by the action of light. A current response is defined as positive when the change in current would indicate a positive voltage response, assuming the resistance of the cell to remain constant.

The current in micromicroamperes per millivolt was determined by the equation

$$I = \frac{f \times d}{V \pm E}$$

with E positive when the external voltage was in the direction of the E.M.F. of the cell, and negative when in the opposite direction. V was, of course, zero for cases of no external voltage. In each case f is the figure of merit of the galvanometer, expressed in micromicroamperes per millimeter, d the deflection in millimeters, E the terminal voltage of the cell, and V the external voltage applied. E and V are in millivolts.

The following symbols will be used in the discussion of results:

D = depolarizer.
D_1 = ethyl bromide as depolarizer.
D_2 = ethyl iodide as depolarizer.
E_1 = ethylmagnesium bromide as electrolyte.
E_2 = phenylmagnesium bromide as electrolyte.
$E_1 - D_1$ = a cell having E_1 as electrolyte and D_1 as depolarizer.
Pt | E_1 (+D_1) | Pt = a cell having platinum electrodes with E_1 as electrolyte and D_1 as depolarizer.

Tables 1 and 2 are introduced for the purpose of summarizing the results of the whole study. The results given are as nearly typical as could be selected. The blank spaces indicate that no results were obtained. While it was the policy to use the results from the same cell in a given row, this was not always done. For example, in a group Pt | E_1 (+D_1) | Pt cells, the voltage response might be of one cell and the resistance of another. The numbers in parentheses indicate the number of cells from which the most typical result was selected.

The results are set out in such detail by the curves and tables that an extensive discussion seems quite unnecessary. However, a brief summary may not be undue repetition.

Platinum electrodes

An examination of the curves, figures 1 to 3, and tables 1 and 2 shows that (1) responses to light were negative before the addition of a depolarizer,

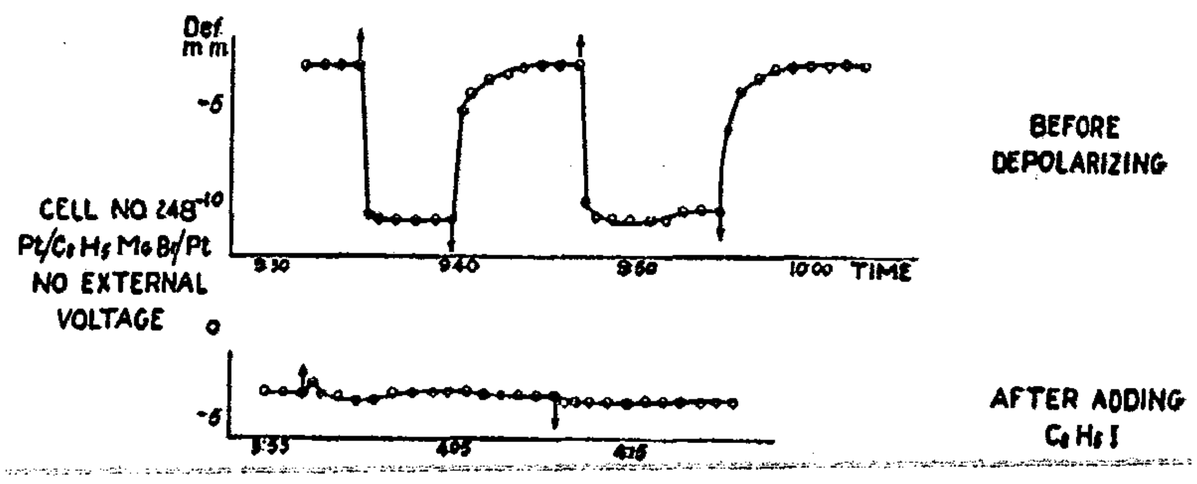

FIG. 1

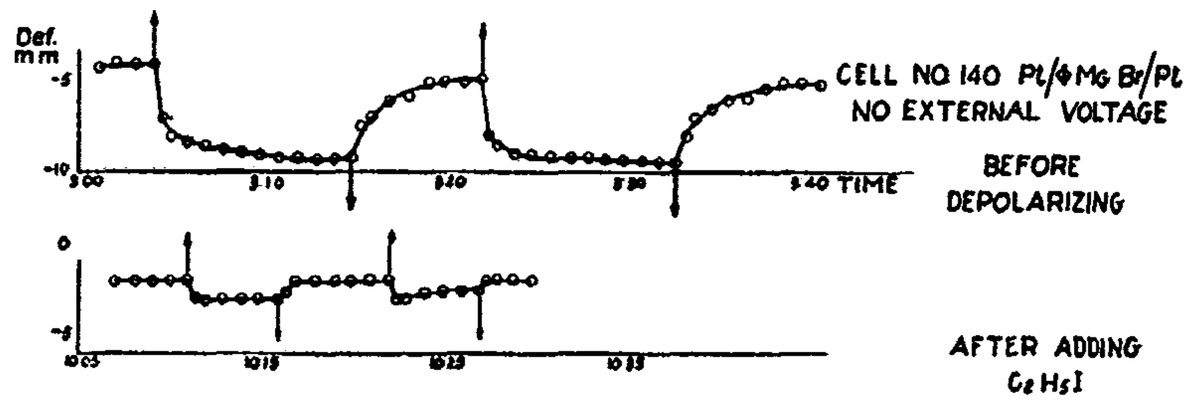

FIG. 2

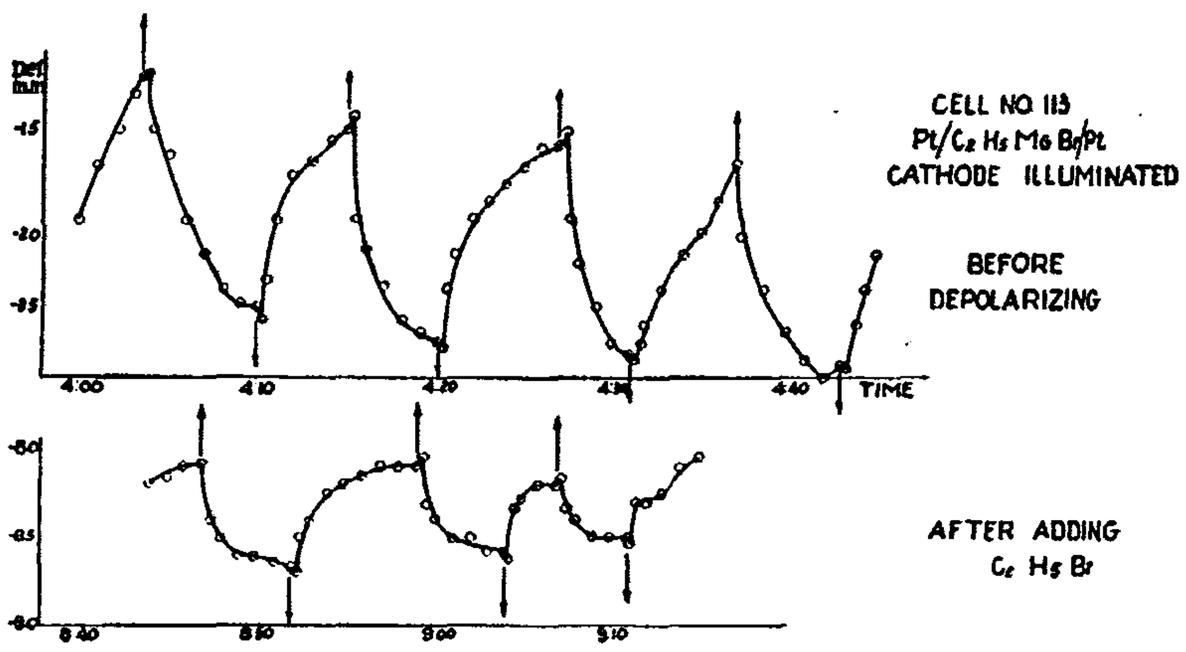

FIG. 3

(2) the addition of either depolarizer reduced the responses, (3) with E_2 the addition of either depolarizer produced no change in the direction of the

responses, and (4) the addition of D_1 to E_1 caused a reversal of the direction of the responses.

The dark E.M.F. was not consistently affected by either depolarizer, but the dark current was usually greatly increased. Increases as great as twelvefold were observed when D_1 was added to E_1.

The resistance of cells containing E_1 was increased by adding either depolarizer, while that of cells containing E_2 was decreased by D_1. Insufficient data are available to show the effect of D_2 on the resistance of E_2 cells.

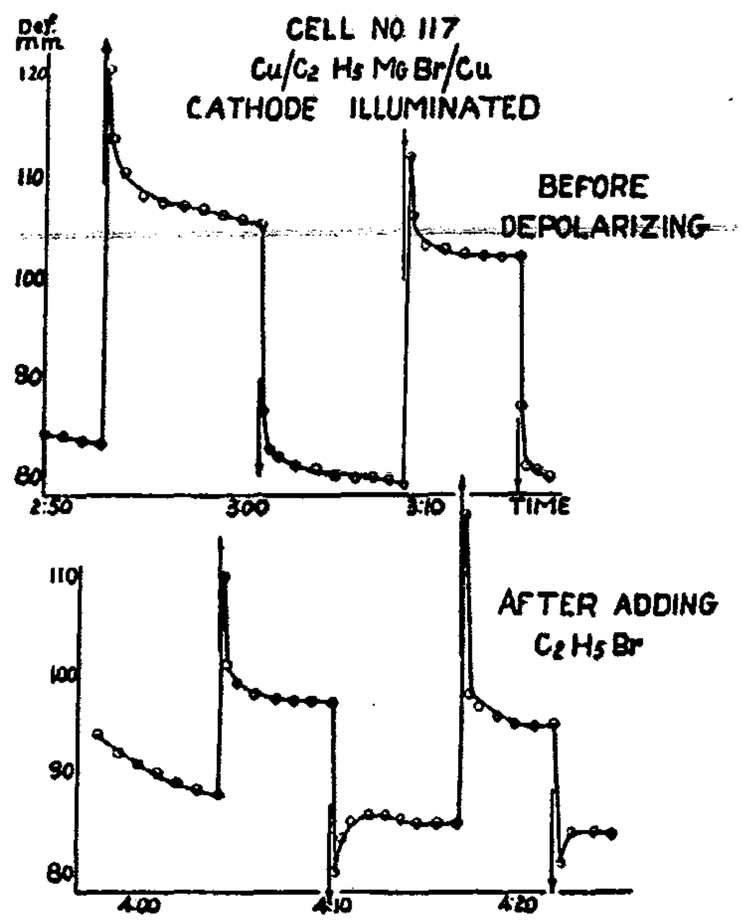

FIG. 4

Capacitance ranged from 0.10 microfarad to 4.65 microfarads, varying widely with the same type of cell. The addition of D_1 or D_2 to E_1 produced a decrease in capacitance.

The results with platinum electrodes, shown in table 2, on resistance and capacitance responses are no more than slightly indicative since only one cell is reported.

Copper electrodes

The curves for cells having copper electrodes are quite characteristic. Figure 4 shows that the responses were almost instantaneous. Within a very few seconds after the light was turned on or off, the galvanometer (in the case of current responses) reached a maximum deflection and started

back. This peculiar effect may be due, at least in part, to an exceedingly thin coating of cuprous oxide.

Voltage and current responses to light are in general positive both before and after the addition of depolarizers. The effect of either depolarizer on the magnitude of the responses is much less in evidence with copper than with platinum electrodes, but where consistent effects were observed the responses were found to be reduced.

Both depolarizers seem to have increased the resistance of cells containing E_1. Cells containing E_2 showed much smaller resistances after adding D_1, but apparently were little affected by the addition of D_2. Resistance responses were uniformly small and positive with one exception. The

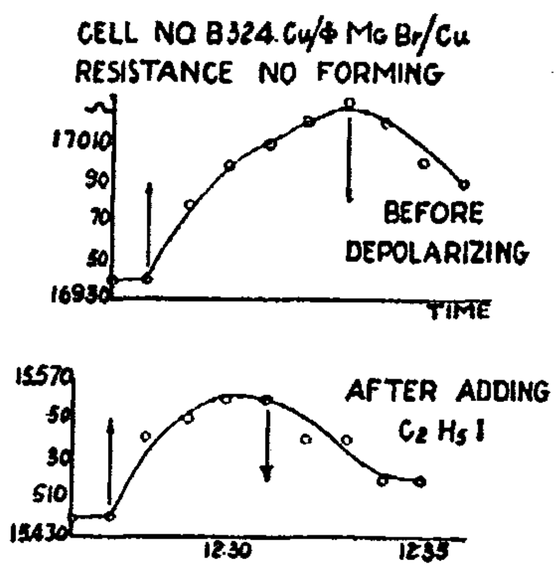

Fig. 5

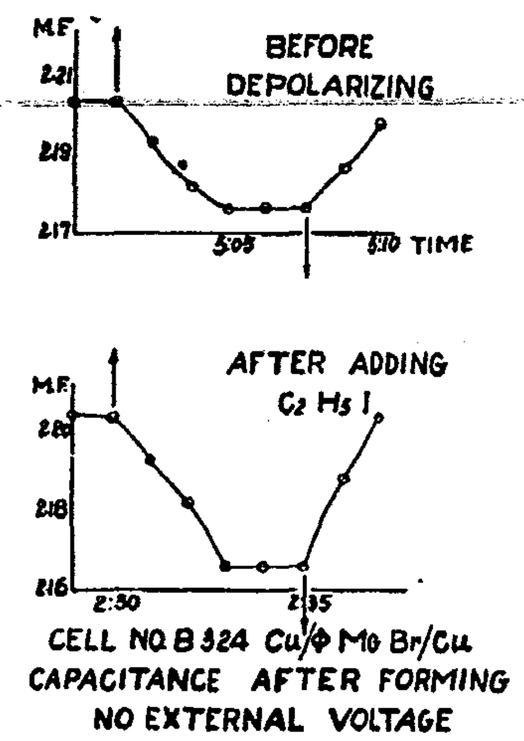

Fig. 6

response was greater with E_1 cells after adding either depolarizer, but with E_2 cells the response was less after adding D_2.

E_1 cells had a much higher capacitance than E_2 cells. The capacitance of E_1 cells was strikingly smaller after adding either depolarizer, but D_1 seemed more effective than D_2. Cells containing E_2 exhibited slight increases in capacitance on adding D_1, but rather large decreases after the addition of D_2. Capacitance responses were almost uniformly negative. The writer believes that the exceptions are due to some extraneous cause. While the responses are small, there seems to be little doubt that they are present. Figure 6 shows two capacitance curves exhibiting the responses quite clearly. A decrease in capacitance response was observed in cells containing E_1 after adding either D_1 or D_2, but D_1 apparently increased slightly the response in the one cell containing E_2.

Iron electrodes

Reference here will be made only to resistance and capacitance measurements. The resistance of E_2 cells was higher than the resistance of E_1 cells. The resistance of E_1 cells was decreased by D_1, while the resistance of E_2 cells was decreased by both D_1 and D_2. Resistance responses were as a rule relatively large, though barely over 1 per cent. Figure 7 shows an

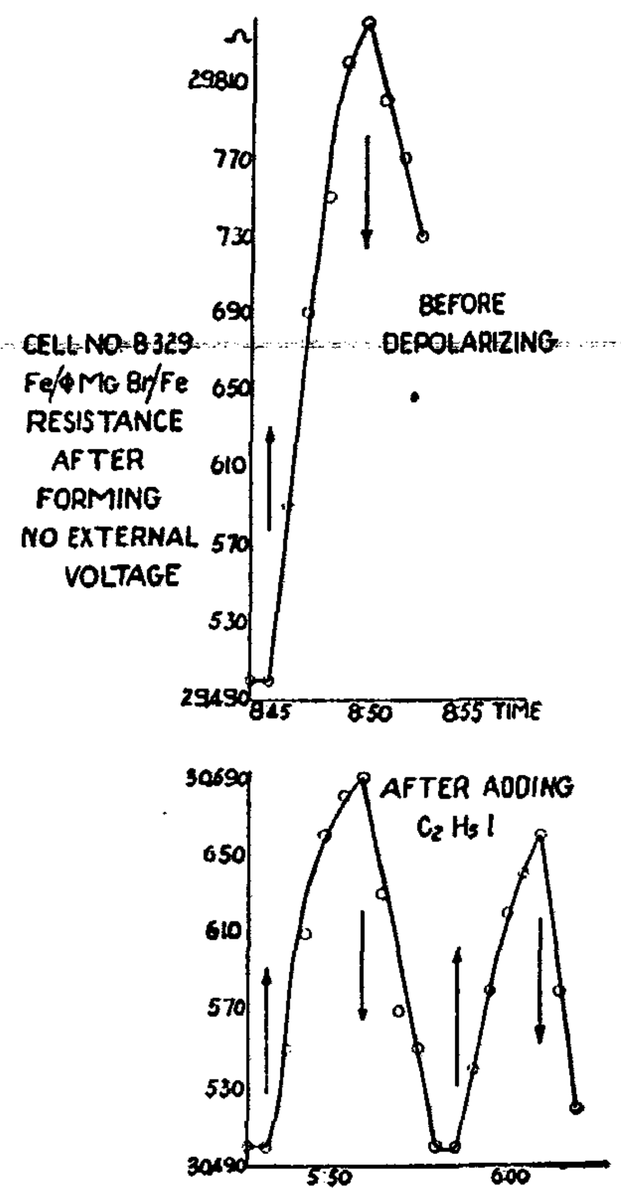

FIG. 7

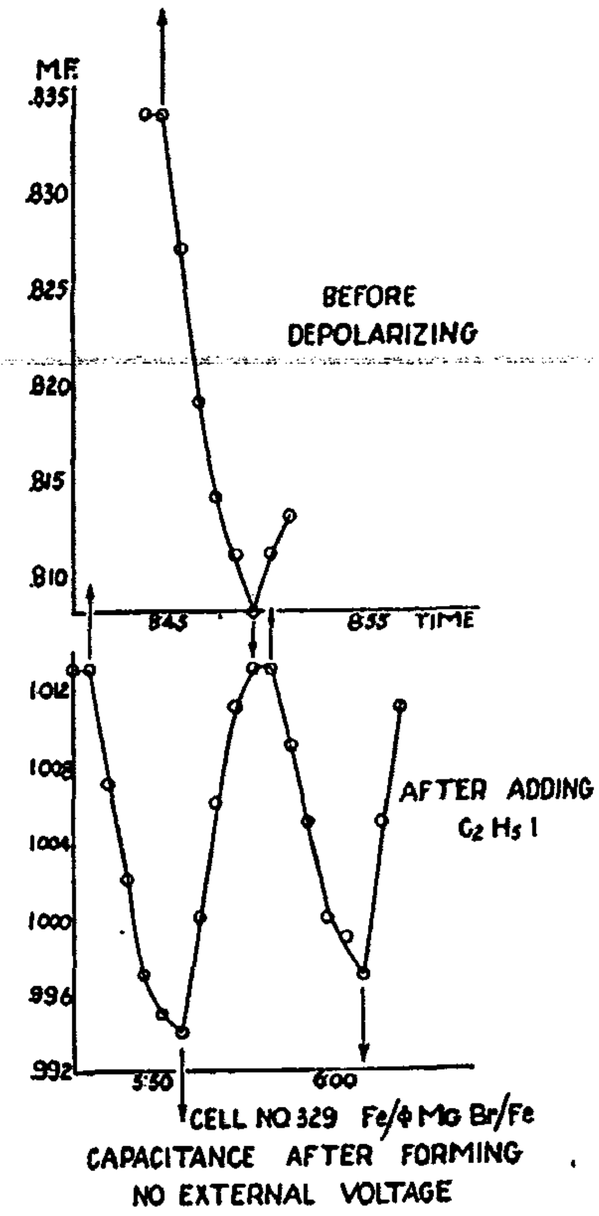

FIG. 8

example of the responses obtained. No case of negative response was found.

The capacitance of iron cells was unusually low, seldom reaching 1 microfarad. While the E_1 cells showed a higher capacitance than the E_2 cells, the difference was less conspicuous for iron electrodes than for any other. D_1 apparently produced a decrease in the capacitance of E_1 cells, while both depolarizers seemed to have increased the capacitance of E_2 cells. Capacitance responses were uniformly negative. A typical response is exhibited in figure 8.

Among the iron cells were a few that produced alternating current. Figure 9 is a current–time curve of such a cell.

A GENERAL VIEW OF THE RESULTS

Further details of results cannot be given in this paper, but as stated above, the curves and tables are purposely made self-explanatory.

Nothing was said in the previous discussion regarding the dark voltage. There was nothing to say. The value of the dark voltage occurs, within limits, as if it were a matter of chance. It ranges usually from 0 to 40 millivolts, but sometimes runs to more than 100. There is no doubt that there are sufficiently good reasons for this behavior, but they have not yet been discovered.

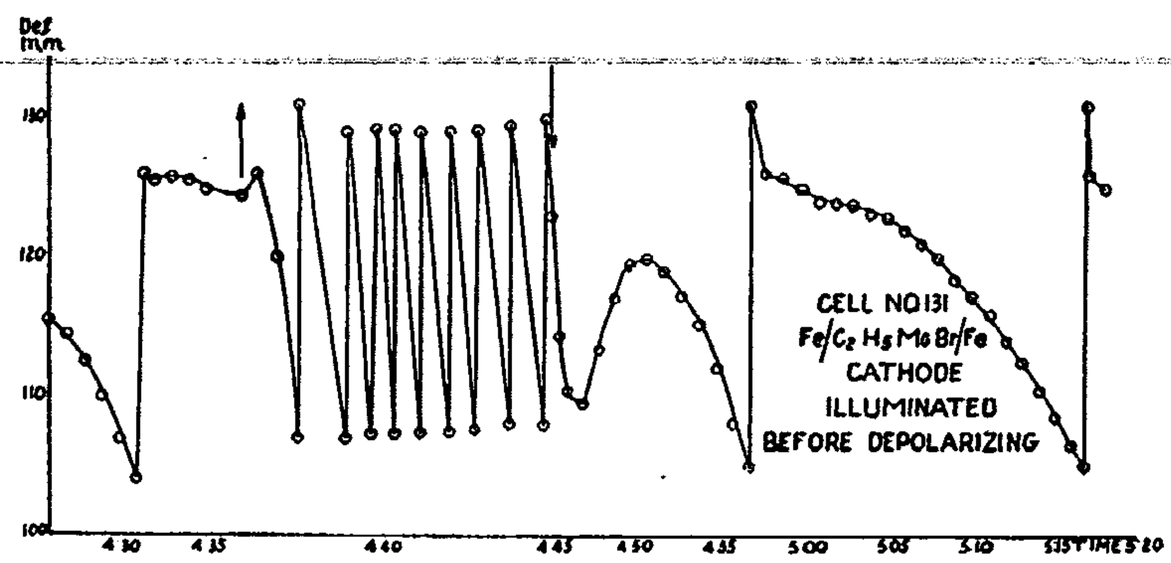

FIG. 9

The effect of the "forming" process, i.e., of polarizing the electrodes either anodically or cathodically, has been apparently ignored, but again the omission was intentional. An examination of the data fails to reveal any uniformity in effects due to the process of "forming."

The so-called Minchin reversal is very clearly shown in figure 3. Unusual care is necessary to catch and record these quick reversals. They take place as a rule, within 3 to 6 seconds.

THEORETICAL CONSIDERATIONS

A consideration of the theories that have been advanced to explain the photovoltaic effect shows that each is based upon either the chemical action of light, the photoelectric effect, or the effect of excited molecules on or near the electrode. The general arguments for and against these theories may be found in the references cited above. The arguments favoring the excited molecule theory seem to be most convincing just now,

and the findings herein reported are certainly more in line with this theory than with any other.

The size of a molecule of a short-chain, aliphatic compound, like ethylmagnesium bromide, is believed to be smaller than that of a molecule of an aromatic compound, such as phenylmagnesium bromide. If the layer on an electrode is monomolecular in thickness, as Hammond's calculations indicate, the layer of ethylmagnesium bromide should be thinner than the layer of phenylmagnesium bromide. Consequently the capacitance of the condenser composed of the film separating the electrolyte and the surface of the plate should be greater for the cells filled with ethylmagnesium bromide. This agrees with the experimental findings. On the other hand, the resistance offered by the film might be expected to be proportional to some function of the thickness, leading to the conclusion that the phenylmagnesium bromide cells should have the higher resistance to direct current. This was found to be true.[2]

In studies by Langmuir and others, it has been found that in certain monomolecular layers the molecules are particularly oriented with respect to the surface. It is then not unreasonable to suppose a similar condition in the cases under consideration.

Now, if light produces in and near these layers a number of excited molecules which have different dipole moments from normal molecules, and which have the property of displacing normal molecules from the layers, an altered difference of potential would result. The change in difference of potential would increase until a kind of saturated layer of excited molecules was built up on the electrode. The life period of these excited molecules may be short, so that when the light is turned off and thus no more are being produced to replace the "dead" ones on the surface, the electrode "recovers in the dark" and the difference of potential becomes normal.

Change in A. C. resistance must indicate a change in the electrolyte, which at present is thought to be due to change in condition of solvation of ions, resulting in their altered mobility.

The assumption that a double layer, containing in the outer film only a comparatively few molecules, is formed, or altered, when the light is turned on, would explain the negative capacitance response. This assumption becomes quite plausible when one considers the polarized condition of the excited molecules.

By assuming that the negative "ends" of the polarized molecules attach themselves to some metals, while with other metals the positive "ends" are so attached, one can explain the fact of positive and negative voltage and current responses.

[2] Hammond arrived at these same conclusions.

Any substance, such as the depolarizers used in this study, when added to a cell, would quite likely disturb the layer on the electrodes. Just what effect the added substance would have would probably depend upon the electrolyte, the electrodes, and the substance added.

To explain completely, on the basis of this theory, the observed effects of the depolarizers, would require more information on the chemical reactions involved, and especially on the structure of the molecules, than is at present available.

The writer desires to acknowledge his indebtedness and express his appreciation to Professors R. T. Dufford and H. E. Hammond of the Department of Physics of the University of Missouri, to President Eugene Fair of the Northeast Missouri State Teachers College, and to Mrs. Harty for assistance in this study. Professor Dufford suggested and directed the investigation, Professor Hammond helped in perfecting the experimental arrangements, President Fair furnished much-needed financial assistance, and Mrs. Harty took many of the readings. The work was begun and carried about half through at the University of Missouri, and completed at the Teachers College.

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ON THE MECHANISM OF POTENTIAL FORMATION IN A SOLUTION OF FOREIGN IONS

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Received March 5, 1934

As was shown by us previously (1) in the most simple cases of the sharply expressed selective adsorption of one of the sort of the foreign solution ions by the metal, the connection between the potential and the concentration (more accurately, the activity) of the ions may be written:

$$E = \pm \frac{2RT}{nF} \ln \frac{K_1}{K_2} \pm (2m - 1) \frac{RT}{nF} \ln cf \qquad (1)$$

The experiments described in the preceding paper have confirmed this equation for the potential of gold in the solutions of copper sulfate, copper nitrate, and silver nitrate.

In the present paper are offered the results of further experiments on the study of the potentials of metallic silver in solutions of copper salts. To this end, exactly as with the earlier method, were measured the E.M.F. of the cells

$$Ag \mid CuSO_4 \mid NH_4NO_3 \text{ saturated} \mid 1N\ KCl, Hg_2Cl_2 \mid Hg$$

and

$$Ag \mid Cu(NO_3)_2 \mid NH_4NO_3 \text{ saturated} \mid 1N\ KCl, Hg_2Cl_2 \mid Hg$$

from the values of which were calculated the potentials of silver in corresponding concentrations of solutions. Simultaneously the potentials of copper in the same electrolytes were measured. The graphic and analytic comparisons of both potentials show that between them there is rectilinear dependence, that is:

$$\left.\begin{aligned} E_{Ag/CuSO_4} &= a + bE_{Cu/CuSO_4} \\ \text{and} \quad E_{Ag/Cu(NO_3)_2} &= a + bE_{Cu/Cu(NO_3)_2} \end{aligned}\right\} \qquad (2)$$

The values for the potentials of silver and copper, found by experiment, and the values of the constants a and b are given in tables 1 and 2.

As the potential of copper in a solution of copper salts may be expressed by Nernst's equation, that is,

$$E_{Cu/CuSO_4} = E^0_{Cu/CuSO_4} + \frac{RT}{2F} \ln C_{Cu^{++}} f_{Cu^{++}}$$

TABLE 1

$CuSO_4$	$E_{Ag/CuSO_4}$ (at 20°C.)	$E_{Cu/CuSO_4}$	$\Delta_1 = E_{Ag/CuSO_4} - 0.420$	$\Delta_2 = E_{Cu/CuSO_4} - 0.2725$	$b = \frac{\Delta_1}{\Delta_2}$
N					
2.0	+0.5430	+0.3215	+0.1230	0.0490	2.53
1.5	0.5351	0.3185	0.1151	0.0460	2.50
1.0	0.5313	0.3150	0.1113	0.0425	2.61
0.75	0.5284	0.3120	0.1084	0.0395	2.74
0.5	0.5145	0.3095	0.0945	0.0370	2.55
0.25	0.4933	0.3030	0.0733	0.0305	2.40
0.125	0.4831	0.2990	0.0631	0.0265	2.38
0.0125	0.4440	0.2820	0.0240	0.0095	2.52
Mean value of *b*					2.54
Mean value of *a*					−0.296

TABLE 2

$Cu(NO_3)_2$	$E_{Ag/Cu(NO_3)_2}$	$E_{Cu/Cu(NO_3)_2}$	$\Delta_1 = E_{Ag/Cu(NO_3)_2} - 0.32$	$\Delta_2 = E_{Cu/Cu(NO_3)_2} - 0.182$	$b = \frac{\Delta_1}{\Delta_2}$
N					
7.0	+0.5609	+0.4298	+0.2409	+0.2478	0.97
5.0	0.5312	0.4082	0.2112	0.2262	0.93
3.0	0.5127	0.3820	0.1927	0.2000	0.96
2.0	0.5060	0.3658	0.1860	0.1838	1.01
1.5	0.4934	0.3569	0.1734	0.1749	0.99
1.0	0.4868	0.3468	0.1668	0.1648	1.01
0.75	0.4800	0.3402	0.1600	0.1582	1.01
0.50	0.4770	0.3331	0.1570	0.1511	1.04
0.0125	0.4365	0.3079	0.1165	0.1259	0.92
0.00125	0.4240	0.2979	0.1040	0.1159	0.90
Mean value of *b*					0.97
Mean value of *a*					+0.1431

and

$$E_{Cu/Cu(NO_3)_2} = E^0_{Cu/Cu(NO_3)_2} + \frac{RT}{2F} \ln C_{Cu^{++}} f_{Cu^{++}}$$

then by substituting the value for the potential of copper in equation 2, and by putting in the numerical values of the constants *a* and *b*, we have:

$$E_{Ag/CuSO_4} = (2.54\, E^0_{Cu/CuSO_4} - 0.296) + 2.54\, \frac{RT}{2F} \ln C_{Cu^{++}} f_{Cu^{++}}, \text{ i.e., } m = 1.77$$

and

$$E_{Ag/Cu(NO_3)_2} = (0.974\, E^0_{Cu/Cu(NO_3)_2} + 0.143) + 0.974\, \frac{RT}{2F} \ln C_{Cu^{++}} f_{Cu^{++}}, \text{ i.e., } m = 0.987$$

TABLE 3

KBr	$E_{Cu/KBr}$ (AT 18°C.) (A. Schmid)	$f_{Br^-/KBr}$ (AT 25°C.) (Landolt)	$E_{Br_2/KBr} = 1.087 - 0.058 \ln cf$	$\Delta_2 = E_{Br_2/KBr} - 1.138$	$b = \frac{E_{Cu/KBr}}{\Delta_2}$
N					
0.01	+0.144	0.90	+1.2056	+0.0676	2.13
0.10	−0.034	0.776	+1.1514	+0.0134	(−2.53?)
1.00	−0.037	0.630	1.098	−0.0400	2.17
2.00	−0.121	0.614	1.0818	−0.0562	2.15
3.00	−0.144	0.616	1.0715	−0.0665	2.16
4.00	−0.171	0.626	1.0639	−0.0741	2.30
Mean value of *b*					2.18
Mean value of *a*					−2.484

TABLE 4

KBr	$E_{Cu/KBr}$ (AT 18°C.) (A. Schmid)	$f_{Br^-/KBr}$ (AT 25°C.) (Haas-Jellinek)	$E_2 = E_{Br_2/KBr} = 1.087 - 0.058 \ln cf$	$\Delta_2 = E_2 - 1.14$	$b = \frac{E_{Cu/KBr}}{\Delta_2}$
N					
0.01	+0.144	0.895	+1.2057	+0.0657	2.19
0.10	−0.034	0.720	1.1533	+0.0133	(−2.55?)
1.00	−0.087	0.590	1.1002	−0.0398	2.18
2.00	−0.121	0.584	1.0832	−0.0569	2.12
3.00	−0.144	0.577	1.0732	−0.0668	2.15
4.00	−0.171	0.570	1.0663	−0.0737	2.32
Mean value of *b*					2.19
Mean value of *a*					−2.500

Thus the potential of silver in solutions of copper salts, like the potential of gold, is caused by the selective adsorption of the cations of the electrolyte (Cu^{++}) on the surface of the metal, and obeys equation 1.

In order to check the theory advanced by us here on the measurements of A. Schmid and Winkelmann (4), we have proceeded as follows: As the potentials of copper in solutions of halogen salts of potassium and sodium become more electronegative by an increase of solution concentration, i.e., as if they had an anion character, then it may be assumed that the potentials are explained by the selective adsorption of the anion. Therefore the

values of the potentials of chlorine and bromine were calculated (according to Nernst's equation) for the corresponding concentrations of the solutions of sodium chloride, potassium chloride, and potassium bromide. The values of the activity coefficients for these electrolytes were taken from two sources,—the "mean" activity coefficients from Landolt's tables (3), and the "true" from the paper of Haas and Jellinek (2).

TABLE 5

NaCl	$E_1 = E_{Cu/NaCl}$ (at 18°C.) (A. Schmid)	$f_{Cl^-/KCl}$ (at 25°C.) (Landolt)	$E_2 = E_{Cl_2/KCl} = 1.36 - 0.058 \ln cf$	$\Delta_1 = E_1 + 0.13$	$\Delta_2 = E_2 - 1.30$	$b = \frac{\Delta_1}{\Delta_2}$
N						
0.01	+0.123	0.904	+1.4785	+0.253	0.1785	1.4?
0.10	+0.076	0.789	1.4240	0.206	0.1240	1.6?
1.00	+0.002	0.659	1.3705	0.132	0.0705	1.9
2.00	−0.026	0.667	1.3528	0.104	0.0528	1.9
3.00	−0.052	0.709	1.3410	0.078	0.0410	1.9
4.00	−0.087	0.767	1.3318	0.043	0.0318	1.3?
5.00	−0.096	0.860	1.3233	0.034	0.1233	1.4?
Mean value of *b*						1.63
Mean value of *a*						−2.245

TABLE 6

KCl	$E_1 = E_{Cu/KCl}$ (at 18°C.) (A. Schmid)	$f_{Cl^-/KCl}$ (at 25°C.) (Landolt)	$E_2 = E_{Cl_2/KCl} = 1.36 - 0.058 \ln cf$	$\Delta_1 = E_1 + 0.13$	$\Delta_2 = E_2 - 1.138$	$b = \frac{\Delta_1}{\Delta_2}$
N						
0.01	+0.123	0.899	+1.4787	+0.253	+0.1620	1.6 (?)
0.10	+0.086	0.764	1.4248	0.216	0.1081	2.0
1.00	−0.008	0.597	1.3730	0.122	0.0563	2.1
2.00	−0.043	0.569	1.3573	0.087	0.0406	2.1
3.00	−0.070	0.570	1.3465	0.060	0.0298	2.0
4.00	−0.087	0.581	1.3398	0.043	0.0231	1.9
Mean value of *b*						2.0
Mean value of *a*						−2.78

The comparison of the potentials of copper with those of chlorine and bromine show that in these cases the rectilinear dependence of type

$$E_{Cu/MeX} = a + bE_{X_2/MeX}$$

holds, but there are certain deviations, especially for sodium chloride. The data from A. Schmid's papers, the potentials of chlorine and bromine, calculated by "mean" and "true" activity coefficients, and the values of constants *a* and *b* are given in tables 3, 4, 5 and 6.

As there are no marked differences between a and b for potassium bromide in both cases, in the future the values for f will be taken only from Landolt's tables.

Thus the potentials of copper in solutions of halide salts of alkali metals, measured by A. Schmid and his collaborators, are explained by the selective adsorption of electrolyte anions and are subordinated to equation 1, taken in this case for anion adsorption, i.e., with the minus sign placed before the logarithm of activity. In agreement with the values of a and b given in the tables, equation 1 may be written:

For Cu/KBr:

$$E_{Cu/KBr} = (2.18\, E^0_{Br/KBr} - 2.484) - 2.18 \frac{RT}{F} \ln C_{Br^-} f_{Br^-}, \text{ i.e., } m = 1.59$$

For Cu/NaCl:

$$E_{Cu/NaCl} = (1.63\, E^0_{Cl_2/NaCl} - 2.245) - 1.63 \frac{RT}{F} \ln C_{Cl^-} f_{Cl^-}, \text{ i.e., } m = 1.31$$

For Cu/KCl:

$$E_{Cu/KCl} = (2\, E^0_{Cl_2/KCl} - 2.78) - 2 \frac{RT}{F} \ln C_{Cl^-} f_{Cl^-}, \qquad \text{i.e., } m = 1.5$$

Taking into consideration the imperfection in the calculations of the same manner (the potentials of chlorine and of bromine are not found experimentally, but only by calculation), it is possible to consider that there is satisfactory agreement between equation 1 and the given experimental data of A. Schmid.

SUMMARY

1. In addition to the preceding measurements of the potential of gold in solutions of copper and silver salts, the potentials of silver in solutions of copper sulfate and copper nitrate were measured.

2. The dependence (deduced earlier on the basis of the adsorption theory for such potential) between the potential and the activity of the selectively adsorbed ions, proved on the potential of gold, was confirmed by the potential of silver and by the experimental data of A. Schmid and his collaborators (the potential of copper in the halogen solutions of alkali metals).

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OXIDATION AND REDUCTION WITH HYDROGEN PEROXIDE

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Received August 30, 1934

In suitably acid solutions and with suitable concentrations hydrogen peroxide reduces the following: cobaltic sulfate to cobaltous sulfate; lead peroxide to lead sulfate; permanganic acid, manganese dioxide, and manganic sulfate to manganous sulfate; chlorine and hypochlorous acid to hydrochloric acid; bromic acid to hydrobromic acid and bromine; chromic acid to chromic sulfate; chloric acid at 80°C. to hydrochloric acid and chlorine; hypobromous acid to hydrobromic acid; thallic sulfate to thallous sulfate; bromine to hydrobromic acid; periodic acid to iodic acid; iodic acid to iodine; 95 per cent nitric acid to oxides of nitrogen; bismuth pentoxide to bismuth trioxide; pentavalent vanadium to tetravalent vanadium.

In suitably acid solutions and with suitable concentrations hydrogen peroxide oxidizes the following: hydrochloric acid to chlorine; hydrobromic acid to bromic acid; hydriodic acid to iodine and to iodic acid; ferrous chloride to ferric chloride; nitrous acid to nitric acid; mercurous nitrate to mercuric nitrate; silver to silver sulfate; tetravalent vanadium to pentavalent vanadium; cuprous chloride to cupric chloride; ferrocyanic acid to ferricyanic acid; stannous chloride to stannic chloride; hydroxylamine and nitrous acid to nitric acid; nickel and lead to the corresponding sulfates.

In suitably alkaline solutions and with suitable concentrations hydrogen peroxide reduces the following: potassium permanganate and manganate to manganese dioxide; potassium ferrate to ferric oxide; silver peroxide and silver oxide to silver; potassium hypobromite to bromide; potassium ferricyanide to ferrocyanide; nickelic oxide to nickelous oxide; bismuth pentoxide to bismuth tetroxide (or Bi_4O_7); potassium periodate to iodate; and potassium hypoiodite to iodide. It is said, though wrongly, to reduce mercuric oxide to mercurous oxide.

In suitably alkaline solutions and with suitable concentrations hydrogen peroxide oxidizes the following: potassium cyanide to cyanate; sodium sulfite to sulfate; lead and lead monoxide to lead peroxide; bismuth trioxide to bismuth tetroxide (or Bi_4O_7); cobaltous oxide to cobaltic oxide or peroxide; manganous and manganic oxides to manganese peroxide; vanadium tetroxide to vanadium pentoxide; chromic oxide to potassium

chromate; thallous oxide to thallic oxide; nitric oxide and potassium nitrite to potassium nitrate; cuprous oxide to cupric oxide; hydroxylamine to nitrogen; ferrous and stannous oxides to ferric and stannic oxides, respectively; zinc to sodium zincate.

It is not claimed that this is a complete list of the oxidations and reductions with hydrogen peroxide, but these instances will suffice to show the apparent complexity of the problem. So far as the theoretical side of the subject is concerned, the literature is in a state of chaos because the "misleading experiment" has tripped up everyone. The problem has not been and cannot be solved by a phenomenological study alone. The Baconian method is not adapted to this sort of work.

Fredenhagen (11) and Bornemann (4) both accept Haber's view of two potentials for hydrogen peroxide in acid solution, a reducing potential at about $E_h = +0.8$ volt and an oxidizing potential at about $E_h = +1.4$ volts. Bornemann says that "a substance with a potential in a dilute acid solution smaller than $E_h = +0.8$ volt, such as hydriodic acid with about $E_h = 0.5$ volt, can only be oxidized by molar hydrogen peroxide. If the potential of the reacting substance is higher than $E_h = +1.4$ volts, such as $E_h = +1.5$ volts for potassium permanganate, there can only be reduction by hydrogen peroxide. Substances with potentials between $E_h = +0.8$ volt and $E_h = +1.4$ volts may be either reduced or oxidized by hydrogen peroxide. When the nature of the substance permits of either reduction or oxidation, which will happen or whether both will happen simultaneously to an appreciable extent depends only on relative reaction velocities; catalytic agents play an important part within this range."

Our experiments show that there are no true electromotive forces for dilute hydrogen peroxide in acid solution at about $E_h = +0.8$ volt and about $E_h = +1.4$ volts, and that there is no range within which it is a question of reaction velocity whether reduction or oxidation occurs. There is also no true electromotive force for hydrogen peroxide at about $E_h = +1.66$ volts as postulated later by Haber (16). In the same way the normal electrode potential $E_h = +1.8$ volts, as given by Kremann and Müller (18) for the alleged reaction $H_2O_2+2H = 2H_2O$, is entirely mythical. Bray (5) gives $E_h = +1.78$ volts.

The real relation is quite simple. If the true electromotive force, referred to the normal hydrogen electrode, for any oxidizing or reducing agent in any solution is larger than the true electromotive force of hydrogen peroxide in the same solution, that substance will be reduced by hydrogen peroxide. If the true electromotive force, referred to the normal hydrogen electrode, of any oxidizing or reducing agent in any solution is smaller than the true electromotive force of hydrogen peroxide in the same solution, that substance will be oxidized by hydrogen peroxide. As will

be shown later, the reason why this relation has not been clear from the beginning is that people talked about measured electromotive forces and not about true electromotive forces.

In tables 1 and 2 are given data for some of the oxidizing and reducing agents which are on record as reacting with hydrogen peroxide. The figures under E_c(Murphy) were obtained at Cornell and are measurements made against the normal calomel electrode. Platinum wires were used and were heated electrically (34) to bring them approximately to equilibrium. The plus sign denotes that the calomel electrode is anode. The E_c data have been converted into E_h values by adding 0.300 volt, with no other correction for liquid-junction potentials except for the reversible reaction between iodic acid and iodine, where the measurements were made against hydrogen in molar sulfuric acid. The E_c data are not necessarily right, but they are comparable. The E_h data, not based on our E_c measurements, are taken from the literature and are not comparable among themselves or with the Cornell data. So far as can be judged, they are right relatively to hydrogen peroxide; but no guarantee can be given that they are right absolutely or right relatively to each other.

To many people this will seem a deplorable state of affairs. They will feel that we should have corrected all these data and that we should have given our data at least to millivolts and probably to tenths of millivolts. T. W. Richards once said that to measure a thing ten times as accurately meant one hundred times the work. There is a great deal of time wasted on unnecessary accuracy in measurements. If we wish to know whether hydrogen peroxide will oxidize ferrous chloride at all, we must determine the electromotive force of a practically pure ferrous chloride solution. If we wish to know whether hydrogen peroxide will oxidize ferrous chloride completely, we must determine the electromotive force of a practically pure ferric chloride solution. The spread in this case is more than 0.2 volt, so an accuracy of millivolts means nothing. The corresponding spread for tetravalent to pentavalent vanadium is apparently nearly half a volt. From the admittedly inaccurate data in table 1 we shall see that the best measurements of the electromotive force for appreciable concentrations of hydrogen peroxide in acid solution may be roughly 0.3–0.4 volt too low.

There will undoubtedly come a time when it will be desirable to measure these electromotive forces to millivolts or less. For the moment the important thing is the determination of general relations. That has been overlooked entirely in the forty years of exact measurements and elaborate thermodynamics. It is usually stated that it is a waste of time to measure the electromotive forces of practically pure ferrous sulfate and ferric sulfate, because the electromotive force measurement means nothing unless we define the concentrations of the reaction products. This may be true

theoretically; but we deny it very often when we do a potentiometric analysis. It would be a distinct help if people made and tabulated the electromotive forces which are involved in potentiometric analyses, instead of ignoring them or treating them as belonging in an entirely independent chapter.

It is quite clear from table 1 that, in approximately molar solutions of hydrochloric or sulfuric acid, all oxidizing and reducing agents having an electromotive force for the reaction and concentrations in question larger than about $E_h = +1.16 \pm 0.3$ volts are reduced by hydrogen peroxide. All having an E_h value smaller than about 1.16 ± 0.03 volt are oxidized

TABLE 1

Behavior of hydrogen peroxide in acid solutions

E_c (Murphy) data are mostly in M HCl or M H_2SO_4. Parentheses denote that the enclosed constituent is present in relatively small amounts

REACTION	REDUCTION		REACTION	OXIDATION	
	Approximate E_h	E_c (Murphy)		Approximate E_h	E_c (Murphy)
$O_3 \rightarrow O_2$*	+1.80		$I_2 \rightarrow (HIO_3)$	+1.15†	+0.850
$Co_2(SO_4)_3 \rightarrow CoSO_4$	+1.79		$HBr \rightarrow (Br_2)$	+1.09	+0.790
$PbO_2 \rightarrow PbSO_4$	+1.63	+1.325	$HNO_2 \rightarrow HNO_3$	+0.94	
$HMnO_4 \rightarrow MnSO_4$	+1.54	+1.237	$(FeCl_2) \rightarrow FeCl_3$	+0.90	+0.60
$HBrO_3 \rightarrow Br_2$	+1.44	+1.14	$Hg_2(NO_3)_2 \rightarrow Hg(NO_3)_2$	+0.87	
$MnO_2 \rightarrow MnSO_4$	+1.43		$Ag \rightarrow Ag_2SO_4$	+0.67	+0.37
$Cl_2 \rightarrow HCl$	+1.37		$HI \rightarrow I_2$	+0.62	
$HBrO \rightarrow HBr$	+1.35		$Cu_2Cl_2 \rightarrow CuCl_2$	+0.55	
$HClO_3 \rightarrow HCl$	+1.34	+1.058	$H_2SO_3 \rightarrow H_2SO_4$	+0.49	+0.19
$H_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3$	+1.29	+0.99	Ferrocyanic acid → ferricyanic acid	+0.44	
$Br_2 \rightarrow (HBr)$	+1.26	+0.96	$NH_2OH \rightarrow HNO_2$	+0.35	+0.05
$Tl_2(SO_4)_3 \rightarrow TlSO_4$	+1.21		$SnCl_2 \rightarrow SnCl_4$	+0.2	
$(HIO_4) \rightarrow HIO_3$	+1.20	+0.899	$Pb \rightarrow PbSO_4$	−0.29	−0.589
$HIO_3 \rightarrow (I_2)$	+1.17†	+0.867			

* One-way reactions; not strictly reversible.

† Measured directly and not calculated.

by hydrogen peroxide. This does not mean that hydrogen peroxide will oxidize ferric chloride higher because the reaction measured is $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$. If we should or could measure the reaction $Fe^{III} \rightleftharpoons Fe^{VI}$ that electromotive force would be found to be larger than $E_h = +1.16$ volts.

The data in table 1 show that the true electromotive force of hydrogen peroxide in a solution approximately molar with respect to hydrogen ion is about $E_h = +1.16 \pm 0.3$ volts, and that there is no intermediate range within which relative reaction velocities determine whether oxidation or reduction will occur. The directly measured value of about $E_h = +0.8$ volt and the deduced value of $E_h = +1.66$ volts go by the board.

It is quite clear from table 2 that, in approximately molar solutions of

potassium hydroxide, all oxidizing and reducing agents having an electromotive force for the reaction and concentrations in question larger than about $E_h = +0.30 \pm 0.03$ volt are reduced by hydrogen peroxide. All having an electromotive force smaller than about $E_h = +0.30 \pm 0.03$ volt are oxidized by hydrogen peroxide, with the exception of potassium iodide to potassium iodate, which will be discussed later. When an oxidation or reduction can only go one way under the conditions of the experiment, the predictions apply only to the reaction measured. We can obtain approxi-

TABLE 2

Behavior of hydrogen peroxide in alkaline solutions

E_c (Murphy) data are mostly in M KOH

REACTION	REDUCTION		REACTION	OXIDATION	
	Approximate E_h	E_c (Murphy)		Approximate E_h	E_c (Murphy)
$KMnO_4 \rightarrow K_2MnO_4$	+0.73	+0.43	$PbO \rightarrow PbO_2$	+0.27	−0.030
$K_2FeO_4 \rightarrow Fe_2O_3$	+0.71	+0.41	$KI \leftarrow KIO_3$*	+0.16	−0.145
$NaClO \rightarrow NaCl$*	+0.70	+0.40	$Hg \rightarrow HgO$	+0.15	−0.15
$K_2MnO_4 \rightarrow MnO_2$	+0.59	+0.294	$KCN \rightarrow KCNO$	+0.13	−0.175
$Ag_2O_2? \rightarrow Ag_2O$	+0.58		$Na_2SO_3 \rightarrow Na_2SO_4$*	+0.11	−0.19
$Bi_2O_5 \rightarrow Bi_2O_4$	+0.58	+0.279	$Bi_2O_3 \rightarrow Bi_2O_4$	+0.11	−0.19
Ferricyanide→ferrocyanide	+0.51	+0.214	$MnO \rightarrow MnO_2$	+0.11	−0.19
			$CoO \rightarrow Co_2O_3$	+0.10	−0.20
$Ni_2O_3 \rightarrow NiO$	+0.51	+0.21	$Cr_2O_3 \rightarrow K_2CrO_4$*	+0.08	−0.22
$KIO_4 \rightarrow KIO$	+0.44		$Tl_2O \rightarrow Tl_2O_3$	+0.05	
$Ag_2O \rightarrow Ag$	+0.34	+0.038	$KNO_2 \rightarrow KNO_3$	+0.01	
			$Cu_2O \rightarrow CuO$	−0.08	
			$NH_2OH \rightarrow N_2$*	−0.29	−0.59
			$Pb \rightarrow PbO$	−0.56	
			$FeO \rightarrow Fe_2O_3$	−0.83	
			$SnO \rightarrow SnO_2$	−0.87	
			$Zn \rightarrow Na_2ZnO_2$	−1.118	

* One-way reactions; not strictly reversible.

mate values for the oxidation of sulfurous acid to sulfuric acid and for the oxidation of alkaline sodium sulfite to alkaline sodium sulfate, but the reverse reaction does not take place at all in alkaline solutions; in acid solutions it takes place only at very high concentrations of sulfuric acid.

The data in table 2 show that the true electromotive force for hydrogen peroxide in a solution approximately molar with respect to hydroxyl ion is about $E_h = +0.3 \pm 0.03$ volt, and that there is no intermediate range within which relative reaction velocities determine whether oxidation or reduction will occur. This compares with an apparent value as measured directly and not corrected for diffusion potentials of about $E_h = +0.04$ volt.

It must be remembered that the value of $E_h = +0.3 \pm 0.03$ volt con-

tains the acid–alkali liquid-potential difference, which is not present in the value of $E_h = +1.16 \pm 0.03$ volts. Consequently these two values cannot be compared directly.

There is independent evidence for $E_h = +1.16$ volts being somewhere near the true electromotive force for hydrogen peroxide in approximately molar hydrochloric acid or sulfuric acid. No one has ever obtained the theoretical value of 1.23 volts for the oxyhydrogen gas cell, but values up to 1.15 volts have been measured by independent observers. Over fifty years ago Traube (48) showed that hydrogen peroxide is formed when oxygen is reduced at the cathode. Both G. N. Lewis (21) and Haber (15) drew the natural conclusion that the primary reaction in the oxyhydrogen gas cell is the formation of hydrogen peroxide. This view has not yet been accepted (14), but it is unquestionably right (47). Richarz and Lonnes (35) obtained an 88 per cent current efficiency for hydrogen peroxide exclusive of what had been lost by catalytic decomposition. Quite recently Fisher and Krönig (7) have obtained a 93.5 per cent current efficiency under favorable conditions. It seems to be practically certain that 100 per cent current efficiency would be obtained if catalytic decomposition could be avoided.

Another argument in favor of this is that the decomposition–voltage curve for sodium peroxide between platinum electrodes is of the same type as that for copper sulfate between copper electrodes, an approximately straight line starting from the origin. This means that the reactions at the two electrodes are the same in fact but opposite in sign.

Consequently the value of $E_h = +1.16 \pm 0.03$ volts must be very close to the true value for the reaction $H_2 + O_2 = H_2O_2$ in a suitably acid solution. It would be more difficult to prove that $E_h = +0.30 \pm 0.02$ volt is approximately the true value for alkaline solutions because of the higher rate of catalytic decomposition of hydrogen peroxide in alkaline solutions. This is not necessary, however, because the close agreement between the chemical and electrical results in acid solution establishes the validity of the chemical method.

Fredenhagen (12) objected to Haber's calling hydrogen peroxide a reducing agent, because Fredenhagen found that hydrogen peroxide oxidizes ferrous chloride completely, even though the measured electromotive force of a hydrogen peroxide electrode relative to the ferro–ferric electrode is the same as that of an acidified solution containing about 10 per cent molar ferrous chloride and 90 per cent molar ferric chloride. There are two mistakes here. The true electromotive force of a hydrogen peroxide electrode is larger than that of a ferric chloride solution, and consequently hydrogen peroxide should oxidize ferrous chloride completely. Also, if Fredenhagen had made up a cell Pt|10 per cent H_2O_2 in $N/10$ HCl|N $FeCl_3$ in $N/10$ HCl|Pt, he would have observed a reduction of ferric chloride in the cell, as we did.

Ferrous salts combine with α,α'-dipyridyl (19) to give complexes in which the concentration of ferrous ions is apparently vanishingly small. This makes the ferric salt a stronger oxidizing agent; consequently it is not surprising that hydrogen peroxide reduces ferric salts quantitatively in presence of α,α'-dipyridyl. As we had none of this substance, we could not make any electromotive force measurements, but they would undoubtedly have fallen in line. It has long been known that hydrogen peroxide in alkaline solutions reduces potassium ferricyanide to potassium ferrocyanide. All who have measured the electromotive force of this reaction have found it come out as it should relatively to our value for hydrogen peroxide.

Since the formation of hydrogen peroxide is the primary reaction in the oxyhydrogen gas cell, it must take 2 faradays to form one gram-molecular weight of hydrogen peroxide. Consequently the oxygen anion concerned must be O_2'', corresponding to the mercurous cation $Hg_2^{\cdot\cdot}$. This is in accord with the experiments of Tanatar (46), who determined the volumes of oxygen set free at the anode from certain hydrogen peroxide solutions and those set free in a sulfuric acid coulometer. The conditions could be so adjusted that two volumes of oxygen were set free from hydrogen peroxide as against one volume of oxygen from the coulometer. This was after correcting for oxygen set free in consequence of catalytic decomposition. In an alkaline barium peroxide solution the anion must be bivalent diatomic oxygen.

If we have a case of reversible oxidation and reduction, such as $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$, the extreme values for a practically pure ferrous salt solution and for a practically pure ferric salt solution will be either on the same side of the true hydrogen peroxide potential for that solution or on opposite sides. If both are on the same side, the reaction will run to an end. Hydrogen peroxide oxidizes ferrous salts completely to ferric salts either in acid or in alkaline solutions. Permanganate is reduced completely both in acid and in alkaline solutions. Lead peroxide is reduced completely to lead sulfate in acid solutions, and lead monoxide is oxidized completely to lead dioxide or sodium plumbate in alkaline solutions. Hydriodic acid is oxidized completely to iodine in acid solutions.

If the two extreme values lie on opposite sides of the true electromotive force for hydrogen peroxide in that solution, a state of equilibrium occurs. Liquid bromine with a low concentration of hydrobromic acid gives a value of $E_h = +1.26$ volts and is reduced by hydrogen peroxide. Bromine with a high concentration of hydrobromic acid gives a value of $E_h = +1.09$ volts, and the hydrobromic acid is oxidized by hydrogen peroxide. The zero point at which traces of hydrogen peroxide are in equilibrium with liquid bromine and hydrobromic acid is at about $E_h = +1.16$ volts, apparently between $+1.17$ and $+1.15$.

The conversion of iodine into iodic acid and back is a very good illustra-

tion of this. As the literature at present is in a hopelessly confused state, this case brings out the advantage of our viewpoint. Iodine dissolved in M sulfuric acid is converted nearly completely into iodic acid. The reverse reaction does not take place to an extent which can be detected by the casual observer. If one adds a little carbon tetrachloride to a solution of iodic acid in 2 normal sulfuric acid before adding the hydrogen peroxide, the existence of an equilibrium will be shown by the development of a pink color in the carbon tetrachloride. Using dilute hydrogen peroxide a pink color develops with $M/2$ and $M/50$ iodic acid but not with $M/200$ iodic acid. When 30 per cent hydrogen peroxide is added, a pink color is obtained even with $M/2000$ iodic acid. This shows again that hydrogen peroxide is a stronger reducing agent in more concentrated solution. If the carbon tetrachloride is added after the hydrogen peroxide has decomposed completely, no pink color is obtained even with $M/2$ iodic acid.

If one adds iodine crystals to a solution of hydrogen peroxide in 2 normal sulfuric acid, the solution does not become colored by the iodine and the oxidation to iodic acid takes place very slowly. This apparent paradox is due to the catalytic decomposition of the hydrogen peroxide at the surface of the iodine crystals. These crystals become coated with a film of oxygen, which protects them pretty well from the solvent action of the solution. The rate of oxidation can be accelerated by stirring the solution vigorously, or by starting with a saturated solution of iodine in carbon tetrachloride and adding excess iodine. The zero point is about $E_h = +1.16$ volts, apparently between $+1.17$ and $+1.15$.

Auger (1) obtained visible amounts of iodine by starting with a dilute iodic acid solution. We have improved on that technique by starting with a concentrated potassium iodate solution, adding a few drops of hydrochloric acid or sulfuric acid, and then adding 30 per cent hydrogen peroxide. A heavy precipitation of iodine occurs, which stops when the solution becomes neutralized. Further addition of hydrochloric acid causes additional precipitation of iodine. If concentrated hydrochloric acid is added, the iodine is oxidized to iodic acid by the hydrogen peroxide. If caustic potash is then added, iodine will come down again on addition of hydrogen peroxide, provided the solution has not become too dilute. This makes a very striking lecture experiment.

In our experiments the change from reduction to oxidation occurs at about pH = 1.2 to 1.4, apparently regardless of whether one uses hydrochloric acid or sulfuric acid. If one adds the acid in several portions, each one after the preceding portion has been neutralized, one can get a good deal of reduction. If the same amount of acid is added all at once, the pH drops below 1.2 and there is practically no reduction. Since the change occurs at approximately the same pH both with hydrochloric acid

and with sulfuric acid, the intermediate formation of iodine monochloride or trichloride cannot be of vital importance as Auger assumed it to be.

The electromotive force measurements on periodic acid and potassium periodate confirm the chemical findings by Tanatar (45) that hydrogen peroxide reduces periodic acid and sodium periodate to iodic acid and sodium iodate, respectively. With potassium iodide and potassium iodate we ran into a serious difficulty which we had not foreseen, although perhaps we should have. The electromotive force of $E_h = +0.16$ should mean that sodium peroxide oxidizes alkaline potassium iodide to potassium iodate. In spite of all our efforts to the contrary, we were forced to confirm the results of our predecessors that sodium peroxide produces practically no potassium iodide from potassium iodate.

A way out of this impossible situation was found at last. One can obtain an electromotive force measurement for sodium sulfite as a reducing agent and one can oxidize sodium sulfite to sodium sulfate; but one cannot reduce sodium sulfate to sodium sulfite. In the presence therefore of a suitable reducing agent, both sodium sulfite and sodium sulfate would be practically stable. The conversion of sodium iodide to sodium iodate is not quite a parallel case to that of sodium sulfate to sodium sulfite, because a sufficiently strong oxidizing agent, such as ozone, will oxidize alkaline sodium iodide to sodium iodate (20) and even to sodium periodate (36). We have found that alkaline permanganate is bleached by alkaline sodium iodide. The difficulty with the hydrogen peroxide is that potassium hypoiodite is the first stage in the oxidation of iodide, and that hydrogen peroxide reduces hypoiodite. To oxidize alkaline potassium iodide to iodate, one must use an oxidizing agent, such as ozone or alkaline permanganate, with a higher oxidizing potential than alkaline potassium hypoiodite. On the reduction side there is no difficulty. Either an alkaline hydrazine or hydroxylamine solution will reduce alkaline potassium iodate to iodide. The reason that hydrogen peroxide can oxidize hydriodic acid to iodic acid is that the first stage is the oxidation to iodine. A strong enough oxidizing agent should oxidize alkaline sodium chloride to sodium hypochlorite and sodium chlorate. Alkaline permanganate will not do it, and we have not tried ozone. Fluorine will do it.

We can now consider the problem of where the oxygen gas comes from when hydrogen peroxide reacts with lead peroxide in sulfuric acid solution. This is simpler than the case of permanganate, and just as typical. There are many differences in detail, but, speaking broadly, there are two schools of thought. One school—led originally by Schönbein, Brodie, and Berthelot—believes that half the oxygen gas comes from the lead peroxide and half from the hydrogen peroxide. The other school—led originally by Weltzien, Traube, and Baeyer—believes that all the oxygen gas comes from the hydrogen peroxide and none of it from the lead peroxide.

Most textbooks adopt the first view—that of Schönbein, Brodie and Berthelot—for no apparent reason. Roscoe and Schorlemmer (38) say: "The oxides of metals such as gold, silver, and platinum immediately cause decomposition of hydrogen dioxide into water and oxygen even in dilute aqueous solutions, and the oxides themselves are simultaneously reduced to the metallic state, the reduction with silver oxide being represented by the equation:

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$$

"We have here the remarkable phenomenon of a powerful oxidizing agent exerting a reducing action on metallic oxides with formation of the metal. The explanation of this fact is, however, not far to seek. The above-named metals only combine somewhat feebly with oxygen, and their oxides decompose easily into the elements. When they are brought into contact with hydrogen dioxide, which contains one atom of oxygen but feebly united, mutual reduction takes place, the one atom of oxygen in the dioxide combining with one atom of oxygen in the metallic oxide to form a molecule of free oxygen."

If we ear-mark the oxygen which is to go off as gas by italicizing it, we can make clear the difference between the two points of view. According to Roscoe and Schorlemmer one should write the equation:

$$Ag_2\mathit{O} + H_2O\cdot\mathit{O} = 2Hg + H_2O + \mathit{O}_2 \text{ (alkaline)}$$

and

$$PbO\cdot\mathit{O} + H_2O\cdot\mathit{O} = PbO + H_2O + \mathit{O}_2 \text{ (acid)}$$

According to the other view, which we endorse, one should write:

$$Ag_2O + H_2\mathit{O}_2 = 2Ag + H_2O + \mathit{O}_2 \text{ (alkaline)}$$

and

$$PbO_2 + H_2\mathit{O}_2 = PbO + H_2O + \mathit{O}_2 \text{ (acid)}$$

The oxidation—not reduction—of hydrogen peroxide by ozone should be written:

$$H_2\mathit{O}_2 + \mathit{O}_2O = H_2O + 2\mathit{O}_2$$

We will now give the reasons (39) for adopting the view put forward by Weltzien, Traube, and Baeyer. Hydrogen peroxide may be considered as dissociating reversibly to a very slight extent into monatomic, electrically neutral hydrogen and activated diatomic oxygen: $H_2O_2 \rightleftharpoons 2H + O\cdot O$. Reductions are effected by the monatomic hydrogen and oxidations by the

activated diatomic oxygen, which differs from molecular oxygen by only having one bond between the oxygens. It is an unsaturated oxygen molecule.

If we arrange a cell, Pt | H_2O_2 in H_2SO_4 | H_2SO_4, PbO_2 | Pb, the current will flow from left to right through the cell, lead peroxide will be reduced to lead sulfate at the cathode, and two oxygens will be evolved at the platinum anode for one gram-molecular weight of lead peroxide reduced. The anode reaction is precisely similar to the one studied quantitatively by Tanatar. In this case there can be no question but that the two oxygens come from the hydrogen peroxide and neither one from the lead peroxide. Similar cells can be set up in all cases in which the error in the potential measured at the platinum electrode, due to the difference between the apparent and true electromotive force of hydrogen peroxide or of the reacting substance, is not sufficiently large to obscure things. With platinum in acidified hydrogen peroxide against platinum in acidified permanganate, manganese dioxide, or chromic acid, the peroxide electrode is the anode, as it should be. With platinum in alkaline hydrogen peroxide against platinum in alkaline permanganate, the hydrogen peroxide electrode is the anode, as it should be.

With platinum in alkaline manganous hydroxide against platinum in alkaline hydrogen peroxide, the hydrogen peroxide electrode is the cathode. Theoretically it should be the cathode, when platinum in alkaline lead monoxide is the other electrode; but actually that is not the case. Apparently the reason why this experiment is unsuccessful with normal alkali is that hydrogen peroxide is catalyzed so rapidly by platinum in such a solution that it is impossible to build up the proper potential at the electrode. Once the cause of the trouble was recognized, it was easy to get around the difficulty. Alkaline hydrogen peroxide oxidizes manganous hydroxide to manganese dioxide and is therefore a stronger oxidizing agent than alkaline manganese dioxide. A cell was accordingly made up: Pt | PbO, N KOH | N KOH, MnO_2 | Pt. The manganese dioxide electrode is the cathode; consequently the stronger oxidizing agent, hydrogen dioxide, would also be at the cathode if the catalytic decomposition were eliminated. A similar arrangement made it possible to show that alkaline chromic oxide and alkaline cobaltous oxide are really anodic to hydrogen peroxide of the same general alkalinity.

In every case the current in an electrolytic cell containing hydrogen peroxide flows in the direction predicted by the chemical reaction, or can be made to do so by eliminating the unessential disturbing factors. It is not safe to say that the type of reaction as postulated by Schönbein and Brodie cannot be arranged as an electrolytic cell, but no one has yet done it and it is not clear what would be anode and what cathode. It has also never been explained why hydrogen peroxide and lead peroxide or manga-

nese dioxide should be compatible in alkaline solution and incompatible in acid solution. In the reaction between barium peroxide and iodine, $BaO_2 + I_2 = BaI_2 + O_2$, all the oxygen must come from the peroxide. We may therefore consider the question of the source of the oxygen gas as settled in the way it should have been settled a long time ago—in favor of the view advanced by Weltzien, Traube, and Baeyer. As late as 1858 Schönbein (40) explained the reaction $H_2O_2 + Cl_2 = 2HCl + O_2$ on the basis that chlorine was murium peroxide and not an element.

An additional argument is to be found in the experiments of Fowler and Grant (10) on the effect of heating lead peroxide with potassium chlorate. From Schönbein's point of view the result should have been evolution of oxygen with the formation of lead monoxide and potassium chloride, both substances losing oxygen. Actually there was a nearly quantitative oxidation of potassium chlorate to potassium perchlorate. When dry sodium peroxide is ground with iodine and heated suitably, there is formation of sodium periodate (17).

Raikow (33) takes the ground that a substance cannot have the same formula as a reducing agent and as an oxidizing agent. He therefore considers that the reducing agent is HO—OH and that the oxidizing agent is $H_2{=}O{::}O{=}$. This seems quite unnecessary. We have postulated the reversible dissociation $H_2O_2 \rightleftharpoons 2H + O{-}O$. When hydrogen peroxide acts as a reducing agent, we have 2H reacting with the substance to be reduced and the O—O going off as molecular oxygen. When hydrogen peroxide acts as an oxidizing agent, the activated oxygen reacts both with the substance to be oxidized and with the monatomic hydrogen. For lead oxide in alkaline solution we have, for instance:

$$2H + O{-}O + PbO = H_2O + PbO_2$$

For hydriodic acid in acid solution we have as the first stages:

$$2H + O{-}O + HI = H_2O + HIO$$

Starting with this point of view one cannot admit that the catalytic decomposition of hydrogen peroxide can be represented by the equation $H_2O_2 \rightarrow H_2O + O$. It must be that one molecule of hydrogen peroxide reduces a second one in exactly the same manner that one molecule of hydrogen peroxide reduces one molecule of lead peroxide. The equation would be written:

$$H_2O_2 + H_2O_2 = 2H_2O + O_2$$

After this conclusion had been reached independently, it was a great pleasure to find that Wieland (51) had said the same thing more than a dozen years ago. He considers that the first stage in the catalytic decom-

position is the dehydrogenation of one molecule, the hydrogen from which reacts very rapidly with a second molecule. Wieland writes the equations:

$$HO{\cdot}OH \rightarrow O{:}O + 2H$$
$$HO{\cdot}OH + 2H \rightarrow 2H_2O$$

The only difference between Wieland's point of view and ours is that we postulate a reversible dissociation and consequently the formation of O—O with subsequent formation of molecular oxygen, O:O.

If hydrogen peroxide decomposed, as is usually assumed, according to the equation $H_2O_2 \rightarrow H_2O + O$, it would necessarily be one of the most powerful oxidizing agents, because it would be setting free nascent oxygen which is, next to fluorine, the most powerful oxidizing agent that we have at ordinary temperatures. As a matter of fact this work was started with the idea that one could do chemical electrolyses with hydrogen peroxide nearly as well as with fluorine. That view was given up when it was found experimentally that hydrogen peroxide is a rather weak oxidizing agent. This is quite reasonable now that we see that what is first evolved is O·O and not O. While molecular oxygen is not as effective an oxidizing agent as hydrogen peroxide, because of its inertness, molecular oxygen in contact with platinum is a stronger oxidizing agent than hydrogen peroxide, though not so convenient a one. If one writes hydrogen peroxide with the unsymmetrical formula, one gets into difficulty because the dissociation $H_2O{:}O \rightleftharpoons 2H + O{:}O$ gives molecular oxygen.

The catalytic decomposition by platinum may be written:

$$H_2O_2 + Pt = Pt(2H) + O_2$$
$$H_2O_2 + Pt(2H) = Pt + 2H_2O$$

The measured reaction is therefore monomolecular. For this particular case we have practically eliminated the distinction between contact catalysis and reaction catalysis made by Bray (5) and Livingston (22). We do not agree with the conclusions drawn by Bray and Livingston in regard to catalysis in homogeneous solutions, though their premises are right. They have shown "that in acid solution hydrogen peroxide oxidizes bromide to bromine, and reduces bromine to bromide, and that these two reactions can take place independently in the same solution. When the rates of these two compensating reactions are equal, the net result is the catalytic decomposition of hydrogen peroxide. This constitutes a 'steady state,' in which the concentrations of bromine, bromide, and acid remain constant in a single experiment."

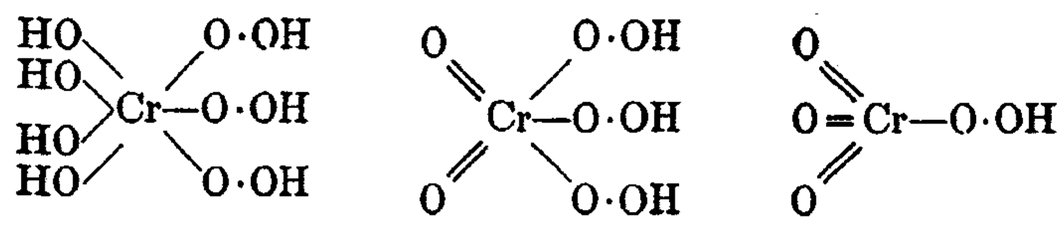
Bray postulates two electromotive forces for molal hydrogen peroxide in molal acid, a reducing one of $E_h = +0.56$ volt and an oxidizing one of $E_h = +1.78$ volts. He considers that an oxidation-reduction catalysis of

hydrogen peroxide occurs when the electromotive forces of the oxidation-reduction couple lie between these two limiting values. In the first place, the steady state is not really one, because the concentrations vary with the concentration of hydrogen peroxide. If the catalysis is to continue until all the hydrogen peroxide is used up, the final electromotive force involved is ours of $E_h = +1.16$ volts and not the hypothetical ones given by Bray.

What Bray should have said is that one gets an oxidation-reduction catalysis of hydrogen peroxide when one electromotive force lies above $E_h = +1.16$ volts and the other below it. Bray came to grief with the ferric salt catalysis of hydrogen peroxide, because there is no evidence of any reduction of ferric ion to ferrous ion by hydrogen peroxide. Bray mentions the possibility of oxidation to ferrate, but does not dwell on it. We explain the catalysis by the temporary formation of the instable ferric acid. When neutral hydrogen peroxide is added to neutral ferric chloride solution, a dark red color is formed temporarily, which is undoubtedly due to a higher valence of iron.

This is confirmed by the work of Bohnson (3) and Robertson (37), who photographed the absorption spectra of solutions of ferric chloride alone, barium ferrate dissolved in acetic acid, potassium ferrate, and mixtures of hydrogen peroxide and ferric chloride. There is a striking similarity between the bands for the two ferrates and those for the reaction mixture. On the other hand, a solution of ferric chloride shows no such characteristic bands in the yellow and green, and is totally opaque to the violet. When hydrogen peroxide is added to the ferric chloride, transmission of violet lines takes place and absorption bands appear in the yellow and green.

One of the very interesting things about hydrogen peroxide is the alleged presence of perchromic acid in the blue solution obtained temporarily by adding hydrogen peroxide to a suitably acidified chromic acid solution. It is a regular experiment in all introductory courses in chemistry. As the name "perchromic acid" implies, most people consider that chromium has been oxidized to a higher valence than it has in chromic acid. Friend (13) writes the formulas for the perchromic acids as



giving chromium a valence of seven.

As a matter of fact, the evidence against the existence of a higher oxide of chromium in perchromic acid is conclusive. Chromic acid does not

bleach acidified permanganate and is therefore not oxidized by it, although acidified permanganate is a stronger oxidizing agent than chromic acid. The blue compound does bleach acidified permanganate even after the free hydrogen peroxide has been removed.

Lead peroxide does not give rise to the blue color. Platinum causes the blue color to fade more rapidly than it would otherwise, but takes quite a while. In spite of this we have been unable to produce the blue oxide by electrolysis with a platinum anode. The only agents which will give rise to the blue color are hydrogen peroxide and compounds which set free hydrogen peroxide, such as ozomolybdic acid, pervanadic acid, pertitanic acid, pertantalic acid, perzirconic acid, peruranic acid, pertungstic acid, perboric acid (8), copper peroxide, mercury peroxide, etc. These are substances whose scientific names do not describe the products. These experiments were done before we had read the paper by Moissan (28), but our line of reasoning is identical with his.

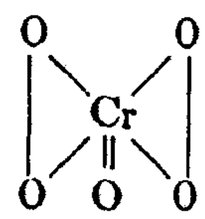
Consequently the blue compound is not a higher oxide of chromium, any more than barium peroxide involves a higher valence of barium. The blue compound is either an addition product or a metathetical product of chromic acid and hydrogen peroxide. It cannot possibly be chromium with a valence of seven, as many people assume. Addition of hydrogen peroxide to a chromic acid electrode does not raise the potential even when a blue color is formed temporarily.

Spitalsky (44) found that in 3 normal sulfuric acid hydrogen peroxide reduces chromic acid practically instantaneously to chromic sulfate. Traube (49) showed that persulfuric acid dissolved in 70 per cent sulfuric acid causes chromic acid to go to chromic sulfate because a sulfuric acid of this concentration converts persulfuric acid rapidly into hydrogen peroxide. With persulfuric acid dissolved in a 40 per cent sulfuric acid no appreciable reduction occurs. This means that persulfuric acid does not oxidize chromic acid to any of the so-called perchromic acids.

There is nothing really new about this. Werther (50), Péchard (30), Melikoff and Pissarjewsky (26), and Pissarjewsky (32) have pointed out more or less clearly that the colored products obtained by adding hydrogen peroxide to acidified chromic acid, vanadic acid, molybdic acid, and tungstic acid do not correspond to higher oxidation stages of these metals.

Schwarz and Giese (43) say that it is very improbable that chromium, which is in the sixth group, should ever have a valence of seven. Also, in all the other cases in which hydrogen peroxide reacts with an acid radical containing a metal, peroxide compounds are formed with an —O:O— group and no increase in the valence of the central atom (pertitanate (2), perzirconate, pervanadate (27), perphosphate, etc.). They come to the conclusion that the so-called perchromic acid is not an acid at all, but a

peroxide of the composition CrO_5 and the formula



Over fifty years ago Moissan (28) wrote the formula $CrO_3 \cdot H_2O_2$, which is still good.

Since hydrogen peroxide reduces quadrivalent lead to bivalent lead in acid solutions and reverses this reaction in alkaline solutions, there must be a transition at some point which will not necessarily come at pH=7. Schönbein (37) fixed the point between lead acetate and basic lead acetate. Zotier (52) confirmed this. With neutral lead acetate and hydrogen peroxide he got no lead peroxide; with basic salts he got a slight formation of lead peroxide; and with alkaline solutions he got plenty of lead peroxide. It is not certain just what is meant by basic lead acetate, so we have checked Zotier's results. Addition of hydrogen peroxide to a solution of lead acetate and lead monoxide in the proportions necessary to form $Pb_2(CH_3COO)_3OH$ caused precipitation of lead peroxide. Addition of increasing amounts of 0.766 *N* potassium hydroxide to 5 cc. of a solution of lead acetate (50 g. of $(CH_3COO)_2Pb \cdot 3H_2O$) in 100 cc. of water followed by addition of 5 cc. of a 30 per cent hydrogen peroxide gave the following results. With 1 cc. of potassium hydroxide no lead peroxide. The pH of the solution, as determined by the indicator method, was 6.5. With 2 cc. of potassium hydroxide there was formed lead peroxide. The pH of this solution was 7.0. The zero point for lead acetate to lead peroxide in the presence of potassium hydroxide is between pH 6.5 and 7.0. Substitution of sodium hydroxide does not affect the zero point within these limits of accuracy.

Addition of increasing amounts of *N*/100 acetic acid to 5 cc. of a basic lead acetate solution (10 g. of basic lead acetate, $Pb_2(CH_3COO)_3 \cdot OH$, in 100 cc. of water), followed by addition of 5 cc. of 30 per cent hydrogen peroxide gave the following results. With 35 cc. of acetic acid lead peroxide was still formed, but 40 cc. of acetic acid prevented its formation. The pH values of these solutions were 7.0 and 6.4, respectively. When *N*/100 hydrochloric acid was added, 35 cc. did not prevent the formation of lead peroxide while 40 cc. did. This corresponds to pH values of 6.2 and 5.8, distinctly smaller than the 7.0 and 6.5 found with caustic alkali and acetic acid. This may have been a chloride effect. This seems to have been proved by experiments in which a 1 per cent solution of potassium chloride was substituted more or less completely for the hydrochloric acid. The results in table 3 were obtained for the varying amounts

of potassium chloride necessary to prevent the formation of lead peroxide. When only potassium chloride was added to the basic lead acetate, the decrease in pH must have been apparent and not real. The basic lead acetate gives lead peroxide at a platinum anode.

Schönbein (40) reports that hydrogen peroxide reduces alkaline cupric oxide to cuprous oxide, and Brodie (6) says that sodium peroxide oxidizes ammoniacal cupric chloride temporarily to a higher oxide. Both are wrong. Schönbein mistook the yellow of the so-called copper peroxide for the yellow of cuprous oxide. Parnell (29) made the same mistake about ten years later. Brodie did not realize that the so-called copper peroxide is really just that. It does not represent a higher valence for copper, any more than the so-called perchromic acid represents a higher valence of chromium. Cuprous salts are oxidized to cupric salts by hydrogen peroxide both in acid and alkaline solutions just as ferrous salts are oxidized to ferric salts.

TABLE 3

Potassium chloride necessary to prevent the formation of lead peroxide

VOLUME OF KCl (1 PER CENT)	VOLUME OF HCl (*N*/100)	pH
cc.	*cc.*	
0.0	35–40	5.8–6.2
0.7	30–35	6.4
1.0	20–25	6.6
1.5	0	6.4

Curiously enough a somewhat similar mistake has been made with regard to mercuric oxide. Martinon (25) says that mercuric oxide is reduced to black mercurous oxide in alkaline solution by hydrogen peroxide. The electromotive force measurements for Hg | HgO and Pt | HgO contradict this. When pure mercuric oxide is treated with hydrogen peroxide in alkaline solution, it turns black as Martinon says, but the product is not mercurous oxide. By working at 0°C. as Pellini (31) did, one can isolate the red mercury peroxide, which is formed metathetically and which gives a blue solution with chromic acid. On addition of alkali there is an evolution of oxygen and the red compound turns black. That is impure metallic mercury. If it is dissolved in dilute nitric acid, one can then precipitate mercurous chloride, but this is no evidence for the prior existence of mercurous oxide.

It is not really surprising that one cannot measure the true electromotive forces of hydrogen peroxide in acid and in alkaline solutions. One can see the evolution of oxygen as a danger signal. There are other cases where one does not measure the true electromotive forces. Ozone is a stronger oxidizing agent than cobaltic sulfate, but electromotive force

measurements do not show it. Luther (24) has given a long list of criteria which should be met before one can postulate that a given electromotive force connotes a given reaction. We do not care for the stipulation that the Peters equation is a necessary criterion. That way leads to the activity concept. Loimaranta (23) cites the cases of trivalent and pentavalent arsenic and trivalent and hexavalent chromic acid where iodine serves profitably as electromotive promoter.

Of especial interest to us is the work of Forbes and Bartlett (9), who found that the apparent electromotive force of acidified chromic acid was raised considerably by addition of ammonium ferrous sulfate. We have confirmed this. With molar chromic acid in molar sulfuric acid an apparent value was obtained of $E_c = +0.990$ volt as given in table 1. On addition of ammonium ferrous sulfate this rose to $E_c = +1.150$ or $E_h = +1.45$ volts. Chromous sulfate, stannous chloride, arsenious acid, and potassium ferrocyanide produce similar though smaller effects.

Forbes and Bartlett at first considered this to be due to a change in the platinum electrode, but pointed out that the effect cannot be obtained with sulfurous acid or with hydrazine. No satisfactory explanation for this phenomenon has yet been given.

Luther (24) obtained a rise of electromotive force by reducing an oxidizing agent instead of oxidizing a reducing agent. A dilute chloric acid has almost no effect on hydrobromic acid. If reduced to chlorine dioxide by means of tetravalent vanadium, the chlorine dioxide oxidizes hydrobromic acid practically instantaneously.

In molar sulfuric acid the apparent electromotive force of hydrogen peroxide increases somewhat with increasing concentration of hydrogen peroxide, whereas the true electromotive force must decrease.

The following general conclusions can be drawn:

1. When the true electromotive force of any oxidizing or reducing agent, with reference to any electrode and in any solution, is larger than the true electromotive force of hydrogen peroxide in the same solution, that substance will be reduced by hydrogen peroxide, provided such a reaction is possible. If the true electromotive force is smaller than the true value for hydrogen peroxide, that substance will be oxidized by hydrogen peroxide, provided such a reaction is possible.

2. The true electromotive force, relatively to the hydrogen electrode, of hydrogen peroxide in M hydrochloric or sulfuric acid is about $+1.16 \pm 0.03$ volts; the corresponding value in M potassium hydroxide is about $+0.30 \pm 0.02$ volt, subject to a correction for diffusion potential. The zero points for iodine to iodic acid in M sulfuric acid and for hydrobromic acid to bromine are apparently $E_h = +1.16$ volts.

3. The primary reaction in the oxyhydrogen gas cell is the formation of hydrogen peroxide, as postulated years ago by G. N. Lewis and by Haber.

4. The oxygen anion in hydrogen peroxide is O_2'', as shown by Tanatar.

5. The current-voltage curve for a sodium peroxide solution between platinum electrodes is the same type as that for a copper sulfate solution between copper electrodes.

6. Hydrogen peroxide may be considered as dissociating reversibly into $2H + O{\cdot}O$. Reduction is done by the two hydrogen atoms and oxidation by the $O{\cdot}O$. The symmetrical structure for hydrogen peroxide is indicated.

7. In the reaction between hydrogen peroxide and lead peroxide in acid solution, the lead peroxide is reduced by the hydrogen from the hydrogen peroxide, and all the oxygen gas comes from the hydrogen peroxide. This is the view put forward by Weltzien, Traube, and Baeyer.

8. In the catalytic decomposition of hydrogen peroxide the reaction is

$$2H + O{\cdot}O + H_2O_2 \rightarrow 2H_2O + O_2$$

and not

$$H_2O_2 \rightarrow H_2O + O$$

This is the view advocated by Wieland. In the presence of platinum the reactions may be written

$$H_2O_2 + Pt = Pt(2H) + O_2$$

and

$$H_2O_2 + Pt(2H) = Pt + 2H_2O$$

The measured reaction is therefore monomolecular.

9. Bray should have said that we get an oxidation-reduction catalysis of hydrogen peroxide when one electromotive force is larger than $E_h = +1.16$ volts and one is smaller. He was led astray by Haber's hypothesis of an oxidation value for hydrogen peroxide greater than $E_h = +1.16$ volts.

10. The blue so-called perchromic acid does not contain chromium with a higher valence than six. This is the view upheld by Moissan. The so-called pertungstates, pertantalates, pervanadates, permolybdates, pertitanates, perzirconates, peruranates, perborates, etc., do not contain higher oxides; nor do copper peroxide and mercury peroxide. Acid permanganate is reduced by the blue compound just as it is by hydrogen peroxide. It is not reduced by chromic acid.

11. When a substance is reduced by hydrogen peroxide in strongly acid solution and oxidized in a strongly alkaline solution, or the other way around, there must be an intermediate pH at which neither change takes place for any given concentration of hydrogen peroxide. With lead acetate this point comes between pH = 6.5 and 7.0. Presence of chloride displaces the apparent position of the point.

12. No satisfactory explanation has yet been given for the rise of

electromotive force when ammonium ferrous sulfate, chromous sulfate, stannous chloride, arsenious acid, or potassium ferrocyanide is added to an acidified chromic acid solution.

13. In molar sulfuric acid the apparent electromotive force of hydrogen peroxide increases with increasing concentration of hydrogen peroxide, whereas the true electromotive force must decrease.

14. Hydrogen peroxide reduces acidified potassium iodate to iodine when the pH is larger than about 1.2 to 1.4, and oxidizes iodine to iodic acid when the pH is smaller than that.

15. In approximately molar caustic potash, hydrogen peroxide should apparently oxidize potassium iodide to iodate, but the first step in such an oxidation is the formation of potassium hypoiodite and this substance is reduced by hydrogen peroxide. Consequently both potassium iodide and potassium iodate are practically stable to hydrogen peroxide in alkaline solutions.

16. To oxidize alkaline potassium iodide to iodate, one must use a more powerful oxidizing agent than potassium hypoiodite. Ozone and alkaline permanganate meet this requirement.

17. It is now possible to draw a sharp dividing line between peroxides and dioxides. The term lead peroxide is so well established that it is doubtful whether a change in nomenclature is wise.

18. The chemistry of hydrogen peroxide is a hopeless subject for the phenomenological, or Baconian, experimenter, because the misleading experiment is everywhere.

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PHOTOSYNTHESIS OF FORMALDEHYDE IN TROPICAL SUNLIGHT

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Received May 22, 1934

The review of the literature on the subject of photosynthesis, from the advancement of Baeyer's hypothesis as regards assimilation of carbon dioxide up to the position of the work as it stands at the present time, leads one to believe that it demands (a) an investigation of the likely impurities besides organic matter, dust, etc., present at the seat of the evolution of carbon dioxide which is to be exposed to light, and (b) suggestions as to an apparatus which can be used everywhere under identical conditions.

Results obtained in an investigation carried out with a view to find out the likely impurities and to suggest an apparatus, are embodied in the present paper.

EXPERIMENTAL

The experiments were carried out in sunlight using the apparatus shown in figure 1 and also in glass bulbs joined together, as will be described. Figure 1 indicates an apparatus made of soft glass having three bulbs a, b, and c. The bulbs a and b are joined together with a tube which is connected with the delivery tube d through which the liberated carbon dioxide passes into the solution in the bulb c; e is a passage to take out and fill in any solution in the bulb c. The passage e is covered with a test tube containing conductivity water. The bulbs a and b contain the carbonates under conductivity water or in solution, and hydrochloric acid, respectively. The carbonate and the acid are introduced into the bulbs through the mouth f, which is afterwards sealed in a blow-pipe flame. By tilting the apparatus towards the bulb a, the acid in b is allowed to come in contact with the carbonate in a and thus the evolution of carbon dioxide takes place; the gas passes through the delivery tube d into the solution in the bulb c. The acid is poured on the carbonate gradually from day to day while the apparatus is sealed at f and the passage e is covered with conductivity water, which is replaced from time to time, in a test tube. There is no possibility of any organic matter or dust entering the bulbs a, b, and c. Thus the necessity of corks, rubber tubing, or an exit tap-way arrangement can be easily dispensed with.

Another apparatus wherein carbon dioxide, in the presence of water, is to be exposed has two glass bulbs joined together and sealed at the other ends. The bulbs contain carbonate or marble pieces and hydrochloric acid, respectively. The bulb containing the acid is tilted towards the other bulb, and thus the acid is allowed to come in contact with the carbonate or marble pieces, or the carbonate with metallic magnesium or tin foil. Carbon dioxide and hydrogen, thus formed, are in a nascent state and can be conveniently exposed to light at the time of their liberation, in the presence of water.

Before use the apparatus was carefully cleaned with hot chromic acid mixture and washed several times with distilled and finally with conductivity water. Merck's extra pure guaranteed reagents were used after necessary precautions.

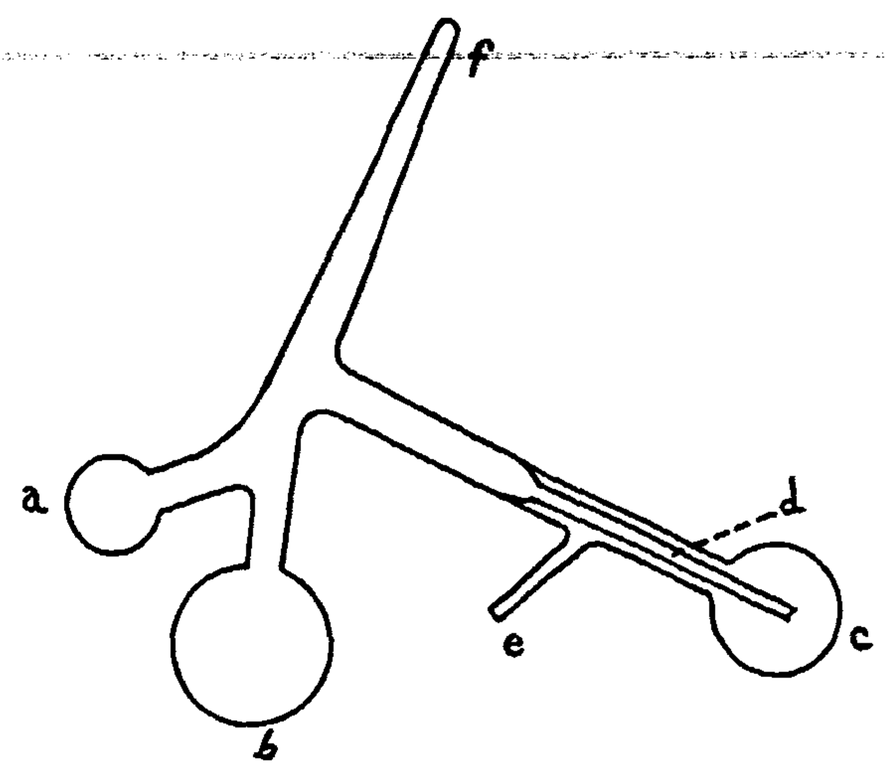

FIG. 1. THE APPARATUS

Schryver's and Rimmi's tests were applied for the detection of formaldehyde. The contents of the apparatus were taken out in beakers after exposure to sunlight, neutralized, and distilled. The distillates were tested for formaldehyde. The marble pieces, barium carbonate, magnesium powder, and carbonates of nickel and cobalt, were well washed with hot conductivity water before use.

DISCUSSION OF RESULTS

The carbon dioxide, obtained from barium or sodium carbonate and hydrochloric acid, though exposed to light for forty-four hours, in the presence of water and in "statu nascendi," does not indicate the formation of formaldehyde. However, if the source of carbon dioxide is changed to marble pieces and hydrochloric acid there is a clear formation of formalde-

hyde, even for an exposure of eight hours. This must be due to certain impurities present in marble pieces (vide experiments 1, 2, and 3, table 1).

L. Moser (2) has discussed the purification of the carbon dioxide gas

TABLE 1

Experiments performed in the double-bulbed apparatus

EXPT. NO.	CONTENTS OF		TIME OF EXPOSURE	RESULTS
	Bulb 1	Bulb 2		
			hours	
1*	$BaCO_3$ under conductivity water	$N/10$ HCl	44	No formaldehyde detected
2*	10 per cent Na_2CO_3 solution	$N/10$ HCl	44	No formaldehyde detected
3†	Marble pieces	$N/10$ HCl	8	Small quantities of formaldehyde detected
4†	$BaCO_3$ and Mg powder	$N/10$ HCl	8	Odor of formaldehyde; formaldehyde detected
5†	$BaCO_3$ and Sn foil	$N/10$ HCl	8	Formaldehyde detected; no odor of formaldehyde

* These experiments were repeated four times.

† These experiments were carried out in the dark with negative results.

TABLE 2

Experiments performed in the apparatus shown in figure 1

EXPT. NO.	CONTENTS OF			TIME OF EXPOSURE	RESULTS
	Bulb a	Bulb b	Bulb c		
				hours	
6	$BaCO_3$	$N/10$ HCl	Conductivity water	43	No formaldehyde detected
7	$BaCO_3$	$N/10$ HCl	Dilute solution of $FeCl_3$	44	No formaldehyde detected
8	$BaCO_3$	$N/10$ HCl	$NiCO_3$ suspended under conductivity water	40*	No formaldehyde detected
9	Marble pieces	N HCl	Conductivity water	8	Small quantities of formaldehyde detected
10	$BaCO_3$	$N/10$ HCl	Dilute solution of H_2S	8	Small quantities of formaldehyde detected
11	$BaCO_3$	$N/10$ HCl	Dilute solution of H_2SO_3	8	Small quantities of formaldehyde detected
12	$BaCO_3$	$N/10$ HCl	Mg powder suspended under conductivity water	8	Formaldehyde detected; odor of formaldehyde

All of these experiments were carried out in the dark with negative results.

from marble pieces and hydrochloric acid and recommends the use of cupric sulfate on pumice to remove hydrogen sulfide and a solution of potassium permanganate to remove sulfur dioxide. Thus the impurities which are likely to be present and can be removed completely by using such reagents as copper sulfate on pumice and potassium permanganate, are the well-known reducing agents. The presence of these substances at the seat of reaction is responsible for definite tests of the formation of formaldehyde as is indicated by the results of experiments Nos. 3 and 5 (table 1) and Nos. 9, 10, and 11 (table 2). Great care is, therefore, essential to remove the above "impurities" when marble with hydrochloric acid is used as a source of carbon dioxide. It is quite clear from experiments No. 4 and 12 that, by using magnesium powder as a reducing agent, there is a distinct formation of formaldehyde so as to give off its odor even after an exposure of about eight hours to sunlight, while in the dark under the same conditions no formaldehyde is formed. Even Fenton (1) could not get the results so clearly in an ordinary "dark reaction" when a stream of carbon dioxide was passed to saturation for about eighteen to twenty-four hours through pure water in contact with several rods of amalgamated magnesium. He obtained slight indication of formaldehyde formation. It seems that the nascent state of both carbon dioxide and hydrogen is responsible for distinct formation of formaldehyde in the results mentioned above.

Further work has been undertaken to study the effect of different and increased periods of exposure to light by using the above apparatus and purest carbon dioxide.

SUMMARY

1. The experiments carried out reveal that the photoreduction of carbon dioxide to formaldehyde is facilitated by the presence of hydrogen in a nascent state, the nascent state of carbon dioxide being another condition.

2. An apparatus has been suggested wherein both carbon dioxide and hydrogen can be exposed to light at the time of their liberation by avoiding the use of corks, rubber tubing, exit tap-way arrangements, etc., and with the exclusion of organic matter, dust, etc.

3. Impurities which are much discussed in the literature might be hydrogen sulfide and sulfur dioxide in small quantities.

The author gratefully acknowledges the help of his senior colleague, Prof. Chandorkar, with whose skill in glass blowing it was possible to prepare the apparatus.

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THEOREMS CONCERNING THE ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENTS OF STRONG AND WEAK ELECTROLYTES

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Received May 22, 1934

I. INTRODUCTION

From a strictly thermodynamic point of view we may study the properties of solutions of electrolytes by considering the solute as undissociated, completely dissociated, or incompletely dissociated. We thus have three corresponding "descriptions" of the same solution and three sets of activity coefficients. Thermodynamics imposes definite mathematical relations between these various sets. The straightforward derivation of these relations is the purpose of the present paper. We shall make use of the thermodynamic method of Gibbs, as expounded for instance in Guggenheim's (2) recent book or in De Donder's "Affinity" (1). A comparison will be made with the method of Lewis and Randall (4). The results thus obtained are general. They lead to simple formulas for the particular cases of extremely low concentrations and of very weak electrolytes.

II. LIST OF SYMBOLS AND FUNDAMENTAL RELATIONS

T = absolute temperature; P = exterior pressure

Description No. 1: the solute is assumed to be undissociated.

$\left.\begin{array}{l}\mu_1^{(1)} = \text{chemical potential}\\ N_1^{(1)} = \text{mole fraction}\\ f_1^{(1)} = \text{activity coefficient}\\ g_1^{(1)} = \text{osmotic coefficient}\end{array}\right\}$ of the solvent.

$\left.\begin{array}{l}\mu_2^{(1)} = \text{chemical potential}\\ N_2^{(1)} = \text{mole fraction}\\ f_2^{(1)} = \text{activity coefficient}\end{array}\right\}$ of the solute.

m = molality of the solution

M = number of moles corresponding to 1000 g. of solvent (for water M = 55.51).

Between these various quantities the following relations hold:

$$\mu_1^{(1)} = \mu_1^{(1)0}(T, P) + RT \ln N_1^{(1)} f_1^{(1)} \tag{1.1}$$

$$\mu_1^{(1)} = \mu_1^{(1)0}(T, P) + g_1^{(1)} RT \ln N_1^{(1)} \tag{1.2}$$

$$\mu_2^{(1)} = \mu_2^{(1)0}(T, P) + RT \ln N_2^{(1)} f_2^{(1)} \tag{1.3}$$

The μ^0's are for a given solvent functions of temperature and pressure only. We also have:

$$N_1^{(1)} = \frac{M}{m + M} \tag{1.4}$$

$$N_2^{(1)} = \frac{m}{m + M} \tag{1.5}$$

Description No. 2: the solute is regarded as completely dissociated, each molecule breaking up into ν_+ positive ions and ν_- negative ions, the sum $\nu_+ + \nu_-$ being represented by ν.

$$\left.\begin{array}{ll} \mu_1^{(2)} & = \text{chemical potential} \\ N_1^{(2)} & = \text{mole fraction} \\ f_1^{(2)} & = \text{activity coefficient} \\ g_1^{(2)} & = \text{osmotic coefficient} \end{array}\right\} \text{of the solvent.}$$

$$\left.\begin{array}{ll} \mu_+^{(2)}, \mu_-^{(2)} & = \text{chemical potentials} \\ N_+^{(2)}, N_-^{(2)} & = \text{mole fractions} \\ f_+^{(2)}, f_-^{(2)} & = \text{activity coefficients} \end{array}\right\} \text{of the positive and negative ions.}$$

We have:

$$\mu_1^{(2)} = \mu_1^{(2)0}(T, P) + RT \ln N_1^{(2)} f_1^{(2)} \tag{2.1}$$

$$\mu_1^{(2)} = \mu_1^{(2)0}(T, P) + g_1^{(2)} RT \ln N_1^{(2)} \tag{2.2}$$

$$\mu_+^{(2)} = \mu_+^{(2)0}(T, P) + RT \ln N_+^{(2)} f_+^{(2)} \tag{2.3}$$

$$\mu_-^{(2)} = \mu_-^{(2)0}(T, P) + RT \ln N_-^{(2)} f_-^{(2)} \tag{2.4}$$

$$N_1^{(2)} = \frac{M}{\nu m + M} \tag{2.5}$$

$$N_+^{(2)} = \frac{\nu_+ m}{\nu m + M} \tag{2.6}$$

$$N_-^{(2)} = \frac{\nu_- m}{\nu m + M} \tag{2.7}$$

Description No. 3: the solute is regarded as incompletely dissociated into single ions, the molality of the undissociated solute being $(1 - \alpha)m$,

that of the positive ion $\alpha\nu_+m$, and that of the negative ion $\alpha\nu_-m$. A more detailed treatment could take into account the possible presence of intermediate and complex ions.

$\mu_1^{(3)}$	= chemical potential	of the solvent.
$N_1^{(3)}$	= mole fraction	
$f_1^{(3)}$	= activity coefficient	
$g_1^{(3)}$	= osmotic coefficient	
$\mu_+^{(3)}, \mu_-^{(3)}$	= chemical potentials	of the positive and negative ions.
$N_+^{(3)}, N_-^{(3)}$	= mole fractions	
$f_+^{(3)}, f_-^{(3)}$	= activity coefficients	
$\mu_u^{(3)}$	= chemical potential	of the undissociated solute.
$N_u^{(3)}$	= mole fraction	
$f_u^{(3)}$	= activity coefficient	

We have:

$$\mu_1^{(3)} = \mu_1^{(3)0}(T, P) + RT \ln N_1^{(3)} f_1^{(3)} \tag{3.1}$$

$$\mu_1^{(3)} = \mu_1^{(3)0}(T, P) + g_1^{(3)} RT \ln N_1^{(3)} \tag{3.2}$$

$$\mu_+^{(3)} = \mu_+^{(3)0}(T, P) + RT \ln N_+^{(3)} f_+^{(3)} \tag{3.3}$$

$$\mu_-^{(3)} = \mu_-^{(3)0}(T, P) + RT \ln N_-^{(3)} f_-^{(3)} \tag{3.4}$$

$$\mu_u^{(3)} = \mu_u^{(3)0}(T, P) + RT \ln N_u^{(3)} f_u^{(3)} \tag{3.5}$$

$$N_1^{(3)} = \frac{M}{[1 + (\nu - 1)\alpha]m + M} \tag{3.6}$$

$$N_+^{(3)} = \frac{\alpha\nu_+ m}{[1 + (\nu - 1)\alpha]m + M} \tag{3.7}$$

$$N_-^{(3)} = \frac{\alpha\nu_- m}{[1 + (\nu - 1)\alpha]m + M} \tag{3.8}$$

$$N_u^{(3)} = \frac{(1 - \alpha)m}{[1 + (\nu - 1)\alpha]m + M} \tag{3.9}$$

Since the μ^0's are independent of composition, it is evident that they are related as follows:

$$\mu_1^{(1)0} = \mu_1^{(2)0} = \mu_1^{(3)0} \tag{4.1}$$

$$\mu_+^{(2)0} = \mu_+^{(3)0} \tag{4.2}$$

$$\mu_-^{(2)0} = \mu_-^{(3)0} \tag{4.3}$$

$$\mu_2^{(1)0} = \mu_u^{(3)0} \tag{4.4}$$

III. FREE ENERGY OF THE SOLUTION IN THE THREE "DESCRIPTIONS"

Let us apply the well-known relation between the free energy, F, the chemical potentials, μ_i, and the numbers of moles, n_i, of the various constituents:

$$F = \sum_i \mu_i n_i \tag{5}$$

The free energy of an amount of solution consisting of 1000 g. of solvent and m moles of electrolyte is given in description No. 1 by

$$F = M\mu_1^{(1)} + m\mu_2^{(1)} \tag{6.1}$$

in description No. 2 by

$$F = M\mu_1^{(2)} + m(\nu_+\mu_+^{(2)} + \nu_-\mu_-^{(2)}) \tag{6.2}$$

in description No. 3 by

$$F = M\mu_1^{(3)} + m[\alpha(\nu_+\mu_+^{(3)} + \nu_-\mu_-^{(3)}) + (1-\alpha)\mu_u^{(3)}] \tag{6.3}$$

These three expressions of F for the same solution should of course be identical. Moreover, the contribution of the solvent is the same in the three cases, as well as that of the solute. Equations 6.1, 6.2, and 6.3 give then:

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} \tag{7.1}$$

and

$$\mu_2^{(1)} = \nu_+\mu_+^{(2)} + \nu_-\mu_-^{(2)} = \alpha(\nu_+\mu_+^{(3)} + \nu_-\mu_-^{(3)}) + (1-\alpha)\mu_u^{(3)} \tag{7.2}$$

IV. ACTIVITY AND OSMOTIC COEFFICIENTS OF THE SOLVENT

A. Relations between the three activity coefficients of the solvent

From equations 7.1, 4.1, 1.1, 2.1, and 3.1 we deduce

$$N_1^{(1)}f_1^{(1)} = N_1^{(2)}f_1^{(2)} = N_1^{(3)}f_1^{(3)} \tag{8}$$

and, thanks to equations 1.4, 2.4, and 3.6,

$$\frac{f_1^{(1)}}{m+M} = \frac{f_1^{(2)}}{\nu m+M} = \frac{f_1^{(3)}}{[1+(\nu-1)\alpha]m+M} \tag{9}$$

B. Relations between the three osmotic coefficients of the solvent

Thanks to equations 1.2, 2.2, and 3.2, equation 8 also gives:

$$g_1^{(1)} \ln N_1^{(1)} = g_1^{(2)} \ln N_1^{(2)} = g_1^{(3)} \ln N_1^{(3)} \tag{10.1}$$

$$g_1^{(1)} \ln\left(1+\frac{m}{M}\right) = g_1^{(2)} \ln\left(1+\frac{\nu m}{M}\right) = g_1^{(3)} \ln\left[1+\frac{\{1+(\nu-1)\alpha\}m}{M}\right] \tag{10.2}$$

C. Special case of extremely dilute solutions

m, νm, $[1 + (\nu - 1)\alpha]m$ are then negligible compared to M. Equations 9 and 10.2 become

$$f_1^{(1)} = f_1^{(2)} = f_1^{(3)} \tag{11}$$

$$g_1^{(1)} = \nu g_1^{(2)} = [1 + (\nu - 1)\alpha] g_1^{(3)} \tag{12}$$

V. RELATIONS BETWEEN THE SETS OF ACTIVITY COEFFICIENTS OF THE SOLUTE

A. General relations

In description No. 3 the ions are regarded as being in equilibrium with the undissociated part of the solute. We thus have the equilibrium condition:

$$\mu_u^{(3)} = \nu_+ \mu_+^{(3)} + \nu_- \mu_-^{(3)} \tag{13}$$

Equation 7.2 can then be written:

$$\mu_2^{(1)} = \nu_+ \mu_+^{(2)} + \nu_- \mu_-^{(2)} = \nu_+ \mu_+^{(3)} + \nu_- \mu_-^{(3)} = \mu_u^{(3)} \tag{14}$$

From this relation and from equations 1.3, 2.3, 2.4, 3.3, 3.4, and 3.5, modified on account of equations 4.1, 4.2, 4.3, and 4.4, we deduce:

$$\begin{aligned} &\ln [N_2^{(1)} f_2^{(1)}] + \frac{\mu_2^{(1)0} - \nu_+ \mu_+^{(2)0} - \nu_- \mu_-^{(2)0}}{RT} \\ &= \ln [(N_+^{(2)})^{\nu_+} (N_-^{(2)})^{\nu_-} (f_+^{(2)})^{\nu_+} (f_-^{(2)})^{\nu_-}] = \ln [(N_+^{(3)})^{\nu_+} (N_-^{(3)})^{\nu_-} (f_+^{(3)})^{\nu_+} (f_-^{(3)})^{\nu_-}] \\ &= \ln [N_u^{(3)} f_u^{(3)}] + \frac{\mu_2^{(1)0} - \nu_+ \mu_+^{(2)0} - \nu_- \mu_-^{(2)0}}{RT} \end{aligned} \tag{15}$$

Introducing the equilibrium constant K (T, P) defined by

$$\ln [K(T, P)] = \frac{\mu_u^{(3)0} - \nu_+ \mu_+^{(3)0} - \nu_- \mu_-^{(3)0}}{RT} = \frac{\mu_2^{(1)0} - \nu_+ \mu_+^{(2)0} - \nu_- \mu_-^{(2)0}}{RT} \tag{16}$$

equation 15 becomes

$$\begin{aligned} KN_2^{(1)} f_2^{(1)} &= (N_2^{(2)})^{\nu_+} (N_-^{(2)})^{\nu_-} (f_+^{(2)})^{\nu_+} (f_-^{(2)})^{\nu_-} \\ &= (N_+^{(3)})^{\nu_+} (N_-^{(3)})^{\nu_-} (f_+^{(3)})^{\nu_+} (f_-^{(3)})^{\nu_-} = KN_u^{(3)} f_u^{(3)} \end{aligned} \tag{17}$$

It has been pointed out by Guggenheim (3) that ionic activity coefficients are thermodynamically undetermined. Thermodynamically determined are only combinations of ionic activity coefficients of the form

$$\prod_i f_i^{\lambda_i} \tag{18.1}$$

in which the quantities λ_i are related to the algebraic valences z_i of the ions by the relation:

$$\sum_i \lambda_i z_i = 0 \tag{18.2}$$

In the case of a single electrolyte an expression of the form of equation 18.1 is the mean activity coefficient of the ions $f_\pm$ defined by

$$(f_\pm)^\nu = (f_+)^{\nu_+}(f_-)^{\nu_-} \tag{19}$$

It has thermodynamic significance because

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{20}$$

It is also convenient to define mean mole fractions $N_\pm$

$$(N_\pm)^\nu = (N_+)^{\nu_+}(N_-)^{\nu_-} \tag{21}$$

and mean molalities

$$(m_\pm)^\nu = (m_+)^{\nu_+}(m_-)^{\nu_-} = \nu_+^{\nu_+}\nu_-^{\nu_-}\cdot m^\nu \tag{22}$$

These mean quantities (19, 21, and 22) may be used both in description 2 and in description 3.

Equation 17 then becomes

$$KN_2^{(1)}f_2^{(1)} = [N_\pm^{(2)}f_\pm^{(2)}]^\nu = [N_\pm^{(3)}f_\pm^{(3)}]^\nu = KN_u^{(3)}f_u^{(3)} \tag{23}$$

or, thanks to equations 1.5, 1.6, 2.6, 2.7, 3.7, 3.8, and 3.9 ,

$$K\frac{m}{m+M}f_2^{(1)} = \left[\frac{m_\pm^{(2)}f_\pm^{(2)}}{\nu m+M}\right]^\nu = \left[\frac{m_\pm^{(3)}f_\pm^{(3)}}{\{1+(\nu-1)\alpha\}m+M}\right]^\nu$$

$$= K\frac{m_u^{(3)}}{[1+(\nu-1)\alpha]m+M}\cdot f_u^{(3)} \tag{24}$$

Equation 23 could be decomposed into the two symmetrical relations:

$$N_2^{(1)}f_2^{(1)} = N_u^{(3)}f_u^{(3)} \tag{25.1}$$

$$N_\pm^{(2)}f_\pm^{(2)} = N_\pm^{(3)}f_\pm^{(3)} \tag{25.2}$$

The corresponding relations deduced from equation 24 are less symmetrical:

$$\frac{mf_2^{(1)}}{m+M} = \frac{m_u^{(3)}f_u^{(3)}}{[1+(\nu-1)\alpha]m+M} \tag{26.1}$$

$$\frac{m_\pm^{(2)}f_\pm^{(2)}}{\nu m+M} = \frac{m_\pm^{(3)}f_\pm^{(3)}}{[1+(\nu-1)\alpha]m+M} \tag{26.2}$$

We have

$$m_u^{(3)} = (1-\alpha)m \tag{27.1}$$

$$m_\pm^{(3)} = \alpha m_\pm^{(2)} \tag{27.2}$$

Equations 26.1 and 26.2 become:

$$\frac{f_2^{(1)}}{m+M} = \frac{(1-\alpha)f_u^{(3)}}{[1+(\nu-1)\alpha]m+M} \tag{28.1}$$

$$\frac{f_\pm^{(2)}}{\nu m+M} = \frac{\alpha f_\pm^{(3)}}{[1+(\nu-1)\alpha]m+M} \tag{28.2}$$

B. Special case of extremely dilute solutions

When m, νm, $[1+(\nu-1)\alpha]m$ are negligible compared to M, equations 12, 23.1, and 23.2 become:

$$K\frac{m}{M}f_2^{(1)} = \left[\frac{m_\pm^{(2)}f_\pm^{(2)}}{M}\right]^\nu = \left[\frac{m_\pm^{(3)}f_\pm^{(3)}}{M}\right]^\nu = K\frac{m_u}{M}f_u^{(3)} \tag{29}$$

$$f_2^{(1)} = (1-\alpha)f_u^{(3)} \tag{30.1}$$

$$f_\pm^{(2)} = \alpha f_\pm^{(3)} \tag{30.2}$$

These equations are approximate but general, since they do not involve non-thermodynamic assumptions.

VI. THE LIMITING VALUES OF THE ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENTS AT INFINITE DILUTION

The coefficients

$$f_1^{(1)},\quad f_1^{(2)},\quad f_1^{(3)}$$
$$g_1^{(1)},\quad g_1^{(2)},\quad g_1^{(3)}$$
$$f_2^{(1)},\quad f_\pm^{(2)},\quad f_\pm^{(3)},\quad f_u^{(3)}$$

are all thermodynamically indeterminate when m tends towards 0. It is necessary, in order to determine them all, to make non-thermodynamic assumptions regarding: (a) the limiting values for $m = 0$ in one of the descriptions, and (b) the behavior of the function $\alpha = \alpha(m)$ as m approaches 0. We shall assume that the solution becomes ideal in description No. 2 when m tends towards 0. We thus have:

$$[\lim f_1^{(2)}]_{m=0} = 1 \tag{31.1}$$

$$[\lim g_1^{(2)}]_{m=0} = 1 \tag{31.2}$$

$$[\lim f_\pm^{(2)}]_{m=0} = 1 \tag{31.3}$$

Moreover we shall assume that

$$[\lim \alpha]_{m=0} = 1 \tag{31.4}$$

regardless of the actual form of the function $\alpha = \alpha(m)$. We then deduce from equation 11 (the formulas obtained above for small molalities become more and more accurate as m tends towards 0):

$$\lim f_1^{(1)} = \lim f_1^{(2)} = \lim f_1^{(3)} = 1 \tag{32}$$

From equation 12

$$\lim g_1^{(1)} = \nu \lim g_1^{(2)} = \nu \tag{33.1}$$

$$\lim g_1^{(3)} = \lim g_1^{(2)} = 1 \tag{33.2}$$

From equations 29 and 22:

$$\lim f_2^{(1)} = \frac{\nu_+^{\nu_+}\nu_-^{\nu_-}}{K} \lim \left(\frac{m}{M}\right)^{\nu-1} (f_\pm^{(2)})^\nu = 0 \tag{34.1}$$

or

$$\lim f_2^{(1)} = 0 \tag{34.2}$$

From equation 30.1:

$$\lim f_u^{(3)} = \lim \frac{f_2^{(1)}}{1-\alpha} \tag{35}$$

Since $\lim f_2^{(1)} = 0$ and $\lim (1 - \alpha) = 0$, $f_u^{(3)}$ is indeterminate. From equation 30.2

$$\lim f_\pm^{(3)} = \lim \frac{f_\pm^{(2)}}{\alpha} = 1 \tag{36}$$

VII. PARTICULAR CASE OF VERY WEAK ELECTROLYTES

Instead of making use of the assumptions 31.1, 31.2, and 31.3 of the foregoing section, it will be more convenient, in the case of very weak electrolytes, to assume that:

$$[\lim f_1^{(3)}]_{m=0} = 1 \tag{37.1}$$

$$[\lim g_1^{(3)}]_{m=0} = 1 \tag{37.2}$$

$$[\lim f_\pm^{(3)}]_{m=0} = 1 \tag{37.3}$$

$$[\lim f_u^{(3)}]_{m=0} = 1 \tag{37.4}$$

$$[\lim \alpha]_{m=0} = 1 \tag{37.5}$$

If the electrolyte is so weak that $f_u^{(3)}$ and $f_\pm^{(3)}$ approach unity much more rapidly than α, equations 30.1 and 30.2 become:

$$f_2^{(1)} = 1 - \alpha \tag{38.1}$$

$$f_\pm^{(2)} = \alpha \tag{38.2}$$

These relations, approximately valid for small molalities, are thus partly non-thermodynamic.

For electrolytes obeying exactly Ostwald's dilution law:

$$\frac{\alpha^{\nu} m^{\nu-1}}{1-\alpha} = K \tag{39}$$

we may replace our assumptions (37) by:

$$f_1^{(3)} = 1 \tag{40.1}$$

$$g_1^{(3)} = 1 \tag{40.2}$$

$$(f_{\pm}^{(3)})^{\nu} = f_u^{(3)} \tag{40.3}$$

relations holding in the same range of extreme dilutions as the dilution law (39).

Equation 38.2 is a justification for referring, as is often done, to $f_{\pm}^{(2)}$ as to a "thermodynamic degree of dissociation." The considerations developed in the present paper should clearly indicate the limitations of this concept (5).

VIII. COMPARISON WITH THE METHOD OF LEWIS AND RANDALL

The activity a_2 and the activity coefficient γ_2 of a solute species are defined by Lewis and Randall (reference 4, p. 255) as follows:

$$F - F^0 = RT \ln a_2 = RT \ln (m\gamma_2) \tag{41}$$

F and F^0 are molal free energies. The superscript 0 refers to a "standard state." For given temperature and pressure F^0 is independent of composition. It is moreover assumed that

$$(\lim \gamma_2)_{m=0} = 1 \tag{42}$$

In the notation of the present paper equation 41 would read:

$$\mu_2^{(1)} = \mu_2^{(1)0\prime}(T, P) + RT \ln (m\gamma_2^{(1)}) \tag{43}$$

From equations 1.3 and 1.5 we deduce:

$$\mu_2^{(1)} = \mu_2^{(1)0} + RT \ln\left[\frac{mf_2^{(1)}}{m+M}\right] = \mu_2^{(1)0} - RT \ln M + RT \ln\left[\frac{mf_2^{(1)}}{1+\frac{m}{M}}\right] \tag{44}$$

Comparing equations 43 and 44 we get:

$$\mu_2^{(1)0\prime} = \mu_2^{(1)0} - RT \ln M \tag{45}$$

and

$$\gamma_2^{(1)} = \frac{f_2^{(1)}}{1+\frac{m}{M}} \tag{46}$$

or, in terms of the mole fraction $N_1^{(1)}$ of the solvent,

$$\gamma_2^{(1)} = f_2^{(1)} \cdot N_1^{(1)} \tag{47}$$

The activity coefficients γ of Lewis and Randall coincide with the "rational" activity coefficients f only at very low concentrations. From equation 47 we see that, even for ideal solutions, γ_2 will be appreciably different from unity at high concentrations. In the same way we have in description No. 2:

$$\gamma_\pm^{(2)} = \frac{f_\pm^{(2)}}{1 + \frac{\nu m}{M}} \tag{48}$$

and in description No. 3:

$$\gamma_\pm^{(3)} = \frac{f_\pm^{(3)}}{1 + [1 + (\nu - 1)\alpha] \frac{m}{M}} \tag{49.1}$$

$$\gamma_u^{(3)} = \frac{f_u^{(3)}}{1 + [1 + (\nu - 1)\alpha] \frac{m}{M}} \tag{49.2}$$

Replacing the various f's by the various γ's in equation 24 we obtain, thanks to equations 46, 48, 49.1, and 49.2,

$$K \frac{m}{M} \gamma_2^{(1)} = \left[\frac{m_\pm^{(2)} \gamma_\pm^{(2)}}{M}\right]^\nu = \left[\frac{m_\pm^{(3)} \gamma_\pm^{(3)}}{M}\right]^\nu = K \frac{m_u^{(3)}}{M} \gamma_u^{(3)} \tag{50}$$

a remarkably symmetrical relation.

In terms of activities we then have

$$K \frac{a_2^{(1)}}{M} = \frac{(a_+^{(2)})^{\nu_+} (a_-^{(2)})^{\nu_-}}{M^\nu} \tag{51}$$

or

$$\frac{(a_+^{(2)})^{\nu_+} (a_-^{(2)})^{\nu_-}}{a_2^{(1)}} = KM^{\nu-1} = K' \tag{52}$$

As shown before (equation 16), K is the true "dissociation constant" of the electrolyte. It is hence not allowed by thermodynamics to assume arbitrarily, as do Lewis and Randall at the starting point of their treatment of strong electrolytes (reference 4, p. 326), that

$$\frac{(a_+^{(2)})^{\nu_+} (a_-^{(2)})^{\nu_-}}{a_2^{(1)}} = 1 \tag{53}$$

Fortunately this relation is never used, the significant relations being:

$$(a_+^{(2)})^{\nu_+}(a_-^{(2)})^{\nu_-} = (a_\pm^{(2)})^{\nu} \tag{54}$$

and

$$(\gamma_+^{(2)})^{\nu_+}(\gamma_-^{(2)})^{\nu_-} = (\gamma_\pm^{(2)})^{\nu} \tag{55}$$

which are in no way expressions of the law of mass action. Equation 52 is the mathematical formulation of a "comparison" between descriptions 1 and 2.

As long as no use is made of the third description, assumption 53, although unnecessary, is perhaps permissible but, on the other hand, when all the descriptions are used (cf. Randall and Allen (5)) equations 24, 50, or 52 must be obeyed and one should not write separately:

$$\frac{(a_+^{(2)})^{\nu_+}(a_-^{(2)})^{\nu_-}}{a_2^{(1)}} = 1, \qquad \frac{(a_+^{(3)})^{\nu_+}(a_-^{(3)})^{\nu_-}}{a_u^{(3)}} = K \tag{56}$$

IX. RÉSUMÉ. LIST OF THEOREMS

A certain number of the results obtained in the present paper may be considered as theorems. They are:

A. General theorems valid for all types of electrolytes and all concentrations

1. The activity coefficients of the solvent corresponding to the three descriptions of the solution (no dissociation, complete dissociation, incomplete dissociation) obey the relation:

$$\frac{f_1^{(1)}}{m + M} = \frac{f_1^{(2)}}{\nu m + M} = \frac{f_1^{(3)}}{[1 + (\nu - 1)\alpha]\, m + M}$$

2. The osmotic coefficients obey the relation:

$$g_1^{(1)} \ln\left[1 + \frac{m}{M}\right] = g_1^{(2)} \ln\left[1 + \frac{\nu m}{M}\right] = g_1^{(3)} \ln\left[1 + \frac{[1 + (\nu - 1)\alpha]m}{M}\right]$$

3. The activity coefficient of the solute in the first description (no dissociation) and that of the undissociated solute in the third description (incomplete dissociation) are connected by the relation:

$$\frac{f_2^{(1)}}{m + M} = \frac{(1 - \alpha) f_u^{(3)}}{[1 + (\nu - 1)\alpha]\, m + M}$$

4. The average activity coefficients of the ions in the second and third descriptions are connected by the relation (see equations 19, 22, and 23):

$$\frac{f_\pm^{(2)}}{\nu m + M} = \alpha \frac{f_\pm^{(3)}}{[1 + (\nu - 1)\alpha]\, m + M}$$

B. Theorems valid for very low concentrations

Theorem 1:

$$f_1^{(1)} = f_1^{(2)} = f_1^{(3)}$$

Theorem 2:

$$g_1^{(1)} = \nu g_1^{(2)} = [1 + (\nu - 1)\alpha]\, g_1^{(3)}$$

Theorem 3:

$$f_2^{(1)} = (1 - \alpha)\, f_u^{(3)}$$

Theorem 4:

$$f_\pm^{(2)} = \alpha\, f_\pm^{(3)}$$

C. Theorems valid for very weak electrolytes at very low concentrations

When α is very small and $f_\pm^{(3)}$ is practically equal to unity, the solution being apparently ideal, theorems 3 and 4 of the foregoing series become:

$$f_2^{(1)} = 1 - \alpha \tag{1}$$

$$f_\pm^{(2)} = \alpha \tag{2}$$

X. SUMMARY

Three thermodynamic descriptions of solutions of electrolytes corresponding respectively to an undissociated, a completely dissociated, and an incompletely dissociated solute have been studied. Between the three sets of activity and osmotic coefficients certain thermodynamic relations are shown to hold. These are obtained in general form, and some interesting simple formulas are deduced for the particular case of very low concentrations and that of very weak electrolytes.

In concluding we wish to express our gratitude to Dr. J. W. McBain and Dr. F. O. Koenig, of this laboratory, for their valuable suggestions and comments.

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THE ACTIVITY AND OSMOTIC COEFFICIENTS OF AQUEOUS SOLUTIONS OF ACETIC ACID AT THE FREEZING POINT

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Received July 9, 1934

The purpose of the present investigation is to calculate from the freezing point data of Hausrath (2) and of Jones and Bury (3, 4) the activity and osmotic coefficients of aqueous solutions of acetic acid. As a typical illustration of the foregoing theory we shall determine these coefficients in the three thermodynamic descriptions corresponding respectively to an undissociated, a completely dissociated, and an incompletely dissociated solute. (Descriptions No. 1, 2 and 3.) The notation is the same as that of the previous paper (5).

For an electrolyte of the type of acetic acid ($\nu_+ = \nu_- = 1, \nu = 2$) it can easily be deduced from the theorems of the preceding paper (5) that:

$$[f_{\pm}^{(2)}]^2 = f_2^{(1)} \cdot K \cdot \frac{(2m + M)^2}{m(m + M)} \tag{1}$$

$$[f_{\pm}^{(3)}]^2 = f_2^{(1)} \cdot K \cdot \frac{[(1 + \alpha)m + M]^2}{\alpha^2 m(m + M)} \tag{2}$$

$$f_u^{(3)} = f_2^{(1)} \cdot \frac{(1 + \alpha)m + M}{(1 - \alpha)(m + M)} \tag{3}$$

We shall restrict ourselves to concentrations such that m, $2m$, $(1 + \alpha)m$ are small compared to M. Neglecting these quantities whenever they should be added to M amounts to using the Lewis-Randall coefficients γ. Therefore we shall write our formulas in terms of these γ's.

Remembering that

$$KM = K' \tag{4}$$

equations 1, 2, 3 become, in terms of the γ's,

$$[\gamma_{\pm}^{(2)}]^2 = \gamma_2^{(1)} \cdot \frac{K'}{m} \tag{5}$$

$$[\gamma_{\pm}^{(3)}]^2 = \gamma_2^{(1)} \cdot \frac{K'}{\alpha^2 m} \tag{6}$$

$$\gamma_u^{(3)} = \gamma_2^{(1)} \cdot \frac{1}{1 - \alpha} \tag{7}$$

From equations 5 and 6 we deduce:

$$\gamma_\pm^{(2)} = \alpha\gamma_\pm^{(3)} \tag{8}$$

Between the three osmotic coefficients we have the relation:

$$g_1^{(1)} = 2g_1^{(2)} = (1 + \alpha)\, g_1^{(3)} \tag{9}$$

Calling θ the freezing point lowering and λ the molar freezing point lowering (for water $\lambda = 1.858$), we have:

$$g_1^{(1)} = \frac{\theta}{\lambda m} \tag{10}$$

The divergence function j_1 of Lewis and Randall is given by:

$$j_1 = 1 - g_1^{(1)} = 1 - \frac{\theta}{\lambda m} \tag{11}$$

The activity coefficient $\gamma_2^{(1)}$ at a certain molality m and the activity coefficient $\gamma_{2,0}^{(1)}$ at another molality m_0 are connected by the relation:

$$\ln \frac{\gamma_2^{(1)}}{\gamma_{2,0}^{(1)}} = j_{1,0} - j_1 - \int_{m_0}^{m} j_1 \cdot d \ln m \tag{12}$$

On figure 1 the values of $-j_1$, deduced from the experimental results of Hausrath (2) and of Jones and Bury (3), are plotted against $\log_{10} m$. It will be seen that within the limits of experimental error the variation of $-j_1$ in terms of $\log_{10} m$ is linear. We found that it can be represented by the equation:

$$j_1 = 0.0371 \log_{10} m + 0.01484 \tag{13}$$

Equation 12 thus becomes:

$$\log_{10} \frac{\gamma_2^{(1)}}{\gamma_{2,0}^{(1)}} = \frac{j_{1,0} - j_1}{2.303} - 0.01855\, [(\log_{10} m)^2 - (\log_{10} m_0)^2] - 0.01484\, [\log_{10} m - \log_{10} m_0] \tag{14}$$

Equations 5, 6, 7, and 14 form a system of four equations with six unknowns: $\gamma_2^{(1)}$, $\gamma_{2,0}^{(1)}$, $\gamma_\pm^{(2)}$, $\gamma_\pm^{(3)}$, $\gamma_u^{(3)}$, and α.

In order to determine all these quantities we shall assume that the Debye-Hückel theory applies to the dissociated part of the solute, and we shall determine $\gamma_{2,0}^{(1)}$ at a certain low concentration from a knowledge of the true dissociation constant of acetic acid. From the value of $\gamma_{2,0}^{(1)}$ we

shall then calculate $\gamma_2^{(1)}$ by means of equation 14 at concentrations for which j_1 is known. This procedure will thus enable us to avoid the graphic extrapolation of the j_1 curve to infinite dilution, which is particularly uncertain in this case.

By means of careful measurements of the E. M. F. of cells without liquid junction of the type

$$H_2 \mid HAc(m_1),\ NaAc(m_2),\ NaCl(m_3),\ AgCl \mid Ag$$

Harned and Ehlers (1) were able to determine the true dissociation constant of acetic acid at various temperatures. At 0°C. they found:

$$K' = \frac{\alpha^2 m}{1 - \alpha} \cdot \frac{[\gamma_{\pm}^{(3)}]^2}{\gamma_u^{(3)}} = 1.653 \times 10^{-5} \tag{15}$$

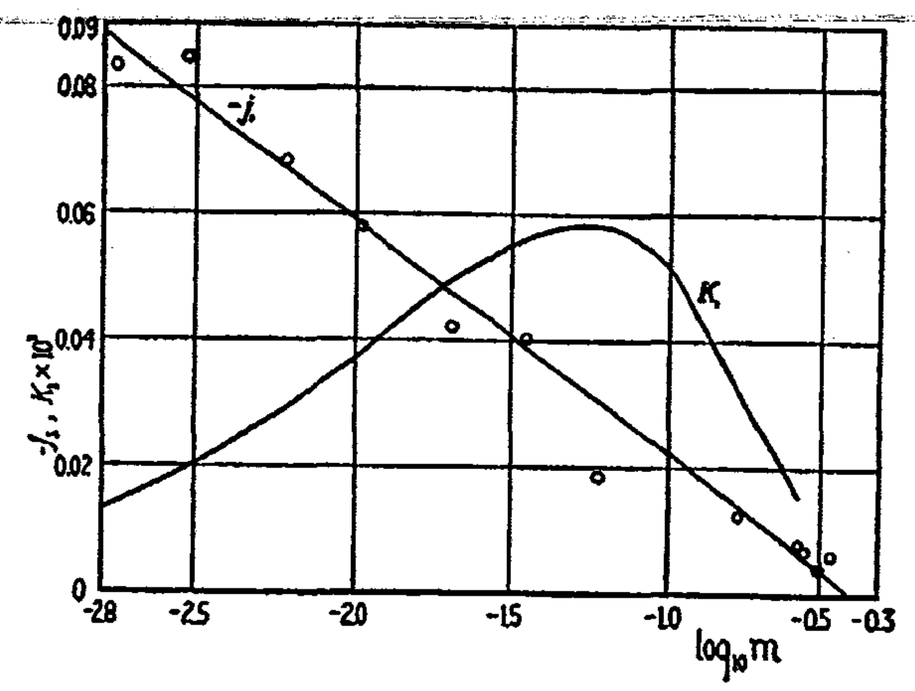

FIG. 1. j_1 AND $K_1 = \dfrac{j_1^2 m}{1 + j}$ FOR AQUEOUS SOLUTIONS OF ACETIC ACID

Freezing point measurements of Hausrath and of Jones and Bury

As shown by equation 9, $g_1^{(1)}$ and $1 + \alpha$ are practically identical at very low concentrations, since $g_1^{(3)}$ should then be very nearly equal to unity. We thus have approximately, at low concentrations,

$$-j_1 = \alpha \tag{16}$$

On figure 1 are plotted against $\log_{10} m$ the values of

$$K_1 = \frac{j_1^2\, m}{1 + j_1} \tag{17}$$

It will be seen that K_1 is by no means constant. At the concentration $m = 0.002138$ however, K_1 is exactly equal to K', i.e., 1.653×10^{-5}.

From equations 15, 16, and 17 we then deduce that at this particular concentration m_0 the following relation holds:

$$[\gamma_{\pm,0}^{(3)}]^2 = \gamma_{u,0}^{(3)} \tag{18}$$

For this concentration m_0 we have:

$$\alpha_0 = -j_{1,0} = 0.0843$$

The ionic strength $\alpha_0 m_0$ being very small we may assume, with a very high degree of approximation, that the mean activity coefficient of the ions obeys the Debye-Hückel limiting law, which in this case becomes:

$$\log_{10} \gamma_{\pm}^{(3)} = -0.5 \sqrt{\alpha m} \tag{19}$$

TABLE 1

Activity and osmotic coefficients of aqueous solutions of acetic acid at 0°C.

m	$-j_1$	$g_1^{(1)}$	$g_1^{(2)}$	$g_1^{(3)}$	$\gamma_2^{(1)}$	$\gamma_{\pm}^{(2)}$	$\gamma_{\pm}^{(3)}$	$\gamma_{\mu}^{(3)}$	α
0.002138	0.0843	1.0843	0.5421	1.000	0.888	0.083	0.985	0.970	0.084
0.005	0.0705	1.0705	0.5352	1.008	1.122	0.061	0.980	1.199	0.062
0.01	0.0595	1.0595	0.5297	1.014	1.161	0.044	0.975	1.219	0.045
0.02	0.0485	1.0485	0.5242	1.016	1.192	0.031	0.971	1.232	0.032
0.05	0.0337	1.0337	0.5168	1.012	1.219	0.020	0.963	1.245	0.021
0.1	0.0225	1.0225	0.5112	1.007	1.229	0.014	0.956	1.248	0.015
0.2	0.0114	1.0114	0.5057	1.000	1.230	0.010	0.948	1.246	0.011
0.5	−0.0034	0.9966	0.4983	0.990	1.139	0.006	0.934	1.145	0.007

At the concentration m_0

$$\gamma_{\pm,0}^{(3)} = 0.9847$$

and, thanks to equation 18,

$$\gamma_{u,0}^{(3)} = 0.9696$$

The thermodynamic relation 7 gives then:

$$\gamma_{2,0}^{(1)} = (1 - \alpha)\, \gamma_{u,0}^{(3)} = 0.8879$$

and equation 14 becomes:

$$\log_{10} \gamma_2^{(1)} = 0.08362 - \frac{j_1}{2.303} - 0.01855\, (\log_{10} m)^2 - 0.01484 \log_{10} m \tag{20}$$

The values of j_1 corresponding to a certain number of round concentrations between m_0 and 0.5 are obtained from figure 1, and the corresponding coefficients $\gamma_2^{(1)}$ are then calculated by means of equation 20. From $\gamma_2^{(1)}$ we calculate $\gamma_{\pm}^{(2)}$ by means of equation 5. Knowing $\gamma_2^{(1)}$ we deduce α and $\gamma_{\pm}^{(3)}$ from the two simultaneous equations 8 and 19, which when combined give,

$$\frac{\gamma_{\pm}^{(2)}}{\alpha} = e^{-1.15 \sqrt{\alpha m}} \tag{21}$$

or, at very low values of $\sqrt{\alpha m}$,

$$\frac{\gamma_{\pm}^{(2)}}{\alpha} = 1 - 1.15\sqrt{\alpha m} \tag{22}$$

$\gamma_{\pm}^{(2)}$ and m being known, we deduce from equation 22 a first and apparently sufficient approximation for α. $\gamma_{\pm}^{(3)}$ is then calculated by means of equation 19. $\gamma_2^{(1)}$ and α being known, $\gamma_u^{(3)}$ is calculated by means of equation 7. $g_1^{(1)}$ is known, $g_1^{(2)}$ and $g_1^{(3)}$ are calculated by means of equation 9.

All the numerical results are given in table 1. Those which are directly derived from the measurements ($-j_1$, $g_1^{(1)}$, $g^{(2)}$) are given to four decimal points. The others are given to only three decimal points.

As was to be expected, $\gamma_{\pm}^{(2)}$ is slightly smaller than α.

At infinite dilution we have:

$$\lim \gamma_{\pm}^{(3)} = 1 \tag{23}$$

From the theorems of our previous paper we then deduce:

$$\lim \gamma_{\pm}^{(2)} = 1 \tag{24}$$

We may assume that

$$\lim \gamma_u^{(3)} = 1 \tag{25}$$

We have shown that equation 24 leads to

$$\lim \gamma_2^{(1)} = 0 \tag{26}$$

An examination of table 1 will show that, somewhere at extremely low concentrations, $\gamma_{\pm}^{(2)}$ will increase rapidly so as to reach the value 1 at $m = 0$ and $\gamma_2^{(1)}$ will decrease to the value 0 at $m = 0$.

SUMMARY

The various activity and osmotic coefficients corresponding to the three thermodynamic descriptions (undissociated, completely dissociated, incompletely dissociated solute) for aqueous solutions of acetic acid are deduced from the best available freezing point data.

The value 1.653×10^{-5} of the dissociation constant at 0°C., determined by Harned and Ehlers, is used. The activity coefficients are obtained without the usual graphic extrapolation to infinite dilution, thanks to the combined use of the dissociation constant, of the Debye-Hückel limiting law, and of an empirical relation giving the dependence of the Lewis-Randall deviation function on molality.

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CATALYTIC DECOMPOSITION OF ACETALDEHYDE[1]

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Received May 29, 1934

I. INTRODUCTION

Acetaldehyde is a compound of very considerable activity. In gaseous form, under different conditions, it will undergo a number of different reactions of which the predominant one is the simple decomposition,

$$CH_3CHO \rightarrow CO + CH_4$$

A study of the equilibrium that results, with the possible reversal of the reaction to synthesize acetaldehyde from carbon monoxide and methane, is of interest from both theoretical and practical standpoints.

Thermodynamical calculations for this reaction have been made. Those based on generally accepted values (e.g., Parks and Huffman (5)) of free energies for the compounds involved indicate an equilibrium very unfavorable to synthesis. There is some uncertainty involved in such calculations, but to indicate a measurable partial pressure of acetaldehyde under the experimental conditions, the error in such free energy calculations would have to be at least 15,000 cals. It is true, however, that small amounts of acetaldehyde have been produced in the electric spark (3) and by the use of silent electric discharge (4). This paper gives the results of research on catalysts for this reaction.

II. CATALYSTS

Obviously the decomposition reaction is in this case most convenient for study of the catalysts; a dynamic method was first used. In order to test a material for catalytic activity some of it was placed in glass in a furnace, and activated by a stream of hydrogen. Then several grams of acetaldehyde were passed over the activated material by use of nitrogen as the inert carrier gas. Liquid products were removed by strong cooling, and were weighed and examined; fixed gases remaining were measured and then analyzed by the usual methods of absorption and combustion. Tem-

[1] From the thesis submitted to the Graduate School of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1932.

[2] Bill Raskob Foundation Fellow, 1929-33.

perature, rate of flow of gases, volume changes, and presence of color, odor, and high-boiling fractions in the recovered liquids were also noted on each of the sixty-six runs.

Metals for the catalysts were precipitated in the form of hydroxides, either pure or with supporting materials admixed. After being washed and dried, they were reduced in a stream of hydrogen at 300°C. for copper, 400°C. for nickel, and 500°C. for iron and cobalt, and cooled in an atmosphere of purified nitrogen.

Results indicate that copper is not a catalyst for this reaction. Other investigators (2) found that copper, on the contrary, favors condensation to form paraldehyde, metaldehyde, and crotonaldehyde. Iron shows very little activity, even at 300°C. Cobalt is more active than iron, but less so than nickel, which shows marked activity even below 200°C. Cobalt catalysts produce a relatively high hydrogen content in gaseous products, and are also sensitive to a slow poisoning effect, which Russel and Marschner (6) attribute to formation of crotonaldehyde.

Supported catalysts resemble the corresponding pure metals, but siliceous supporting materials also favor extensive side reactions, producing high-boiling liquids and a very low $CO:CH_4$ ratio. Catalysts made from amalgams were less active than the corresponding reduced metal, probably because of remaining traces of mercury, exceedingly difficult to remove.

A dark green, gel-like precipitate, formed by action of excess sodium hydroxide on an 8 per cent nickel nitrate solution was, after reduction, the material showing greatest activity and most freedom from side reactions. This catalyst was used in all subsequent equilibrium studies.

III. EQUILIBRIUM STUDIES

Preliminary studies indicated that in a steel bomb the decomposition of acetaldehyde was quite slow, the reaction continuing for at least one hundred and fifty hours. It also became evident that the temperature must be limited to 175°C. or above to prevent formation of nickel carbonyl, and to 225°C. or below to prevent formation of carbon dioxide and carbon. The presence of much carbon dioxide was found to aid in preventing resin formation as well as in suppressing carbon deposition, therefore its use was adopted.

In the adopted procedure, 25 g. of acetaldehyde was sealed in one thin-walled glass tube; in a similar tube 15 g. of catalytic material was reduced with hydrogen at 400°C. for three hours and sealed. Both sealed tubes were placed in the 485-cc. steel bomb, the bomb then closed, evacuated, filled with carbon dioxide to a pressure of 735 lbs. per square inch, and finally the glass tubes were smashed. Small samples of the contents were blown off at about twelve-hour intervals for analysis by a method similar to that of Ripper (1). This method involved collection of the sample over

mercury, absorption in strong sodium bisulfite solution, and determination of acetaldehyde by the use of strong iodine solution and dry sodium bicarbonate, and titration with standard iodine solution. The method is reported to be satisfactorily specific for acetaldehyde in the presence of only small amounts of higher aldehydes, and involves a possible experimental error in absorption and titration estimated to be equivalent to 0.03 "per cent by volume." Residual gases were analyzed by absorption and combustion for carbon dioxide, carbon monoxide, methane, ethane, hydrogen and unsaturated hydrocarbons.

Table 1 contains the results of one run made according to the above procedure. The temperature was first held at 200°C., then lowered and held at 175°C. The increase in aldehyde content following the lowering of

TABLE 1

Change of aldehyde in bomb

TEMPERATURE	ELAPSED TIME	ALDEHYDE
degrees C.	*hours*	*per cent by volume*
200 ±2	12	1.85
	35	1.74
	60	1.01
	108	0.38
	117	0.36
	141	0.28
	167	0.25
	179	0.25
175 ±2	204	0.28
	494	0.34
	515	0.31

the temperature seems to indicate attainment of equilibrium, although the actual amounts present are quite small. A corresponding slight decrease of both carbon monoxide and methane content also occurred. On opening the bomb a very slight amount of free carbon and several cubic centimeters of liquid but no resinous material was found.

Previously in the course of catalyst studies, an approximately equimolar mixture of carbon monoxide and methane was passed over an active catalyst at 175°C. and atmospheric pressure and through a liquid air trap. After the liquefied methane had boiled away, a definite odor of acetaldehyde was observed, and the rinsings of the bulb gave a weak positive test to fuchsine reagent. The results, however, could not be repeated.

Three attempts at synthesis were made by sealing in a glass tube of about 15-cc. volume, approximately 5.0 g of activated catalyst, 0.01 mole of liquid methane, and 0.02 mole of carbon monoxide in the form of nickel

carbonyl, then heating the tube under high external pressure in a bomb at 170–190°C. for about sixty hours. Neither acetaldehyde nor any resin which would be evidence of temporary existence of acetaldehyde could be detected.

IV. SUMMARY

Numerous catalysts for the decomposition of acetaldehyde into carbon monoxide and methane have been studied; nickel precipitated by sodium hydroxide and reduced with hydrogen at 400°C. proved to be the best. Equilibrium conditions have apparently been attained in one direction, but attempts to approach them in the direction of synthesis were not very successful.

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ADSORPTION AT CRYSTAL-SOLUTION INTERFACES. VII[1]

EFFECT OF STIRRING AND GROWTH RATES ON THE HABIT AND DYE ADSORPTION OF ALUM CRYSTALS. INFLUENCE OF ACID AND ALKALI MEDIA ON THE HABIT OF ALUM CRYSTALS

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Received June 5, 1934

The present study is an extension of previous work carried out in this laboratory on adsorption at crystal-solution interfaces (2, 3, 4, 5, 10). Part I is concerned primarily with the effect of stirring on the habit of alum crystals, grown both from pure solutions and from solutions containing small quantities of dye. Part II deals with the influence of acids and alkalies on the habit of alum crystals.

I. EFFECT OF STIRRING AND RATE OF GROWTH ON THE HABIT AND DYE ADSORPTION OF ALUM CRYSTALS

Observations were made of the habit of individual potassium alum crystals grown both from stirred and from unstirred solutions. Quantitative measurements of the change in the relative growth rates of the cube and octahedral faces caused by stirring and by the adsorption of diamine sky blue were made and expressed in terms of the growth ratio V_{100}/V_{111} where V_{100} and V_{111} represent the relative rate of growth (i.e., perpendicular displacements) of the cube and octahedral forces respectively. The measurements were made by photographing the growing crystal every hour over periods ranging from twenty-four to forty-eight hours, using the apparatus and method described in previous papers. The growth ratios so obtained are given in table 1.

The above work was carried out in a constant temperature room held at 30°C. in which the humidity was controlled by the presence of open jars of calcium chloride. Further studies were made at about 23°C. (room temperature) with no effort to control the humidity. Potassium alum solutions containing varying concentrations of diamine sky blue were allowed to evaporate both with and without stirring and the resulting crystals analyzed colorimetrically to determine the amount of dye adsorbed. The results are given in table 2.

[1] Presented in part before the Division of Colloid Chemistry at the Eighty-sixth Meeting of the American Chemical Society held in Chicago, September, 1933.

Ammonium alum solutions containing varying concentrations of crystal violet were allowed to crystallize by cooling solutions saturated at 30°C. to room temperature (23°C.). The crystals were filtered off and the filtrate allowed to evaporate at room temperature until another crop of crystals was obtained. The results of the colorimetric analysis of these crystals are given in table 3, in which the column headed "hot solution" refers to solutions saturated at 30°C. and "cold solution" to those saturated at 23°C.

From the results given in table 1 it is evident that the effect of stirring on potassium alum crystals grown both from pure solutions and from

TABLE 1

Growth ratios of potassium alum crystals

SUBSTANCE	V_{100}/V_{111}	
	Stirred	Unstirred
Pure potassium alum	1.75	1.61*
Potassium alum + 0.002 g. of diamine sky blue per 100 cc.	1.66	
Potassium alum + 0.004 g. of diamine sky blue per 100 cc.	0.75	0.38
Potassium alum + 0.006 g. of diamine sky blue per 100 cc.	0.79	0.29
Potassium alum + 0.008 g. of diamine sky blue per 100 cc.	0.45	0.00

* Keenen and France (4).

TABLE 2

Adsorption of diamine sky blue by potassium alum crystals

DIAMINE SKY BLUE PER 100 CC. OF SOLUTION	PER CENT OF DYE ADSORBED	
	Stirred	Unstirred
grams		
0.002	0.008	0.01
0.004	0.017	0.04
0.006	0.055	0.09
0.008	0.080	0.13

solutions containing varying concentrations of diamine sky blue is to decrease the size of the cube faces, i.e., to increase the V_{100}/V_{111} ratio. Other workers have observed a similar decrease in the size of cube faces in the case of potassium alum grown from supersaturated (8), rapidly cooling, or rapidly evaporating solutions (1). A consideration of Valeton's theory (9) of crystal growth suggests a plausible explanation. Valeton assumes that the actual rate of growth of any crystal face depends on two factors: (1) the specific rate of growth of that face (i.e., perpendicular displacement) which is dependent only on its ionic character, and (2) the speed with which the ions can diffuse to the face. Since the specific growth rate of the cube face is very high (because the face is populated by ions of like charge),

the actual growth rate is determined by the rate of diffusion to the face. Any condition (such as stirring or growth from supersaturated, rapidly cooling, or rapidly evaporating solutions) which increases the rate of diffusion will increase the actual growth rate of the cube face and hence the V_{100}/V_{111} ratio.

The relatively greater size of the cube faces on crystals grown from unstirred solutions containing dyes than from stirred solutions can undoubtedly be accounted for in part by the same explanation that holds for crystals grown from pure solution. A second factor, smaller dye adsorption from stirred solutions as is shown in table 2, also is involved. The dye is adsorbed on the cube faces only, so that obviously the less color is adsorbed, the less the inhibiting effect on the growth rate of the cube faces, and the larger the V_{100}/V_{111} ratio. This lesser adsorption of color from stirred solutions can be explained by the increased rate of diffusion of the

TABLE 3

Adsorption of crystal violet by ammonium alum crystals

CRYSTAL VIOLET PER 100 CC. OF SOLUTION AT 23°C.	PER CENT OF DYE ADSORBED	
	Hot solution	Cold solution
grams		
0.03	0.0035	0.025
0.03	0.0028	0.023
0.04	0.0540	0.076
0.04	0.0550	0.084

alum ions; since these ions are available, they will deposit on the crystal in preference to the foreign dye particles.

It has previously been stated that the rate at which ions can reach the cube faces of alum is increased when crystals are obtained by rapid cooling or evaporation as well as by stirring. It should follow, then, that less color should be adsorbed by crystals grown by cooling warm solutions than by those produced by slow evaporation at room temperature. The results given in table 3 show that this prediction is verified experimentally.

II. INFLUENCE OF ACIDS AND ALKALIES ON THE HABIT OF ALUM CRYSTALS

Numerous workers have reported that alum crystallizes as cubes from alkaline solution; other investigators have reported changes in the habit of alum crystals grown in solutions containing various acids. Saylor (7) states that the influence of acid and alkaline solutions "upon external crystal form has served as a key to the entire field of adsorption and has tied in with those examples where adsorption has actually been demonstrated. The new technique is absolutely general"; and, further, "Nega-

tive ions are adsorbed on the octahedron faces of the alkali halides and barium nitrate, on the cube faces of potassium alum, and on the pyramids of sodium nitrate. The other principal faces adsorb positive ions." He has used as one of his examples the formation of large cube faces on alum crystals presumably grown from alkaline solutions or from other solutions containing readily adsorbable anions.

The present study was made to determine the influence of acid and alkaline media on the crystal habit of potassium and ammonium alum. The solutions were made up by adding the proper amounts of the foreign materials to saturated alum solutions. Individual seed crystals mounted on copper or nichrome wires were suspended in the solutions and allowed to grow over periods ranging from a few days to several weeks. The concentrations are expressed as the number of grams or per cent of foreign material per 100 grams of saturated solution.

Up to 25 or 30 per cent concentrations of hydrochloric, nitric, acetic, sulfuric, and phosphoric acids the crystals showed the usual cuboöctahedral form; the 110 face which frequently occurred in pure or slightly acid solutions tended to disappear at higher concentrations. Above 25 or 30 per cent, clumps of tiny crystals or needle-like formations formed in the nitric and phosphoric acid solutions, while crystal growth almost completely ceased in the other acids.

Crystals of potassium alum grown in 1 per cent sodium carbonate solution were similar to those grown from pure solution. When a 2 per cent sodium carbonate solution was used, some aluminum hydroxide precipitated; when this was filtered off and crystals allowed to grow in the clear filtrate, cubic crystals were formed and more aluminum hydroxide precipitated as the solution evaporated. Ammonium alum crystals in 1 per cent to 2 per cent sodium carbonate solutions were normal in habit. In 3 per cent solutions aluminum hydroxide was precipitated; crystals grown in the clear filtrate were cubic and more aluminum hydroxide precipitated as the solution evaporated.

The above results indicate that crystals grown from acid solutions do not show the enlargement of the octahedral faces predicted by Saylor's "absolutely general technique." Crystals grown in sodium carbonate solutions from which no aluminum hydroxide had precipitated showed no change in form; the cubic crystals obtained in solutions where some aluminum hydroxide had precipitated were not alum crystals but sodium or potassium sulfate.

III. SUMMARY

Stirring causes a decrease in the size of the cube faces of potassium alum crystals grown both from pure solution and from solutions containing varying concentrations of diamine sky blue. For a given concentration of

dye, less color is adsorbed by crystals grown from stirred than from unstirred solutions, and by those obtained by rapid cooling than by slow evaporation at room temperature. An explanation is offered to account for these facts.

No appreciable change in habit occurs when alum crystals are grown from acid solutions or from solutions containing sodium carbonate from which no aluminum hydroxide has been precipitated.

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INFLUENCE OF THE PRESENCE OF A SOLUTE ON RATE OF OSMOSIS

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Received July 10, 1934

Most studies of osmotic phenomena have dealt with measurements of pressure with little reference to rates of transfer of material across the membrane. Although it is generally recognized that the presence of dissolved material affects the osmotic pressure exerted by a liquid, the influence of a solute on the rate of passage of the solvent through a semipermeable membrane has not been given serious consideration. For such a study two miscible liquids should be separated by a membrane which is permeable to one liquid and not to the other. Various substances should be dissolved in one of the liquids and the rates of osmosis compared with those obtained using the pure solvents. In the work described below a system composed of pyridine–rubber–water was used.

If a water-soluble salt such as silver nitrate is dissolved in the pyridine, the flow through the rubber should be retarded, but not to the same extent as when a water-insoluble compound, such as anthracene, is dissolved in the pyridine. On the other hand an aqueous solution of potassium chloride, a salt which is insoluble in pyridine, should also retard the flow, because the aqueous solution has less attraction for the pyridine and thus should pull it through the rubber membrane less rapidly.

EXPERIMENTAL

The apparatus, materials, and method of experimentation were identical with those described in a paper (1) dealing with the effect of temperature on rate of osmosis. Since 35°C. was a convenient temperature at which to work and gave rates of flow large enough to be conveniently measured, the experiments were conducted at that temperature. It was pointed out in the previous paper that at 35°C. the determination of rates in the pyridine–rubber–water system could be duplicated with a high degree of accuracy.

Early in the investigation it was noticed that pyridine, after standing in contact with the same rubber membrane for some time, contained fine particles of dispersed material. Substituting this contaminated pyridine for the pure solvent showed that the suspended particles and dissolved

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material which were present exerted a definite retarding action on the passage of the liquid through the membrane. It was this discovery that prompted the use of freshly distilled pyridine and a new rubber membrane in each determination.

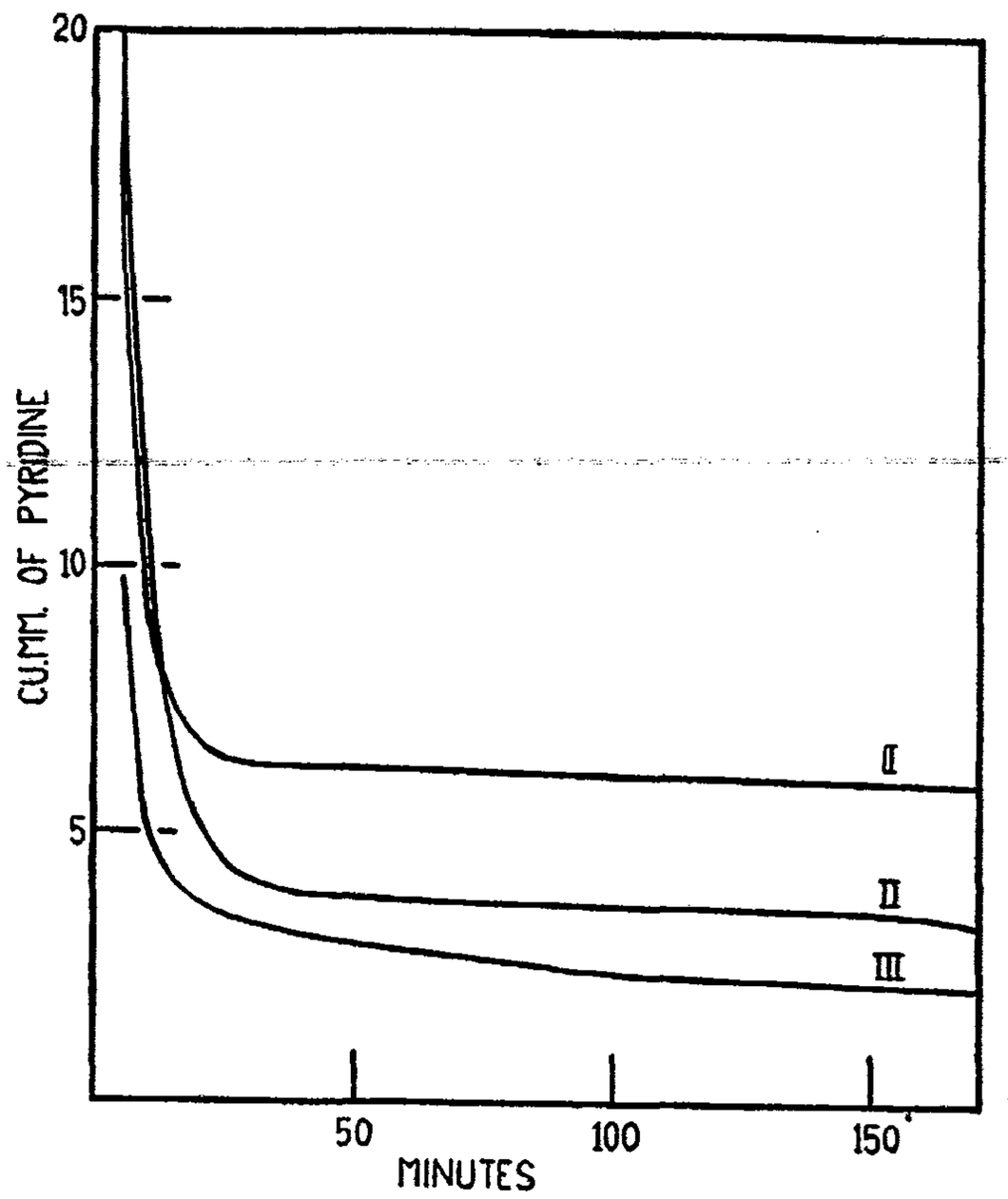

FIG. 1. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY DISSOLVING SILVER NITRATE IN THE PYRIDINE

Curve I, pyridine-water; curve II, 0.5 *N* silver nitrate in pyridine-water; curve III, 1.0 *N* silver nitrate in pyridine-water.

The data obtained are given in figures 1 to 4 inclusive.

DISCUSSION

The rates of osmosis are found to be very regular except at the beginning of the experiments. Irregularities may occur at the start of each experiment because a few minutes must elapse before the membrane becomes saturated with pyridine and a steady rate of flow is attained. For this

reason no deductions should be made until about thirty minutes after the beginning of the experiment, when the rates become constant. From thirty minutes on up to seven to ten hours the rates of osmosis at 25°C. to 35°C. are very uniform for every combination studied.

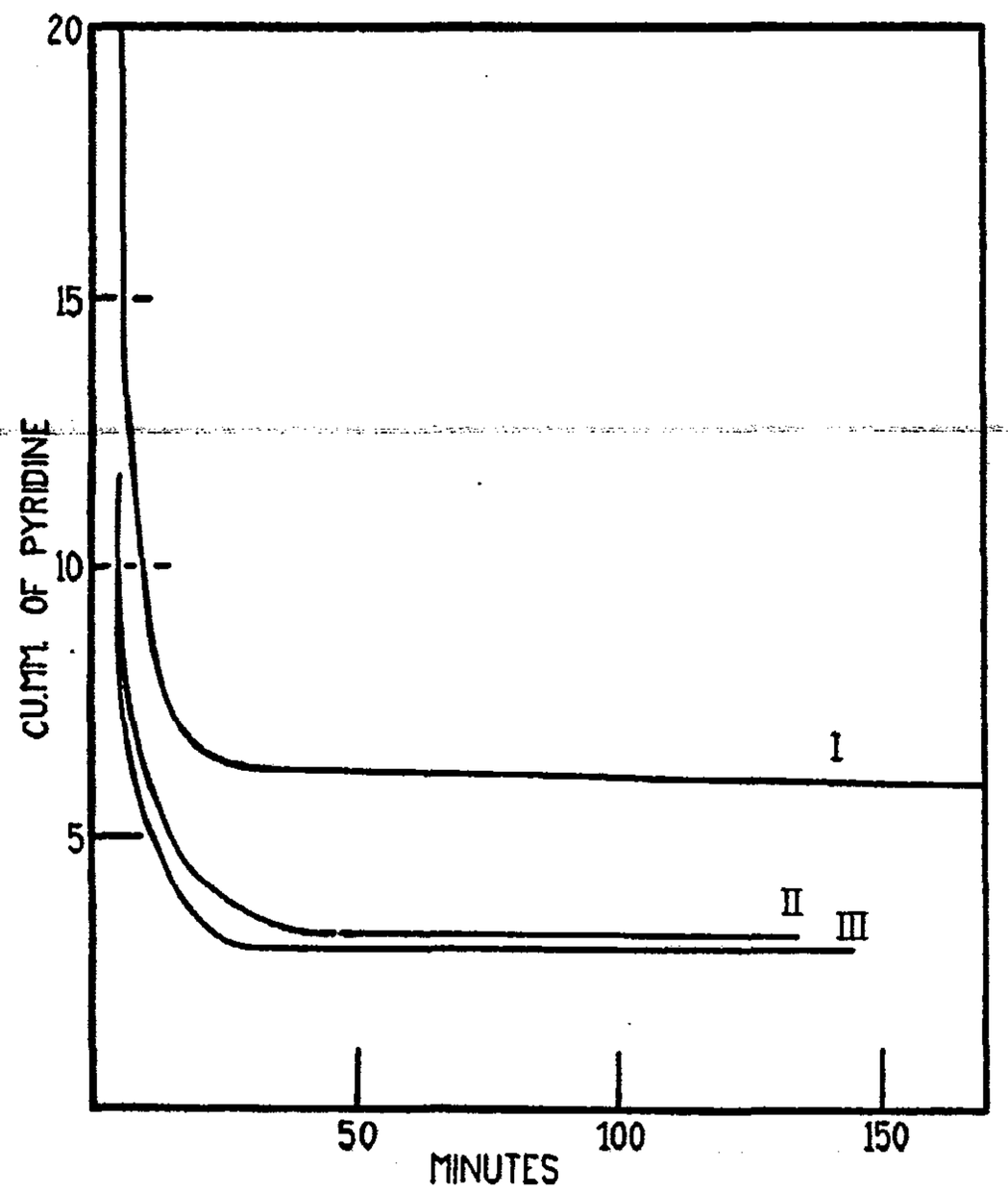

FIG. 2. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY DISSOLVING ANTHRACENE IN THE PYRIDINE

Curve I, pyridine-water; curve II, 0.08 *M* anthracene in pyridine-water; curve III, 0.16 *M* anthracene in pyridine-water.

Organic and inorganic solvents in either of the liquids retard the dialysis rate. It might be expected that a molar solution of silver nitrate in pyridine would hold back the pyridine twice as much as a half molar solution, but this is not found to be true (figure 1). Successive equal amounts of added solute make increasingly smaller changes in the rate of passage. Doubling the amount of anthracene in the pyridine (figure 2) has a smaller relative effect than doubling the concentration of silver

nitrate. Considering the effects of equal molar quantities of anthracene and silver nitrate, the organic compound is more effective than the silver salt in retarding the passage of the pyridine through the rubber membrane.

Figure 3 shows that an aqueous molar solution of sucrose draws pyridine through a rubber membrane more slowly than a molar solution of potassium

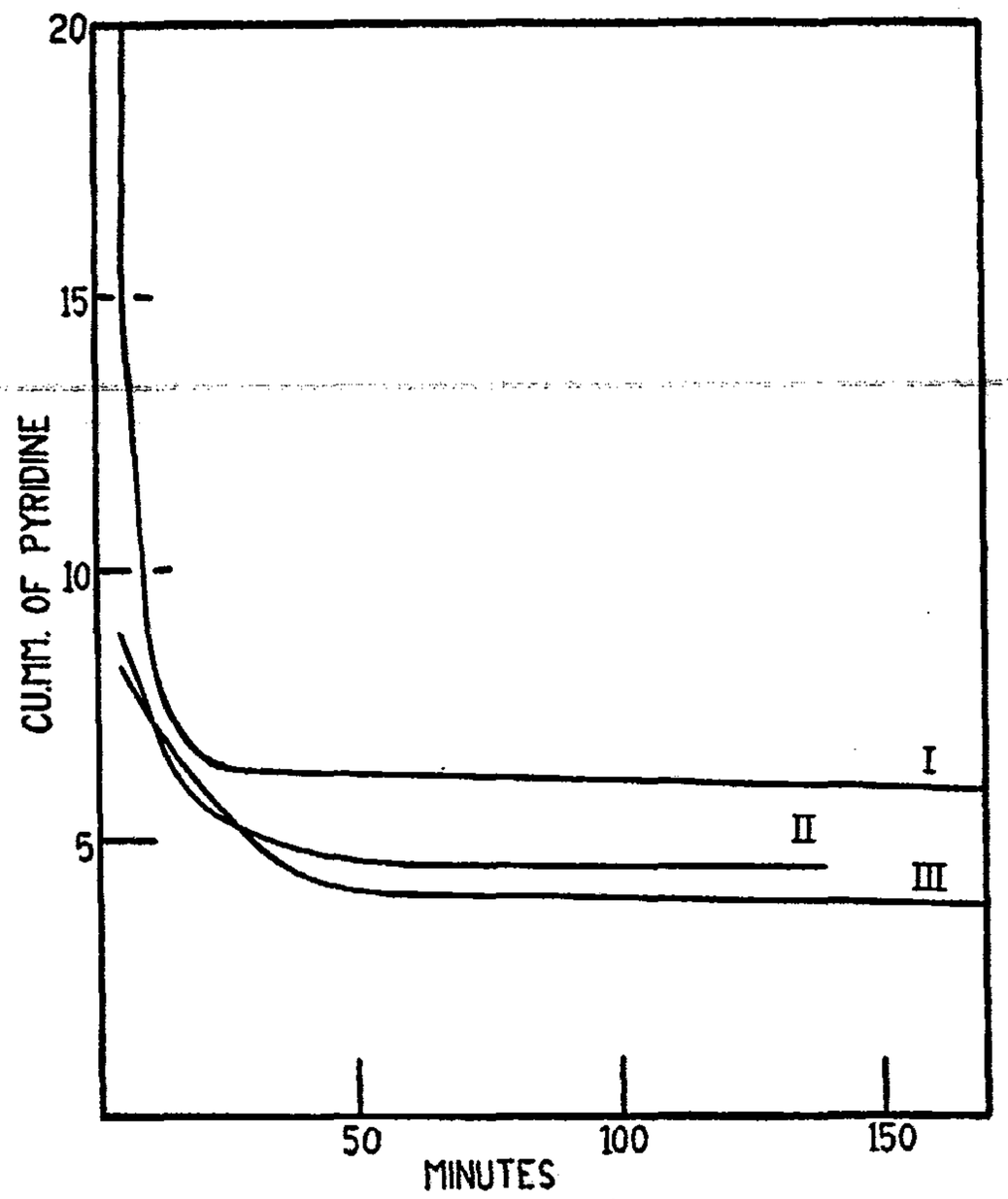

FIG. 3. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY DISSOLVING POTASSIUM CHLORIDE AND SUCROSE IN THE WATER

Curve I, pyridine-water; curve II, pyridine-molar solution of potassium chloride in water; curve III, pyridine-molar solution of sucrose in water.

chloride. However, with both solutions the rate of passage is slower than with pure water.

As mentioned above, when pyridine is allowed to stand in contact with rubber for many hours the liquid becomes contaminated with dissolved and dispersed material derived from the membrane. If such contaminated pyridine is used in a new experiment with a fresh rubber membrane the

rate of passage of the pyridine into the water is found to be greatly retarded (figure 4).

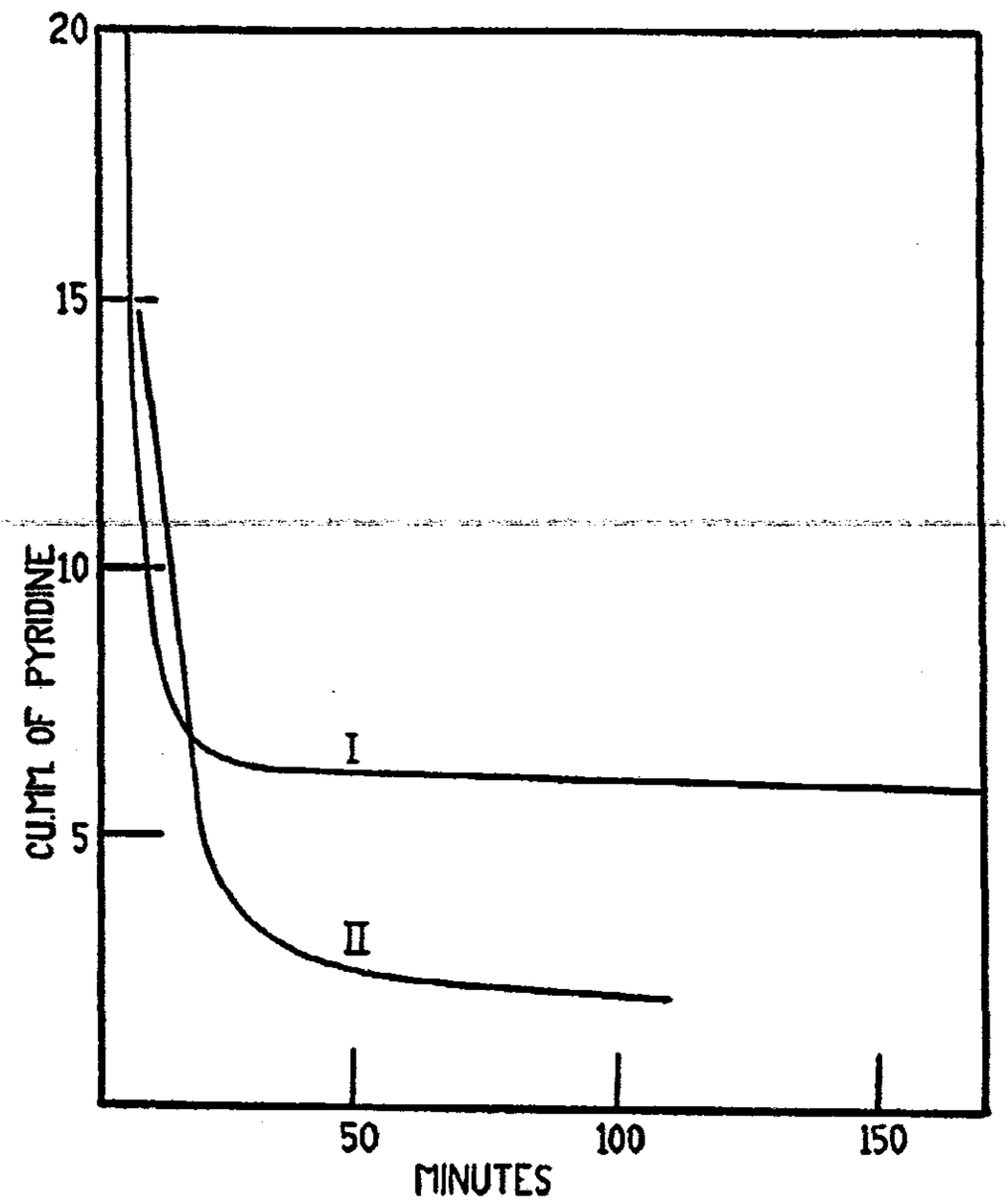

FIG. 4. RETARDATION OF THE RATE OF OSMOSIS OF PYRIDINE THROUGH RUBBER TO WATER CAUSED BY THE PRESENCE OF FOREIGN PARTICLES IN THE PYRIDINE

Curve I, pyridine-water; curve II, foreign particles in pyridine-water

SUMMARY

1. The retardation of the rate of osmosis of pyridine through a rubber membrane into water, which is caused by dissolving silver nitrate and anthracene in the pyridine, was determined at 35°C.

2. The effect of dissolving sucrose and potassium chloride in the water was determined for a pyridine-rubber-water system at 35°C.

3. The influence of dissolved and dispersed rubber in the pyridine on the rate of osmosis was determined.

REFERENCE

(1) TRAXLER, R. N.: J. Phys. Chem. 32, 127-41 (1928).

NEW BOOKS

Volumetric Analysis. By H. P. STARCK. 228 pp. Baltimore: William Wood & Company, 1934. Price: bound, $3.00.

This book is written primarily for pharmaceutical and medical students and seems to be suitable for the purpose. However, it cannot be recommended as a text for students in chemistry, since the theory is entirely inadequate, a great many of the procedures are repetitions and not up-to-date, and some of them are highly inaccurate.

I. M. KOLTHOFF.

Dipole Moments. A General Discussion held by the Faraday Society. 25 x 16 cm.; lxxxvi + 227 pp. London: Gurney and Jackson, 1934. Price: (in stiff cloth covers) 21s.

This volume, reprinted from the Transactions of the Faraday Society, contains twenty-four papers and a general discussion on dipole moments and related topics, which were communicated at the Faraday Society's Symposium at Oxford in April, 1934.

The papers, which include contributions from the leading workers in this field in America and Europe, are divided into three groups: Part I. Dielectric Constant; Part II. Determination of Dipole Moments; Part III. Interpretation of Dipole Moments.

The first section begins, as is fitting, with a paper by Debye, on "Energy Absorption in Dielectrics with Polar Molecules." The other two papers in this section deal with the temperature variation of the dielectric constant of some crystalline solids.

The nine papers in the second section are mainly concerned with the dielectric behavior of concentrated solutions, dipole association, and cohesion, and with the difficulties encountered in the calculation of dipole moments from polarization measurements in solution, in particular, the vexed question of the atom polarization, and the effect of the non-polar solvent on the apparent dipole moment. These papers constitute a valuable summary of the present position in these matters.

The third section contains papers which cover a very wide field of the application of dipole moment measurements to problems of molecular and stereochemical structure.

An appendix of some eighty-six pages contains an excellently arranged catalogue of dipole moment data compiled by Dr. N. V. Sidgwick and his collaborators. This is the most complete list of dipole moments which has been published, and would in itself render the volume invaluable as a book of reference. In this list are given, not only the actual dipole moments, the authors, and references, but also the temperature or temperature range of measurement, the solvent or medium in which the measurement was carried out, the method used for the elimination of P_e, the allowance which has been made for P_a, and the observed value of ∞P_2 where this is given by the author.

The book is indispensable to workers in the field of dipole moments and contains much of interest to the general reader.

F. FAIRBROTHER.

Leitfähigkeitstitrationen und Leitfähigkeitsmessungen. Visuelle und akustische Methoden. By G. JANDER and O. PFUNDT. 25 x 16 cm.; viii + 88 pp. Stuttgart: F. Enke Verlag, 1934. Price: unbound, 7.40 RM; bound, 8.80 RM.

This book constitutes the second edition of Prof. Jander's excellent monograph on visual conductometric titrations. Since its appearance, he and his pupils have made several improvements in the technique of these methods, and these are described in the present volume. As its name implies, the new edition has been extended so as to cover the whole field of conductometric analysis, including its technical applications. Coming, as it does, from the pens of well-known authorities in the field of physico-chemical analysis, the volume will be heartily welcomed by physical chemists, analysts, and especially those engaged in many chemical industries.

The introduction of satisfactory and accurate visual methods has undoubtedly rendered conductometric methods available in noisy works laboratories, in which the ordinary telephone method cannot be used, and it is there that Jander's technique will find ever-increasing adoption.

The second half of the book deals with analytical processes. Although, from the purely practical standpoint, the descriptions are adequate, it is felt that too little attention is given to the principles underlying the procedures, and this is especially the case in the section on acidimetry and alkalimetry, in which no attempt is made to correlate the shape of the titration graphs with the dissociation constants of acids and bases and the concentrations of the solutions being titrated and their titrants. On titrations themselves, the book can hardly be regarded as exhaustive.

H. T. S. BRITTON.

The Electronic Structure and Properties of Matter. By C. H. DOUGLAS CLARK. 22 x 14 cm.; xxv + 374 pp. London: Chapman and Hall, Ltd., 1934. Price: 21s.

This book is the first volume of a Comprehensive Treatise on Atomic and Molecular Structure, of which two further volumes, treating of the fine structure of matter and the interpretation of band spectra, respectively, are in preparation. This volume consists of two parts, a general introduction and a treatment of physical properties and molecular constitution.

The general introduction gives a survey of modern views on the Periodic Table, the electronic configuration of atoms, quantum numbers, the transition elements, valency, and the nature of chemical linkages. The treatment is brief, accurate, and reasonably clear, though too condensed to be of much value to the student approaching the subject of electronic structure for the first time. It is a pity that Dr. Clark has not given a fuller and clearer treatment to this portion, and so made it a very valuable textbook for the university student.

The second portion collects a great number of facts which have not been assembled before in a single volume. This section will certainly be of great value. It contains excellent surveys of melting and boiling points, atomic and molecular volumes, atomic and ionic radii, electrical conductivity, magnetic and cohesional properties. The reviewer, though naturally unable to test the accuracy of the whole of a work of this type, has found no errors other than minor misprints.

Full references are given to the author's sources, and their clear and detailed presentation is a valuable feature of the work. The indexes are not so complete. A short examination revealed the absence of the names of Wasastjerna and Kerschbaum from the author index and of permutites (pp. 150, 151), rectification (p. 190), and complex compounds (pp. 225–8) from the subject index.

FRANK SHERWOOD TAYLOR.

THE ELECTROCAPILLARY CURVE AND ITS DISPLACEMENT WITH CONCENTRATION AND TEMPERATURE[1]

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Received June 14, 1934

INTRODUCTION

A change in the electrical potential across the interface formed by an aqueous solution in contact with mercury is accompanied by a change in interfacial tension which can be measured directly. The relationship between interfacial tension and applied potential may be represented graphically, forming the so-called electrocapillary curve. If we plot some function of interfacial tension as ordinate with applied potential as abscissa a curve of parabolic shape is usually obtained.

Before a difference of potential is applied across the interface the mercury is positively charged and anions are preferentially adsorbed in the solution side of the interface. Usually the anions are capillary-active. In this event the more capillary-active the anion is, the greater will be the depression in the rising branch of the curve. As the applied potential difference is increased the charge of the mercury surface is lowered, thus increasing the interfacial tension and causing the electrocapillary curve to rise. A maximum in the curve is reached when the charge on the mercury surface has been neutralized. Further increase in applied potential causes the mercury to become negatively charged, and the curve descends. If the cations are capillary-active, the descending branch of the curve will be depressed because of the increased concentration of these ions at the interface. The general mathematical theories of the electrocapillary curve have been presented and discussed in a number of places in the literature. Reference may be made at this time to articles by Lippmann (11), Gouy (5), Frumkin (3), Koenig (8), and Craxford, Gatty, and Philpot (1).

The electrochemical study of the interfacial potential difference between mercury and a solution containing electrolytes, or electrolytes and neutral

[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14-16, 1934.

More complete details of this work may be found in the thesis of L. A. Hansen, presented to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy and filed in the Library of the University of Wisconsin, June, 1934.

molecules, is important because a knowledge of the effects produced gives information about the properties and arrangement of the ions and molecules present in the interface. In this report it will be our purpose to give the results of a study of the effect of changes in temperature and concentration of ammonium nitrate in aqueous solution on the position and shape of the electrocapillary curve.

In a later report there will be presented the results of similar electrocapillary studies with solutions of sodium sulfate and of certain nonelectrolytes.

PREPARATION OF MATERIALS

Mallinckrodt's "Reagent Quality" sodium sulfate was used. Mallinckrodt's "C.P." quality ammonium nitrate was recrystallized from water and dried in a desiccator over concentrated sulfuric acid for use. The mercury was purified by placing concentrated sulfuric acid over it and passing air through the liquids. This process was continued for a period of a week, the sulfuric acid being changed several times. After this treatment the mercury was thoroughly washed to remove all traces of acid; then it was dried and distilled. Mercurous nitrate was prepared by allowing concentrated nitric acid to react with an excess of the purified mercury. The mercurous nitrate was removed from the solution by filtration through a sintered glass filter and was dried over concentrated sulfuric acid in a desiccator.

All of the solutions were prepared by dissolving the proper weights of the materials in conductance water. The final distillation of the conductance water was carried out in quartz.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus employed in this research was constructed of Pyrex glass. It is shown diagrammatically in figure 1. The liquid to be studied was placed in the cell T, which was connected to the electrometer proper by means of the ground glass joint S. The side arm U was joined with K, a reflux condenser. Because of the fact that temperatures of from 25° to 75°C. were to be used, it was necessary to employ this reflux condenser to keep the pressure in the cell equal to the atmospheric pressure without changing the composition of the solution.

The column of mercury P ends in the capillary L. The inside radius of the capillary was approximately 6×10^{-4} centimeter. Because the capillary was so small, the technique ordinarily used in sealing capillary tubing to larger tubing could not be employed. Eight-millimeter Pyrex tubing was used, because the outside diameter of the capillary tubing was just slightly less than the inside diameter of tubing of this size. The capillary tube was inserted to a distance of about one-fourth of an inch into the 8-

mm. tubing. The two tubes were then clamped in this position on a ring stand. The glass tubing which extended over the capillary tubing was heated gently with a hand blast torch until a small portion of it became soft. This pliable portion was pressed against the capillary tubing by rolling a carbon rod over the surface. This process was continued until the capillary tubing was entirely sealed into position. By following this method it was possible to seal capillary tubes without collapsing their inner walls. The stopcock J and the ground glass joint R made it possible to take the apparatus apart whenever it was necessary to replace the capillary tip L. Two brass rings were clamped on the tube; one above, and

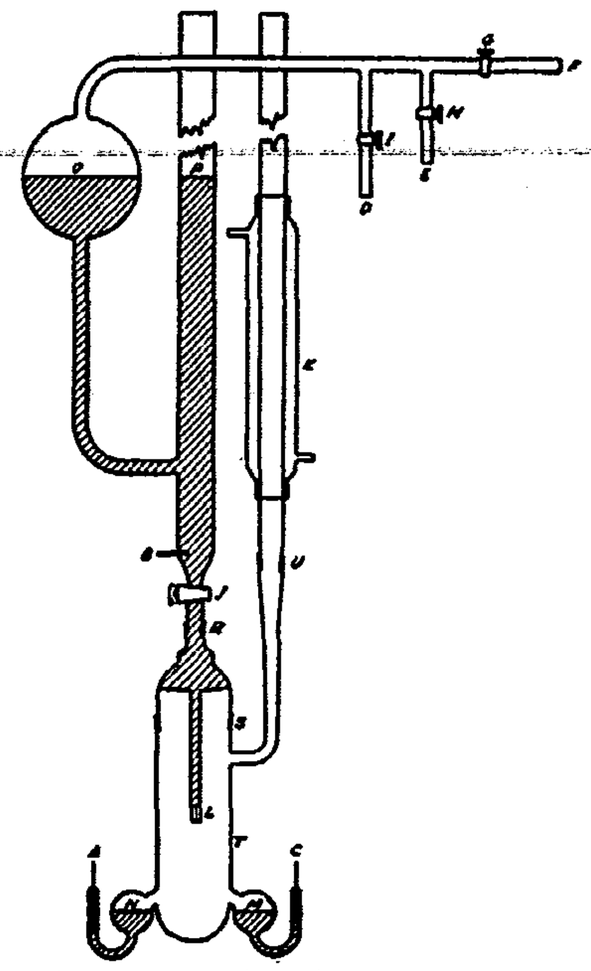

FIG. 1. APPARATUS

one below, the joint R. Metal springs were suspended between the two brass rings, thus holding the ground glass joints securely in position. The height of the mercury in column P could be changed by applying pressure from a nitrogen tank through the tube F.

The negative electrode, located at B, consisted of a tungsten wire sealed into the glass tube. The tungsten wires A and C were sealed into the glass vessel coming in contact with the duplicate anodes of mercury, N and M respectively.

The stopcock H allowed the pressure in the reservoir O to be reduced by allowing nitrogen gas to escape to the atmosphere through it. When the

stopcock I was opened, the pressure was moderated by having another reservoir connected to the outlet D.

The entire electrometer was placed in a well-insulated air thermostat. The heating elements consisted of nichrome wire wound in spiral form. The air was thoroughly circulated by means of a fan, the blades of which were placed inside the air bath, while the motor which drove the fan was located outside the thermostat. The temperature was regulated by means of relay and deKhotinsky regulator.

The difference of potential to be applied across the electrodes A and B was obtained by means of an ordinary potentiometric circuit.

The mercury in the capillary tip L was illuminated by means of an automobile spotlight and a lens which focused the light on the capillary. The source of light was placed at right angles to the telescope of the comparator. It was found that by having the distance from the objective of the comparator to the mercury capillary very slightly greater than the focal length of the telescope, the mercury in the capillary took on the appearance of a wide ribbon with well-defined tip. If the comparator was so arranged that it was sharply in focus, it was observed that the mercury in the capillary would take on the appearance of a fine thread with a diffuse or ill-defined tip. Instead of measuring the change of position of the mercury in the capillary, it was more convenient to keep the mercury at a constant level by increasing or decreasing the height of the mercury in the column P.

The position of the mercury in the capillary L was kept constantly at a point 0.05 cm. from the lower tip of the capillary. It was found by Koenig (9) that if the mercury was kept at a position such that it was more than 0.1 cm. from the end of the capillary the slight amount of hydrogen which was slowly liberated at the capillary cathode could not diffuse out fast enough but would form bubbles of hydrogen inside.

The height of the mercury in column P was measured by means of a traveling telescope suspended on a $\frac{3}{4}$-in. cold rolled steel rod and a steel scale graduated to millimeters. The distance from the mercury meniscus in the capillary to the bottom of the steel scale was a constant for each capillary, so the height actually measured with the traveling telescope is the difference between the bottom of the scale and position of the mercury meniscus in the tube P. The distance from the mercury meniscus in the capillary to the bottom of the steel scale was measured by means of a cathetometer.

The solution in the cell T extended a short distance above the bottom of the capillary tip L. In order to make the correction for the hydrostatic pressure of this column of solution from the bottom of the mercury meniscus to the top of the solution it was necessary to measure this height accurately. This measurement was made by means of the comparator.

To obtain the values of the interfacial tension in absolute units from the

corresponding heights of the mercury column the following procedure was adopted. The value of the interfacial tension at the maximum of the electrocapillary curve for a half-molar aqueous solution of sodium sulfate has been determined by Gouy (6). The apparatus was calibrated by means of this solution for each capillary used.

EXPERIMENTAL RESULTS

Electrocapillary curves were obtained at 25°, 50°, and 75°C. for the following solutions of ammonium nitrate: (1) 1.0 *M* ammonium nitrate in a solution 0.002 *M* with respect to mercurous nitrate and nitric acid. (2) 0.2 *M* ammonium nitrate in a solution 0.002 *M* with respect to mercurous nitrate and nitric acid. (3) 0.02 *M* ammonium nitrate in a solution 0.002 *M* with respect to mercurous nitrate and nitric acid.

The electrocapillary data are collected to form table 1. In the first column are found the values of ϕ, the applied potential difference. The second, third, and fourth columns contain values of interfacial tension corresponding to the several applied potential differences at 25°, 50°, and 75°C., respectively, for 1.0 *M* ammonium nitrate solution; the fifth, sixth, and seventh columns are made up of similar data for the 0.2 *M* solution; and the eighth, ninth, and tenth columns contain the results for the 0.02 *M* solution. Representative electrocapillary curves which show the effect of change in concentration and temperature, plotted from these data, are shown in figures 2 and 3.

In order to determine accurately the position of the maximum of an electrocapillary curve, an equation for a portion of the curve extending to a short distance on either side of the apparent maximum was obtained by the method of the least squares. The first derivative $\frac{d\sigma}{d\phi}$, when equated to zero, gave the exact position of the curve. This method of obtaining the maximum was used in all cases. In table 2 there are given representative results obtained at 25°C. The heading for each column is self-explanatory. Such results are shown graphically in figure 4. The curves of this figure are from values obtained by using the mathematical equations, but the points on the curves are experimental values.

The results of calculations for ϕ (max.) and for the coefficients $\frac{\partial\sigma\text{ (max.)}}{\partial T}$ and $\frac{\partial\phi\text{ (max.)}}{\partial T}$ for the ammonium nitrate solutions are summarized in table 3. In the third column are given the values of the applied potential which correspond to the maxima of the electrocapillary curves. The fourth column presents the differential coefficient of change of σ (max.) with temperature, and the last column gives the corresponding coefficient for change of ϕ (max.) with temperature.

TABLE 1

Electrocapillary data for ammonium nitrate solutions

ϕ	1.0 *M* NH_4NO_3 25°C.	1.0 *M* NH_4NO_3 50°C.	1.0 *M* NH_4NO_3 75°C.	0.2 *M* NH_4NO_3 25°C.	0.2 *M* NH_4NO_3 50°C.	0.2 *M* NH_4NO_3 75°C.	0.02 *M* NH_4NO_3 25°C.	0.02 *M* NH_4NO_3 50°C.	0.02 *M* NH_4NO_3 75°C.
volts	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$
0.000	312.57	314.78	315.61	306.27	306.99	307.74	310.46	311.32	310.64
0.025	319.26	321.52	322.20	312.73	313.93	313.98	317.03	317.59	316.97
0.050	325.41	327.72	328.17	319.18	319.93	320.22	322.67	323.98	322.59
0.075	331.43	333.21	333.80	325.37	325.92	326.08	329.12	329.39	328.41
0.100	337.11	338.82	339.11	331.47	331.77	331.86	334.72	334.89	333.80
0.125	342.47	343.96	344.31	337.34	337.22	337.02	339.73	340.07	339.07
0.150	347.48	348.99	349.12	342.27	342.52	342.10	344.82	345.13	344.19
0.175	352.33	353.62	353.89	347.13	347.39	347.18	350.41	349.92	349.15
0.200	356.95	358.22	358.42	351.94	352.22	351.95	355.30	354.56	353.96
0.250	365.75	366.52	366.64	361.41	360.99	360.67	363.95	363.29	361.91
0.300	373.85	374.43	374.17	369.90	369.32	368.47	372.29	371.47	369.79
0.350	380.94	381.64	381.07	377.57	376.96	375.84	379.88	378.83	376.81
0.400	387.71	388.10	387.32	384.77	383.89	382.70	386.96	385.88	383.36
0.450	393.85	393.91	392.94	391.19	390.32	388.48	393.38	392.04	389.68
0.500	399.45	399.28	397.98	397.45	396.17	394.41	399.33	397.72	394.84
0.550	404.34	403.88	402.44	403.08	401.43	399.30	404.54	402.44	399.53
0.600	408.65	407.74	405.93	407.82	405.94	403.60	409.31	406.92	403.64
0.650	412.48	411.48	409.23	412.48	410.62	407.17	413.65	410.85	406.90
0.675	414.16	412.68	410.27	414.63	412.22	409.03	415.57	412.41	408.49
0.700	415.65	414.40	411.40	416.24	413.85	410.58	417.65	413.93	409.77
0.725	416.82	415.37	412.37	417.80	415.45	411.71	419.17	415.33	411.01
0.750	418.00	416.35	413.11	419.25	416.81	412.68	420.78	416.50	411.98
0.775	419.05	417.24	413.53	420.54	417.75	413.49	421.99	417.63	412.91
0.800	420.07	417.71	414.08	421.72	418.53	414.42	422.85	418.45	414.00
0.825	420.66	417.98	414.39	422.81	419.35	414.93	423.44	419.15	414.58
0.850	421.09	418.10	414.42	423.59	420.01	415.39	424.30	419.81	415.39
0.875	421.21	418.10	414.27	424.06	420.36	415.63	424.69	420.36	415.98
0.900	421.21	418.02	413.80	424.30	420.52	415.78	425.04	420.79	416.40
0.925	421.05	417.75	413.34	424.49	420.59	415.78	425.39	421.18	416.52
0.950	420.62	417.36	412.72	424.49	420.52	415.70	425.47	421.37	416.52
0.975	419.92	416.39	411.90	424.34	420.36	415.55	425.47	421.22	416.44
1.000	419.09	415.37	410.78	424.02	419.97	415.00	425.36	421.06	416.25
1.025	418.15	414.52	409.62	423.28	419.11	414.23	425.28	420.79	413.05
1.050	417.14	413.23	408.53	422.41	418.06	413.45	424.85	420.40	415.70
1.075	416.16	411.59	407.13	421.17	416.58	412.49	423.91	419.62	415.04
1.100	414.40	410.31	405.58	419.99	415.65	411.44	423.05	418.84	414.35
1.125	412.68	408.40	404.22	418.70	414.13	410.35	422.07	418.02	413.53
1.150	410.91	406.53	402.56	417.18	412.68	408.88	421.17	416.89	412.37
1.175	408.92	404.66	400.77	415.65	411.17	407.64	419.88	415.61	411.13
1.200	406.88	402.91	398.91	414.08	409.30	405.85	418.43	414.28	409.93
1.225	404.65	401.23	396.82	412.32	407.66	404.65	416.94	413.00	408.80
1.250	402.27	398.62	394.57	410.33	406.06	402.79	415.38	411.67	407.68
1.275	399.76	396.13	392.32	408.25	404.31	401.01	413.42	410.23	406.47
1.300	397.37	393.56	389.68	406.26	401.78	399.18	411.58	408.36	404.88
1.350	391.93	388.88	384.33	401.52	397.69	394.76	408.14	404.39	401.94
1.400	385.87	382.65	378.63	396.55	392.70	389.95	403.67	400.69	397.44
1.450	379.45	376.49	372.97	391.58	387.75	385.03	399.17	396.05	392.86
1.500	372.52	369.71	365.99	385.13	382.22	379.13	393.62	390.99	388.21
1.550	365.52	362.78	359.20	378.59	375.95	373.20	388.02	385.65	383.48
1.600	357.81	355.03	351.83	371.86	369.21	367.11	381.68	383.74	377.58

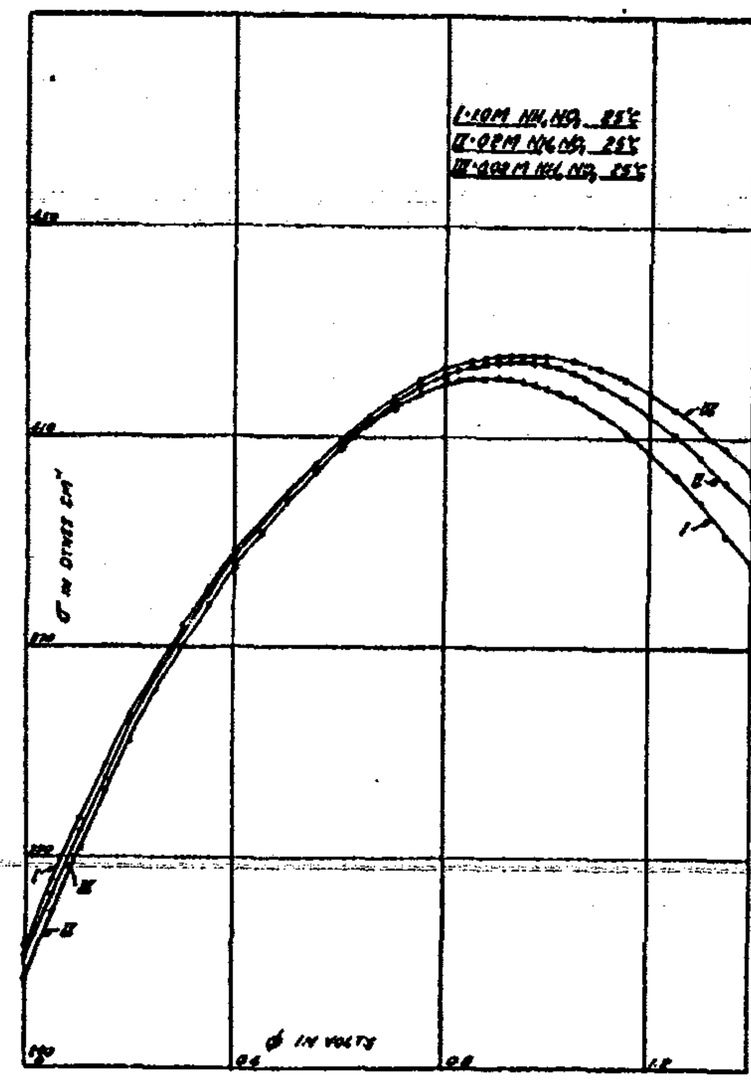

FIG. 2. ELECTROCAPILLARY CURVES FOR 1.0 *M*, 0.2 *M*, AND 0.2 *M* AMMONIUM NITRATE SOLUTIONS AT 25°C.

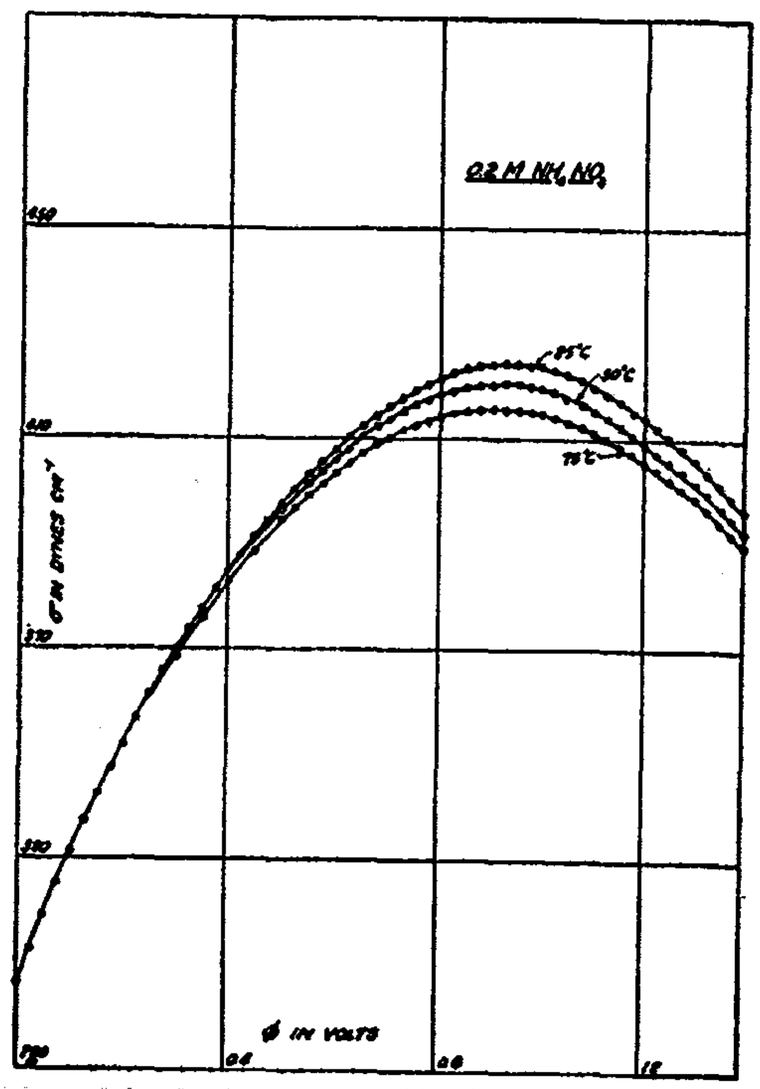

FIG. 3. ELECTROCAPILLARY CURVES FOR 0.2 *M* AMMONIUM NITRATE SOLUTION AT 25°, 50°, AND 75°C.

TABLE 2

Data for 0.2 M ammonium nitrate solution at 25°C.

ϕ	σ OBSERVED	σ CALCULATED	DEVIATION	DEVIATION SQUARED
volts	*dynes cm.*$^{-1}$	*dynes cm.*$^{-1}$		
0.825	422.81	422.81	0.00	0.0000
0.850	423.59	423.52	−0.07	0.0049
0.875	424.06	424.06	0.00	0.0000
0.900	424.30	424.39	+0.09	0.0081
0.925	424.49	424.54	+0.05	0.0025
0.950	424.49	424.51	+0.02	0.0004
0.975	424.34	424.29	−0.05	0.0025
1.000	424.02	423.88	−0.14	0.0196
1.025	423.28	423.28	0.00	0.0000
1.050	422.41	422.48	+0.07	0.0049
			−0.03	0.0429

σ (max.) = 424.49 dynes cm.$^{-1}$ ϕ (max.) = 0.933 volt

$$\sigma = 293.52 + 280.96\phi - 150.60\phi^3$$

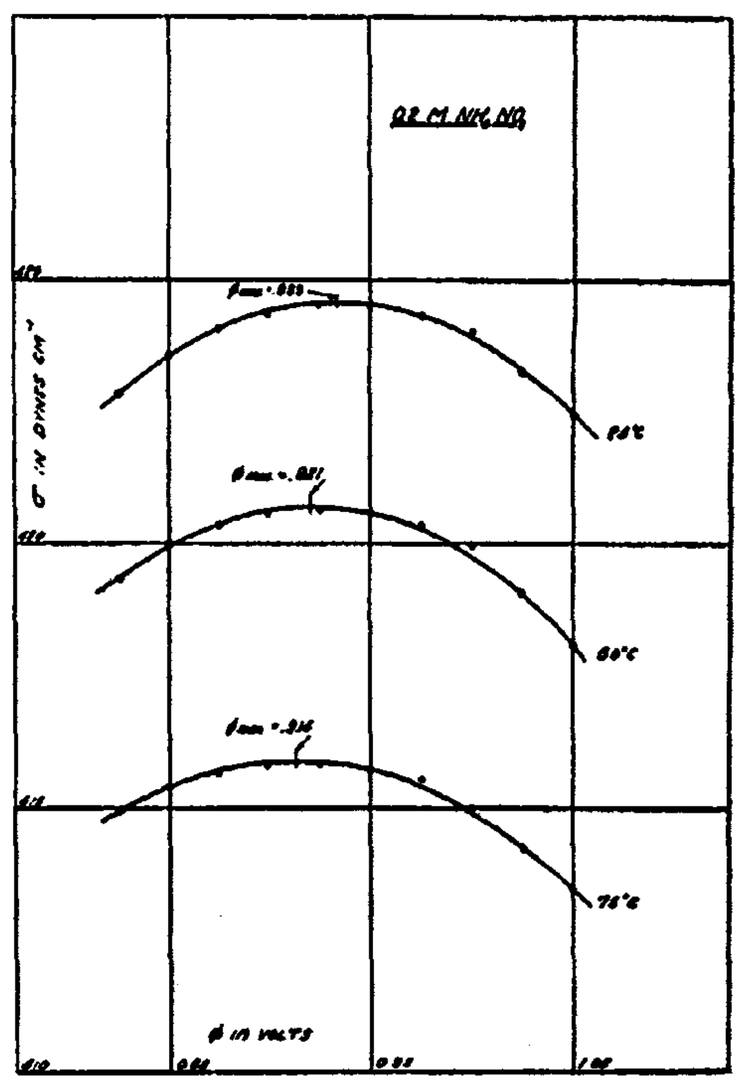

FIG. 4. ELECTROCAPILLARY CURVES FOR 0.2 *M* AMMONIUM NITRATE SOLUTION IN THE REGION OF THE MAXIMA OF THE CURVES AT 25°, 50°, AND 75°C.

In measurements carried out at 27.5°C., the potential of the 1.0 *M* ammonium nitrate solution in contact with mercury with respect to the normal calomel electrode was found to be 0.338 volt, that of the 0.2 *M* solution 0.385 volt, and that of the 0.02 *M* solution 0.414 volt.

TABLE 3

Summary of electrocapillary data

SOLUTION	TEMPERATURE	ϕ(max.)	$\frac{\partial\sigma(\text{max.})}{\partial T}$	$\frac{\partial\phi(\text{max.})}{\partial T}$
	°C.	*volts*	*dynes cm.*$^{-1}$ *degree*$^{-1}$	*volts degree*$^{-1}$
1.0 *M* NH_4NO_3	25	0.887		
1.0 *M* NH_4NO_3	50	0.862	−0.12	−0.00100
1.0 *M* NH_4NO_3	75	0.846	−0.15	−0.00064
0.2 *M* NH_4NO_3	25	0.933		
0.2 *M* NH_4NO_3	50	0.921	−0.16	−0.00048
0.2 *M* NH_4NO_3	75	0.914	−0.19	−0.00028
0.02 *M* NH_4NO_3	25	0.961		
0.02 *M* NH_4NO_3	50	0.961	−0.16	−0.0000
0.02 *M* NH_4NO_3	75	0.953	−0.19	−0.00032

TABLE 4

Electrical capacity data for 0.2 M ammonium nitrate solution at constant potential values

ϕ	$\frac{d\sigma}{d\phi}$ IN COULOMBS CM.$^{-1}$ × 10^7		
	At 25°C.	At 50°C.	At 75°C.
0.825	32.47	28.61	22.71
0.850	24.94	21.21	16.34
0.875	17.41	13.74	9.97
0.900	9.88	6.27	3.60
0.925	2.35	−1.20	−2.77
0.950	−5.18	−8.67	−9.13
0.975	−12.71	−16.14	−15.50
1.000	−20.24	−23.61	−21.87
1.025	−27.77	−31.08	−28.24
1.050	−35.30	−38.55	−34.61

The Lippmann equation for the electrocapillary curve is $\frac{d\sigma}{d\phi} = \epsilon$, where ϵ is the electrical capacity of the surface at constant potential. The value of ϵ can be calculated from the slope of the electrocapillary curve. If the equations for these curves, $\sigma = a + b\phi - c\phi^2$, are differentiated with respect to ϕ, values of ϵ are obtained. Data of this sort are presented in table 4.

DISCUSSION

For discussion it is convenient to divide the electrocapillary curves into three parts, an ascending branch, a maximum, and a descending branch.

The ascending branch

Along the ascending branch the mercury is positively charged and, as a result, there is an excess of anions in the water side of the interface. From an inspection of figure 3 it would appear that a change in temperature has

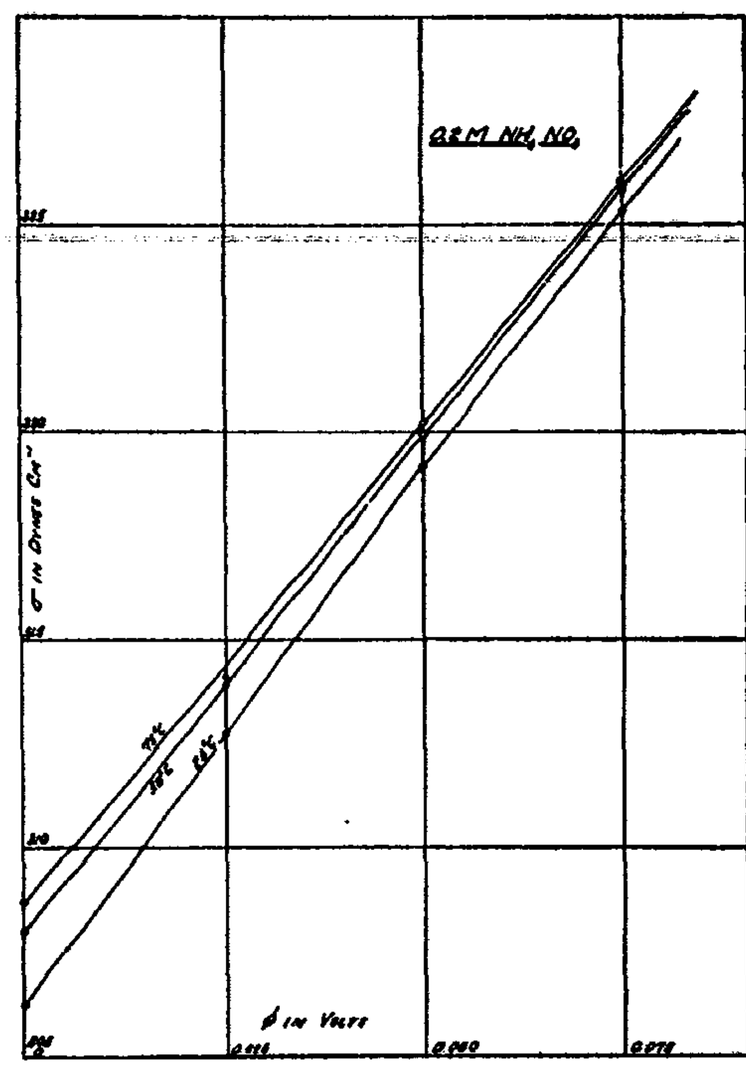

FIG. 5. ELECTROCAPILLARY CURVES FOR 0.2 *M* AMMONIUM NITRATE SOLUTION IN THE REGION OF THE ORIGIN OF THE CURVES AT 25°, 50°, AND 75°C.

no effect on the position of the first portions of the ascending branch of the curve. However, if these portions of the ascending branches are plotted on a larger scale, as shown in figure 5, it is observed that at the higher temperatures the interfacial tension values are higher. As the applied potential difference is increased the curves cross each other in such a manner that, at the higher temperatures, the interfacial tensions eventually become lower. This can be explained in the following manner (10). There are two factors operative. An increase in thermal agitation serves to lower the interfacial tension, and an increase in temperature decreases

the adsorption of mercury salt and acts to increase the interfacial tension. It is apparent that the effect of the adsorption is the more important one near the origin of the curves, but as the curves rise the effect of thermal agitation becomes more and more important and eventually causes reversal in the position of the curves.

The maximum

At the maximum of the electrocapillary curve the charge on the mercury should be zero, but Gouy (7) considered that additional ions will be present on the surface if they are capillary-active, so that at the maximum of the electrocapillary curve there may be still a considerable potential difference between the solution and the mercury due to this layer of capillary adsorbed ions. According to Freundlich (2), if the anions are capillary-active, the mercury must carry a negative charge at the maximum in order to balance the tendency of anion adsorption. In the same way, with capillary-active cations present the mercury must have a positive charge at the maximum.

It will be observed from an inspection of table 3 that the values of ϕ (max.) for the ammonium nitrate solutions become smaller as the temperature is increased. This is consistent with expectation and in agreement with the results published by Koenig (10) for potassium nitrate solutions. Formally, the situation may be discussed with the use of the equation,

$$\phi = \phi_{ref.} - \phi_P \tag{1}$$

in which $\phi_{ref.}$ is the potential of reference, and ϕ_P may be described as the potential of the double layer at the polarized electrode. For the temperature variation of the maximum we have,

$$\frac{\partial\phi(\text{max.})}{\partial T} = \frac{\partial\phi_{ref.}}{\partial T} - \frac{\partial\phi_P}{\partial T} \tag{2}$$

Contributions to ϕ_P result from the presence in the interface of ions and dipole molecules; in addition, the distribution of electrons and mercury ions in the charged surface of the metal itself is a factor.

At the present time it is impossible to determine ϕ_P and $\frac{\partial\phi_P}{\partial T}$ with any degree of accuracy, because the available methods for the estimation of $\phi_{ref.}$ and $\frac{\partial\phi_{ref.}}{\partial T}$ are not entirely satisfactory. But even if ϕ_P and $\frac{\partial\phi_P}{\partial T}$ could be determined, it would be a matter of extreme difficulty to separate the amounts contributed by the three factors,—ions, dipoles, and metal. For solutions of ammonium nitrate there are good reasons to believe the contributions of both ions and dipoles to be finite. In the maximum region of the curve the double layer at the interface contains some adsorbed

anions. It also contains water molecules which are partially oriented in such a way that the negative end of the dipole is turned toward the mercury side of the interface. Now, since increasing temperature favors a decrease in the adsorption of anions and tends to increase the randomness of any effective orientation, a shift of the position of ϕ (max.) toward smaller values with increase in temperature is explained. As would be expected, the actual value of the interfacial tension decreases with increasing temperature and the entire curve is flattened out.

From the observed vertical shift of the maximum with concentration of added ammonium nitrate, calculations can be made for the surface densities at the maximum, Γ (max.), in equivalents per unit area ($\overline{\text{cm}}.^2$), by using

TABLE 5

Surface density data for ammonium nitrate solutions

T IN °C.	$\Gamma^{(max.)}_{NH_4NO_3}$ 1.0 M – 0.2 M NH_4NO_3	$\Gamma^{(max.)}_{NH_4NO_3}$ 0.2 M – 0.02 M NH_4NO_3
25	5.3×10^{-11}	1.0×10^{-11}
50	3.7×10^{-11}	0.7×10^{-11}
75	1.9×10^{-11}	0.6×10^{-11}

an equation of Gibbs. The chemical potential of the electrolyte, $\mu_{NH_4NO_3}$, is defined by the expression,

$$\mu_{NH_4NO_3} = \text{Const.} + RT \ln C_{NH_4^+} \cdot f_{NH_4^+} + RT \ln C_{NO_3^-} \cdot f_{NO_3^-}$$

Therefore,

$$d\mu_{NH_4NO_3} = 2\,RT\, d \ln C_{NH_4NO_3} \cdot f_{NH_4NO_3} = 2\,RT\, d \ln a_{NH_4NO_3}$$

The equation of Gibbs, in the form assigned it by Koenig (8), is

$$\frac{\partial\sigma(\text{max.})}{\partial\mu_{NH_4NO_3}} \cong -\,\Gamma^{(max.)}_{NH_4NO_3}$$

The numerical results of table 5 for $\Gamma^{(max.)}_{NH_4NO_3}$ have been obtained from graphs in which logarithms of ammonium nitrate activity were plotted as a function of the maximum interfacial tensions. The surface densities are seen to decrease with an increase in temperature and with a decrease in concentration. Also, since

$$\frac{\partial\sigma\ (\text{max.})}{\partial\mu_{NH_4NO_3}}$$

is negative, we may conclude that ammonium nitrate is a capillary-active electrolyte.

The descending branch

Along the descending branch the mercury side of the interface acquires a greater and greater negative charge and the anions are replaced by cations at the interface. In figure 3 it is observed that the descending branches of the electrocapillary curves are more or less uniformly displaced with a change in temperature. Higher temperatures lower the interfacial tension.

The effect of a change in concentration of ammonium nitrate on the position of the descending branch of the curve is shown in figure 2. As the concentration of the ammonium nitrate is lowered, the interfacial tension for equal values of applied potential increases. It was shown by Frumkin (4), and later by Koenig (8), that one can predict the effect of a change in concentration of the electrolyte on the shape of the electrocapillary curve. According to Gibbs there exists a simple relationship between the adsorbed quantity of a substance and the change of surface tension with concentration, which is expressed by the equation

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\ln a} \tag{3}$$

In this expression Γ is the excess of the solute in gram-moles per square centimeter of the dividing surface, a is the effective concentration or activity of the solute, and σ is the surface tension. Frumkin has shown that the equation for the electrocapillary curve can be written in the form,

$$d\sigma = \epsilon d\phi - \Sigma\Gamma_i d\mu_i \tag{4}$$

where μ_i is the chemical potential of the ith species present at the interface. It can be shown from equations 3 and 4 that

$$\left(\frac{\partial\phi}{\partial\ln a}\right)_\sigma = \frac{RT}{F}\frac{\Gamma_A + \Gamma_K}{n_A\Gamma_A - n_K\Gamma_K} \tag{5}$$

Here the subscripts A and K refer to the anion and cation, respectively, and n represents the valence of the ion. Along the descending branch of the curve only the cations are adsorbed at the interface, therefore the terms referring to the anions can be neglected, and we obtain the equation

$$\left(\frac{\partial\phi}{\partial\ln a}\right)_\sigma = \frac{RT}{n_K F}$$

When integrated between limits this equation gives

$$\phi_2 - \phi_1 = \frac{RT}{n_K F}\ln\frac{a_2}{a_1} \tag{6}$$

In a similar manner one obtains the following expression for the ascending branch.

$$\phi_2 - \phi_1 = \frac{RT}{n_A F} \ln \frac{a_2}{a_1} \tag{7}$$

Equation 7 has not been applied with any degree of success because anions are usually capillary-active.

The application of equation 6 to the data for the ammonium nitrate solutions now can be illustrated. There are given in table 6 values calculated for the quantity $\frac{RT}{n_K F} \ln \frac{a_2}{a_1}$ at 25°, 50°, and 75°C., together with observed values of $\phi_2 - \phi_1$. The data may be considered to confirm the identity required by the equation.

TABLE 6

Electrocapillary data for 0.02 and 0.2 M ammonium nitrate solutions

AT 25°C.		AT 50°C.		AT 75°C.	
σ	$\phi_2 - \phi_1$	σ	$\phi_2 - \phi_1$	σ	$\phi_2 - \phi_1$
410	0.041	410	0.051	405	0.054
405	0.039	405	0.053	400	0.054
400	0.043	400	0.053	395	0.054
395	0.047	395	0.055	390	0.051
390	0.048	390	0.051	385	0.053
385	0.044	385	0.053	380	0.053
380	0.043			375	0.057
Average =	0.044	Average =	0.053	Average =	0.054
$-\frac{RT}{F} \ln \frac{a_2}{a_1}$ =	0.053	$-\frac{RT}{F} \ln \frac{a_2}{a_1}$ =	0.058	$-\frac{RT}{F} \ln \frac{a_2}{a_1}$ =	0.062

Activity coefficient data of Scatchard and Prentiss (12), obtained by the freezing point method, have been used in our calculations. It was necessary to assume these coefficients to be constant over the entire temperature range.

SUMMARY

1. A modified Lippmann electrometer was designed and built. With this apparatus electrocapillary curves were obtained for 1.0 molar, 0.2 molar, and 0.02 molar aqueous ammonium nitrate solutions at the temperatures 25°, 50°, and 75°C. The position of the maximum in each curve was located by means of an analytical procedure.

2. An explanation based upon the capillary activity of the ammonium

nitrate has been presented for the displacement of these curves toward lower values of interfacial tension with increase in temperature and with increase in concentration.

3. A displacement of the maxima of the curves toward lower values of applied potential at the higher temperatures has been partially accounted for on the basis of a decreased adsorption of anions and an increased tendency toward random distribution of solvent dipoles caused by the rise in temperature.

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OBSERVATIONS ON THE EFFECT OF MECHANICAL AGITATION ON ELECTRODE POTENTIAL[1]

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Received June 14, 1934

I. INTRODUCTION

The effect of mechanical agitation on the potential of an electrode immersed in an electrolyte solution is of interest because of its bearing on electrokinetics. In the experiments hitherto carried out on this effect the mechanical agitation has been produced in three different ways: (i) by moving the electrode (15, 6); (ii) by moving the electrolyte (3); (iii) by scraping the surface of contact between the electrode and the electrolyte with some suitable foreign body (2). In this note only the first two methods are considered.

The effect is conveniently described in terms of the quantity $\Delta\varphi$ given by

$$\Delta\varphi = \varphi_m - \varphi_r \tag{1}$$

where φ_r is the electric potential of the electrode with respect to the solution when the system is at rest, and φ_m the potential when the system is subjected to agitation. The quantity $\Delta\varphi$ can evidently be measured by means of a suitable reference electrode.

In recent years the quantities $\Delta\varphi$ have been extensively investigated for various metal electrodes in various electrolyte solutions by Stephan Procopiu (15, 16). This author does not describe his procedure in detail, but seems to have used method i exclusively, the electrode being attached to the armature of an electromagnetic vibrator. Procopiu's conclusions may be summarized by the equation

$$-\Delta\varphi = \zeta \tag{2}$$

where ζ is the electrokinetic potential of the electrode in the solution in question, defined in the usual manner. Equation 2 may be called the "electrokinetic theory" of the effect.

It is possible to account for equation 2 by making a number of assumptions as to the mechanism of the effect. Let that part of the double layer which, in the usual electrokinetic phenomena of electrosmosis etc., is

[1] Presented before the Eleventh Colloid Symposium, held at Madison, Wisconsin, June 14–16, 1934.

displaced relative to the solid phase be called the mobile part; it extends from the "rigidity boundary" (12) out into the interior of the solution and contains a certain net electric charge, say $-\sigma$ coulombs $\times$ cm^{-2}. It is assumed (i) that the mobile part of the double layer is completely removed by the mechanical agitation, thereby removing $-\sigma$ coulombs $\times$ cm^{-2}. of charge from the liquid side of the rigidity boundary, (ii) that the electroneutrality (10) of what is left of the double layer is restored by the simultaneous disappearance of $+\sigma$ coulombs $\times$ cm^{-2}. from the solid side of the rigidity boundary. As a result the potential of the electrode with respect to the solution will be changed by an amount

$$\Delta\varphi = \varphi_m - \varphi_r$$

which is such that σ and $-\Delta\varphi$ have the same sign (if $\sigma \lesseqgtr 0$, then $\Delta\varphi \gtreqless 0$). But from the definition of ζ it follows that σ and ζ have the same sign (if $\sigma \lesseqgtr 0$, then $\zeta \lesseqgtr 0$). Hence it follows from assumptions i and ii that ζ and $-\Delta\varphi$ have the same sign (if $\zeta \lesseqgtr 0$, then $\Delta\varphi \gtreqless 0$). Finally it is assumed (iii) that $-\Delta\varphi$ and ζ have also the same magnitude.[2] It is to be noted that the picture contained in assumptions i and ii implies that the effect is qualitatively of an entirely different kind from the usual electrokinetic effects, in which the mobile part of the double layer is not removed, but is displaced parallel to itself without disturbance of its average structure.

The validity of equation 2 is a question of some importance on account of the uncertainty (11) of the ζ values calculated from the usual electrokinetic measurements and the special difficulty of obtaining such measurements for metals. The uncertainty of the ordinary ζ values also makes it impossible to test equation 2 rigorously. Nevertheless, the best that can be done at the present time is to compare $\Delta\varphi$ and ζ for the same system, the ζ being obtained in the usual way. To this end Procopiu (16) has compared his $\Delta\varphi$ values for the metals platinum, silver, copper, bismuth, lead, and iron in water, with the ζ values obtained by Burton (5) from the electrophoretic velocities of colloidal particles of the same metals in water. For the metals silver and lead good agreement was found between $-\Delta\varphi$ and ζ, the metals platinum and iron agreed in sign but not in magnitude, and finally copper showed a discrepancy in both sign and magnitude. The deviations from equation 2 found here may be due to the fact that the colloidal metal particles, owing to their method of preparation, are in many cases covered with a layer of oxide or hydrated oxide (14). The comparison is therefore not decisive, and there are to the author's knowl-

[2] This picture of the electrokinetic theory of the effect differs in several features from that of Procopiu (16).

edge no other data available which could lead to a similar comparison. What evidence does exist for equation 2 is therefore even more incomplete than that obtainable from a comparison of the usual calculated ζ values with $\Delta\varphi$. This evidence may be summarized under three heads: (i) The observed $\Delta\varphi$ values are always of the same order of magnitude as the ζ values calculated from the usual electrokinetic data. (ii) For the metals silver, platinum, nickel, lead, iron, and zinc in water the sign of $-\Delta\varphi$ is the same as that of ζ as found by Burton (5) or by Coehn and Schafmeister (7). (iii) The curves obtained by Procopiu (16) for $\Delta\varphi$ as a function of the electrolyte concentration, c, have the same general shape as the familiar $\zeta - c$ curves (extrema, isoelectric points).

The chief purpose of this note is to suggest that the electrokinetic theory is not the only possible explanation of the effect, a reasonable alternative being the theory that irreversible chemical reactions at the electrode are partly or wholly responsible. The following observations lend support to this idea.

II. EXPERIMENTS

The electrodes used in the experiments were of pure soft silver wire about 1 mm. in diameter, of the sort used as anode in a silver coulometer. The mechanical agitation was produced both by causing the electrode to vibrate (method i) and by stirring the solution (method ii). The vibrating electrode was made by soldering a copper lead onto one end of a 4-cm. piece of the silver wire and then sealing the silver wire with DeKhotinsky cement into one end of a Pyrex tube 3 mm. in diameter and 8 cm. long, in such a way that about 2 cm. of the silver wire projected beyond the seal. The copper lead was passed out through a small hole blown through the wall of the glass tube near its other end, which was attached, also by means of deKhotinsky cement, to the arm of a vibrator made by sawing off the gong and the clapper from a small electric bell. Three such electrodes were prepared; they all gave the same results. Before use, the silver electrodes were always thoroughly polished first with dry rouge and filter paper and finally with dry filter paper alone to remove traces of the rouge.

The solution into which the electrode dipped was contained in a short-necked wide-mouthed 200-cc. flask. Dipping into the latter were, besides the vibrating electrode, a glass stirrer run by a small A.C. motor of 2000 R.P.M. and finally a glass siphon leading to another flask of the same solution, into which the snout of the reference electrode, a calomel electrode with 3.5 N potassium chloride, was immersed. With this arrangement the effects of vibrating and stirring could be studied side by side on the same system.

The potentials were measured with a Type K potentiometer in conjunction with a Leeds and Northrup HS galvanometer.

Preliminary experiments showed that only such solutions as enter into a fairly definite and reproducible electrochemical equilibrium with the silver give even approximately reproducible $\Delta\varphi$ values. Thus in an attempt to check Procopiu's (16) value, $\Delta\varphi = 15$ millivolts for silver in 0.2 N sulfuric acid, values were obtained lying anywhere between 6 and 30 millivolts depending on the length of time the electrode was allowed to remain immersed in the solution. Except where otherwise stated, the following experiments were carried out with potassium chloride solutions of various concentrations, saturated with silver chloride.

1. *Nature of the vibration effect in time*

A few minutes after the silver electrode is plunged into a potassium chloride solution saturated with silver chloride, it reaches a state in which

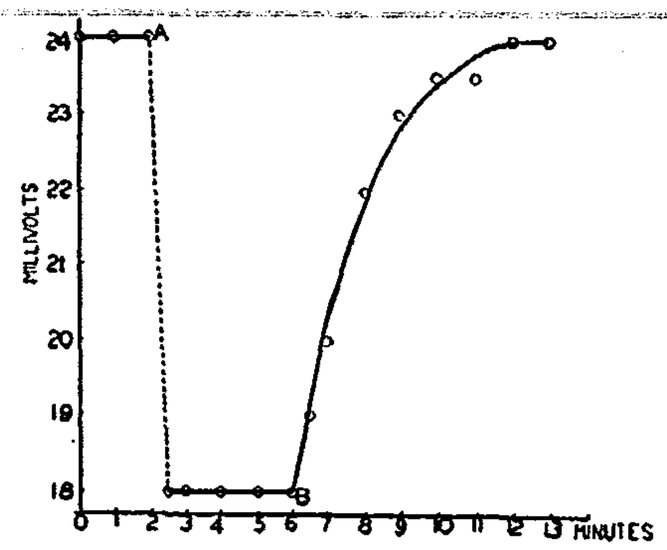

FIG. 1. E.M.F. OF THE CELL Ag|3.0 M KCl SATURATED WITH AgCl|3.5 N KCl SATURATED WITH HgCl|Hg, AS A FUNCTION OF THE TIME

A, vibration started; B, vibration stopped. The silver electrode is the negative pole, so that $\Delta\varphi>0$.

its potential changes less than 0.0001 volt per minute and may be regarded as constant. If then the electrode is caused to vibrate, its potential *immediately* increases ($\Delta\varphi > 0$) to a new practically constant value which is maintained as long as the vibration lasts. On stopping the vibration the potential *gradually*, during the course of five to eight minutes, returns to the value before vibration. Figure 1, showing an experiment with 3.0 N potassium chloride, illustrates this behavior. $\Delta\varphi$ is always taken as the difference (with proper sign) between the steady values.

2. *Dependence of $\Delta\varphi$ on the frequency of the vibrator*

From the sound of the vibrator it was evident that its frequency increased with the voltage used to run it. Figure 2, in which the observed $\Delta\varphi$ for 1.0 N potassium chloride is plotted against the voltage applied to

the vibrator, is typical of all the experiments with potassium chloride solutions and shows that $\Delta\varphi$ increases somewhat with the frequency, at least up to 6 volts. The application of 10 volts to the vibrator caused a sudden jump in frequency of two octaves. This increase in frequency in no case changed the $\Delta\varphi$ values appreciably from those obtained at 6 volts. This fact makes it probable that the $\Delta\varphi$ for 6 volts is practically a "saturation value." It is this "saturation value" which was always taken as the

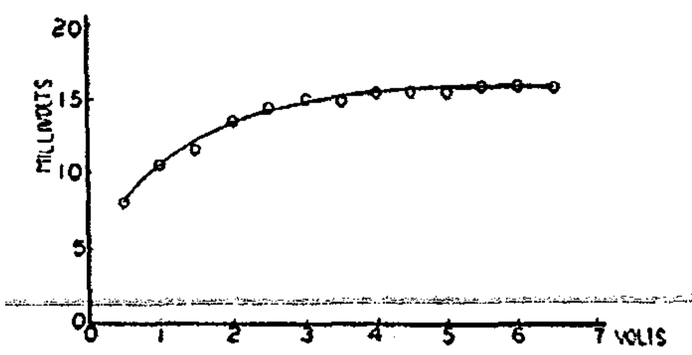

FIG. 2. $\Delta\varphi$ FOR 1 N KCl SATURATED WITH SILVER CHLORIDE, AS A FUNCTION OF THE VOLTAGE APPLIED TO THE VIBRATOR

TABLE 1

$\Delta\varphi$ values as a function of the potassium chloride normality

c, MOLES OF KCl PER LITER OF SOLUTION	$\Delta\varphi$
	millivolts
10^{-3}	27 ± 2
10^{-2}	25 ± 2
10^{-1}	32 ± 2
1.0	17 ± 2
3.0	6 ± 2

$\Delta\varphi$ of the system. For a potassium chloride solution of a given concentration the $\Delta\varphi$ so obtained is reproducible to ± 2 millivolts.

3. *The $\Delta\varphi$ — c curve*

Table 1 gives the $\Delta\varphi$ values obtained by vibration, as a function of the potassium chloride normality, c. Each of the $\Delta\varphi$ values is the average of nine experiments (three electrodes, three sets of solutions). Figure 3 shows $\Delta\varphi$ plotted against log c. Each of the five points is represented by a vertical line indicating the limits of reproducibility of $\Delta\varphi$ (± 2 millivolts). The curve has the general characteristics of the familiar ζ — c curves.

4. *The effect of stirring*

If the solution is stirred, as described above, an effect of the same sign as that produced by vibration of the electrode results. The $\Delta\varphi$ increases

slightly with the rate of stirring, but the values obtained for the maximum rate of 2000 R.P.M. were 2 to 5 millivolts less, in the different solutions, than the maximum vibration values given in the above table.

5. *Effect of the removal of air*

The stirring experiment was carried out in an atmosphere of nitrogen as follows. Nitrogen from a tank was purified by passing it first through a strongly alkaline solution of sodium anthraquinone-β-sulfonate and sodium hyposulfite, then over dry calcium chloride, and finally over copper gauze at a dull red heat. An apparatus was set up in which the potassium chloride–silver chloride solutions to be investigated could be boiled and cooled while the pure nitrogen was bubbled through them, and then forced into a stoppered flask, previously filled with nitrogen and containing a glass stirrer introduced through an air-tight mercury seal, a silver electrode, and

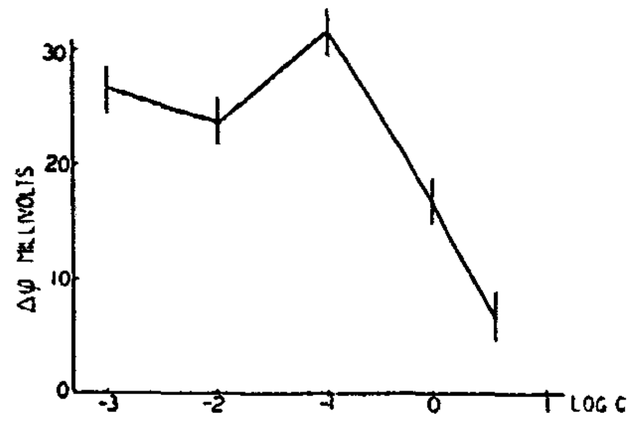

FIG. 3. $\Delta\varphi$ FOR KCl SOLUTIONS SATURATED WITH SILVER CHLORIDE, AS A FUNCTION OF THE LOGARITHM OF THE POTASSIUM CHLORIDE NORMALITY, c

a siphon to the reference electrode. It was found that stirring gave $\Delta\varphi$ values of the same magnitude as in the presence of air, but that when, after conclusion of the experiment in nitrogen, air was bubbled through the solutions, the potential φ_r of the silver electrode at rest increased by 3 to 5 millivolts. That is, the $\Delta\varphi$ effect persists when the air is replaced by nitrogen, but the silver electrode at rest is more positive in the presence of air than of pure nitrogen.

6. *Effect of sodium bisulfite*

The addition of 1 g. of sodium bisulfite to 100 cc. of potassium chloride solution caused the complete disappearance of the effect in solutions of all concentrations up to 3 N.

7. *Silver nitrate solutions*

Finally, the effect of vibration and stirring was investigated with the silver electrodes immersed in silver nitrate solutions. It was found that $\Delta\varphi = 0$ for silver nitrate concentrations between 10^{-3} N and 1 N.

III. DISCUSSION

The above observations can all be qualitatively explained either by the electrokinetic theory described above or by the following "chemical theory." It is assumed that the silver immersed in potassium chloride solutions saturated with silver chloride tends towards electrochemical equilibrium not only with respect to the Ag^+ ions:

$$Ag^+ \text{ (metal)} \rightleftharpoons Ag^+ \text{ (solution)}$$

but also with respect to the dissolved oxygen:

$$4OH^- \text{ (solution)} \rightleftharpoons 2H_2O \text{ (solution)} + O_2 \text{ (solution)} + 4\ominus \text{ (metal)}$$

i.e., the silver metal functions also as an oxygen electrode, and is therefore the more positive the greater the concentrations of dissolved oxygen in its immediate neighborhood. It is furthermore assumed that the following irreversible chemical reaction:

$$4Ag \text{ (metal)} + 4H^+ \text{ (solution)} + 4Cl^- \text{ (solution)} + O_2 \text{ (solution)} = 4AgCl \text{ (solid)} + 2H_2O \text{ (solution)}$$

is always proceeding slowly at the metal surface. This reaction tends to decrease the concentration of dissolved oxygen in the immediate neighborhood of the electrode. Vibrating and stirring aid diffusion and therefore keep the oxygen concentration closer to its value in the bulk of the solution, thus producing a positive $\Delta\varphi$.

That an oxygen electrode effect is present at the silver surface in potassium chloride solutions saturated with silver chloride is rendered fairly certain by observation 5 above, that the electrode is more positive in the presence of air than of pure nitrogen. That $\Delta\varphi$ nevertheless persists after boiling out the solutions in a current of pure nitrogen may be due to the fact that it is impossible to remove dissolved oxygen completely by this method. Sodium bisulfite, on the other hand, is known to remove the last traces of oxygen from a solution, so that the chemical theory is confirmed by observation 6.

When the silver-ion concentration is appreciable compared with the concentration of dissolved oxygen, the effect of the latter on the electrode potential is negligible compared with that of the former. The chemical theory therefore predicts $\Delta\varphi = 0$ for silver nitrate solutions of moderate concentrations, in accordance with observation 7. In this connection it is to be noted that Henry (9), using the method of the deflection of thin wires in an electric field, found practically zero deflection for the system silver–silver nitrate, but whether this means that ζ is really zero or merely that the specific conductivity of the wire is large compared with that of the solution (1) is not certain.

Regarding the effect of stirring (observation 4), it is to be noted that this effect implies a conflict between the electrokinetic theory of $\Delta\varphi$ and the generally accepted ideas as to the kinetics of heterogeneous reactions. According to the latter, there is generally at the surface of a solid in contact with a solution an unstirrable liquid film (4, 8, 13). If this is true, then the mobile part of the double layer cannot, as demanded by the electrokinetic theory, be removed by stirring, and $\Delta\varphi$ should be zero. From the point of view of the chemical theory there is evidently no conflict of this sort.

Regarding observation 1, it may be noted that practically nothing is known regarding the time necessary for the formation of the mobile part of the double layer. It is no doubt greater than the time required for the formation of an ionic atmosphere ("relaxation time"), which is of the order of $\frac{10^{-10}}{c}$ seconds. But that it should be a matter of minutes seems improbable. The time effect shown in figure 1 would therefore seem to favor the chemical rather than the electrokinetic theory.

It is of course possible that the observed effects result from an overlapping of electrokinetic and chemical processes rather than from either kind of process alone. Finally, it is worth mentioning that the idea that chemical reactions involving dissolved gases are at least partly responsible for $\Delta\varphi$ is strongly supported by the observations of Charmandarjan and Peruschwin (6), who studied the electric current which flows from a platinum electrode agitated in a solution of sulfuric acid, hydrochloric acid, nitric acid, oxalic acid, or phosphoric acid to another platinum electrode at rest in the same solutions. It was found that the magnitude and, for hydrochloric acid, even the sign of the current is different depending on whether or not the solution has been subjected to electrolysis before the measurement.

IV. SUMMARY

The electrokinetic theory of the effect of mechanical agitation upon electrode potential is critically discussed. It is pointed out that this theory is not the only possible explanation, an alternative being the theory that irreversible chemical processes are partly or wholly responsible for the effect. Experiments with silver electrodes in potassium chloride solutions saturated with silver chloride and in silver nitrate solutions are described which lend support to the chemical theory of the effect.

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ELECTROKINETIC POTENTIAL OF SILVER IODIDE

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Received June 15, 1934

I. INTRODUCTION

It might be assumed that the electrokinetic potential of halogen salts of silver against pure water would be zero. However, Labes (8), Mukherjee and Kundu (12), Kruyt and Van der Willigen (7), Lange and Crane (9), and Basinski (3) have shown that the electrokinetic potential, ζ, of these salts (in particular, silver iodide) at the point of equivalence, i.e., at equal concentrations of silver and of halogen ions in solution, has a rather considerable negative value. Zero value of the electrokinetic potential was attained only by having a rather considerable excess of silver ions in solution. At higher concentrations of the soluble silver salt the silver halide is charged positively, but on subsequent dilution of the solution with water the potential falls to lower values and finally becomes negative.

This phenomenon is not confined to silver halides. Lottermoser and Riedel (10) consider the negative charge in pure water to be proper to all substances and confirmed this with many examples.

Labes, Mukherjee and Kundu, as well as Lange and Crane, measured the potential by the rate of the endosmosis, that is, on the boundary of the coarsely dispersed silver halide, while only the last authors measured systematically the whole curve of the dependence of ζ-potential of silver iodide on the concentration of the excess ion constituting the lattice of the salt (silver ion or iodide ion). In other researches electrophoresis of sols was used, but the data obtained were either only approximate or concerned with the influence of the dilution with water on the ζ-potential of the positively charged sol, i.e., the simultaneous change and concentration of the electrolyte and the concentration of the dispersed substance.

My aim has been to measure the curve ζ-potential–concentration of electrolyte, similar to that one obtained by Lange and Crane, but with sols of highly dispersed silver iodide.

II. METHOD OF ζ-POTENTIAL DETERMINATION

ζ-potentials were determined by rate of the electrophoresis of sol observed through an ultramicroscope. The method was that of P. Tuorila (14). Observations were made with the help of the slit ultramicroscope of

C. Zeiss. The cell used was pasted together by means of picein; it contained two platinum electrodes and a tightly fitting glass cover.

The distance between the electrodes was 35 mm., and the depth of the cell 5 mm. On the upper side of the cell a slight scratch was made with a diamond. The cell was set on the vertically displaceable stage of the microscope, and the latter was focused first on the scratch and then on the illuminated layer of sol. If the displacement of the microscope tube, D, is known as well as the true thickness of the glass plate, d, then the thickness of the layer of liquid between the inner surface of the upper glass and the plane under observation will be as follows:

$$x = \frac{n_1}{n_2}D - \frac{d}{n_2}$$

where n_1 and n_2 are the refractive indices at the interfaces glass–exterior medium and glass–sol. Since the objective was used with water immersion, we may put $n_1 - n_2 = n_{H_2O}$

$$x = D - \frac{d}{n_{H_2O}}$$

where $\frac{d}{n_{H_2O}}$ = the optical thickness of the plate, is established.

The observed velocity of electrophoresis of the dispersed phase at different distances from the walls of the cell is the algebraic sum of the true velocity and of that of endosmose of the solution relative to the walls of the cell.

According to Smoluchovsky (13) the velocity of endosmose in the closed cell at the distance x from one of the two parallel sides distant l apart is:

$$U_x = U_0\left[1 - 6\left(\frac{x}{l} - \frac{x^2}{l^0}\right)\right]$$

where U_0 is the velocity of endosmose close to a side. The rate of motion of the particles observed by the ultramicroscope is equal to velocity of electrophoresis, v, at the depth where $U_x = 0$, i.e., when

$$\frac{x}{l} = \frac{1}{2} \pm \frac{1}{2\sqrt{3}}$$

or $x_1 = 0.211l$ and $x_2 = 0.789l$.

The parabolic curve of Smoluchovsky's function near this "neutral layer" is nearly a straight line. Hence, by measuring the velocity of motion of particles in the electric field, once at a depth somewhat smaller and then at one greater than $0.211l$, it is possible to find the true velocity of electrophoresis, v, by interpolation.

A difference of potentials of about 12 volts was applied to the electrodes, about 3.5 volts per centimeter. By means of a stop watch the time of passing of the observed particle between two selected divisions of the ocular-micrometer was measured, first in the field, where the positive pole was on the left, second, in the case of short-circuited electrodes (for in a wide cell there are always curious, partly convectional currents of liquid, more or less constant in velocity), and lastly in the reversed field. Measurements of this kind were repeated at both depths four to seven times.

The potential was calculated with the usual equation for spherical particles, due to Debye and Hückel:

$$\zeta = \frac{6\pi\eta}{HD} v$$

where η is the viscosity, taken as the viscosity of pure water, H is the potential gradient, and D is the dielectric constant, considered equal to 81.

Sols were prepared in the following way. To 37.5 cc. of the solution of one of the electrolytes (potassium iodide or silver nitrate) during exactly 3 minutes and with constant stirring, 12.5 cc. of the second electrolyte was added. The mixture was made in yellow light. The sol was violently shaken and left standing for three to four hours in order to attain a state of comparative equilibrium. After that the ζ-potential was measured.

Two series of experiments were undertaken with three different concentrations of silver iodide in each, viz., $M/400$, $M/4000$, and $M/20{,}000$.

These two series were made at different times and differed from each other by the following conditions: (1) In the first series common distilled water was used, while the water used for the second series was carefully distilled three times through a silver condenser. (2) In the first series, sols were made in such a way that the first solution (37.5 cc.) contained that electrolyte of which there was an excess, while in the second series that electrolyte was used one of the ions of which communicated the charge to sol, which fact was discovered from the results of the first series.

Experiments showed that the potential did not change with time.

$M/4000$ AgI, 10^{-5} M KI	After 2 hours	= −50 mv.
	After 48 hours	= −56 mv.
$M/400$ AgI, 10^{-4} M $AgNO_3$	After 3 hours	= +38 mv.
	After 48 hours	= +37 mv.
$M/20{,}000$ AgI, 10^{-4} M $AgNO_3$	After 3 hours	= −25 mv.
	After 24 hours	= −26 mv.
$M/400$ AgI, 10^{-5} M KI	After ¼ of an hour	= −45 mv.
	After 5½ hours	= −48 mv.

III. POTENTIALS OF SOLS WITH DIFFERENT CONCENTRATIONS OF SILVER IODIDE

The results of measurements made during the *first* series of experiments are shown in table 1. Several values in one column correspond to the potentials of sols made up at different times; these data give an indication of the reproducibility of the experiments.

It should be noted that sols with the contents of $M/10$ potassium iodide are already of great electrical conductivity, and consequently the data obtained are approximate.

TABLE 1

Potentials of sols with different concentrations of silver iodide

CONCENTRATION OF EXCESS ELECTROLYTE		ζ-POTENTIAL		
		Concentration of AgI in sol		
$AgNO_3$	KI	$\frac{M}{400}$	$\frac{M}{4000}$	$\frac{M}{20,000}$
gram-moles per liter	*gram-moles per liter*	*mv.*	*mv.*	*mv.*
10^{-2}		+58	+49, +44	+32
10^{-3}		+55	+21, +36	+12, −2
10^{-4}		+38	+15	+25
$10^{-4.2}$		–	+1	–
10^{-5}		0	−16, −13, −35	−31, −36
10^{-6}		–	−53	−43
10^{-8}	10^{-8}	–	–	−53
	10^{-6}	–	−48	−56
	10^{-5}	−44	−60, −50	−50, −50
	$10^{-4.2}$	–	−62	–
	10^{-4}	−50	−51	−50
	10^{-3}	−44	−53	−53
	10^{-2}	−55	−73	−65, −49
	$10^{-1.2}$	–	approx. −100	–
	10^{-1}	approx. −170	–	approx. −105

ζ-potentials of the *second* series of experiments are given in table 2.

Basinski (3) for the more concentrated sol ($N/50$ silver iodide) obtained the following values of ζ-potential:

	ζ-potential
At 10^{-3} M $AgNO_3$	= +46.9 mv.
At 10^{-3} M $AgNO_3$	= +47.3 mv.
At 10^{-2} M KI	= −70.1 mv.

i.e., values coinciding practically with those which refer to our $M/400$ sol. The results are shown graphically in figures 1 and 2.

The more the sol is diluted, the greater is the difficulty in charging it

TABLE 2

Potentials of sols with different concentrations of silver iodide

CONCENTRATION OF EXCESS ELECTROLYTE		ζ-POTENTIAL		
		Concentration of AgI in sol		
$AgNO_3$	KI	$\frac{M}{400}$	$\frac{M}{4000}$	$\frac{M}{20,000}$
gram-moles per liter	*gram-moles per liter*	*mv.*	*mv.*	*mv.*
10^{-2}		+50	+58	+30
10^{-3}		+43	+37	+10
10^{-4}		+45, +41	+38	−10
10^{-5}		0 (?)	+20, 0	−24
10^{-6}		—	−29	−40
10^{-3}	10^{-3}	−23	—	—
	10^{-6}	—	—	−33, −37
	10^{-5}	−48, −45, −46	−43	−32
	10^{-4}	−36	−41	−39
	10^{-3}	−37	−47	−49
	10^{-2}	−69	−75	−71
	10^{-1}	approx. −135	approx. −115	—

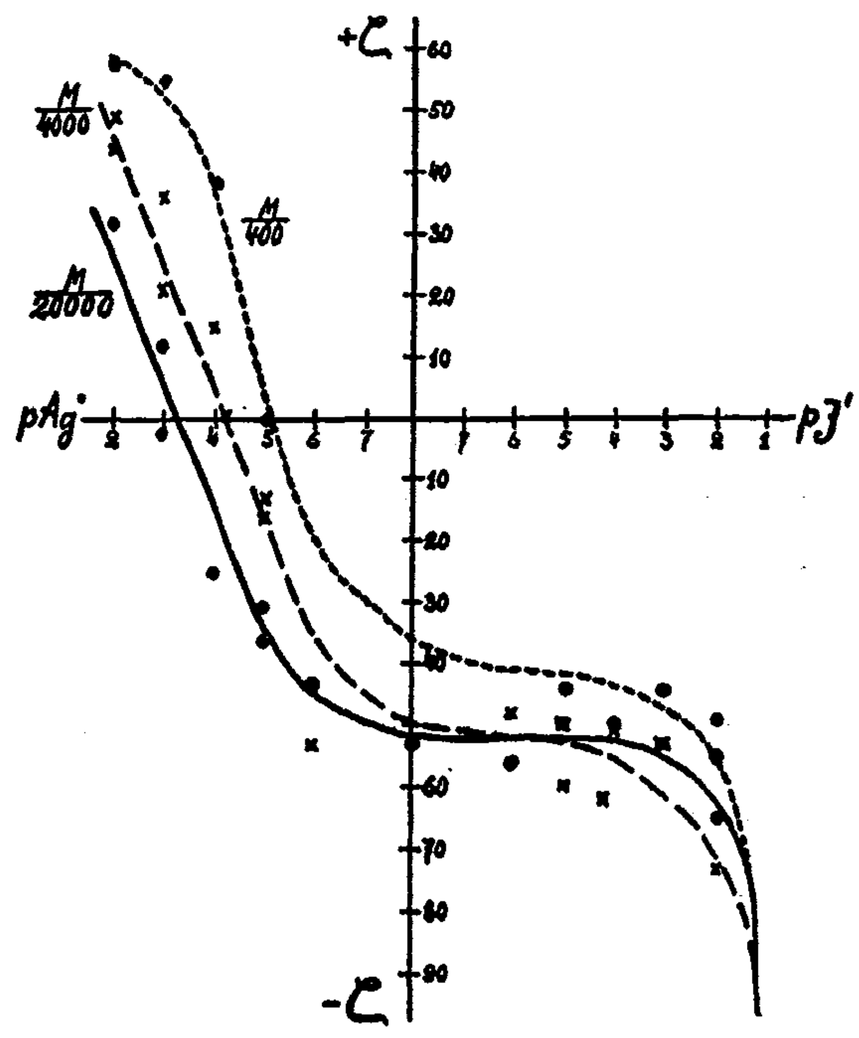

FIG. 1

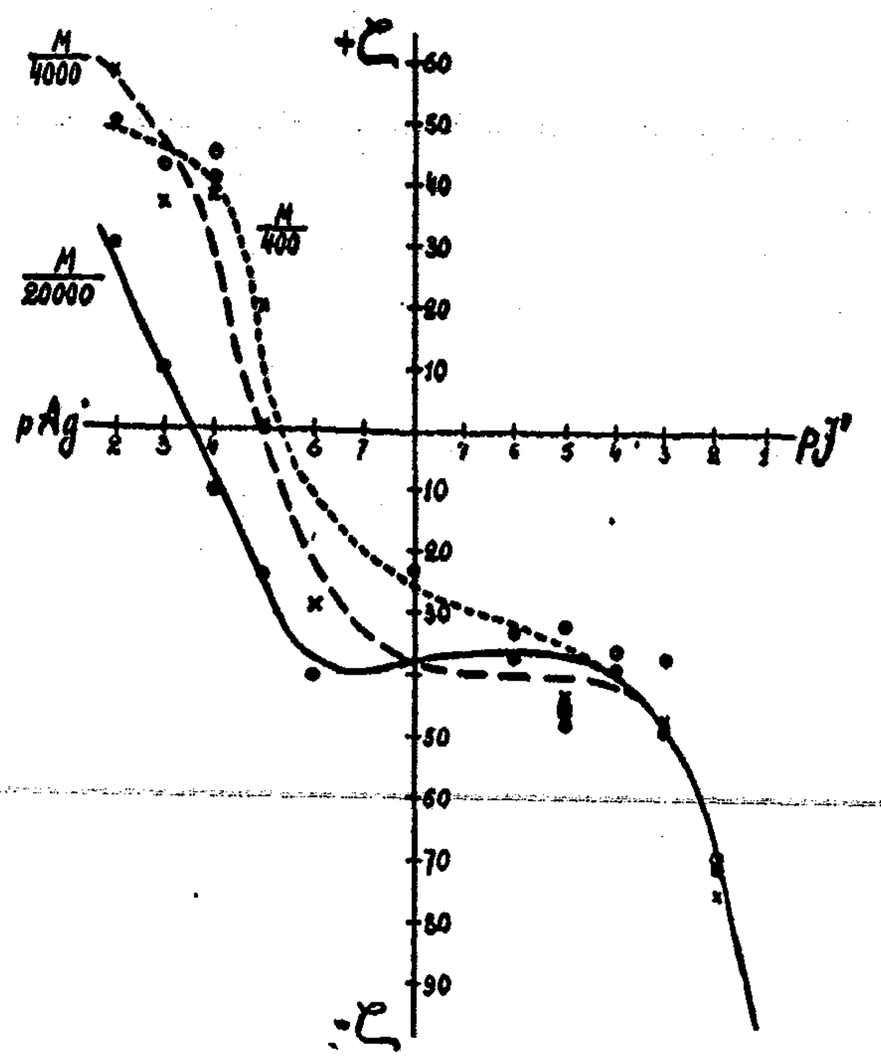

Fig. 2

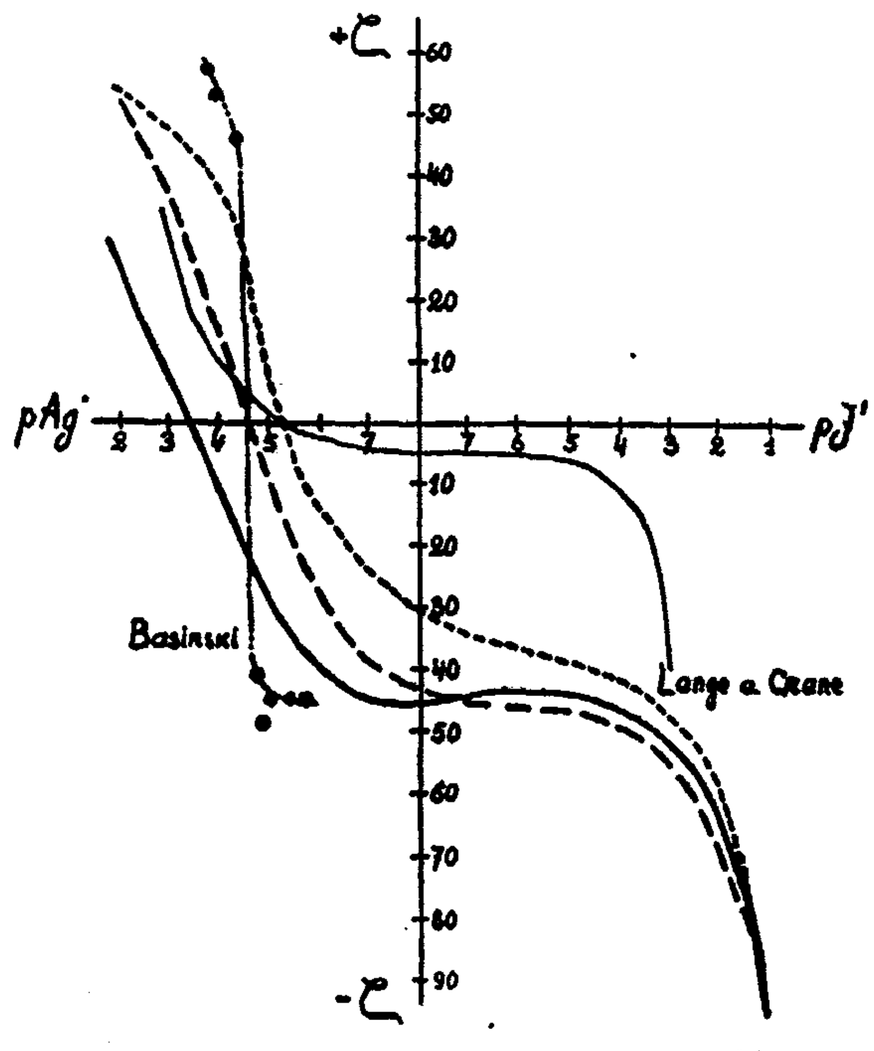

Fig. 3

positively and the less is its ζ-potential in the region of positive charge. Accordingly the isoelectric point ($\zeta = 0$) is shifted; if in the case of the sol of $M/400$ silver iodide, the concentration of silver ion exceeds at this point the concentration of iodide ion by 10^6, then in the case of the sol with content of silver iodide fifty times less, the concentration of silver ion exceeds the concentration of iodide ion by 10^9. Outwardly this change is manifested by a quite obvious shift of the domain of minimum stability of the sols.

The curves obtained differ to a great extent from the endosmotic curve of Lange and Crane (see figure 3, where the average curves of both series of tests are shown).

While it is possible to explain fully this last divergence by the difference of the methods of measurement and by the fact that the conditions of adsorption of ions on silver iodide in statu nascendi can differ considerably from the adsorption on the precipitate previously made, the divergence between the potential curves of sols of dissimilar concentrations requires a special explanation.

IV. INFLUENCE OF DILUTION UPON ζ-POTENTIAL

It may be supposed that ζ-potential depends on the conditions of preparation of the sol. The more the initial solutions are diluted, the larger would be the particles and the less the relative quantity of adsorbed silver ions, which according to Kruyt's view (6) are adsorbed chiefly on the edges of the crystals. Endosmotic experiments of Kruyt showed that fused silver iodide differed from precipitated since it was not possible to charge it positively even with high concentrations of silver nitrate. The possibility indicated is not peculiar to heteropolar crystals, but also occurs with noncrystalline spherical particles. The dependence of the velocity of transference (and consequently of ζ-potential) on the radius was established by means of experiment. Illig and Schönfeld (5) have observed this by the endosmose of water through diaphragms with pores of different size; Mooney (11) with emulsions of oil in water; Alty (1) with bubbles of gas in water. In later researches this dependence is expressed mathematically (2, 4).

In connection with such hypotheses it is interesting to compare the results obtained with phenomena found in the usual dilution of sols.

Basinski[1] showed that there is no marked influence of dilution by ultrafiltrate on the ζ-potential of the positively charged sol, but the same dilution of the negatively charged sol leads to a decrease of the potential. The dilution with water of the positively charged silver iodide sol gives a sharper curve for ζ-potential than that in our work. But it is necessary

[1] Reference 3, pp. 332–9. The curve in our figure 4 is drawn from table 44.

to take into consideration that the reduction of concentration of excess electrolyte and that of the dispersed phase take place simultaneously on dilution with water; thus, the positive potentials (concentration of silver iodide from $M/1250$ to $M/5000$) belong to sols which approach the most concentrated of my sols, and negative potentials (concentration of silver iodide from $M/10{,}000$ to $M/100{,}000$) belong to sols which are for the most part more diluted than the least concentrated of my sols. Under such circumstances I consider that the data given by this author confirm the presence of a concentration dependence of ζ-potentials of sols.

In order to verify these results, I also made experiments on the dilution of the sol of $M/400$ silver iodide by means of isoelectrolytic solutions, that is, by solutions containing the same quantity of excess electrolyte as

TABLE 3

Potentials obtained after dilution of the M/400 silver iodide sol

CONCENTRATION OF EXCESS ELECTROLYTE		ζ-POTENTIAL		
$AgNO_3$	KI	$M/400$ sol AgI	The same but diluted to $M/20{,}000$ AgI	Diluted sol with $M/250$ KNO_3
gram-moles per liter	*gram-moles per liter*	*mv.*	*mv.*	*mv.*
10^{-2}		+56	+30	+27
10^{-3}		+49	+13	+16
10^{-4}		+41	+8	+10
10^{-5}		+23	−23, −28	−27
10^{-6}	10^{-6}	−53 (?)	−26, −32	−22
	10^{-5}	−55	−40	−49
	10^{-4}	−51	−52	−39
	10^{-3}	−51	−56	−51
	10^{-2}	−82	−71	−70
	10^{-1}	approx. −145	approx. −120	−

the initial sol, and also by means of solutions which contained excess electrolyte with $M/250$ potassium nitrate (see table 3). It is difficult to suppose that this electrolyte influences the ζ-potential, but as it was being formed in dissimilar quantities in sols of different concentrations of silver iodide, it was necessary to take this fact into consideration.

It follows from these data that simple dilution of the sol gives exactly the same general results as have already been observed: the diluted sol has a smaller positive charge than the concentrated sol, and the isoelectric point is shifted from the point of equivalence. The presence of potassium nitrate has practically no effect on the value of the ζ-potential. Therefore the conditions of preparing a sol do not cause a dependence of ζ-potential on the concentration of the dispersed phase.

It seemed possible to explain the results otherwise. The fact that the

flocculation value depends on the concentration of sol is generally explained in the following way: the higher the concentration of dispersed phase, the greater will be the proportion of the dissolved electrolyte which partakes in adsorption and the less the equilibrium concentration of electrolyte as compared with the initial concentration. But in our case this reasoning leads to conclusions contrary to experiment.

V. pH OF SOLS OF SILVER IODIDE

Let us examine the problem of the structure of the double electric layer of silver iodide. The rule by Paneth-Fajans states that those ions are adsorbed on the surface of the heteropolar crystal which give, together with the oppositely charged ions of the crystal lattice, the least soluble

TABLE 4

Results of pH measurements

EXCESS CONCENTRATION OF SILVER ION	CONCENTRATION OF DISPERSED AgI				0
	M/400		*M*/20,000		
	The made up sol	Centrifuging	The made up sol	Dilution of sol *M*/400	
10^{-2} *M*		6.05	6.13	6.38	
0					5.70
10^{-3} *M*	5.17		5.32	5.27	
10^{-3} *M*	5.83	5.80		5.73	5.83
0					5.16
10^{-4} *M*		6.68	6.25	6.31	6.40
10^{-5} *M*	6.31	6.27			
0					5.41

compounds. We suppose that the "composition" of the second layer of the double layer is also determined by this rule, i.e., that the latter layer is formed for the most part from ions which give together with ions of the first layer the least soluble compounds.

In the case of negatively charged silver iodide sol, iodide ions constitute the first layer; it is evident that potassium and hydrogen ions can form the second diffuse layer. In positively charged sols silver ions constitute the first layer and either nitrate or hydroxyl ions constitute the second layer. According to what precedes, in the case of the positively charged sol hydroxyl ions form chiefly the second layer, as silver hydroxide is but slightly soluble. In this case the equilibrium $H^+ + OH^- \rightleftarrows H_2O$ is displaced and the intermicellar liquid is slightly acid. The higher the concentration of dispersed phase, the more the liquid will be acidified. In compliance with

the decrease of concentration of "free" hydroxyl ion, the relative amount of hydroxyl ion in the diffuse layer will be less in the concentrated sol than in the diluted one. The layer will be more diffused and the value of the ζ-potential will increase.

In order to verify such an hypothesis, the pH values of sols were measured by means of a glass electrode. The determinations with positively charged sol were rather difficult, since the more positive the sol, the more intensely it was precipitated on the negatively charged glass and on the film of the electrode as well. In consequence, the potential proved to be unstable and badly reproducible (3 to 5 millivolts, and sometimes more).

Table 4 gives the results of the pH measurements made at different times. They give generally a negative answer to our problem.

However, the negative results do not exclude the possibility of such an explanation of the phenomenon. Ions constituting the diffuse layer of the double electric layer can be active in regard to the glass electrode, and then the value of pH will tell us nothing of the structure of the double layer.

VI. SUMMARY

1. Electrokinetic potentials of sols of silver iodide with $M/400$, $M/4000$ and $M/20{,}000$ silver iodide made in different excesses of ions (silver or iodide) were electrophoretically measured.

2. The curves ζ–$C_{\text{electrolyte}}$ of silver iodide sols do not coincide with the curve in the case of endosmose through the precipitate (Lange and Crane).

3. The less the concentration of the dispersed phase in sols, the greater are the concentrations of silver ion necessary to charge it positively and the further the isoelectric point is removed from the point of equivalence in the direction of the excess of silver ions.

4. The dilution of sol $M/400$ silver iodide by means of solutions containing the same quantities of excess electrolyte as the initial sol leads also to decrease of positive charge of the sol.

5. The alteration of the concentration of dispersed phase does not cause any change of pH of the sols.

I wish to express my deepest gratitude to Mr. K. S. Ljalikov, to whose initiative this work was due and who invariably gave it his closest attention.

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TEMPERATURE VARIATION OF IONIZATION CONSTANTS IN AQUEOUS SOLUTIONS

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Received July 23, 1934

According to Harned and Embree (5), the temperature variation of the ionization constant can, as a first approximation, be represented by a quadratic equation of the type

$$\log K - \log K_m = -p(t - \theta)^2 \tag{1}$$

where K is the ionization constant, K_m is the maximum value of the ionization constant, p is a *general* constant and has a value of 5.0×10^{-5} deg.$^{-2}$, t is the Centigrade temperature, and θ is the temperature at which K is equal to K_m. For purposes of theoretical significance to be used later in connection with van't Hoff's isochor and the temperature variation of the heat of reaction, the temperature may be expressed in degrees Absolute without changing the value of p. Equation 1 then becomes

$$\log K - \log K_m = -p(T - \theta_1)^2 \tag{2}$$

where T is the absolute temperature and θ_1 is the absolute temperature at which K is equal to K_m. Thus, log K may be expressed by a quadratic equation

$$\log K = (\log K_m - p\theta_1^2) + 2p\theta_1 T - pT^2 \tag{3}$$

in which K_m and θ_1 are constants characteristic of each substance, and the constant p is general.

Likewise, equation 1 becomes

$$\log K = (\log K_m - p\theta^2) + 2p\theta t - pt^2 \tag{4}$$

By rearranging terms, equations 3 and 4 become, respectively,

$$\log K + pT^2 = \log K_m - p\theta_1^2 + 2p\theta_1 T \tag{5}$$

and

$$\log K + pt^2 = \log K_m - p\theta^2 + 2p\theta t \tag{6}$$

It is the object of this paper to show that p is not a characteristic constant except under certain assumptions. The theoretical significance of p and its relation to $d^2 \log K/dT^2$ will also be pointed out.

By taking the first derivative of log K with respect to temperature in equation 1:

$$\frac{d \log K}{dT} = -2p(t - \theta) \tag{7}$$

Likewise, from equation 2:

$$\frac{d \log K}{dT} = -2p(T - \theta_1) \tag{8}$$

But from van't Hoff's isochor,

$$\frac{d \log K}{dT} = \frac{\Delta H}{2.303RT^2} \tag{9}$$

where ΔH is the heat of reaction, or in this case, the molal heat of ionization.

By taking the second derivative of equation 1,

$$\frac{d^2 \log K}{dT^2} = -2p \tag{10}$$

Likewise, by differentiating equation 9:

$$\frac{d^2 \log K}{dT^2} = \frac{d(\Delta H)}{2.303RT^2\, dT} - \frac{2\Delta H}{2.303RT^3} \tag{11}$$

but

$$\frac{d(\Delta H)}{dT} = \Delta C_p \tag{12}$$

where ΔC_p is the change in specific heat upon ionization. Therefore

$$\frac{d^2 \log K}{dT^2} = \frac{\Delta C_p}{2.303RT^2} - \frac{2\Delta H}{2.303RT^3} \tag{13}$$

If the variation of log K with temperature is not originally expressed as a quadratic equation, and if ΔH and ΔC_p are not calculated from this quadratic equation, the validity of the assumption, namely, that p is a *general* constant, may be tested by combining equations 10 and 13:

$$-2p = \frac{\Delta C_p}{2.303RT^2} - \frac{2\Delta H}{2.303RT^3} \tag{14}$$

and dividing by 2,

$$-p = \frac{\Delta C_p}{4.606RT^2} - \frac{\Delta H}{2.303RT^3} \tag{15}$$

Equation 15 may be tested in two ways. Since $\Delta H = 0$ somewhere at or near the temperatures under consideration, one may determine the value of $-p$ at $\Delta H = 0$. This value will be the value of $-p$ at log K_m because $\frac{d \log K}{dT} = \frac{\Delta H}{RT^2}$ and at K_m, $\Delta H = 0$. Equation 15 then becomes

$$\frac{\Delta C_p}{4.606RT^2} = -p \tag{16}$$

Table 1 shows the values of $-p$ at K_m found in the literature. It shows that $-p$ does not have a constant value of 5.0×10^{-5} as was assumed by Harned and Embree (5).

In order to determine if $-p$ remained constant for any particular acid through a range of temperatures, equation 15 was applied to the series of

TABLE 1

The value of $-p$ at K_m

SUBSTANCE	ΔC_p	T	$-p = \frac{\Delta C_p \times 10^5}{4.606RT^2}$
Formic acid (4)	−41.0	298	5.06
Chloroacetic acid (9)	−48.9	269	7.38
Acetic acid (2)	−33.7	295	4.23
Propionic acid (3)	−37.1	293	4.72
Glycine (K_A) (8)	−45.0	328	4.57
Alanine (K_A) (7)	−23.2	321	2.46
Phosphoric acid (second hydrogen) (6)	−41.0	316	4.50
Sulfuric acid (second hydrogen) (1)	−74.5	269	11.25

acids in table 1. The constants used and the results calculated for these acids are given in table 2.

Table 2 shows that p is not a constant, characteristic of any particular acid, unless the variation of log K with temperature is originally expressed as a quadratic equation. It was observed that p increased with temperature except where log K had been expressed as a quadratic function. Figure 1 shows that equation 13 will have a point of inflection at some temperature above that of the experiment. This fact cannot be true if log K is expressed as a general quadratic equation, as illustrated by lines II and III of figure 1.

At the point of inflection, $\frac{d^2 \log K}{dT^2} = 0$ and equation 13 becomes

$$\frac{\Delta C_p}{2.303RT^2} = \frac{2\Delta H}{2.303RT^3} \tag{17}$$

which, upon simplification, becomes

$$\Delta C_p = \frac{2\Delta H}{T} \tag{18}$$

TABLE 2

Variation in ΔH and ΔC_p with temperature

TEMPERATURE	ΔH	ΔC_p	$\frac{\Delta C_p \times 10^5}{4.606RT^2}$	$\frac{\Delta H \times 10^5}{2.303RT^2}$	$-p \times 10^4$	$\frac{\Delta H \times 10^3}{2.303RT^2}$
			Propionic acid			
273	737	−34.7	−5.090	0.792	5.88	2.162
278	562	−35.3	−4.993	0.572	5.57	1.590
283	384	−35.9	−4.900	0.370	5.27	1.048
288	203	−36.5	−4.811	0.186	5.00	0.535
293	19	−37.1	−4.724	0.017	4.74	0.048
298	−168	−37.7	−4.652	−0.139	4.51	−0.415
303	−358	−38.3	−4.561	−0.282	4.28	−0.853
308	−551	−38.9	−4.483	−0.412	4.07	−1.270
313	−746	−39.4	−4.397	−0.532	3.87	−1.665
318	−945	−40.0	−4.324	−0.643	3.68	−2.043
323	−1147	−40.6	−4.254	−0.744	3.51	−2.404
328	−1351	−41.2	−4.187	−0.837	3.35	−2.746
333	−1559	−41.8	−4.121	−0.923	3.20	−3.074
			Chloroacetic acid			
273	−149	−46.83	−6.869	−0.160	6.71	−0.368
283	−593	−42.04	−5.738	−0.572	5.17	−1.619
291	−914	−38.21	−4.933	−0.811	4.12	−2.360
298	−1170	−34.86	−4.301	−0.967	3.33	−2.821
305	−1402	−31.51	−3.703	−1.080	2.62	−3.295
313	−1639	−27.68	−3.089	−1.169	1.92	−3.658
			Glycine (K_A)*			
283	1562	−23.4	−3.194	1.507	4.70	4.264
288	1439	−25.8	−3.400	1.317	4.72	3.793
293	1305	−28.2	−3.591	1.134	4.73	3.324
298	1159	−30.6	−3.776	0.958	4.73	2.860
303	1000	−33.0	−3.930	0.786	4.72	2.382
308	829	−35.4	−4.079	0.623	4.70	1.911
313	646	−37.8	−4.218	0.461	4.70	1.442
318	449	−40.2	−4.346	0.305	4.65	0.971
			Acetic acid			
273	714	−32.15	−4.716	0.767	5.48	2.095
278	552	−32.50	−4.597	0.562	5.16	1.562
283	389	−32.85	−4.484	0.375	4.86	1.062
288	223	−33.20	−4.376	0.204	4.58	0.588
293	57	−33.55	−4.272	0.050	4.32	0.145
298	−112	−33.91	−4.184	−0.093	4.09	−0.276

* ΔC_p was calculated from Owen's equation, $d(\Delta H)/dt = 18.6 - 48t$. It was observed that log K was expressed as a quadratic function. Calculation of ΔH and ΔC_p from a quadratic equation in t must necessarily produce a constant value of p by this method, because the coefficient of the square term is p. Values from log K_B for glycine were not computed because log K_B had been expressed as a quadratic function of temperature.

TABLE 2—*Concluded*

TEMPERATURE	ΔH	ΔC_p	$\frac{\Delta C_p \times 10^4}{4.606RT^2}$	$\frac{\Delta H \times 10^4}{2.303RT^2}$	$-p \times 10^4$	$\frac{\Delta H \times 10^3}{2.303RT^2}$
			Acetic acid—*Concluded*			
303	−282	−34.26	−4.080	−0.222	3.86	−0.672
308	−455	−34.61	−3.988	−0.342	3.65	−1.049
313	−628	−34.96	−3.901	−0.448	3.45	−1.402
318	−804	−35.31	−3.817	−0.547	3.27	−1.738
323	−982	−35.66	−3.737	−0.637	3.10	−2.058
328	−1161	−36.02	−3.660	−0.736	2.92	−2.360
333	−1342	−36.37	−3.586	−0.795	2.79	−2.646
			Formic acid			
273	931	−34.6	−5.075	1.000	6.08	2.731
278	755	−35.9	−5.078	0.768	5.85	2.136
283	573	−37.1	−5.064	0.553	5.62	1.564
288	384	−38.4	−5.061	0.352	5.41	1.012
293	189	−39.7	−5.055	0.164	5.22	0.481
298	−13	−41.0	−5.059	−0.011	5.05	−0.032
303	−221	−42.3	−5.037	−0.174	4.86	−0.526
308	−436	−43.6	−5.024	−0.328	4.70	−1.005
313	−657	−44.8	−4.999	−0.469	4.53	−1.466
318	−884	−46.1	−4.988	−0.601	4.39	−1.911
323	−1118	−47.4	−4.967	−0.725	4.24	−2.343
328	−1358	−48.7	−4.949	−0.841	4.11	−2.760
333	−1605	−50.0	−4.929	−0.950	3.98	−3.165
			Sulfuric acid (second hydrogen)			
273	−146	−76.0	−11.148	−0.157	10.99	−0.428
278	−533	−78.9	−11.161	−0.542	10.62	−1.508
283	−934	−81.8	−11.165	−0.901	10.26	−2.550
288	−1351	−84.8	−11.177	−1.237	9.94	−3.561
293	−1782	−87.9	−11.173	−1.514	9.68	−4.435
298	−2229	−90.9†	−11.216	−1.842	9.38	−5.501
303	−2692	−94.1	−11.205	−2.165	9.04	−6.411
308	−3172	−97.3	−11.213	−2.374	8.84	−7.311
313	−3665	−100.6	−11.226	−2.613	8.60	−8.179
318	−4176	−103.7	−11.210	−2.833	8.38	−9.029
323	−4704	−107.2	−11.233	−3.052	8.18	−9.858
328	−5249	−110.7	−11.249	−3.255	8.00	−10.668
333	−5811	−114.1	−11.249	−3.441	7.81	−11.458
			dl-Alanine (K_A)‡			
293	913	−39.8	−5.068	0.794	5.86	2.325
298	720	−37.5	−4.627	0.595	5.22	1.777
303	538	−35.1	−4.180	0.423	4.60	1.281
308	369	−32.3	−3.722	0.276	4.00	0.851
313	215	−29.0	−3.236	0.153	3.39	0.480
318	79	−25.4	−2.746	0.054	2.80	0.171

† A mistake in ΔC_p was observed in the original data.

‡ ΔC_p was calculated by approximate methods from ΔH.

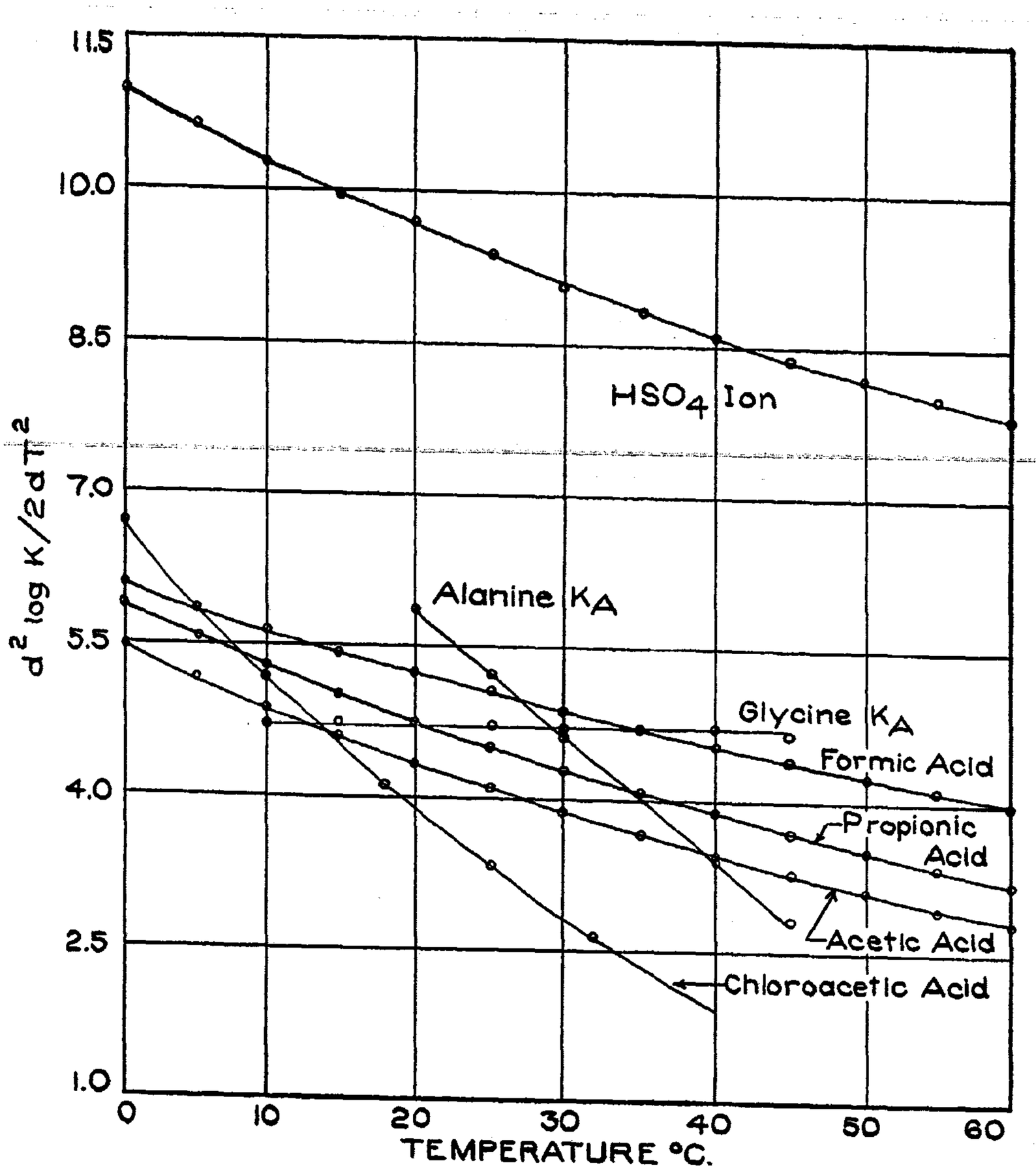

FIG. 1. VARIATION OF SECOND DERIVATIVE OF IONIZATION CONSTANT WITH TEMPERATURE

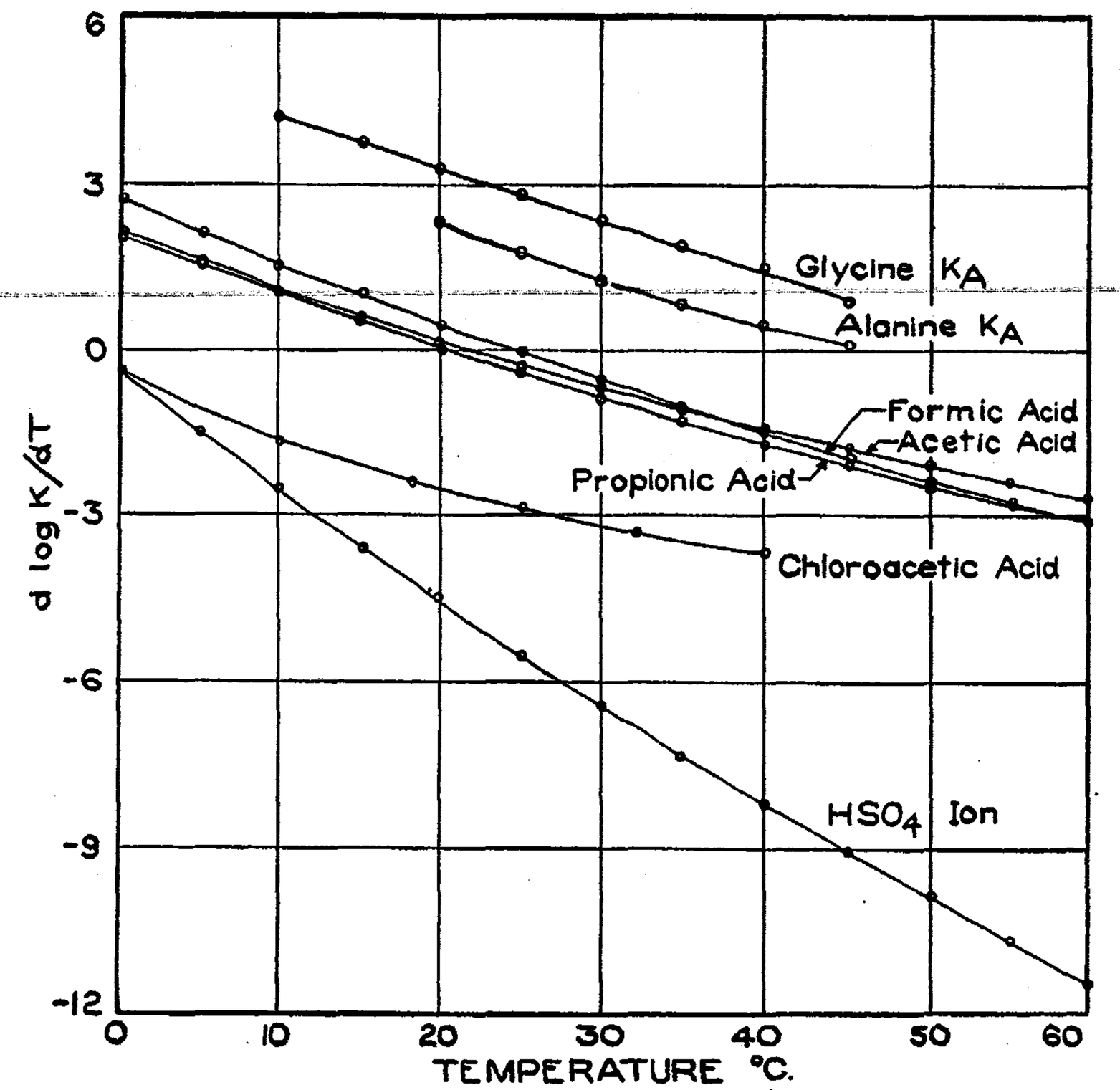

FIG. 2. VARIATION OF FIRST DERIVATIVE OF IONIZATION CONSTANT WITH TEMPERATURE

A tangent to any point on a curve in figure 1 then represents $\frac{\frac{1}{2}d^3 \log K}{dT^3}$, which can be determined by differentiating equation 13:

$$\frac{d^3 \log K}{dT^3} = \frac{-4\Delta C_p}{2.303RT^3} + \frac{6\Delta H}{2.303RT^4} + \frac{1}{2.303RT^2}\frac{d(\Delta C_p)}{dT} \qquad (19)$$

This equation likewise expresses the rate at which $\Delta H/T$ is approaching ΔC_p.

Another method of testing whether or not log K is a quadratic function of temperature is to plot $\frac{d \log K}{dT}$ against temperature. Straight lines having the same slope should be obtained. The expression d log K/dT may be obtained by combining equations 8 and 9:

$$\frac{\Delta H}{2.303RT^2} = -2p(T - \theta_1) = \frac{d \log K}{dT} \qquad (20)$$

The data for $\frac{\Delta H}{2.303RT^2}$ obtained in table 2 have been plotted in figure 2; the values do not fall on straight lines, showing that d log K/dT is not a linear function of temperature. The slopes of the lines are not the same for all acids.

Glycine is found to plot as a straight line. This fact must be true, however, since examination of the original article (8) shows that ΔH and ΔC_p apparently had been calculated under the assumption that log K was a quadratic function of temperature.

CONCLUSION

1. Log K is not a quadratic function of the temperature.
2. The theoretical significance of p and its relation to d log K/dT and d^2 log K/dT^2 have been pointed out.
3. The significance of the third derivative has been pointed out for the first time.

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POTENTIALS OF CELLS INVOLVING MOVING BOUNDARIES[1]

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Received July 23, 1934

The thermodynamic treatment of a cell involving a liquid junction between two electrolytes having a common ion would be greatly simplified if the boundary between the two solutions could be regarded as a moving boundary such as is used in the determination of transference numbers (7), for under these conditions the potential of the cell becomes a simple function of the activity of the water in the two different solutions.

Referring to figure 1, consider, for example, the case of a cell involving a moving boundary, O_1–O_2, between solution I, C_1 normal with respect to lithium chloride, and solution II, C_2 normal with respect to potassium chloride. Using electrodes reversible to chloride ions, let 1 faraday of negative electricity pass through the cell from right to left, causing the boundary to sweep through V liters of solution to the new position O_3–O_4. Letting T_{Li} and T_K be the transference numbers of the cations in solutions I and II, respectively, it is apparent that T_{Li} equivalents of lithium cross O_1–O_2 into V, while T_K equivalents of potassium cross O_3–O_4 out of V. If it is assumed that the boundary is to be maintained without mixing the two solutions or changing their concentrations, the following relations must hold:

$$T_{Li} = VC_1 \tag{1}$$
$$T_K = VC_2 \tag{2}$$

On dividing equation 1 by equation 2 there results the familiar "regulating" equation, first derived in a more general form by Kohlrausch (3):

$$\frac{T_{Li}}{T_K} = \frac{C_1}{C_2} \tag{3}$$

When C_1 and C_2 are chosen so as to satisfy the above equations, the net transfer of chloride ion can be calculated as follows:

[1] This article is based upon a thesis submitted by F. D. Martin to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1931.

PROCESS	GAIN OR LOSS IN EQUIVALENTS PER FARADAY	
	Solution I	Solution II
Electrode reactions	Loses one equivalent	Gains one equivalent
Movement of the boundary	Gains VC_2 equivalents	Loses VC_2 equivalents
Transference across O_3–O_4	Gains $(1 - T_K)$ equivalents	Loses $(1 - T_K)$ equivalents
Net effect	Gains $VC_2 + (1 - T_K) - 1 = 0$	Loses $VC_2 + (1 - T_K) - 1 = 0$
	(For by equation 2, $VC_2 = T_K$)	

Since the concentrations are adjusted so that no mixing or transfer of the cations will occur, there is no net transfer of any of the three ions.

The transfer of water remains to be considered. It has been shown by MacInnes and Dole (6) that transference numbers calculated from experiments with moving boundaries are identical with Hittorf transference numbers, hence the transfer of water by the ions themselves need not be taken into account. There is, however, a transfer of water from solution II to solution I as a result of the movement of the boundary; the water originally present in V liters of II becomes a part of I as the boundary moves from O_1–O_2 to O_3–O_4. Let M_w be the number of moles of water thus transferred, and let a_1 and a_2 be the activities of the water in solutions I and II, respectively. The free energy change, ΔF, of the transfer will be:

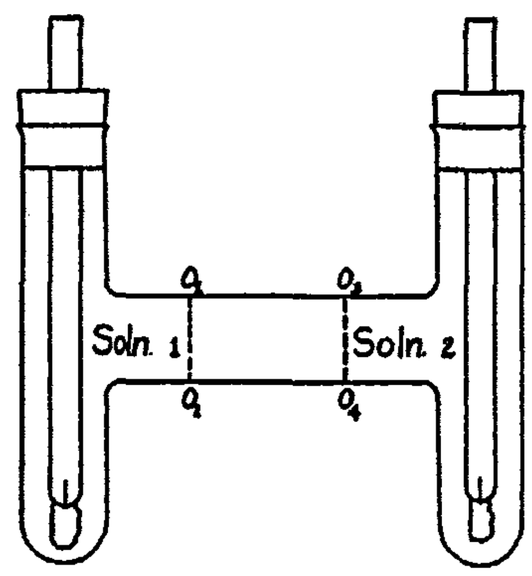

FIG. 1

$$\Delta F = M_w RT \ln \frac{a_1}{a_2} \tag{4}$$

Taking T as 298°K. and noting that M_w represents the number of moles transferred per faraday, the potential, E, of the cell represented in figure 1 becomes

$$E = 0.05915\, M_v \log_{10} \frac{a_2}{a_1} \tag{5}$$

Equation 5 provides a means for calculating the exact potential of such a cell, using data which is readily available. It is valid, however, only in case the passage of electricity through the cell brings about the movement of the boundary. Dole (1) has derived an equation similar to equation 5 to account for the deviations of the glass electrode in acid and in non-aqueous solutions.

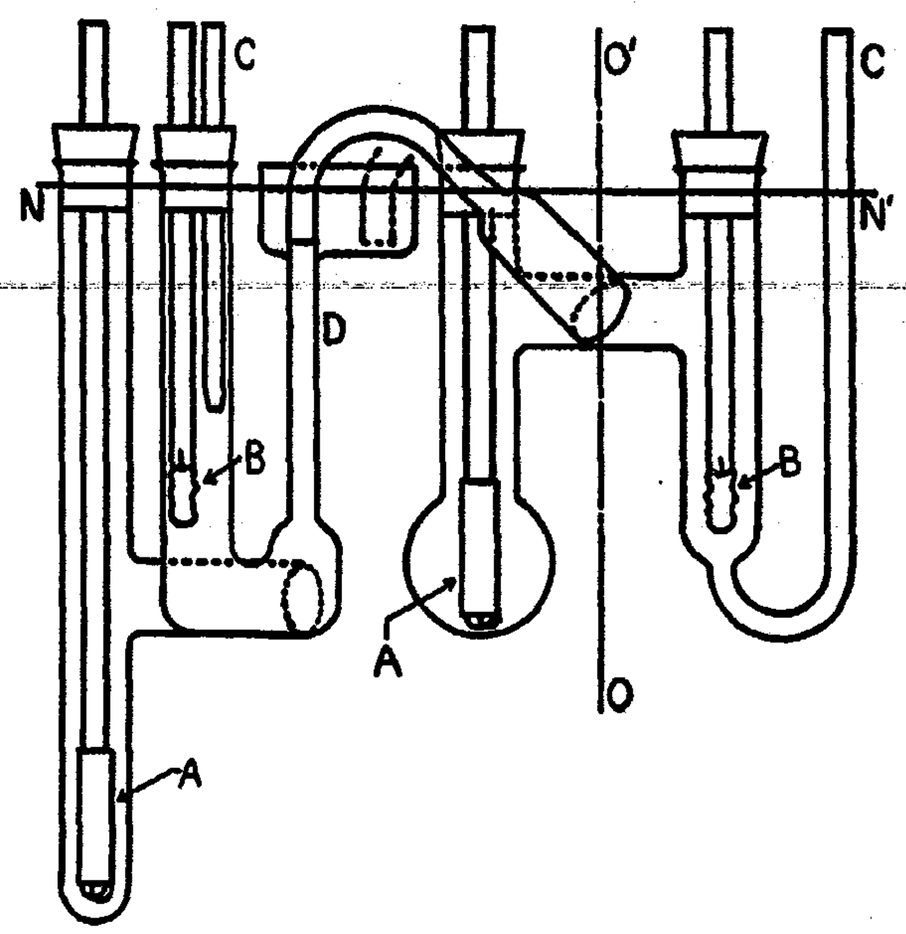

FIG. 2

EXPERIMENTAL

In an effort to test equation 5, a modification of the moving boundary apparatus developed by Brighton (4) was set up. As shown in figure 2, in addition to the compartments AA, containing the working electrodes for carrying the current used to establish the moving boundary, the compartments BB, were added, containing the potential electrodes for measuring the potential of the cell. The tubes CC furnished a means for renewing the electrolyte around the potential electrodes and for adjusting the surfaces of the two solutions before establishing contact. The boundaries were of the descending type and were made visible by an illuminated screen with a black horizon as recommended by MacInnes and Smith (8).

Thermostat. All runs were made in an oil thermostat at a temperature of 25.0°C.

Potentiometer and electrical system. A diagram of the electrical connections is shown in figure 3. The current used to establish the boundary could be regulated by the rheostats to any desired value, as read on the milliammeter, A. When a reading of the potential of the cell was being taken this current was shut off by switch S_1, while contact with the potential electrodes was established by means of switch S_2. A Leeds and Northrup Type K potentiometer was used.

Electrodes and solutions. Both the working and the potential electrodes were of the silver-silver chloride type. The former were made by silver plating cylindrical electrodes of platinum foil, then chloridizing the electrode which was to serve as cathode. The electrodes used for measuring the potential were made by filling platinum spirals, about 1 cm. long, with a paste of pure silver oxide, decomposing the oxide in an electric furnace, then chloridizing the resulting spongy silver in a dilute solution of hydrochloric acid for one to two hours. The electrodes were then thoroughly washed and stored in the solution in which they were to be used. Solutions of the chlorides of sodium, potassium, and lithium were used, solu-

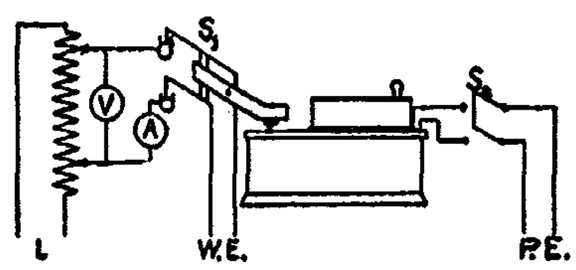

FIG. 3. ELECTRICAL CIRCUIT

L = 110 volts; W. E., to working electrodes; P. E., to potential electrodes

tions of the first two being prepared by direct weighing of the dry, recrystallized salts into calibrated volumetric flasks, while the lithium chloride solutions were prepared by weighing out the calculated amount of one of three different stock solutions, then diluting as before.

Procedure. In the first series of experiments, readings of the potential were taken about one second after the interruption of the current used to establish the boundary. Several different combinations of the three chlorides were used, the concentrations in each case conforming to the requirements of equation 3, as calculated from data in the International Critical Tables. Table 1 gives the results of this series of measurements, as compared with the values calculated from equation 5.

In view of the discrepancy between the observed and the predicted values of the potentials, the first series of runs was discontinued and a search begun for possible causes of the lack of agreement. The results of this investigation may be summarized as follows:

1. There appeared to be no serious error in the data used for calculating the potentials according to equation 5. The ratios of a_2/a_1 were calculated

from the vapor pressure lowerings of the various solutions as recorded in the International Critical Tables. Each value of M_w was calculated by three different methods with concordant results.

2. The experimental error was insufficient to account for differences amounting to several millivolts.

3. There remained to be considered the behavior of the boundary after the working current had been interrupted. In the derivation of equation 5 it was assumed that the boundary was maintained during the measurement of the potential of the cell. The experiments of MacInnes and Cowperthwaite (5) showed that the boundary faded slowly when the current was shut off and regained its original sharpness shortly after the current was turned on again. These observations were repeated and confirmed in this laboratory. In order to study further the effect of the interruption of the working current upon the potential of the cell, a second series of measurements was undertaken. In this series the working current was shut off after the boundary had been established, then readings of the potential were taken at short intervals until no further significant change was noted. The influence of other factors, such as the potential drop used to form the boundary and the concentration of the indicator solution, was also studied.

TABLE 1

Potentials of cells with liquid junction established by a moving boundary

$T = 25°C.$

SOLUTION I	SOLUTION II	POTENTIAL DROP IN II	AVERAGE POTENTIAL OF CELL	POTENTIAL CALCULATED FROM EQUATION 5
		volts per cm.	*millivolts*	*millivolts*
0.594 *N* LiCl	1.00 *N* KCl	2.3–2.7	−17.9	−8.4
0.303 *N* LiCl	0.50 *N* KCl	2.6	−17.9	−8.4
0.064 *N* LiCl	0.10 *N* KCl	2.4–2.8	−18.1	−8.33
0.77 *N* NaCl	1.00 *N* KCl	2.7	−11.0	−4.9
0.40 *N* NaCl	0.50 *N* KCl	2.6–3.0	−10.5	−4.15
0.303 *N* LiCl	0.40 *N* NaCl	2.5–3.0	−7.1	−4.27

The sign on the potential corresponds to the flow of negative electricity through the cell from solution II to solution I.

As the result of nearly one hundred runs using various concentrations of lithium chloride solutions against 0.10 *N* solutions of potassium chloride and sodium chloride, also different concentrations of sodium chloride solutions against 0.10 *N* potassium chloride solution, the following conclusions were drawn:

1. The "instantaneous" potential of a cell involving a moving boundary, taken within a fraction of a second after the interruption of the current used to establish the boundary, is not a constant but varies with the potential gradient used to form the boundary. As shown in figure 4, an

increase in the potential gradient causes a rise in the observed "instantaneous" potential of the cell.

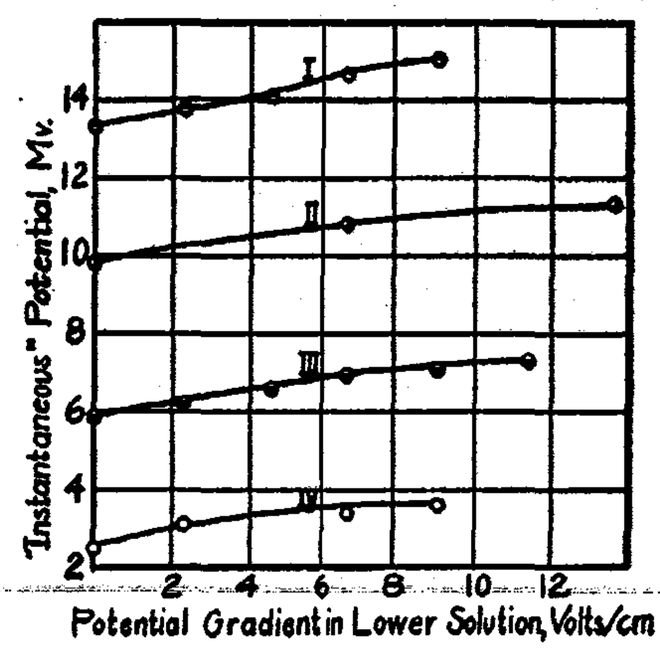

FIG. 4. EFFECT OF POTENTIAL GRADIENT UPON INSTANTANEOUS POTENTIAL

I, 0.1 *N* sodium chloride, using 0.050 *N* lithium chloride as indicator solution; II, 0.1 *N* sodium chloride, using 0.064 *N* lithium chloride as indicator solution; III, 0.1 *N* sodium chloride, using 0.0822 *N* lithium chloride as indicator solution; IV, 0.1 *N* sodium chloride, using 0.1000 *N* lithium chloride as indicator solution.

TABLE 2

Potential of the cell Ag, AgCl, 0.064 *N* LiCl, *junction formed by moving boundary,* 0.10 *N* KCl, AgCl, Ag

$T = 25°C.$

TIME INTERVAL BETWEEN INTERRUPTION OF CURRENT AND MEASUREMENT OF CELL POTENTIAL	POTENTIAL DROP IN KCl SOLUTION IN VOLTS PER CENTIMETER (5.7 MM. TUBE)			
	4.43	3.31	1.66	0.55
	Potential of the cell			
minutes	*mv.*	*mv.*	*mv.*	*mv.*
0.0	−17.9	−17.5	−17.1	−16.7
0.25	−16.5	−16.6	−16.6	−16.5
0.50	−16.5	−16.5	−16.6	−16.4
1.0	−16.4	−16.4	−16.6	−16.4
2.0	−16.4	−16.4	−16.5	−16.4
5.0	−16.4	−16.3	−16.4	−16.4
10.0	−16.4		−16.4	
15.0		−16.3		

Negative current flowed from right to left through the cell. Similar results were obtained for other pairs of solutions.

2. After the current used to form the boundary has been cut off, the potential of the cell diminishes with time, approaching a constant value. Although, as stated above, the instantaneous values of the potential of the

cell vary with potential gradient used to form the boundary, the final or equilibrium value, obtained after the lapse of several minutes, is constant and reproducible, depending only on the concentration and the composition of the solutions used. The data in table 2 furnish a typical illustration of this effect.

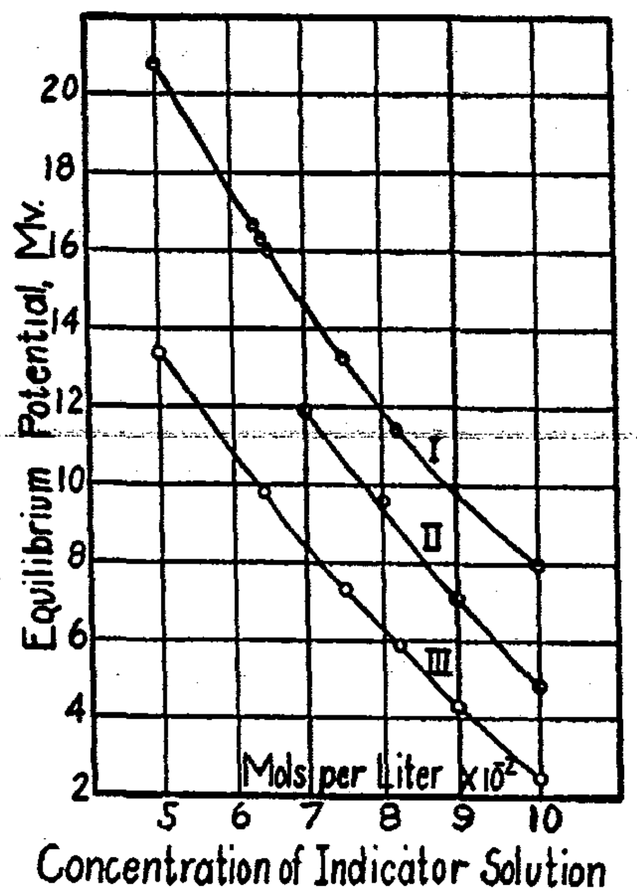

FIG. 5. EQUILIBRIUM POTENTIALS OF CELLS AFTER ESTABLISHING A LIQUID JUNCTION BY MEANS OF A MOVING BOUNDARY

I, 0.10 *N* potassium chloride, using lithium chloride as an indicator solution; II, 0.10 *N* potassium chloride, using sodium chloride as an indicator solution; III, 0.10 *N* sodium chloride, using lithium chloride as an indicator solution.

TABLE 3

Comparison of observed and calculated values of the liquid junction potentials

JUNCTION	LIQUID JUNCTION POTENTIAL	
	Observed by moving boundary method	Calculated from Lewis and Sargent formula
	mv.	*mv.*
0.1 *N* KCl, 0.1 *N* LiCl	8.0	7.4
0.1 *N* KCl, 0.1 *N* NaCl	4.88	4.9
0.1 *N* NaCl, 0.1 *N* LiCl	2.5	2.5

3. These equilibrium values of the potential vary in a regular manner with the concentration of the indicator solution. This is clearly shown in figure 5, where these equilibrium potentials are plotted against the concentrations of the various indicator solutions. Since there is no abrupt

change in the regions in which the concentrations of the indicator solutions are close to the "adjusted" values required by equation 3, there is no reason for believing that lack of agreement with equation 5 was due to any error in selecting an indicator solution of exactly the right concentration.

It may be of interest to point out that these equilibrium potentials for the 0.1 N solutions agree fairly well with the potentials calculated from the Lewis and Sargent formula (9). Table 3 gives a comparison of the observed and calculated values.

4. A possible explanation for the high potentials obtained experimentally, as compared with the values predicted from equation 5, may lie in a peculiar lag effect now being investigated in this laboratory. A preliminary report on this effect by Hunt and Chittum (2) showed that when a direct current is passed through an electrolyte and the fall in potential over a section of the solution measured by means of a set-up similar to that used for measuring the potentials in the present investigation, a distinct lag occurs when the current is interrupted, that is, the potential between the two electrodes dipping in the same solution does not instantly fall to zero when the current is shut off. Further investigation is necessary before deciding whether this lag effect will account for the observed deviations from the values predicted by equation 5.

SUMMARY

1. An equation has been derived for the potential of a cell involving a moving boundary between two electrolytes having a common ion.

2. Potentials of such cells were measured immediately after the interruption of the current used to establish the boundary. The experimental results were not in agreement with the equation.

3. Possible reasons for this disagreement were investigated without revealing the exact cause of the deviation. It is suggested that a lag effect now being studied in this laboratory may be involved.

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THERMOCHEMISTRY AND PHYSICAL PROPERTIES OF BROMIDES AND HYDROSULFIDES

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Received January 26, 1934

In a preceding paper (19) the size and symmetry of the SH^- ion was deduced from the crystal structures of the alkali hydrosulfides MeSH, where Me is Na, K, Rb, Cs, or NH_4. The union of a proton with the S^{--} ion may be considered to take place in either of two ways: first, the proton may enter the S^{--} nucleus with an energy change of the order of 10^6 volts to give a spherical Cl^- ion; second, it may penetrate only the outer electron shells and form an electron pair bond with the sulfur to give a SH^- dipole ion (internuclear distance, 1.4 A.U.; dipole moment, 0.65×10^{-18}), the energy change here being about 10 volts. In all three of these ions the outer electrons have configurations similar to that of argon. The ease with which the SH^- ion assumes effective spherical symmetry in crystals by rotation is evidence that the proton is quite deeply buried in the outer electron shells of the group and leads one to expect that SH^- will be more like a halogen than like the strongly polar OH^-. Because of the increase in radius over Cl^-, SH^- resembles more closely in size the next halogen Br^-, as the following list of crystal radii shows: I^-, 2.19; SH^-, 1.99; Br^-, 1.96; CN^-, 1.93; Cl^-, 1.81; F^-, 1.33. By reason of the similarity in the sizes and charges of their anions, ionic crystals of the type MeX where X is SH, Br, or CN will have similar Coulomb energies and consequently similar lattice energies. It is the purpose of this paper to present some thermochemical calculations based on these lattice energies, and further to extend the comparison of Br and SH compounds to a brief survey of the physical properties of their covalent compounds.

In calculations of the kind to be presented all errors are additive. While a complete elimination of minor inconsistencies in the large variety of data employed has not been attempted because of the considerable labor involved, the majority of derived values appear reliable to 5 kg-cal.; this accuracy is sufficient for the purposes in view. Heat evolved in a reaction is positively signed and is given in kilogram-calories per mole.

I. LATTICE ENERGY OF ALKALI COMPOUNDS MeX

The lattice energy of MeX, defined as the heat of the reaction

$$MeX_{crystal} \rightarrow Me^+ + X^- + (U)$$

may be calculated from the simple Born theory for ionic crystals. The calculations of Sherman (17) for MeBr and for MeCN are reproduced and his method is applied to MeSH. For sodium hydrosulfide, potassium hydrosulfide, and rubidium hydrosulfide the heat absorbed in raising the crystal from 25°C. to 200°C., which includes a heat of transition in addition to the usual specific heat terms, is neglected. For lithium hydrosulfide a hypothetical sodium chloride cubic phase is assumed whose cube edge is predicted from known radii; uncertain or estimated numerical quantities here as elsewhere are enclosed in parentheses (see table 1). Lattice energies for ammonium hydrosulfide and ammonium cyanide will be calculated by an indirect method in section IV.

From these lattice energies we may calculate the proton affinities of the anions, defined as the heat of the reaction

$$H^+ + X^- \rightarrow HX_g + (K)$$

by three independent processes, except in the case of SH^-, to which only two are applicable.

TABLE 1

Lattice energies of alkali compounds MeX

MeX	(a)MeSH	(n)MeSH	−(U)MeSH	−(U)MeBr	−(U)MeCN
LiX	(5.56)	7	(178)	183.1	
NaX	6.05	8	168	171.7	171
KX	6.63	9	155	157.8	156
RbX	6.93	10	150	152.5	150
CsX	4.29	11	143	143.5	142.5
NH_4X			149	147.4	148

II. CALCULATION OF PROTON AFFINITIES BY PROCESS I

This makes use of the cycle

$$\begin{array}{ccccc} Me & + & HX & \xrightarrow{(W)} & MeX + 1/2H_2 \\ & \nwarrow^{(K)X^-} & & & \swarrow^{(U)} \\ (I+S)Me & & Me^+ + X^- + H^+ & & (I+D)H \end{array}$$

The heat of reaction (W) is found by the equation

$$(W) = (Q)MeX - (Q)HX$$

the symbol (Q) denoting here as elsewhere the heat of formation from the elements; numerical values of this quantity are taken from Landolt-Börnstein, tables 320 and 321, except as noted. The constants $(I)H = 312$, $(D)H = 52$ will be used frequently in the following (see table 2).

III. CALCULATION OF PROTON AFFINITIES BY PROCESS II

This process makes use of the heat of solution of the gas ion $(L)X^-$. While this quantity could be calculated from the known radii by the method of Bernal and Fowler (1), a more reliable method combines the lattice energy (U)MeX, the heat of solution (L)MeX, and the heat of solution of the cation $(L)Me^+$; for the latter is used the "experimental"

TABLE 2

Proton affinities by process I

	NaSH	KSH	NaCN	KCN	NaBr	KBr
(U)	−168	−155	−171	−156	−172	−158
(W)	51	58	52	62	78	86
$-(I + D)$H	−364	−364	−364	−364	−364	−364
$(I + S)$Me	144	121	144	121	+144	+121
$(K)X^-$	337	340	339	337	314	315

TABLE 3

Heats of hydration

	NaSH	KSH	NaCN	KCN	NaBr	KBr
U	−168	−155	−171	−156	−172	−158
$-(L)$MeX	−4	−1	0	3	0	+5
$(L)Me^+$	114	94	114	94	114	94
$(L)X^-$	58	62	57	59	58	59

TABLE 4

Proton affinities by process II

	HBr	HSH	HCN
$H^+ \rightarrow H^+_{aq}$	276	276	276
$X^- \rightarrow X^-_{aq}$	58	60	58
$H^+_{aq} + X^-_{aq} \rightarrow HX_{aq}$	>−20<	6	11
$HX_{aq} \rightarrow HX_g$		−5	−6
$H^+ + X^- \rightarrow HX_g + (K)$	314	337	339

value of the same writers as shown in table 3, giving the average values for $(L)X^-$: SH^-, 60; CN^-, 58; Br^-, 58. This calculation neglects hydrolytic effects, which may introduce some uncertainty in the case of the cyanides. Using these values and the known heats of solution of H^+ and of HX, and the heat of dissociation of the weak acids, hydrosulfuric and hydrocyanic (dissociation constants 10^{-7} and 10^{-9}, respectively), we find the results given in table 4, in satisfactory agreement with the results of process I.

Conversely this calculation shows convincingly that the weakness of hydrosulfuric and hydrocyanic acids in aqueous solution is a consequence of the relatively large proton affinity of the anion.

In the case of Br^- and CN^- the lattice energy (U)MeX yields a value for the electron affinity (E)X, or rather of the sum $(E + D)$X, where (D)X is the heat of dissociation of $1/2X_2$ into atoms. From this value of (E)X independent values for $(K)X^-$ are then easily found, in agreement with the foregoing values (see tables 5 and 6), or $(E)Br = 85$, $(E)CN$[1] $= 69$.

The agreement between (K) values calculated by the foregoing three methods points to a consistency in the experimental reaction heats em-

TABLE 5

Electron affinities

	NaBr	KBr	NaCN	KCN
$(D + E)$*	59	58	32	29
(D)†	27	27	38.5	38.5
(E)	86	85	70.5	67.5

* Values from Sherman (17).

† Values of $(D)(CN)_2$ and (D)HCN from Kistiakowsky and Gershinowitz (J. Chem. Physics 1, 432 (1933)).

TABLE 6

Proton affinities by process III

	HSH	HBr	HCN
(D)HX*	87	87	94.5
(I)H	312	312	312
(E)X		−85	−69
$(K)X^-$		314	337.5

* See second footnote to table 5.

ployed, and suggests that the only uncertainty lies in the theoretical lattice energies. We therefore select the following (K) values: Br^-, 314; SH^-, 338; CN^-, 338. This readily gives $(E)SH = 61$, and permits the conclusion that while the covalent bond strengths H:Br and H:SH are equal, the proton affinities and electron affinities of the negative groups differ by 24 kg-cal.

Taken in conjunction with the lattice energies of section I, they also permit the calculation of the following heats of formation: lithium hydrosulfide (hypothetical), (47); rubidium hydrosulfide, (65); cesium hydrosulfide, (65); and of the lattice energy of NH_4X as follows.

[1] Lederle (Z. physik. Chem. 17B, 361 (1932)) gives $(E)(CN) = 92 \pm 2$.

IV. LATTICE ENERGY OF NH_4X

The proton affinity of NH_3

$$NH_3 + H^+ \rightarrow NH_4^+ + (P)$$

enters into the following cycle:

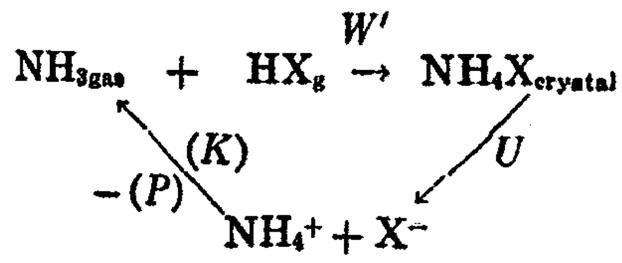


TABLE 7

Lattice energies of ammonium salts

	NH_4Br	NH_4SH	NH_4CN
(W')	45.0	22.4	20.6
(K)	314	338	338
$-(P)$	−211	−211	−211
(U)	148	149	148

TABLE 8

Lattice energies of ammonium salts

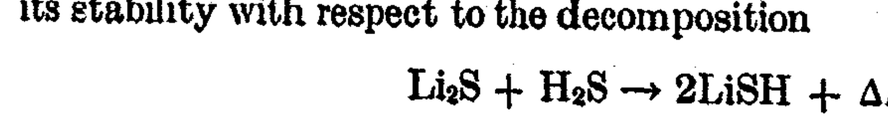
	NH_4Br	NH_4SH
$(L)NH_4X$	−4	−3
$(L)NH_4^+$	−87	−87
$(L)X^-$	−58	−60
$(U)NH_4X$	−149	−150

From W' (Landolt-Börnstein), $(K)HX$ (given in section III), and $(U)NH_4X$ (Sherman) are calculated the following values of (P): ammonium chloride, 214; ammonium bromide, 213; ammonium iodide, 206; or $P_{av.} = 211$. This differs immaterially from Sherman's value for the same constant. From the same cycle are now calculated the lattice energies of ammonium hydrosulfide, which has the PH_4I structure for which the Madelung constant has not yet been given, and of ammonium cyanide whose crystal structure has not been reported (see table 7). This shows that, as in the case of the alkali metals, the three ammonium salts have identical lattice energies and therefore that ammonium hydrosulfide and ammonium cyanide are presumably ionic crystals.

The same value of $(U)NH_4SH$ may be calculated from its reported heat of solution (see table 8).

V. THE STABILITY OF MeSH UNDER VARIOUS CONDITIONS

The ability of lithium hydrosulfide to exist in a stable anhydrous solid form is at least questionable. We are in a position to make an estimate of its stability with respect to the decomposition



$$Li_2S + H_2S \rightarrow 2LiSH + \Delta H$$

and to compare it with the other alkali hydrosulfides.

TABLE 9

Heat of formation of lithium hydrosulfide

(*Q*)LiSH	(47)
(*U*)LiSH	−(178)
(*L*)Li^+	136
(*L*)SH^-	60
(*Q*)$LiSH_{aq}$	(65) calculated
(*Q*)$LiSH_{aq}$	70 observed

TABLE 10

Dissociation of solid alkali hydrosulfides

	Li	Na	K	Rb
−(*Q*)Me_2S	−(111)*	−89	−87	−87
−(*Q*)H_2S	−5	−5	−5	−5
2(*Q*)MeSH	(94)	113	126	(130)
(ΔH)	−(22)	19	34	38
($T\Delta S$)†	−(11)	−(11)	−(11)	−(11)
(ΔF)	−(33)	(8)	(23)	(27)

* (*Q*)Li_2S is assumed equal to (*Q*)SrS; see Guntz and Benoit (Ann. chim. **20**, 5 (1923)).

† The entropy change is a rough estimate and is assumed independent of the alkali metal involved.

In section I it was assumed that if lithium hydrosulfide existed it would have a sodium chloride cubic structure; thus the cube edge, lattice energy, and heat of formation were readily predicted from known radii of crystal ions. These calculated quantities are seen to be consistent when we deduce from them a value for the heat of formation of aqueous lithium hydrosulfide and compare it with the experimental value given in Landolt-Börnstein (see table 9).

The heat and free energy changes of the foregoing decomposition of MeSH, including hypothetical lithium hydrosulfide, are now calculated from heats of formation as given in table 10.

The calculated free energy changes indicate that MeSH is increasingly stable as the atomic number of the cation increases. This is in agreement with the qualitative observations of other writers on the stability of sodium hydrosulfide and potassium hydrosulfide. The negative value of the free energy change for lithium hydrosulfide shows that this hypothetical phase is thermodynamically unstable at ordinary temperatures. Similar deductions could be made from an application of the Nernst approximation formula.

It seems probable that the anhydrous hydrosulfides of the divalent metals—magnesium, calcium, strontium, barium, etc.—will be similarly unstable with respect to this decomposition. An experimental attack on this problem, which apparently has not been tried, would be the determination of equilibrium pressures of hydrogen sulfide over the solid phases MeSH–Me_2S, etc. On the contrary, it is easily shown from known heats of formation that the hydroxides of all the alkali and alkaline earth metals are thermodynamically stable with respect to the corresponding decomposition into water and the metal oxide.

The stability of MeSH in the presence of an alkali metal is also of some interest. When the hydrogens of hydrogen sulfide are successively replaced by Me in the two steps

$$Me + H{-}SH \rightarrow MeSH + 1/2H_2 + (W)$$

and

$$Me + MeSH \rightarrow Me_2S + 1/2H_2 + (Z)$$

each step evolves considerable heat. This is in accord with the observation that the alkali hydrosulfides are readily decomposed by alkali metals. In contrast to this it is known that the molten hydroxides of sodium and potassium are not only stable in contact with the metal but appear to take up a quantity of the metal in true solution (8); this agrees with the calculated negative heats of reaction, Z, for these hydroxides.

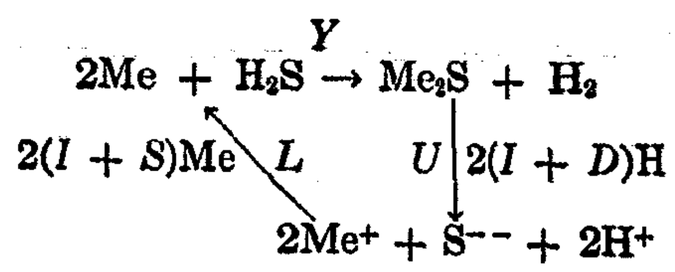
Numerical values of the foregoing reaction heats, including that of the reaction

$$2Me + H_2S \rightarrow Me_2S + H_2 + (Y)$$

are tabulated in table 11.

VI. LATTICE ENERGIES OF ALKALI SULFIDES AND DERIVED CONSTANTS

The lattice energies of the alkali sulfides are now calculated by the Born method (see table 12). Sherman's value for sodium sulfide is reproduced; the cube edge of rubidium sulfide is derived from the reported density 2.912.



The quantities

$$S^{--} + 2H^+ \rightarrow H_2S + (L)$$
$$S^{--} \rightarrow S + 2e + (E')$$

are derived by simple cycles from the lattice energies (U'). They do not differ seriously from values which may be calculated from Sherman's lattice energies of the alkaline earth sulfides.

TABLE 11

Decomposition of alkali hydrosulfides

	Li	Na	K	Rb
$(Q)Me_2S$	(111)	89	87	87
$-(Q)H_2S$	−5	−5	−5	−5
Y	(106)	84	82	82
W	(42)	51	58	(60)
Z	(64)	33	24	(22)

TABLE 12

Lattice energies of alkali sulfides

	a	n	$-U'$	L
Li_2S	5.70	7	576	(872)
Na_2S	6.53	8	516	869
K_2S	7.35	9	465	866
Rb_2S	(7.71)	9.5	(446)	(858)
				868

From the adopted values $(K) = 338$, $(L) = 868$, are found further the reaction heats[2]

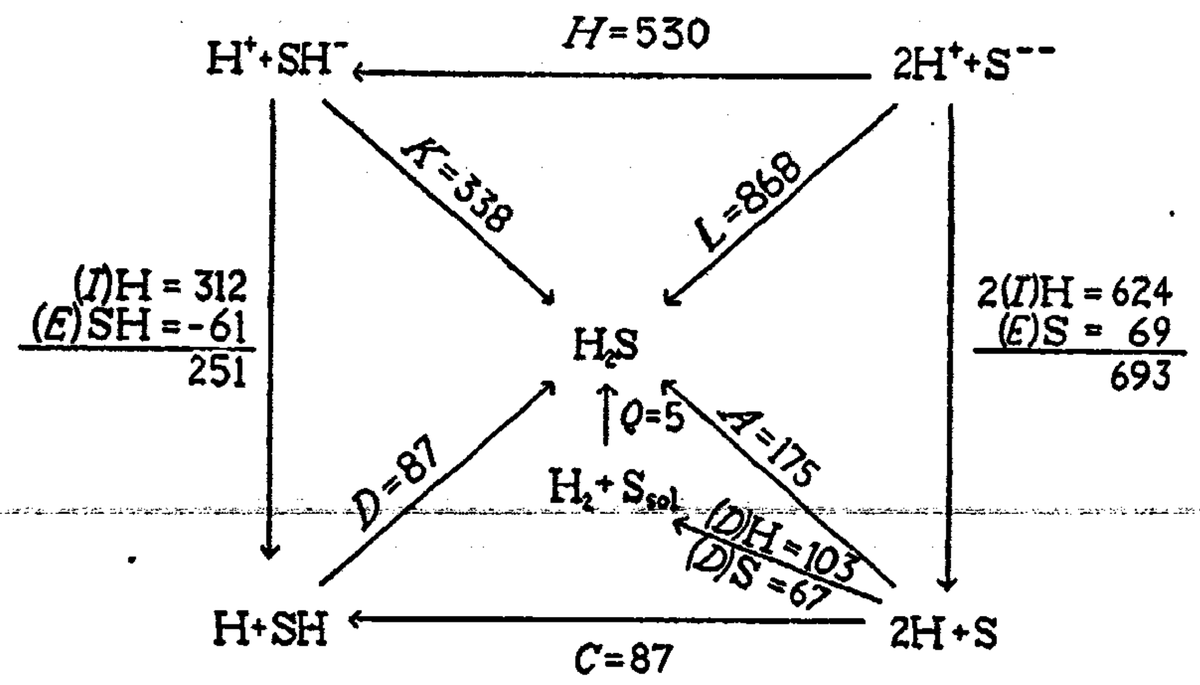
$$S^{--} + H^+ \rightarrow SH^- + (H): H = L - K = 530$$
$$S^{--} + H_2S \rightarrow 2SH^- + (M): M = L - 2K = 192$$

The thermochemical constants for hydrogen sulfide are summarized in diagram 1.

[2] Approximate values for H, K, L have been deduced by Hund (Z. Physik 32, 1 (1925)) from a model for the hydrogen sulfide molecule.

Finally the heat of hydrolysis of the S^{--} gas ion may be calculated by either of two cycles, as given in tables 13 and 14.

$$S_g^{--} + H_2O_{liq} \rightarrow SH^-_{aq} + OH^-_{aq} + (J)$$



Heat cycles for H_2S molecule

DIAGRAM 1

TABLE 13

Calculation of the heat of hydrolysis of the S^{--} gas ion

	Li_2S	Na_2S	K_2S	Rb_2S
U	−576	−516	−405	−(446)†
−$(L)Me_2S$	−(11)*	−16	−23	−25
$2(L)Me^+$	272	228	188	174
J	(315)	304	300	(297)

* From $(Q)Li_2S_{aq} - (Q)Li_2S = 122 - (111) = (11)$.

† Lattice energy calculated from reported density.

TABLE 14

Calculation of the heat of hydrolysis of the S^{--} gas ion

$H^+ \rightarrow H^+_{aq}$	276	$HOH_{liq} \rightarrow HOH_g$	−10
$OH^- \rightarrow OH^-_{aq}$	$(L)OH^-$	$HOH_g \rightarrow H^+ + OH^-$	$-(280 + (L)OH^-)$
$H^+_{aq} + OH^-_{aq} \rightarrow HOH_{aq}$	14	$S^{--} + H^+ \rightarrow SH^-$	530
$HOH_{aq} \rightarrow HOH_g$	−10	$SH^- \rightarrow SH^-_{aq}$	60
		$OH^- \rightarrow OH^-_{aq}$	$+(L)OH$
$(K)OH^-$*	$280 + (L)OH^-$	(J)	300

* Precisely this same value, $(K)OH^- = 280 + (L)OH^-$, follows from the experimental heats of reaction of the alkali metals with water when combined with the ionic heats of hydration used above.

If instead of the alkali sulfides the alkaline earth sulfides are used as a basis of calculation, somewhat larger values of (J) are obtained, similar to the case of the quantities (L), (H), etc., already mentioned.

The second method (table 14) introduces the proton affinity $(K)OH^-$.

The two methods thus give identical results, namely $(J)S^{--} = 300$, or a somewhat greater value from the alkaline earth sulfides.

VII. THE PROTON AFFINITY OF OH^- AND OF SeH^-

The proton affinity $(K)OH^-$ may be calculated in terms of $(U)NaOH$ or of $(L)OH^-$ by the methods outlined in preceding paragraphs. Thus

$$(K)OH^- = 175 - (U)NaOH; \ (L)OH^- = -104 - (U)NaOH$$

Previously proposed values for these constants are as follows:

$(K)OH^- = 370 \pm 30$ Hund from model (10)
$(U)NaOH = 186 \pm 5$, $(K)OH^- = 360 \pm 5$ Garrick (5)
$(L)OH^- = 105$, $(K)OH^- = 385$ Bernal (1) from radius OH^-

From x-ray powder data at 300°C. I have some evidence that the high temperature modification of sodium hydroxide has the sodium chloride structure with $a = 5.00$; from this may be calculated the radius of $OH^- = 1.50$, the lattice energy $(U)NaOH = 201$ kg-cal., and $(L)OH^- = 97$. This gives a fourth value, namely $(K)OH^- = 376$. We take the average of the four values, none of which appears very reliable, as $(K)OH^- = 373 \pm 20$.[3] From this and the heat of dissociation, $(D)HOH = 115$, may be calculated the electron affinity of OH as $(E)OH = 54 \pm 20$.[4]

It is also possible to estimate the proton affinity of SeH^-. By process II, given

$$H_2Se_g \rightarrow H^+_{aq} + SeH^-_{aq} + 3 \ (\pm 10)$$

and assuming $(L)SeH^- = 55 \pm 10$, we find $(K)SeH^- = 328 \pm 20$. Further, given $(W')NH_4SeH = 30$ and assuming $(U)NH_4SeH = -146 \pm 10$ we find $(K)SeH^- = 327 \pm 10$.

Thus 328 ± 20 seems a safe estimate for this quantity, and from it and the known heat of dissociation, $(D)H - SeH = 67$, may be found such further constants as may be desired.

The constants proposed above for SH, CN, OH, and SeH are now tabulated (table 15) for comparison with accepted values for some other univalent anions. These constants are related by the equation

$$(K) - (I)H = (D) + (E)$$

where $(I)H = 312$.

[3] H. Smyth and D. Miller (Phys. Rev. **43**, 116 (1933)) recently found $(K)OH^- = 460 \pm 115$.

[4] E. Lederle (Z. physik. Chem. **17B**, 368 (1932)) gives $(E)OH = 88 \pm 1$.

VIII. COVALENT BOND ENERGIES

It has already been pointed out that the S:H and Br:H covalent bond energies are both equal to 87 kg-cal. Likewise it has been shown (15, 16) that the S:C and Br:C covalent bond energies are both about equal to 67 kg-cal. The consequence of these coincidences is that the thermochemistry of organic bromides and mercaptans will be largely similar. This statement may be verified for such simple reactions as

$$>C{=}C< + HX \rightarrow >CH{-}CX<$$
$$ROH + HX \rightarrow RX + H_2O$$

where X is Br or SH, by the use of the compilation of Parks and Huffman (14).

TABLE 15

Comparison of gas ions and their hydrides

X	$(K)X^-$	$-(E)X$	$(D)HX$	$(L)X^-$	CRYSTAL RADIUS X^-	DISTANCE H – X
I	307	76	71	47	2.19	1.616
Br	314	85	87	58	1.96	1.420
SeH	(328)	(51)	67	(55)		
SH	338	61	87	60	1.99	1.43
CN	338	68.5	94.5	58	1.93	
Cl	326	88	102	65	1.81	1.282
F	361	98.5	148	97	1.33	0.923
OH	(373)	(54)	115	(93)		0.96
H	400	16	103			0.75

According to these figures the difference $(K - L)X^-$ is equal to 260 for the four strong hydrogen halide acids, while for the weak acids HSH, HCN, and HOH it is 20 kg-cal. greater, or 280.

According to this analysis the reactions

$$MeSH_s + HBr_g \rightarrow MeBr_s + HSH_g + \Delta H_1$$
$$MeSH_s + RBr_g \rightarrow MeBr_s + RSH_g + \Delta H_2$$

will have

$$\Delta H_1 = \Delta H_2 = (E)Br - (E)SH = 85 - 61 = 24 \text{ kg-cal.}$$

this statement is also easily verified. The second of these reactions is commonly employed in the preparation of the mercaptans, RSH; in view of the large heat change it is readily understood why they both run to completion. On the contrary the reaction

$$HBr + RSH \rightleftharpoons RBr + HSH$$

would have only a small heat change and therefore might be expected to give an equilibrium of reactants and products. It may also be shown that

the reaction

$$HBr_g + MeCN_s \rightarrow HCN_g + MeBr_s + \Delta H$$

will have

$$\Delta H = (K)CN^- - (K)Br^- = 338 - 314 = 24 \text{ kg-cal.}$$

IX. SOME PHYSICAL PROPERTIES OF COVALENT BROMIDES AND HYDROSULFIDES

Familiar examples of comparable covalent compounds containing Br, SH, and CN radicals are the hydrides (HX), the dimers (XX),[5] and the carbon compounds (RX); of these the hydrides have been the most intensively studied. While it would be unwise to generalize from these to other covalent compounds, nevertheless the similarities in these three types are at least very suggestive. The molecules H:X and R:X, where X is Br or SH, are moderately polar, while the HCN and RCN molecules are strongly polar. The X—X molecules are symmetrical and non-polar. The hydrogen sulfide molecule is angular; hydrogen cyanide is linear.

In these compounds the space requirements of Br, SH, and CN are generally similar as calculated by the numerous methods available. For example, the additive parachors 68.0, 65.3, and 63.9, the additive mole volumes at the boiling point, 27.6, 29.4, and 30.5, respectively, have been proposed for the Br, SH, and CN groups. The mean free paths of hydrogen bromide and hydrogen sulfide at a given temperature, as calculated from gas viscosity data, differ by only 5 per cent, but that of hydrogen cyanide is considerably shorter. Similarly van der Waals' b, as calculated from critical constants, is nearly the same for hydrogen bromide and hydrogen sulfide, but is considerably larger for hydrogen cyanide.

Neither do the additive mole refractions of —Br and —SH differ greatly, however calculated; commonly used values are —Br, 8.87, and —SH, 8.79. This shows that the electrons are similarly bound in the two groups. Bromides and hydrosulfides thus have nearly the same refractive indices under the same conditions, as well as mole refractions. The considerably lower mole refraction of —CN, 5.54, is accounted for by supposing that the electron shells are more tightly bound in this group. Liquid H_2S_2 is distinguished from H_2O_2 in having normal values for its parachor and mole refraction; a rather large electric moment has been attributed to the hydrogen peroxide molecule.

The attractive forces between molecules, indicated by such constants as the heat of vaporization, van der Waals' a, the Sutherland constant C, the critical temperature, etc., are similar where known for corresponding

[5] Physical properties of $(SH)_2$ are given by Butler and Maass (J. Am. Chem. Soc. **52**, 2197 (1930)).

bromides and hydrosulfides; but relative to these they are large for hydrogen cyanide and the nitriles and small for cyanogen. The analysis of these forces according to London's theory shows that while the dispersion effect predominates in hydrogen bromide (13) and hydrogen sulfide (2), the orientation effect is greatest in the hydrogen cyanide (2) molecule.

Finally the valence forces within the molecule have been shown to be similar for the H:Br and H:S and also for the C:Br and C:S linkages by calculation from their characteristic Raman frequency shifts (12).

It is of interest that cubic hydrogen sulfide and hydrogen bromide crystals form an uninterrupted series of solid solutions. The structure is a close packing of rotating molecules and is indistinguishable from that of the rare gases. On further cooling both crystals undergo transitions in which the dipole molecules become rigidly oriented, as shown by the sudden drop in the dielectric constant (9, 11, 18) and specific heat (3, 6) curves. Thus the parallelism in the physical properties of these two substances extends from the critical state down to the lowest temperatures at which they have been investigated. The properties of crystalline hydrogen cyanide have not been studied.

Ellis and Reid (4) have tabulated some physical constants of some liquid *n*-alkyl bromides and mercaptans, although they fail to stress the evident similarities. From the nonyl down through the amyl compounds and in some cases beyond, the following constants lie remarkably close together in the two series: melting point, normal boiling point, expansion coefficient mole volume, refraction, mole refraction. Bromides and mercaptans are normal unassociated liquids, nitriles are highly associated, as shown by fluidity and surface tension measurements. Although bromides and mercaptans differ in chemical properties, it is evident that they form a more logical pair for comparison of physical properties than mercaptans and alcohols as inevitably heretofore. That the SH radical would have this character of a halogen was implied by Grimm's hydride displacement rule (7).

The statements of this section are illustrated by the accompanying tabulations of physical constants (see table 16).

X. SUMMARY

Corresponding alkali bromides and hydrosulfides have nearly the same lattice energies; the proton affinities of Br^- and SH^- differ by about 23 kg-cal. The stability of the alkali hydrosulfides alone and in the presence of an alkali metal is treated from a thermochemical standpoint. Some reaction heats are deduced from the lattice energies of the alkali monosulfides. A brief survey of the physical properties of corresponding covalent bromides and hydrosulfides discloses some notable similarities. The foregoing treatment is extended in some cases to include cyanogen compounds.

TABLE 16

*Physical properties of covalent bromides, hydrosulfides, and cyanides**

	HBr	HSH	HCN	Br_2	$(SH)_2$	$(CN)_2$	EtBr	EtSH	EtCN
Dipole moment	0.79	0.93	2.65	0		(0.3)	1.86	(1.39)	3.4–3.7
Parachor (observed)	85.4	82.9	81.5	132.1	130.0		167.6	159.3	
Mole volume at boiling point (observed)	37.4	35.2	38.8	53.4	53.0	60.4		77.6	78.5
Mole refraction	9.15	9.64	6.48	17.44	17.73	12.32	19.11	19.19	15.78
Refractive index (liquid)	1.325	1.384	1.268	1.648	1.632		1.424	1.427	1.369
Refractive index (gas)†	0.573	0.642	0.438	1.132		0.850			
Melting point	−86	−83	−14	−7	−90	−28	−119	−147	−104
Boiling point	−68	−60	26	59	71	−20	38	35	98
Heat of vaporization	3.9–4.2	4.5–5.2	6.1–6.6	7.0	8.5	5.4–5.8	6.4–6.7	6.9	7.4
Critical temperature	90	100	184	301	(278)	127	236	228	291
Sutherland constant	375	331	901	460		330			
Entropy S_{298}	47.5	48.2	48.2	59.1		57.8			
Raman shift	2558	2615	3220				594	704	
Force constant, f	3.56	3.88					2.61	3.01	
Mass	80.92	34.08	27.02						
Outer electrons	36	18	14						
Nuclear charge of X	35	16 + 1	6 + 7						
Zero point volume	27.3	26.9							
Cube edge	5.78	5.77							
Relative mean free path‡	202.5	214.5	142.4						
Critical pressure	84	89	53						
Van der Waals' a	887	883	2220						
b	1978	1914	3920						

* From Landolt-Börnstein Tabellen, or recent sources.

† $(n_D - 1)\ 10^3$.

‡ Gas viscosity at 20°C. divided by square root of molecular weight.

Dr. Linus Pauling first suggested to me that the thermochemistry of the hydrosulfides might be worth investigating from the point of view adopted in this paper. My best thanks go to Dr. H. M. Smallwood for his generous help in criticising the material here presented.

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THE EFFECT OF CATHODE RAYS ON HYDROPHOBIC SOLS

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Received July 5, 1934

The action of ionizing radiations on colloids was first investigated by Hardy (8) in 1903. He found that positively charged globulin sols were coagulated by β-rays from radium, while negatively charged sols were rendered more disperse. Henri and Meyer (9) reported that β-rays discharged the positively charged ferric hydroxide but not negatively charged sols. Fernau and Pauli (7) obtained coagulation of ceric hydroxide and albumin, by exposure to both β-rays and x-rays. Using x-rays Wels and Thiele (14) found that aggregate formation occurred in globulin sols on both sides of the isoelectric point, and hence was independent of the sign of the particle charge. Nordenson (12) studied the influence of ultra-violet light, x-rays, and β-rays on gold sols, and found that positively and negatively charged sols were coagulated at about the same rate. Crowther and Fairbrother (5) found that copper and iron sols which are positively charged were coagulated on exposure to large quantities of x-rays, and that silver and gold sols, which are negatively charged, were rendered more stable. Clark and Pickett (3) worked with positively charged colloidal lead and found it stabilized by exposure to x-rays. Lal and Ganguly (10) studied the coagulating influence of ultra-violet light and concluded that the stability of the sol was decreased, whether the sol was positively or negatively charged. In a recent paper, Boutaric and Roy (1) report that the γ-rays from radioactive materials do not affect colloid stability, and that the β-rays coagulate positively charged sols but do not affect the stability of negatively charged sols. They investigated sols of ferric hydroxide and gum mastic. Clark (2) states, "At present the results are still so conflicting due to large effects of impurities, sensitiveness to hydrogen-ion concentration, and other unknown eccentricities, such as internal photoelectric action, that no definite conclusions or rules can be established." (See also references 6 and 13.)

The present investigation was undertaken to obtain some definite information regarding the effect of ionizing radiations on colloids. Cathode rays were chosen for the experiments, (1) because of their simple nature and their high energy, (2) because the number of electrons emitted per second and the energy of the electrons could be varied independently,

and (3) because, as far as could be ascertained, the effect of cathode rays on colloids had not previously been investigated.

The cathode-ray tube was of the simple form originally designed by Coolidge. It was operated by a transformer system similar to that described by him (4). The voltage applied to the tube was of the order of 150 kilovolts, and tube currents from 0.15 to 0.25 milliampere were used. The reaction cell was composed of two circular sheets of mica, 5 cm. in diameter and 0.0025 cm. thick, separated by a ring of glass 1.3 cm. thick. Washers were placed on the outer surface of each mica disc, and the combination was tightly clamped in a heavy brass container, by a screw counter cell. The liquid bombarded was thus only in contact with glass and mica, and the cell could easily be taken apart to be cleaned. The cell was connected to earth, and placed directly in front of the window and as close to it as possible.

In the first set of experiments the colloids were simply bombarded with the cathode rays and observed to see if coagulation had occurred. In the second set, samples not coagulated by bombardment were tested with electrolyte for change in stability. In the third set of experiments, the cataphoretic mobility of the sol particles was measured before bombardment, and after various lengths of exposure to the rays. Samples of sols not exposed to the rays, but otherwise subjected to the same manipulation as the treated samples, were used as controls. These controls gave no evidence of decrease in stability. The metallic sols were all made by the high frequency under water sparking method, but differed in concentration, even from sample to sample of sols of the same metal.

The results of the first two sets of experiments are shown in table 1. Two typical series of results of the third set are shown in table 2. Mobilities were measured one hour after the bombardment was completed. The gold sol used had a high conductivity, as it was stabilized with a small amount of potassium hydroxide; the copper sol had a low conductivity, as its dispersion medium was doubly distilled water. On bombardment the conductivity increased for sols of low initial conductivity, but it was not measurably affected when the initial conductivity of the sol was high.

No appreciable change in the conductivity of colloids or water took place on standing in the cell; moreover, no appreciable change in the conductivity of the water was observed due to exposure to cathode rays. This shows that decrease in stability cannot result from absorption of electrolytic impurities from the cell. Under bombardment the sol was never heated to a temperature higher than 40°C.; this rise in temperature does not account for the changes produced, for most of the sols could be boiled without coagulating.

The results thus indicate that the stability of both positively and

negatively charged sols is decreased by exposure to cathode rays. This is in agreement with the theoretical considerations outlined below.

The cathode rays in passing through the sols will, on collision, give up their kinetic energy and their charge. The extra charge introduced by the cathode rays must eventually escape to earth, and can only affect the

TABLE 1

The effect of cathode rays on the stability of sols

SOL	TUBE CURRENT	TUBE VOLTAGE	LENGTH OF EXPOSURE	RESULTS
	milli-amperes	*volts* $\times 10^3$	*hours*	
Copper	0.12	140	5	Coagulated
	0.25	140	1.5	Coagulated
	0.21	150	1	Coagulated
	0.18	150	1.25	Coagulated
	0.25	160	2.5	Less stable to electrolytes
	0.25	160	1	Coagulated on standing
	0.25	160	1.5	Coagulated on standing
	0.25	160	0.5	Coagulated on standing
Gold	0.12	153	3.5	Not coagulated
	0.12	148	4	Not coagulated
	0.25	150	2	Electrolyte test not definite
	0.25	150	0.75	Less stable to electrolytes
		160	2	
	0.25	160	2	Less stable to electrolytes
	0.25	160	3	Coagulated on standing
Silver	0.25	150	2	Less stable to electrolytes
	0.25	160	2.5	Coagulated
	0.21	160	1.5	Coagulated on standing
Ferric hydroxide	0.25	127	1.25	Not coagulated
		150	2	
	0.21	150	2	Less stable to electrolytes
Lead	0.25	160	1.5	Coagulated on standing
Bismuth	0.25	160	1	Coagulated on standing
Platinum	0.25	160	2	Coagulated on standing
Arsenious sulfide	0.25	160	3.5	Very turbid, partially coagulated

sol stability when adsorbed by the sol particles; in this case the stability will be increased or decreased according to whether the sol is negatively or positively charged. The kinetic energy given up by the cathode rays will result in the production of ionization. Ionization of the dispersion medium means an increase in the effective electrolyte concentration, which, in general, will bring about a decrease in sol stability irrespective of the

sign of the charge of the sol particles. Unless some permanent chemical reaction results, the positive and negative ions will recombine and the net result will be the production of heat. On collision some of the energy will be used in the production of x-rays, but the percentage of energy so used will be small, for Clark states that even in an x-ray tube at least 98 per cent of the electron energy goes to the heating of the target. The total change in stability will thus depend on the ratio of the effect produced by the transfer of charge to the sol particles to that produced by the ionization of the medium. For a 0.1 per cent gold sol the ratio of the proba-

TABLE 2

The effect of cathode rays on the mobility of sol particles

Tube voltage, 160 kilovolts; current, 125 milliamperes

DURATION OF CATHODE RAY BOMBARDMENT	CONDUCTIVITY	MOBILITY
Gold sol, 0.0262 g. per 100 cc.		
	ohms⁻¹ cm.⁻¹	*cm. per second per volt per cm.*
Untreated		0.00018
Control		0.00018
0.5 hour		0.00016
1.0 hour	1.9×10^{-4}	0.00013
1.5 hours		0.00011
Untreated		0.00018
Control		0.00018
0.5 hour		0.00016
Copper sol, 0.0128 g. per 100 cc.		
Untreated	7.9×10^{-6}	0.00020
Control	8.0×10^{-6}	0.00020
0.5 hour	11×10^{-6}	0.00015
1.0 hour	16×10^{-6}	0.00015
1.5 hour	17×10^{-6}	0.00012 (Coagulated after 3 hrs.)
Untreated	8.0×10^{-6}	0.00020
0.5 hour	12×10^{-6}	0.00015
1.0 hour	19×10^{-6}	0.00015 (Coagulated after 5 hrs.)
1.5 hours		

bility of collision of a cathode ray with a gold particle to the probability of collision with a water molecule is about $1:10^7$, so that it seems quite reasonable that, in general, decrease of stability will result on exposure.

Lind (11) states, "The chemical effects of α- and β-rays must be attributed to their kinetic energy and ionizing power, not to their own charges, which in comparison with the secondary charges produced are wholly insignificant."

Experiments were also conducted on the rates of heating of water and of colloids under cathode-ray bombardment. One junction of a copper-

constantan thermocouple was kept in ice, and the other was placed in the liquid above the level of the direct cathode ray stream; the heating produced was measured by deflections of a sensitive galvanometer. During the latter part of this work the reaction cell consisted of two circular sheets of mica 5 cm. in diameter and 0.0025 cm. thick cemented to a ring of glass 0.63 cm. thick, and supported by a thin circular brass strip held in a wooden clamp. This apparatus was designed to have as small a water equivalent as possible. The results obtained are shown in table 3.

TABLE 3

Rates of heating of water and of colloids under cathode-ray bombardment

Tube voltage, 155 to 160 kilovolts

COLLOIDAL SOLUTION	TUBE CURRENT	RATE OF HEATING OF SOL RELATIVE TO RATE OF HEATING OF WATER	REMARKS
	milli-amperes		
Silver (0.008 g. per 100 cc.)	0.25	1.26	Conditions as nearly uniform as possible
Silver (0.008 g. per 100 cc.)	0.21	1.09	
Gold (0.038 g. per 100 cc.)	0.18	1.32	
Copper (0.009 g. per 100 cc.)	0.18	1.32	
Gold (0.038 g. per 100 cc.)	0.18	1.06	Position of cell changed relative to window
Copper (0.010 g. per 100 cc.)	0.18	1.14	Readings taken on successive days
Copper (0.010 g. per 100 cc.)	0.18	1.12	
Gold (0.0322 g. per 100 cc.)	0.18	1.31	
Gold (0.0322 g. per 100 cc.)	0.15	1.12	Conditions as nearly uniform as possible
Gold (0.0322 g. per 100 cc.)	0.15	1.10	
Gold (0.0256 g. per 100 cc.)	0.15	1.17	Conditions as nearly uniform as possible
Gold (0.0256 g. per 100 cc.)	0.15	1.15	

* Each of the last five results represents the average of two sets of experiments performed consecutively.

In each case investigated the rate of heating of the sol was greater than the rate of heating of the water; the rates of heating were approximately proportional to the tube current; and the rates of heating of sols on different days under similar conditions were in very good agreement.

The results seem quite definite, but the explanation must be a matter for further research. Intensity measurements indicate that both the water and the sol completely absorb the energy of the cathode ray beams bombarding the liquid, and theoretical calculations show that on passing through the cell the intensity of the cathode ray stream is reduced to 10^{-23} of its initial value. The accepted heats of flocculation are 10^3 times too small to account for the observed differences, the energy due to the charge on the surface of the colloid particles is 10^6 times too small, and the energy

due to the compression of the water around the colloid particle is about 10^{13} times too small; so that it is not at all clear what additional source of energy in the colloid state could account for this phenomenon.

SUMMARY

1. The stability of both positively and negatively charged sols is decreased by exposure to cathode rays.

2. This result is in agreement with the theoretical considerations outlined.

3. The rate of heating of a sol under cathode ray bombardment is slightly greater than the rate of heating of water under similar conditions. Known sources of energy in the colloid state are found inadequate to account for this phenomenon.

In conclusion, the author wishes to express her sincere appreciation to Professor E. F. Burton and to Professor H. J. C. Ireton, of the Department of Physics at the University of Toronto, for their helpful suggestions and advice throughout the investigation.

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MIGRATION STUDIES WITH COLLOIDS. III

The Behavior of Gelatin-protected Ferric Oxide and Manganese Dioxide Sols

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Received July 23, 1934

INTRODUCTION

A characteristic of hydrophilic sols in general, and gelatin in particular, is that they show a diffuse light cone and no "resolvable" particles when viewed under the ultramicroscope. It has been found easier, therefore, to abandon the use of this instrument when making electrophoretic studies with these systems (8, 22, 24, 26, 28). Particles of microscopic size have been suspended in protein sols and their rate of movement in an electric field measured with the aid of a microscope (3, 8, 18a). It has been shown that the particles are coated with an adsorbed film of protein (5, 16; see, however, references 4 and 25), and that their behavior in an electric field is due entirely to the protein covering.

In the present investigation it has been found that the particles in ferric oxide–gelatin sol mixtures and manganese dioxide–gelatin sol mixtures are "visible" in an ultramicroscope, and that their migration velocities under varying conditions can be studied.

EXPERIMENTAL

The ferric oxide sol was made by high temperature hydrolysis of a ferric chloride solution and was dialyzed for a week at 90°C. It was diluted to 0.5 g. of iron per liter for use in preparation of the samples. The manganese dioxide sol was prepared by adding concentrated ammonium hydroxide to boiling potassium permanganate (7) and dialyzing as above.

Stock solutions of gelatin were made from day to day with Eastman de-ashed gelatin. This was dissolved at 50°C. and cooled to room temperature, after which a trace of toluene was added as a preservative.

In the study of the effect of salts on the migration velocity of sol–gelatin mixtures, stock samples were made by adding 0.1 per cent gelatin to the sol in the ratio of 4 cc. to 1 cc. Individual sol–gelatin–electrolyte samples were prepared by adding 50 cc. of electrolyte solution to 50 cc. of the

above sol–gel mixture. Before any observations were made the samples were set aside for about half an hour to permit equilibrium to be established.

Migration velocities were determined by a method previously described (11). Measurements of pH were made with the glass electrode at approximately the same time as the migration velocities.

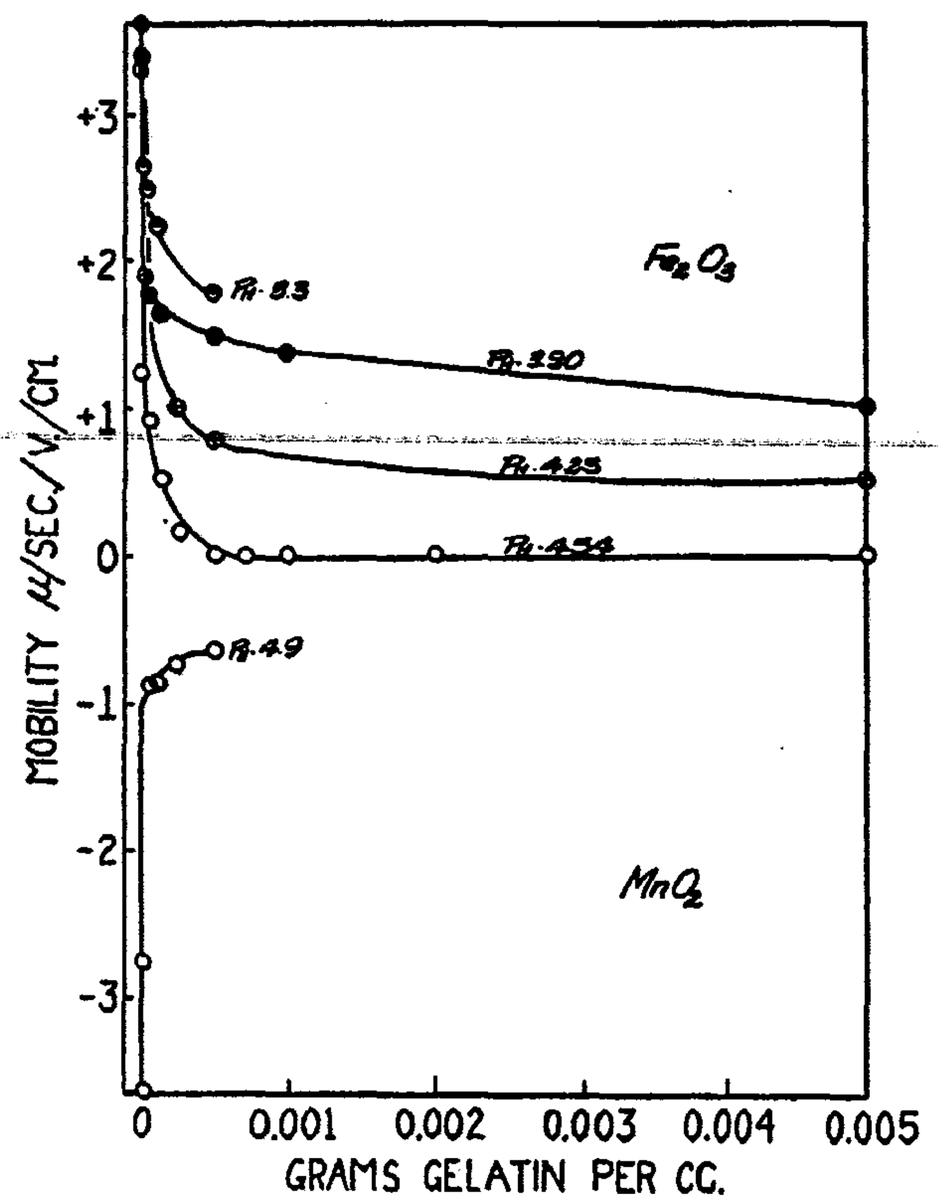


FIG. 1. EFFECT OF GELATIN CONCENTRATION ON FERRIC OXIDE AND MANGANESE DIOXIDE PARTICLES

The effect of gelatin on the migration velocity of ferric oxide and manganese dioxide sols

Some of the results with ferric oxide and gelatin are plotted in figure 1, where it is shown that a limiting value of the electric mobility is approached at about 0.002 g. of gelatin per cm.[3] Samples were made as follows: 10 cc. of sol of the desired pH was diluted to 50 cc. with water of the same pH, and to this were added varying amounts of a 0.1 per cent gelatin solution made up to 50 cc. with water, all of the same pH. The hydrogen-ion activities were adjusted with hydrochloric acid. Results similar to these have been obtained by Limburg (15), who investigated the relation between

the pH value of gelatin and its efficiency as an emulsifier for pure paraffin oil. Limburg made measurements of the cataphoretic velocity of the oil at pH 2.8, 4.7, 5.5 and 9.6, as a function of the concentration of the gelatin. When sufficient gelatin was added, a steady minimum for the migration velocity was reached for any given pH. At pH 4.7 this value was zero.

It has been shown frequently that albumin added in the proper proportions to hydrophobic sols sensitizes and even precipitates the latter (6, 10, 21, 23). Freundlich studied a ferric oxide–crude egg albumin sol and a Carey Lea silver–gelatin sol (9), and observed in both cases that in the presence of small amounts of protein the mobilities of the hydrophobic sols were decreased and the sols coagulated. He further found that increased amounts of gelatin stabilized the silver–gelatin mixture. This author considered that the particles of the hydrophobic sol were enveloped by micells of protein, and that the positive groups of the ampholyte ions were adsorbed by the negative silver particles while the negative groups projected into solution.

Discharge of the system at pH 4.56 led to coagulation at several of the higher concentrations of gelatin. Since at this hydrogen-ion concentration the charge on the gelatin is either neutral or slightly positive, and, in the latter case, of the same sign as the ferric oxide, it would seem that the conditions do not favor an explanation on the basis of mutual coagulation as suggested by Thomas (27). A possible explanation of the precipitation is that owing to the close proximity of the gelatin to its isoelectric point its solubility is near the minimum and when some of the soluble groups are removed from solution by adsorption, the gelatin precipitates with the discharged ferric oxide.

The effect of hydrogen-ion concentration on the mobility of particles in sol–gelatin mixtures

Various minima and maxima properties of gelatin are identified with its isoelectric point. Changes in the magnitude of these properties with pH are associated with its ampholyte behavior, e.g., alteration of the degree of ionization of the acid and basic groups with the acidity of the system. In addition to change of ionization produced by varying the acidity there is evidence (12, 13, 14) that the hydrogen ion also produces changes in the degree of dispersion of the gelatin particles.

Loeb (18) laid great stress on the importance of hydrogen-ion concentration in protein behavior; the correctness of this viewpoint was amply borne out by experiments with gelatin in the present investigation.

The marked influence of hydrogen-ion activity on the mobility of sol–gelatin mixtures is shown in figure 2. The samples were prepared in a uniform manner by mixing 10 cc. of sol with 40 cc. of a 0.1 per cent gelatin solution and diluting with 50 cc. of water, all of the same pH. The fact

that in the presence of gelatin the two oppositely charged hydrophobic sols give a single curve strongly indicates that the systems consist of gelatin-coated particles and that their behavior is that of the protein. The concentration of gelatin in these experiments was 0.0004 g. per cubic centimeter, and is sufficient to cover the particles of the metallic oxide hydrosols with a film of protein. These results may be compared with those of Abramson (1), who also found that concentrations of the order of 10^{-4} g. of gelatin per cubic centimeter were able to convey to quartz particles the properties of the protein.

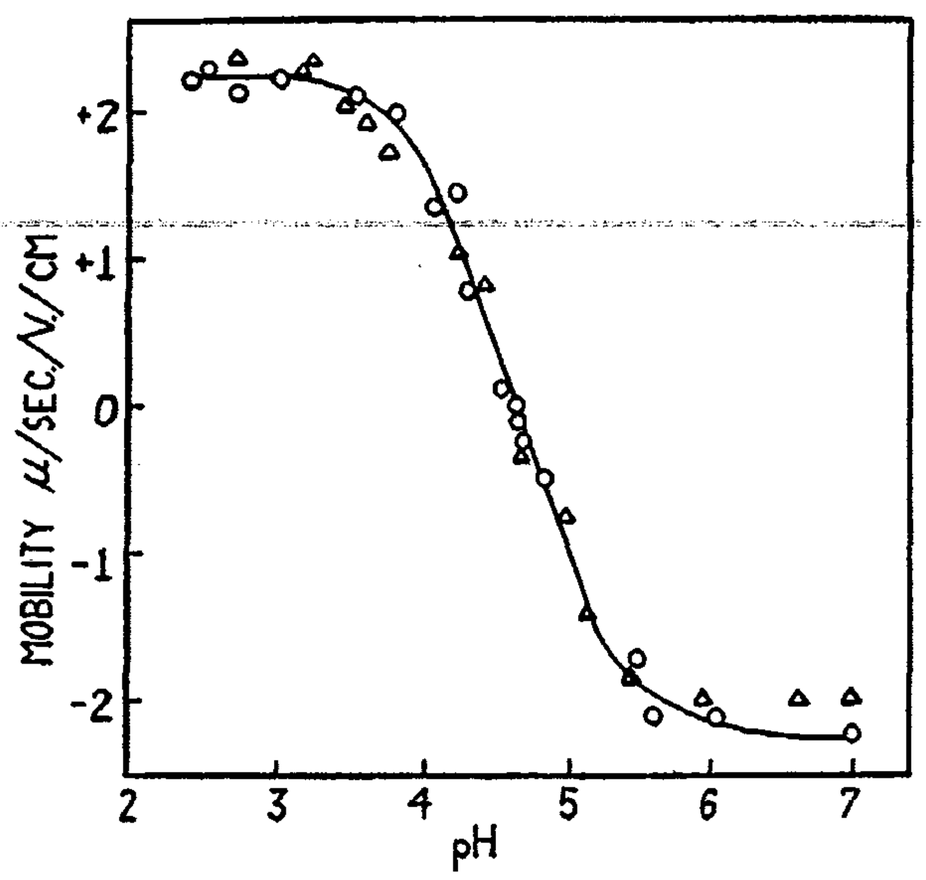


FIG. 2. EFFECT OF HYDROGEN-ION ACTIVITY ON GELATIN-COATED FERRIC OXIDE AND MANGANESE DIOXIDE PARTICLES

○ Fe_2O_3 sol; △ MnO_2 sol

The effect of salts on the migration velocity of sol-gelatin mixtures

When salts of the type KCl, K_2SO_4, KH_2PO_4, and $K_3Fe(CN)_6$, are added to a ferric oxide sol, pH 3.9, it is found that there are marked differences in the ability of the salts to decrease the migration velocity of the particles. Potassium chloride, which furnishes the weakly adsorbed chloride ion, decreases the mobility of ferric oxide particles very slightly. With potassium sulfate the discharging by the bivalent sulfate ion is much more pronounced. Monopotassium phosphate and potassium ferricyanide produce a still greater lowering of the mobility and recharge the ferric oxide to the negative form at low concentrations of the electrolyte.

On the other hand, when these same salts are added to a sol-gelatin

mixture pH 3.9, it is found (figure 3) that the mobility curves lie close together and that the marked differences in discharging power associated with mono-, di- and tri-valent ions are absent. It is apparent, however, that there exists a slight increase in the ability of the ions to lower the mobility of the particles as the valence of the negative ion increases. The discharge curves for potassium chloride and monopotassium phosphate are practically identical, indicating that the phosphate ionizes as a monovalent

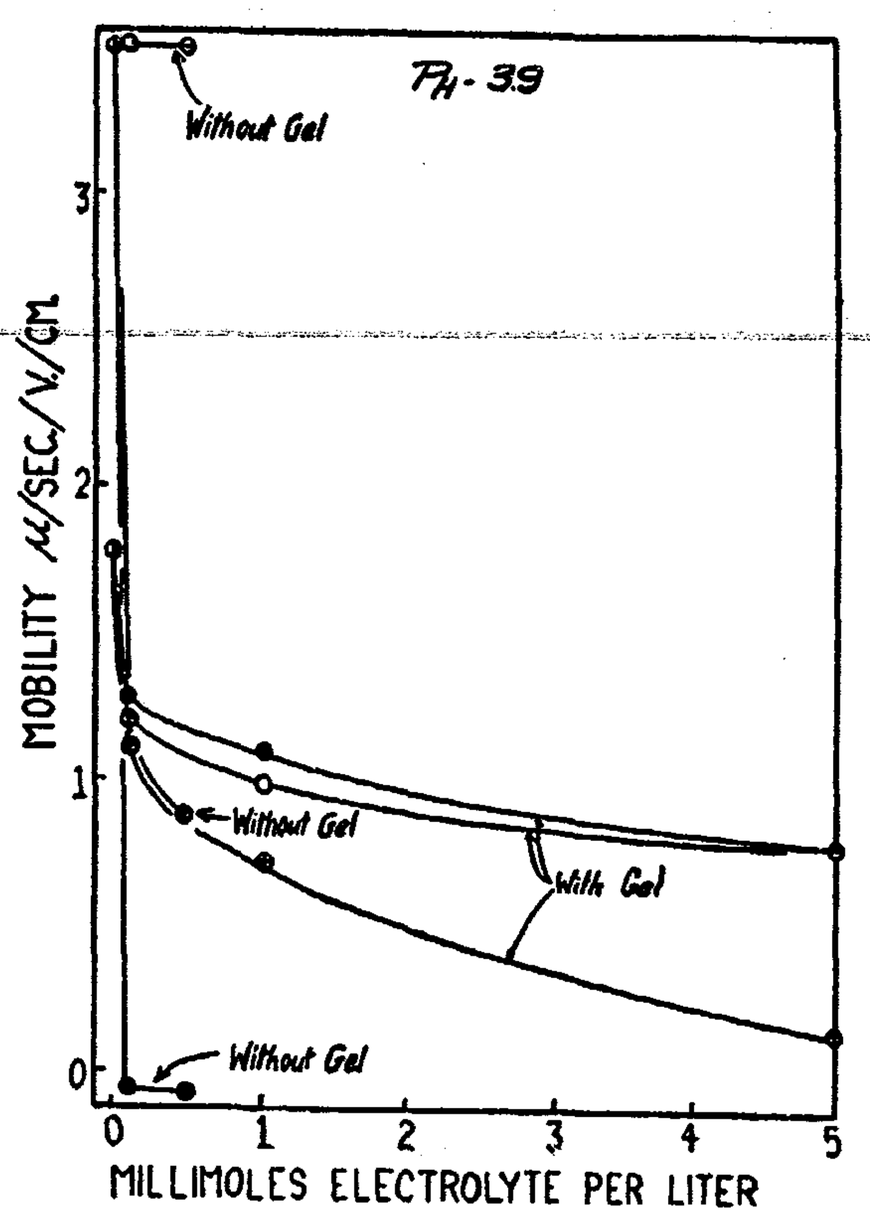


FIG. 3. COMPARISON OF THE EFFECT OF ELECTROLYTES ON UNPROTECTED FERRIC OXIDE AND ON GELATIN-PROTECTED FERRIC OXIDE

○ KCl ● KH_2PO_4 ⊕ K_2SO_4

ion. This is in contrast to the behavior of the salt with unprotected ferric oxide, where it acts as though ionized into trivalent phosphate ions, but is in accord with the experiments of Loeb who found that this salt acted as a monovalent ion with the proteins.

Addition of the electrolytes to a sol–gelatin system of pH 3.9 produced a decrease in acidity of the system. It was found, subsequently, that the major part of the effect of these salts in lowering the mobility of the par-

ticles was due to the pH change. However, the latter is corrected for in figures 4 to 11, and it is evident that there remains a real discharging action by the ions of the electrolytes themselves. The migration data in each figure are for a single electrolyte. Three different concentrations of the salt are plotted at several different pH values. The dotted curve represents the migration velocity in the absence of electrolyte, i.e., the effect of hydrogen-ion activity on the mobility. The divergence of the curves from the dotted line represents the discharging effects of the electrolytes, the order being, for ferric oxide–gelatin, $K_3Fe(CN)_6 > K_2SO_4 > KCl$, KSCN, KH_2PO_4. With the possible exception of monopotassium phosphate the order is the same expected with any positive sol.

In this connection the thing that distinguishes a positive ferric oxide–gelatin system from colloidal systems without gelatin is that the chloride ion produces a lowering of mobility much greater than is to be expected from the well-known low adsorbability of monovalent ions, and also that the sulfate and ferricyanide ions produce a smaller decrease in velocity than is associated with their high adsorbabilities.[1]

DISCUSSION

It is usually adduced from acid and base titration data with the proteins and from the close agreement between the mobilities of freely dispersed proteins as compared with the mobilities of protein-coated surfaces that all of the polar groups are free after adsorption has occurred (2). Thus the fact that the mobility curves of gelatin-coated ferric oxide particles (initially positive) and manganese dioxide particles (initially negative) are the same (figure 2) indicates not only that the mobilities are a function of the protein surface but also suggests, since the isoelectric point (pH about 4.6) under these conditions is in fair agreement with values frequently observed with freely dispersed gelatin, that adsorbed gelatin has ionizing properties similar to dissolved gelatin. However, if gelatin is to be regarded as a polyvalent electrolyte of high molecular weight (which properties together with its degree of ionization are related to the hydrogen-ion activity of the system), one would expect it to be highly adsorbable. The course of the curve in figure 2 might then be interpreted on the premise that gelatin is so strongly adsorbed through its polar groups by hydrophobic particles that the latter acquire a mobility close to the ionic mobility of the dissolved protein. The results in figure 1 are not entirely consistent with a mechanism of adsorption in which polar groups do not take part. The data in this figure show the decrease in mobility of iron oxide with increasing amounts of gelatin. The curves are typical in form to those

[1] There is no reason to question that gelatin adsorbs ions, but from the present data the mechanism of this adsorption does not appear to be one in which the ions enter directly into the double layer, i.e., to decrease its thickness.

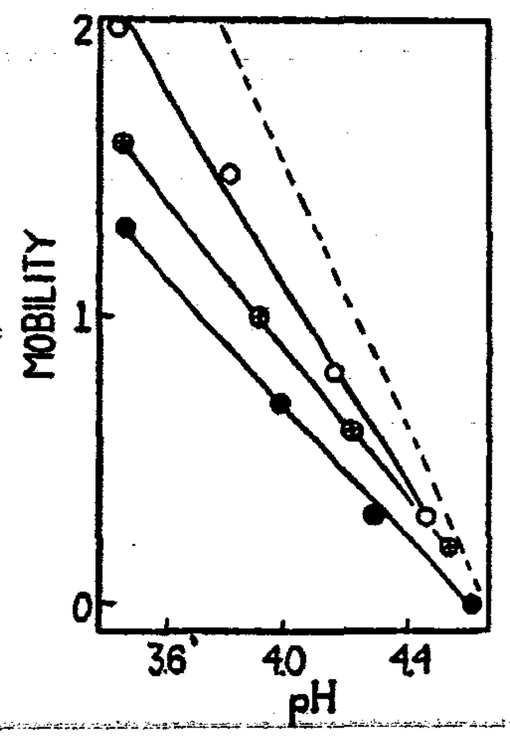


FIG. 4

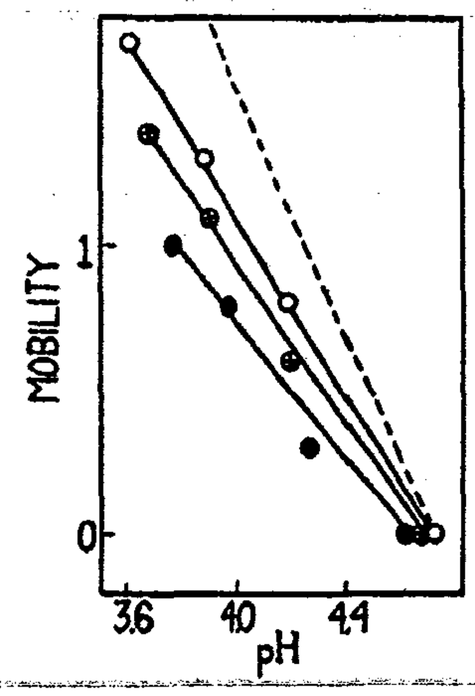


FIG. 5

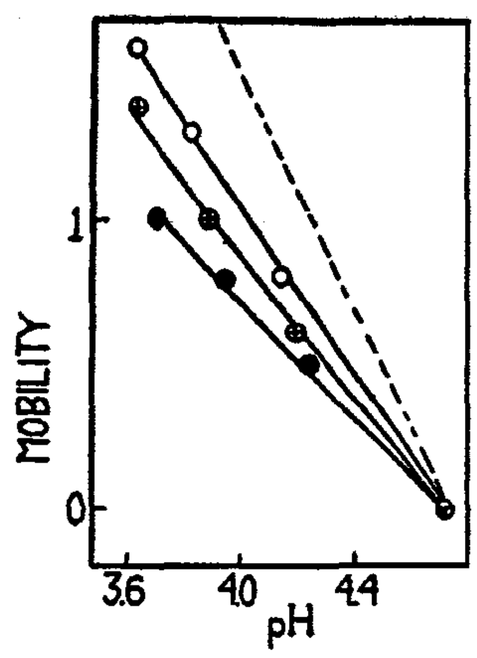


FIG. 6

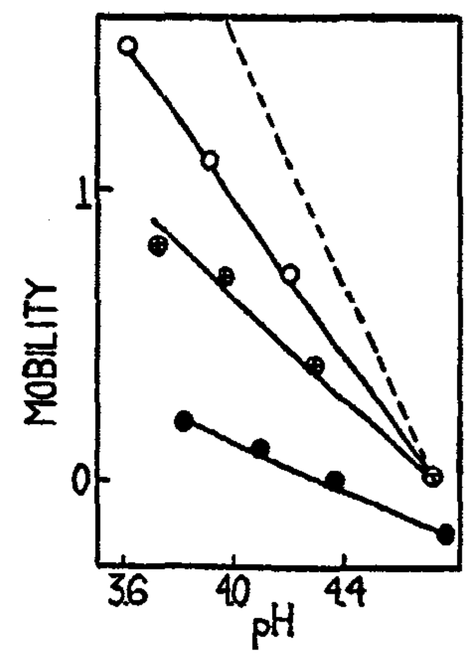


FIG. 7

FIG. 4. FERRIC OXIDE-GELATIN

○ KCNS, 0.1 millimole per liter
⊕ KCNS, 1.0 millimole per liter
● KCNS, 5.0 millimoles per liter

FIG. 5. FERRIC OXIDE-GELATIN

○ KH_2PO_4, 0.1 millimole per liter
⊕ KH_2PO_4, 1.0 millimole per liter
● KH_2PO_4, 5.0 millimoles per liter

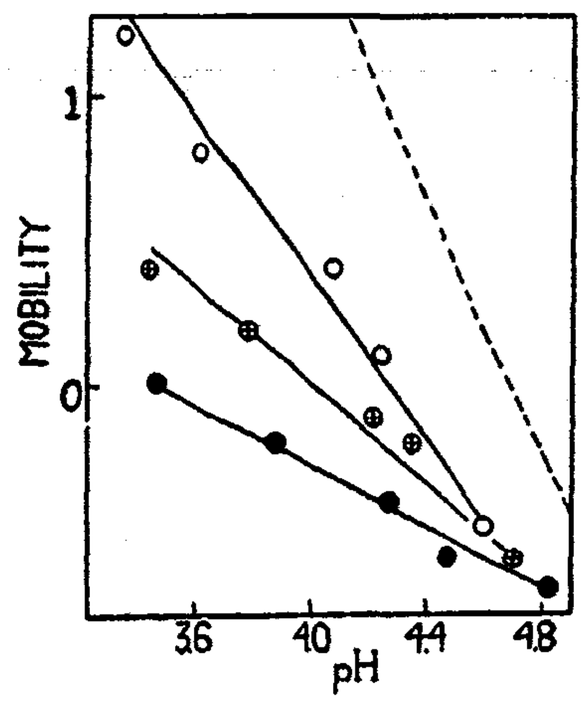
FIG. 6. FERRIC OXIDE-GELATIN

○ KCl, 0.1 millimole per liter
⊕ KCl, 1.0 millimole per liter
● KCl, 5.0 millimoles per liter

FIG. 7. FERRIC OXIDE-GELATIN

○ K_2SO_4, 0.1 millimole per liter
⊕ K_2SO_4, 1.0 millimole per liter
● K_2SO_4, 5.0 millimoles per liter

Fig. 8



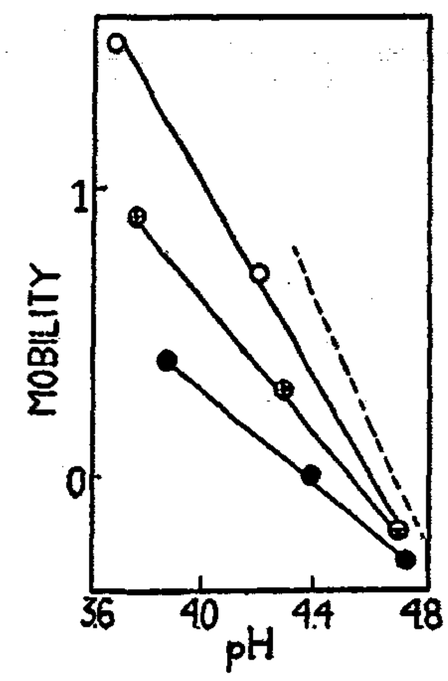
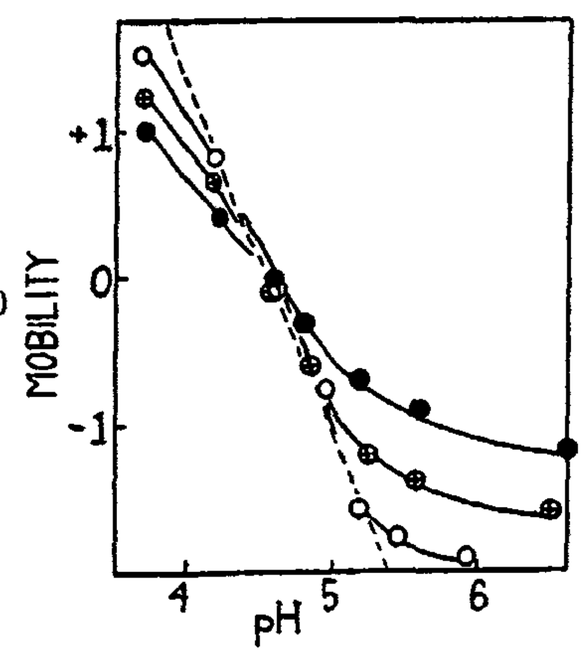


Fig. 9

Fig. 10



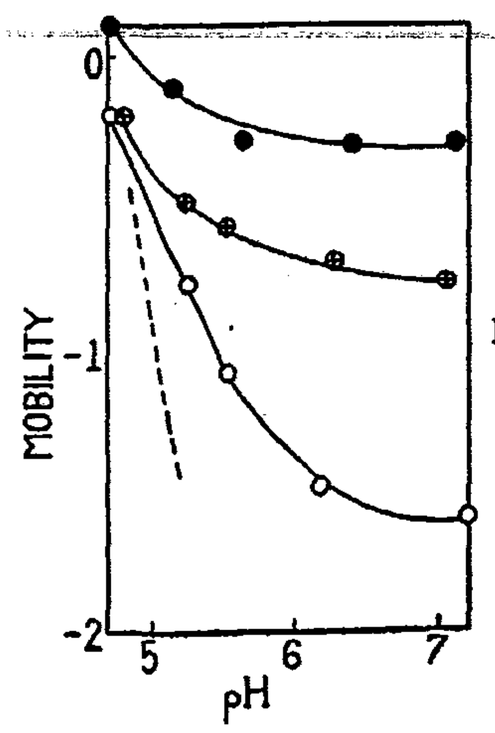


Fig. 11

Fig. 8. Ferric Oxide-Gelatin

○ $K_3Fe(CN)_6$, 0.1 millimole per liter
⊕ $K_3Fe(CN)_6$, 1.0 millimole per liter
● $K_3Fe(CN)_6$, 5.0 millimoles per liter

Fig. 9. Manganese Dioxide-Gelatin

○ K_2SO_4, 0.1 millimole per liter
⊕ K_2SO_4, 1.0 millimole per liter
● K_2SO_4, 5.0 millimoles per liter

Fig. 10. Manganese Dioxide-Gelatin

○ KCl, 0.1 millimole per liter
⊕ KCl, 1.0 millimole per liter
● KCl, 5.0 millimoles per liter

Fig. 11. Manganese Dioxide-Gelatin

○ $BaCl_2$, 0.1 millimole per liter
⊕ $BaCl_2$, 1.0 millimole per liter
● $BaCl_2$, 5.0 millimoles per liter

obtained when electrolytes are added to colloidal ferric oxide and where it is assumed from classical theory that the ions of the electrolyte are adsorbed, i.e., enter into and decrease the thickness of the double layer.

Loeb (19) has shown that the solubility of gelatin is increased by the addition of salts. He has also shown (17) that collodion particles coated with isoelectric gelatin are unstable, but that they are stabilized by small amounts of salts without altering their cataphoretic velocity from zero. Results comparable to these were obtained with iron oxide and gelatin, where it was found that isoelectric mixtures are unstable but that low concentrations of salts produce stability. A possible explanation for the effect of small amounts of electrolytes is that they disperse the gelatin into smaller particles, rendering possible the formation of more soluble groups per unit weight of protein.

The stock solutions of electrolytes used in this study were all of a concentration of $M/100$. It was found that when the acidity of an electrolyte was adjusted to pH of about 4 and then added to an equal volume of a 0.1 per cent gelatin solution of the same pH, the mixed system became more alkaline. The pH change occurred rapidly and without hysteresis. Similar results were obtained with other electrolytes, although the increase was not always the same for different electrolytes. When the hydrogen-ion activities were on the alkaline side of the isoelectric point, the mixed systems were more acid than either of the constituents. Thus it would seem that the changes in hydrogen-ion activity are not due solely to alteration in ionic strength of the solution (since the pH is shifted in opposite directions when the system is on the acid side of the neutral point, pH 7.0). The data are shown in table 1.

Loeb (20) did not give much emphasis to the effect of electrolytes just described, and this fact tends to lend confusion to some of his findings. For example, his results on the mobility of proteins with potassium ferrocyanide are of doubtful significance. It is difficult to hold this salt at a constant pH for any considerable length of time, and, further, when a potassium ferrocyanide solution of a pH such as Loeb used is mixed with gelatin of the same pH there occurs a marked change in acidity with a slow attainment,[2] if any, of equilibrium.[3] In the present work the use of this salt had to be abandoned, although it gave mobility curves similar to Loeb's when only the pH of the original solutions (before mixing) was considered. It should be noted that it does not seem possible to make dilutions with gelatin solutions, electrolyte solutions, and water all of the same pH and obtain a series of samples of the same acidities (unless, possibly, this was done at the isoelectric point).

The order of electrolytes in decreasing the mobility of positive gelatin-

[2] With other salts of this study equilibrium was rapidly established.

[3] In this case Loeb noticed a change in pH after eighteen hours.

coated particles (at a constant hydrogen activity, see figures 4 to 8) is $K_3Fe(CN)_6 > K_2SO_4 > KCl$, KSCN, KH_2PO_4. From table 1 it may be observed that this order is identical with the effectiveness of the salts in decreasing the acidity of gelatin when it is on the acid side of the isoelectric point. In neither instance was there any evidence of lyotropy with the monovalent ions.

The change in acidity produced by salts is consistent with the assumption that salts disperse the protein into smaller particles with the resultant increase in total number of active groups. The groups which are released by dispersion are probably in the isoelectric condition when first formed, but quickly adjust themselves to the acidity of the medium. This readjustment uses up acid or base depending upon the original pH of the system. Thus the shift in pH is toward the isoelectric point.

TABLE 1

Changes in pH values when solutions of electrolytes and of gelatin are mixed

ELECTROLYTE	pH BEFORE MIXING	pH AFTER MIXING
Gel	3.91	
KCl	3.83	3.97
K_2SO_4	3.86	4.05
KH_2PO_4	3.86	3.97
$K_3Fe(CN)_6$	3.85	4.17
$BaCl_2$	3.85	3.99
Gel	3.87	
KSCN	3.88	3.98
Gel	4.95	
KCl	4.98	4.88
$BaCl_2$	4.95	4.72

It has been mentioned that gelatin-coated particles of ferric oxide and manganese dioxide have the properties of the protein itself. It is none the less true that addition of an excess of gelatin (figure 1) over the minimum required to give protein properties to a protected particle results in a still further decrease in velocity of the particle. The decrease in mobility is the result of a decrease in the electrokinetic potential. If the addition of neutral salts to gelatin leads to dispersion and an increase in the concentration of ampholyte groups, the salt which produces this change to the greatest degree should be the most effective in lowering the cataphoretic velocity at a given hydrogen-ion concentration. Thus the reason why electrolytes of different valence do not lower the mobility in proportion to their adsorption isotherms may be explained. The addition of ions of different valence does not lead to an entrance of these ions into the double

layer but instead results in an increase in the concentration of an ion (gelatin) already present.

In conclusion it may be stated that since molecular weight determinations on gelatin (13) have been made with buffer systems and therefore in the presence of salts, any effects of the latter in producing dispersion would be included with those of the hydrogen ion.

SUMMARY

1. An ultramicroscopic method has been used to study the migration velocity of gelatin-coated ferric oxide and manganese dioxide particles.

2. The effects of concentration of gelatin and of the hydrogen-ion concentration of the system are shown in relation to the mobility of the protected particles.

3. The effects of salts of different valence on the mobility of hydrophobic particles covered with a protein film have been found to be more in direct proportion to their valence than with their adsorption isotherms.

4. When the electrolyte solutions and gelatin were adjusted to the same pH and mixed, the hydrogen-ion concentration was altered. The mixed systems became more alkaline when the original acidity was on the acid side of the isoelectric point and more acid when on the alkaline side of the isoelectric point. The order of electrolytes in altering the hydrogen-ion concentration was identical with their effectiveness in decreasing the mobility of gelatin-protected particles.

5. It has been suggested that small amounts of salts disperse gelatin into smaller particles, liberating more active groups.

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THE STABILITY OF EMULSIONS AS DETERMINED BY THE DISTRIBUTION OF SIZES

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Received July 24, 1934

INTRODUCTION

One of the most important characteristics of an emulsion is its stability. This stability has generally been determined by allowing the emulsion to stand until the dispersed phase collects in bulk to an extent decided upon by the individual observer. This method is not only uncertain, but also extremely slow since, for example, emulsions of oil in water prepared in this laboratory have exhibited no separation of oil during a period of five years after their initial preparation. It was suggested by Harkins and Beeman (4) that a determination of the variation of the distribution of sizes of the dispersed droplets of the emulsion with time gives a measure of its stability. Of course, the stability of emulsion systems, like the stability of true colloidal systems, depends not only on the degree of dispersion of the dispersed phase, but also upon certain other factors, such as (1) interfacial tension, which induces the coalescence of globules of the dispersed phase, reducing thereby the total surface, and (2) the electric charge of the globules, tending to repel globules on near approach. As in other colloidal systems, the presence of a large number of small-sized particles characteristic for the permanent state appears to be general. The distribution of sizes for two types of emulsions, octane and heavy paraffin oil (stanolax) in aqueous solutions of sodium oleate, was determined in order to obtain information concerning their stability under various conditions.

APPARATUS AND PROCEDURE FOR OBTAINING NUMBER DISTRIBUTION CURVES

Purification of substances

The accuracy of the determination of the distribution of sizes of the droplets in an emulsion depends not only upon the method used, but also upon the purity of the participating components of the respective system. The purification of the substances used in this investigation and the preparation of the emulsions studied are presented herein in detail.

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It is known that oleic acid, from which oleates used as emulsifiers are prepared, always contains by-products in the form of other fatty acids, and when exposed to air oxidizes readily. Oleates also oxidize readily, but since sodium oleate is oxidized less readily than potassium oleate it was used in the investigation. The method employed for the purification of oleic acid was a modification of one generally recommended: The commercial U.S.P. oleic acid was first shaken with pure granular rice carbon (Kahlbaum). After twenty-four hours standing the oleic acid was filtered from the carbon, water added to form an emulsion, and 0.1 *N* potassium hydroxide solution stirred into this mass until the saponified emulsion dissolved, when a saturated solution of lead chloride was poured in until a white, flocculent precipitate of the lead salts of the fatty acids separated out. The precipitate was filtered, the solution tested for complete precipitation, and the lead salts washed many times by decantation, the water being drawn off by suction on the funnel in the absence of air. These salts were then dissolved in ether by shaking and left standing in ether for four to five days for the complete removal of lead oleate. Other fatty acid salts, such as those of stearic acid, remaining as precipitates in the ether solution were separated by filtration. The lead oleate dissolved in ether was poured into a separatory funnel and repeatedly shaken with fresh portions of 0.1 *N* hydrochloric acid until complete separation was effected. The ether layer was evaporated on a water bath; water was then added to the remaining oleic acid, which was resaponified with 25 per cent ammonia solution, and then diluted with water until all the soap dissolved. Treating with lead chloride does not render the oleic acid completely free from other admixed fatty acids, a small amount always remaining in the ether after the extraction. Therefore the soap solution was treated with barium chloride; a white, flocculent precipitate of barium oleate was obtained, which was allowed to settle for several hours. The precipitate was sucked from the cold solution in the absence of air, the barium oleate decomposed with tartaric acid or hydrochloric acid, and washed to separate the excess of acid. Even after this treatment the purified oleic acid still contained some palmitic and stearic acids, for the complete removal of which the oleic acid was subjected to a fractional distillation.

Oleic acid decomposes, upon distillation under ordinary pressure, into water, carbon dioxide, acetic acid, caprylic acid, capric acid, and elaidic acid; therefore it was distilled under a pressure of 10 to 15 mm. to prevent decomposition (under this pressure oleic acid boils at about 223°C.). The pure oleic acid obtained after final purification was a colorless, odorless liquid, solidifying at a low temperature and in the solid state melting at 14°C. Sodium oleate was then prepared from the purified oleic acid.

Pure metallic sodium was dissolved in pure ethyl alcohol and a calculated amount of oleic acid previously dissolved in ethyl alcohol added to the

sodium ethylate until repeated tests of the alcoholic solution indicated a neutral reaction with a boiling mixture of three parts of alcohol and one part of water containing a few drops of phenolphthalein. The neutral alcoholic solution was evaporated on a water bath to dryness, the residue dissolved in absolute alcohol and refluxed for one hour. The hot solution was filtered through a hot air funnel. The soap obtained was crystallized, the crystals washed well with alcohol and dried in air. The dry powder was rubbed in a mortar with pure absolute ether until the fine soap powder was free from impurities; the ether was then removed by suction. The sodium oleate, obtained in the form of a white powder, was dried over phosphorus pentoxide in a vacuum desiccator for the elimination of water and ether, and ground to extreme fineness; its melting point was found to be 230–232°C., corresponding to that of pure sodium oleate.

Preparation of emulsions

At a definite temperature, an equal volume of the corresponding oil flowing in a thin stream from a pipet was added to an aqueous soap solution stirred by an Arnold drink mixer in a tube with a flat bottom at a constant speed of 3500 revolutions per minute. The emulsion obtained was homogenized by drawing it up into a large 100-cc. pipet by means of a suction pump and rapidly expelling it by compressed air. This operation was repeated five times. Foaming did not occur when the homogenization proceeded comparatively slowly. The emulsion was poured into 10-cc. measuring cylinders having flat bottoms and provided with glass stoppers to prevent evaporation.

Apparatus

The apparatus used for the determination of the distribution of sizes of globules in emulsions was a new type Leitz microprojection equipment with a special collimator of great light-transmitting power. The emulsion was protected from the heat of the arc lamp by the use of a cell containing a solution of ferrous ammonium sulfate to which had been added a few drops of sulfuric acid to prevent its oxidation on exposure to air, also by a green-gold glass (patented) fixed on the wall of the heat-adsorbing cell. In addition, the microscope stand was surrounded by a series of lead tubes of small diameter in which cold water circulated. In this way, drying of the emulsions used in protracted experiments was prevented.

EXPERIMENTAL PART

All emulsions prepared as previously mentioned and before observation under the microscope were diluted three hundred times with distilled water. By means of a projection prism above the ocular, the image obtained in the

microscope was projected on a screen made up of a large sheet of millimeter graph paper attached to a wall opposite the projection prism. The distance of the microscope from the screen was such that each millimeter of the graph paper corresponded to one micron (micrometer calibration). The cell containing the emulsion was identical with that used by Harkins and Beeman (4). Special attention was given to the cleaning of the slide with the cell (similar in construction to a hanging drop slide) which served as the container of the emulsion, as well as the cover glasses. The slide and cover glasses were placed in a cleaning solution for several hours, washed many times with distilled water, and then placed in the funnel of an Ostwald boiler containing distilled water and a solution of potassium permanganate, where they were left for an hour under steam. The fact that the slide and cover glasses when taken from the funnel were not wetted by water and dried quickly was evidence that their surfaces were clean.

The distribution of sizes of globules in emulsions was obtained by calculating the number of droplets of various sizes. The method of obtaining the distribution curves of sizes was a statistical method, using the law of great numbers to increase the probability. Each distribution curve was obtained by calculating and measuring an average of fifteen hundred to two thousand droplets. From the calculated number of droplets of each size and the total number of droplets calculated, the percentage of droplets of each size was determined.

The observation procedure was as follows: Immediately after diluting the emulsion, a sample was pipetted from it, placed upon a slide and covered with a cover glass. Oil contacts between the condenser and the slide and between the cover glass and the objective were made with stanolax, since it is more readily cleaned off than cedar oil and does not harden after exposure to air as does cedar oil, which is usually used. Because of the dilution of the emulsion, only a few droplets were present in the microscopic field. The slide containing the emulsion was moved from one side to the other by means of a modified movable stage operated at a distance, and observations were made, after which the slide was cleaned and refilled with a fresh portion of the diluted emulsion. This procedure was repeated for every curve plotted, fifteen hundred to two thousand globules being measured for every curve.

DISCUSSION

Number distribution curves were obtained for octane–water and stanolax–water emulsions with sodium oleate as the emulsifier. The effects produced by varying the concentration of the emulsifier, and particularly those changes in the distribution with time, were studied in order to draw a relationship between the distribution of sizes of the dispersed phase and the stability of the emulsion system. The figure with curves obtained for

the distribution of sizes of oil droplets in octane–water and stanolax–water emulsions showed clearly: (1) that the maximum number of droplets corresponding in size from 1 to 1.5 microns in diameter is independent of the concentration, high or low, of the emulsifier used to produce a relatively permanent emulsion, and of the age of the emulsion, whether it is a day, a month, or even years since its initial preparation; (2) that the distribution of intermediate size droplets is rather gradual; (3) that deviations in both directions from the maximum size droplets correspond to the peak in the number distribution curve prior to the establishment of a stable static equilibrium of the emulsion, e.g., the course of changes in the distribution of sizes being comparable to the swing of a pendulum at both its extremities; (4) that this method of attaining a state of equilibrium indicates changes occurring in the distribution of sizes with time by the ageing of the emulsion systems and varies with various concentrations of the emulsifier; (5) the percentage of large size droplets, such as those from 10 to 30 microns in size, was extremely small, very few being present in stable emulsion systems, and their appearance indicates a transition to an unstable form (the unstable state was verified by the distortion of the perfectly round shape of the droplets); (6) that the maximum peak in the distribution curve appeared not to be displaced by using a viscous oil instead of a fluid oil in an emulsion.

These are the general results derived from a casual perusal of the data obtained and tabulated with respect to the distribution of sizes of droplets in different emulsion systems in the investigation of which factors influencing their state of permanency were varied.

To study more thoroughly the kinetics of changes as reflected in the distribution of sizes, it was necessary to pursue small rates of changes of the physical quantity; therefore a mathematical analysis of the results obtained was necessitated. The distribution of sizes and the corresponding percentage of droplets obtained experimentally were plotted for each emulsion directly in a coördinate system as integral curves, and from these integral curves derivative curves were constructed. For the evaluation of the derivative $y' - \frac{dy}{dx}$ when the function is known analytically, a differential calculus or a graphical method must be used. Geometrically, the procedure consists in using the principle that the ordinate of the derivative curve at any point $P'(x, y)'$ is equal to the slope of the integral curve at any point, that is, of the tangent at the corresponding point of the integral curve.

The practical construction of the derivative curve is as follows (figure 1): A point $S\ (-2, 0)$ is chosen at a convenient distance to the left of the axis y and a line parallel to the tangent drawn for each point of the integral curve. This parallel cuts the ordinate axis at the point U. Since SU forms with the axis $+x$ the same angle α as the tangent t, then $OU = \text{tg}\alpha = y'$ and the

point U projected horizontally on the ordinate from the point P cuts it at P', which is the point of the derivative curve corresponding to the point P of the integral curve. Since $Y' = 1/a\int y.dx$, then $dy/dx = 1/aY$. The slope of the integral curve at any point is proportional to the ordinate of the derivative curve at the corresponding point. Derivative curves for all integral curves were constructed in this manner.

In comparing derivative curves (figure 2, 0.10 M sodium oleate–octane–water emulsions) corresponding to integral curves expressing a change in the distribution of sizes with time as the emulsion grows older, it is seen that derivative curves A' and C' of aged emulsions have a large number of small size droplets, the maximum not even being indicated. Emulsions one day old and seven days old, respectively, differ from aged emulsions in the shape of the distribution curve in that their maximum is extended, D' indicating that there are several sizes of droplets in the maximum region, while B' limits the maximum to globules of certain definite size. The

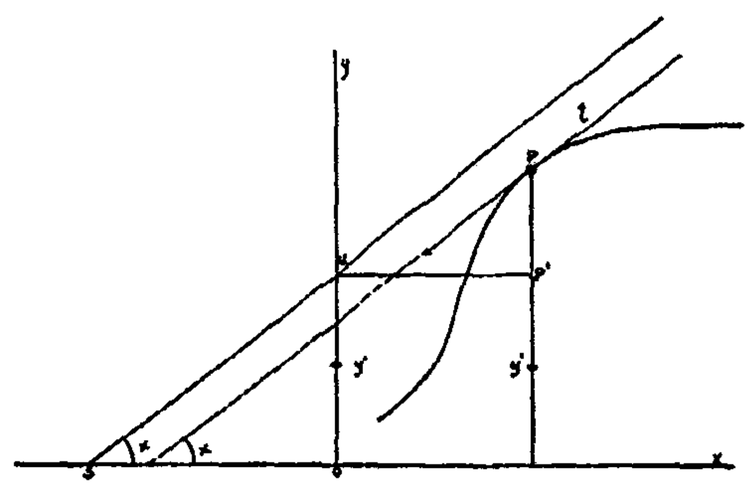

FIG. 1. GRAPHICAL METHOD FOR DERIVING DIFFERENTIAL CURVES

percentage of maximum (number) of globules of large sizes is more pronounced in aged emulsions.

Figure 3 presents the same kind of derivative curves for the corresponding integral curves as figure 2, 0.10 M sodium oleate–octane–water emulsions, except that 0.01 M sodium hydroxide was added for the prevention of hydrolysis usually occurring in these emulsions (1). It was interesting to note the effect of an alkali, added to counteract hydrolysis, on the character of the distribution of sizes in these emulsions, it being found that the dispersion into finer droplets was favored by the addition of alkali and that the distribution curves for emulsions in which hydrolysis was compensated reshaped the derivative curve, that is, a curve with an unexpressed maximum lying in an unmeasurable region (ultramicrons). Depending on the amount of alkali added, hydrolysis is retarded for varying periods of time, and the stability of emulsions containing an excess of alkali is not essentially improved in comparison with emulsions to which no

alkali has been added for, after two months, the maximum level of small size droplets decreases markedly and is almost equal to that of emulsions without alkali (compare figure 3 with figure 2).

A comparison of figure 3 with figure 2 makes evident also that the effect

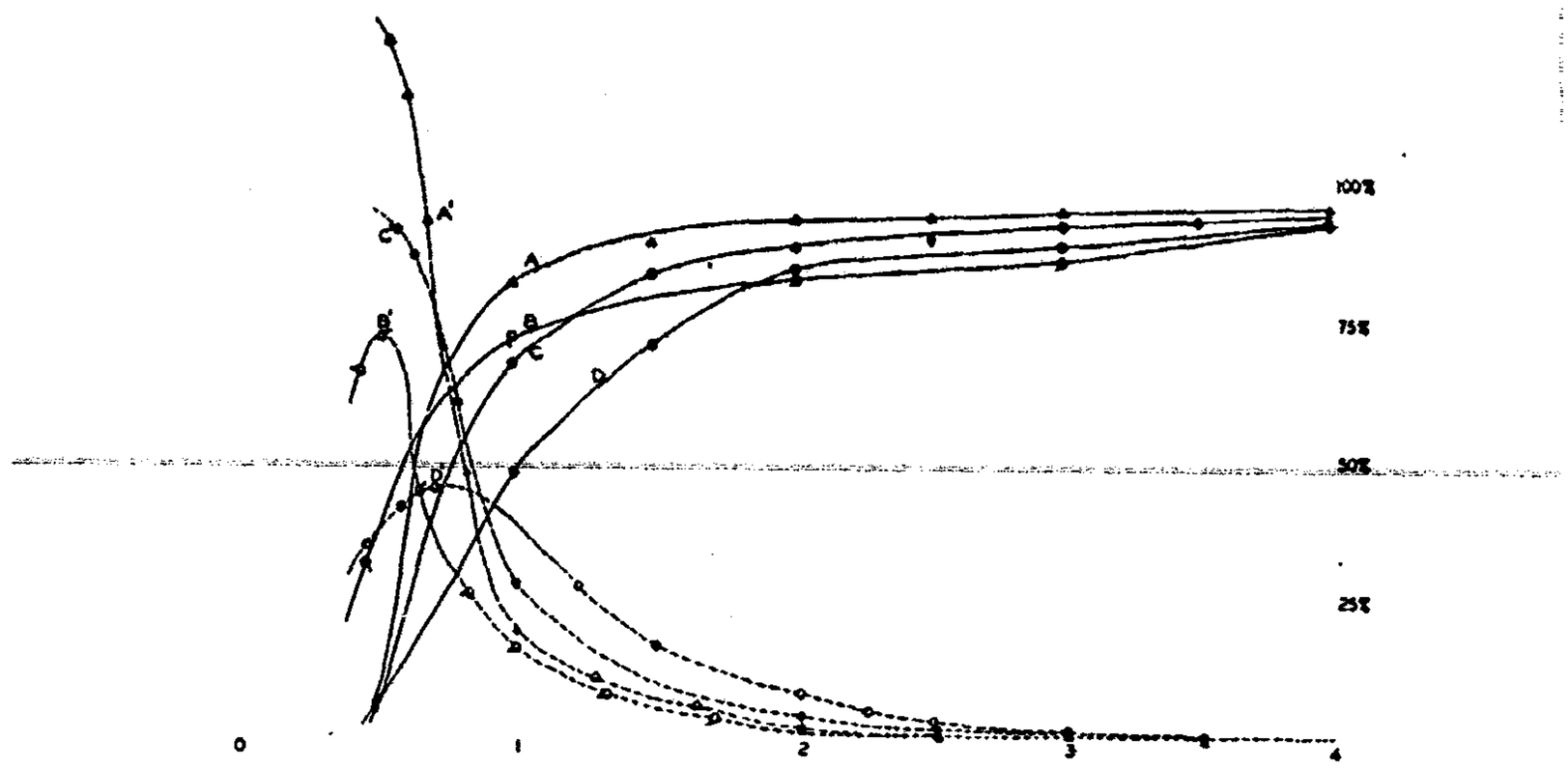

FIG. 2. 0.10 *M* SODIUM OLEATE-OCTANE-WATER EMULSIONS
△, AA′, 12 days old; ⌕, BB′, 7 days old; ●, CC′, 2 months old; ○, DD′, 1 day old

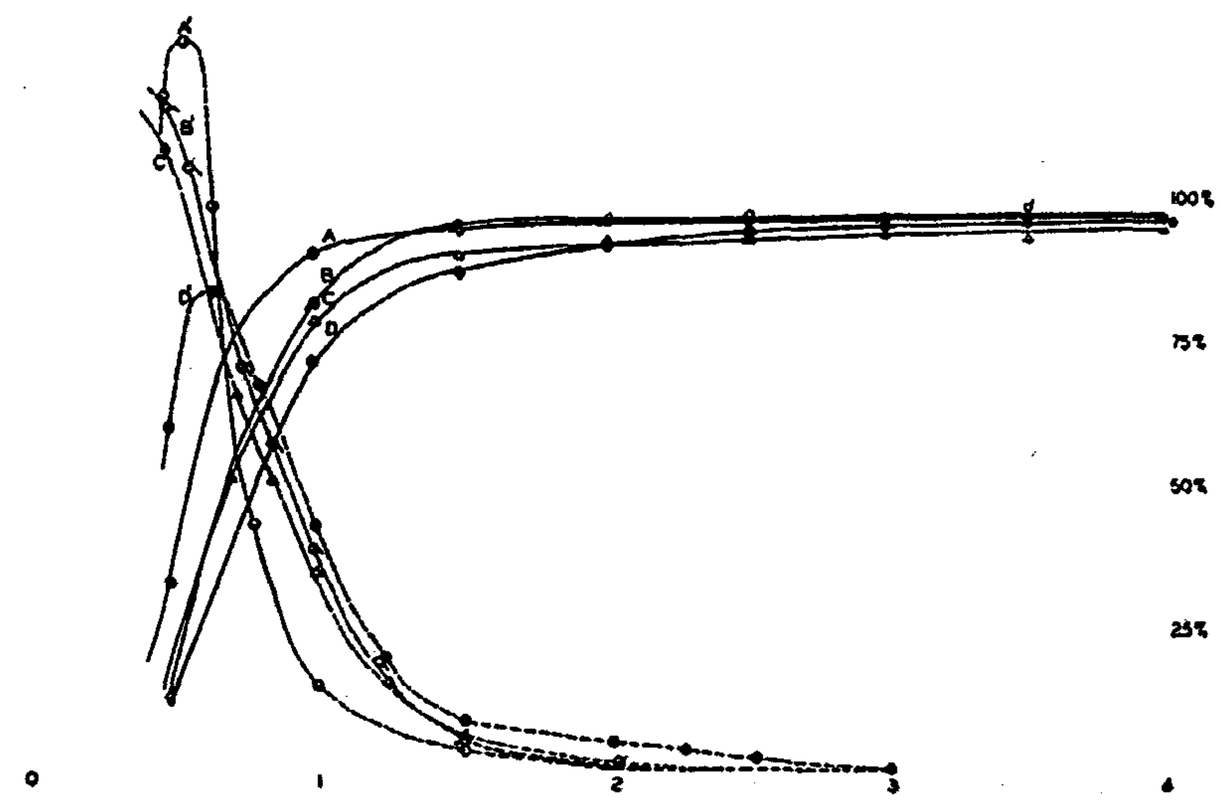

FIG. 3. 0.10 *M* SODIUM OLEATE-OCTANE-WATER EMULSIONS (+ 0.01 *M* SODIUM HYDROXIDE)
○, AA′, 2 days old; ⌕, BB′, 9 days old; △, CC′, 13 days old; ●, DD′, 2 months old

of hydrolysis at this concentration (0.10 *M*) of the emulsifier is sharply pronounced immediately after preparing the emulsion, for it interferes with the dispersing factor. However, as time passes, hydrolysis neither affects nor depresses the state of stability.

Figure 4 presents the rate of changes in the integral curves of size distribution when a smaller amount (0.05 *M* sodium oleate) of the emulsifier is used to produce an emulsion system. The percentage of maximum small size droplets continues in the same direction, and as time goes on an equilibrium is established and stability becomes more pronounced. After a period of two months hydrolysis interferes greatly with the stability, the level of the maximum of small size droplets is displaced, and the emulsion exhibits a smaller percentage of small droplets and greater instability.

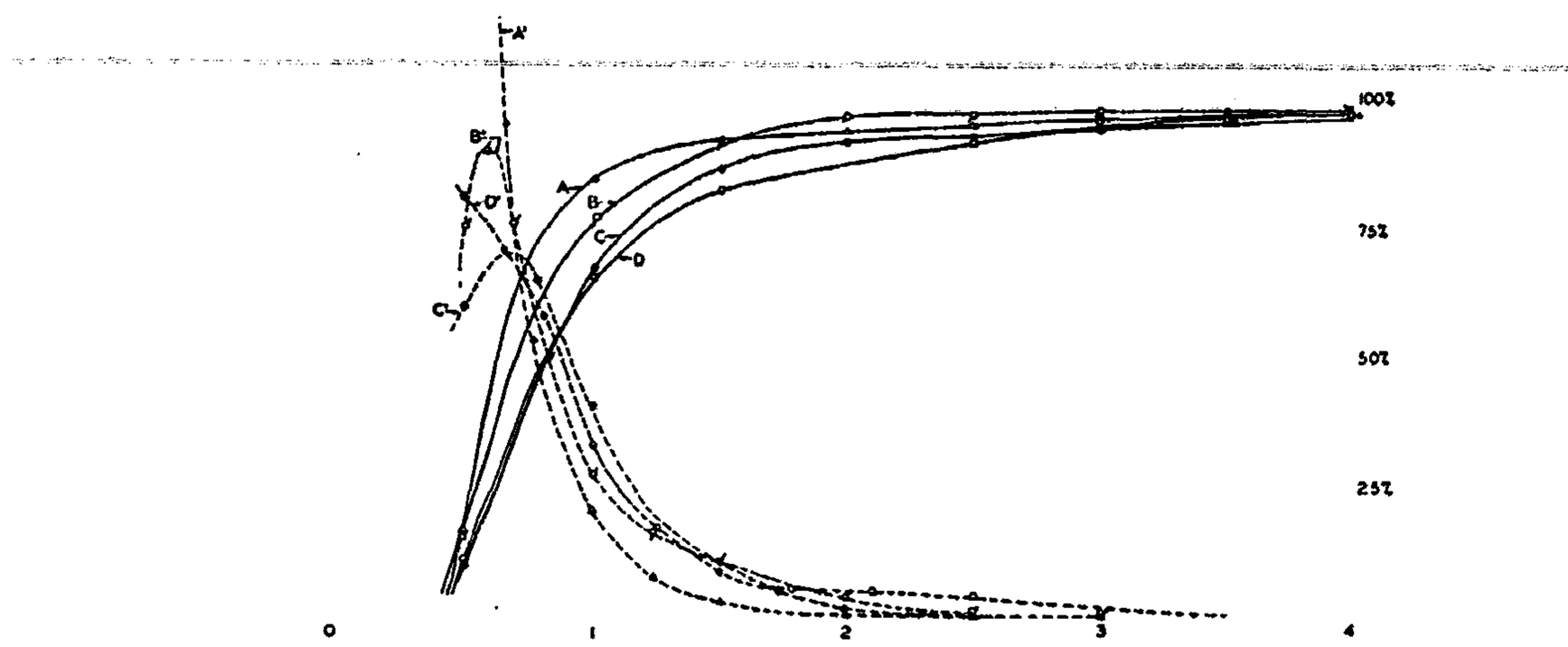

FIG. 4. 0.05 *M* SODIUM OLEATE-OCTANE-WATER EMULSIONS
△, AA', 12 days old; ⌕, BB', 7 days old; ●, CC', 2 months old; ○, DD', 4 days old

A comparison of figure 2 with figure 4 (emulsions of the same age but having different amounts of the emulsifier) shows that curves A' (twelve days old) have identical shapes indicating stability and the absence of hydrolysis. Curves B' (seven days old) have an expressed maximum effect of hydrolysis, and the percentage of small size droplets is slightly higher in the case of the lower concentration of the emulsifier. In figure 2, curve C' (two months old) has a shape suggesting the absence of hydrolysis, while in figure 4, curve C' (two months old) suggests the presence of hydrolysis; the maximum of small size droplets is displaced to a lower level in the case of the lower concentration of the emulsifier.

With a concentration 0.05 *M* of the emulsifier, no marked hydrolysis is apparent after four days, while with a concentration 0.10 *M* the level of

the maximum of small size droplets is the lowest, that is, hydrolysis is present and the emulsion is practically instable. Figure 5 illustrates the ageing process of octane–water emulsions with a still smaller amount of the emulsifier, 0.01 *M* sodium oleate. Curves A′, C′, and D′ exhibit a flat maximum, indicating the least stability of these emulsions. The percentage of the small size droplets increases with time and hydrolysis ceases its interference with the presentation of the actual distribution of sizes, an equilibrium apparently being established between dispersion; later, the action of hydrolysis is reëstablished. The curve obtained for a three-months old emulsion is typical of a stable emulsion in which no hydrolysis has occurred.

In the consideration of a still lower concentration of the emulsifier, the reverse with regard to stability is seen. The amount of the emulsifier seems

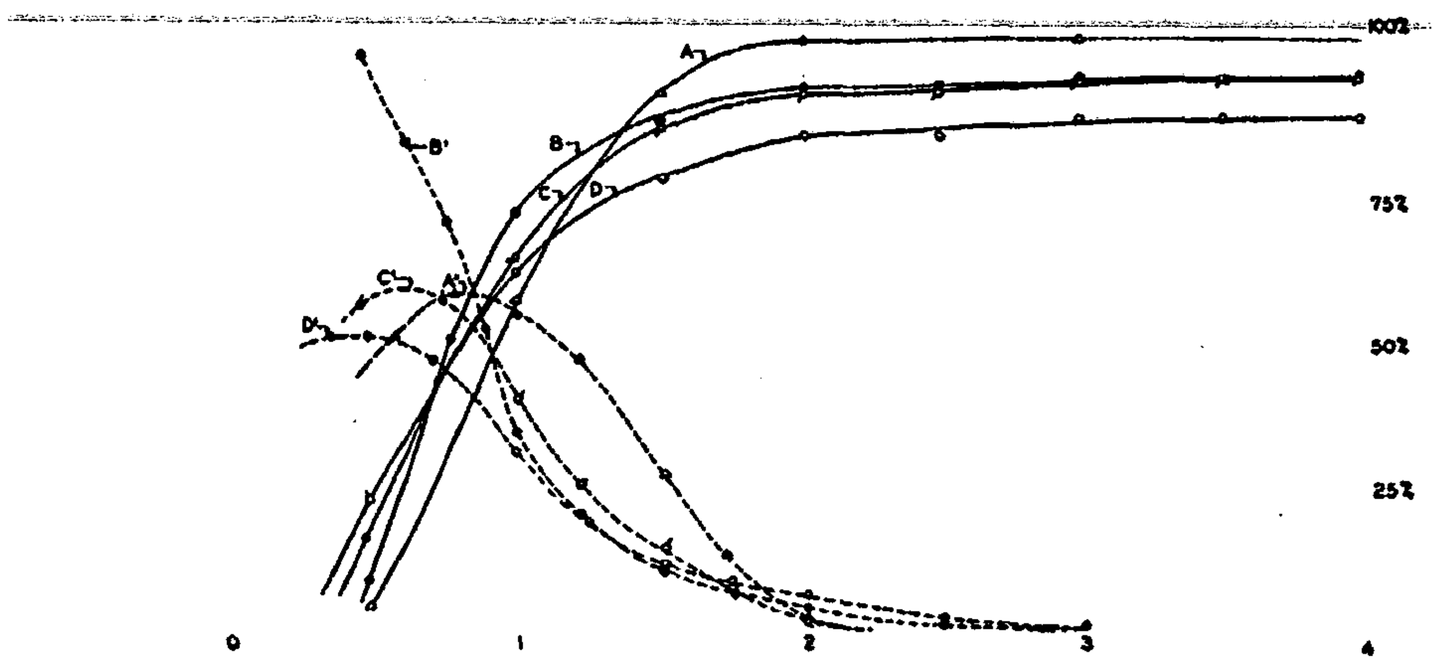

FIG. 5. 0.01 *M* SODIUM OLEATE-OCTANE-WATER EMULSIONS
△, AA′, 2 months old; ●, BB′, 3 months old; ⌕, CC′, 15 days old; ○, DD′, 2 days old

to be insufficient in maintaining the stability of an emulsion, although readily attained in the beginning; after three days the emulsion has a high per cent of small droplets.

Figure 6 presents curves for 0.005 *M* sodium oleate–octane–water emulsions. The shape of the derivative curves changes greatly. In a comparatively short time, after fifteen days, curve C′ has a very extended maximum peak and the percentage decreases rapidly. With an emulsion one month old, curve B′ is obtained, the shape of which is similar to that of a fifteen-day old emulsion, but the decrease in per cent is more gradual and to a lesser extent. It must also be emphasized that emulsions containing a very small amount of the emulsifier are short-lived, lasting only about one month. There is a great resemblance between the shape of curves

A′, C′ of figure 5 and B′, C′ of figure 6, but a striking difference between D′ of figure 5 and A′ of figure 6. That is where the amount of the emulsifier, and correspondingly the weakening in the stabilization action, becomes sharply pronounced.

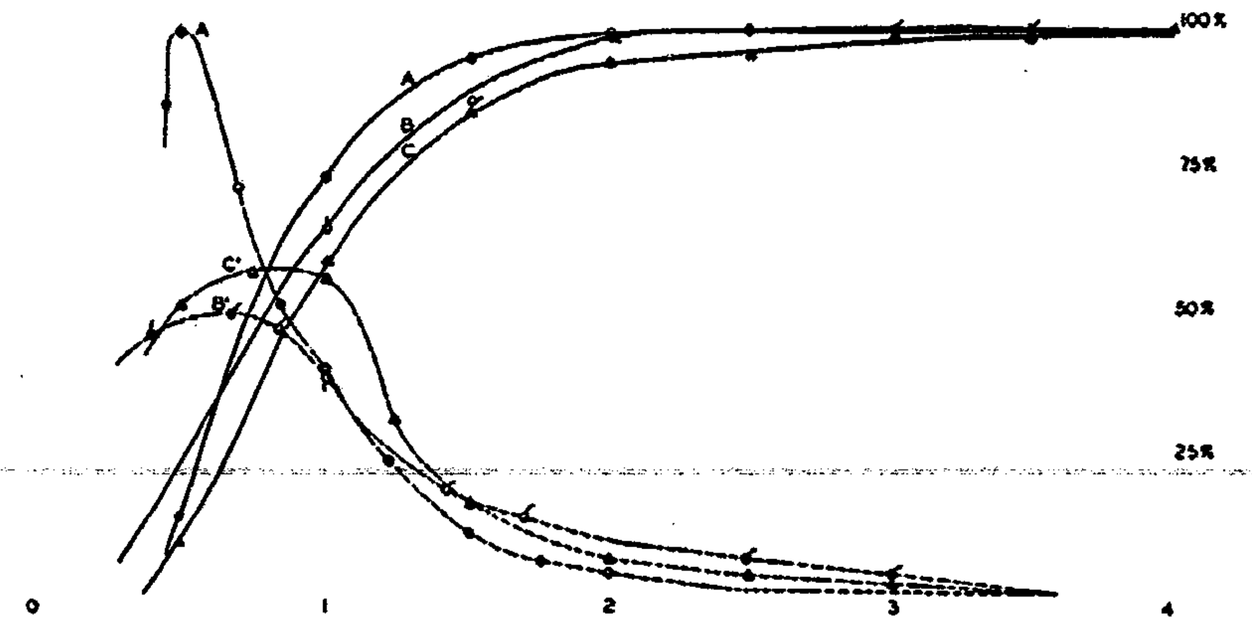

FIG. 6. 0.005 *M* SODIUM OLEATE-OCTANE-WATER EMULSIONS
○, AA′, 3 days old; ⌕, BB′, 1 month old; △, CC′, 15 days old

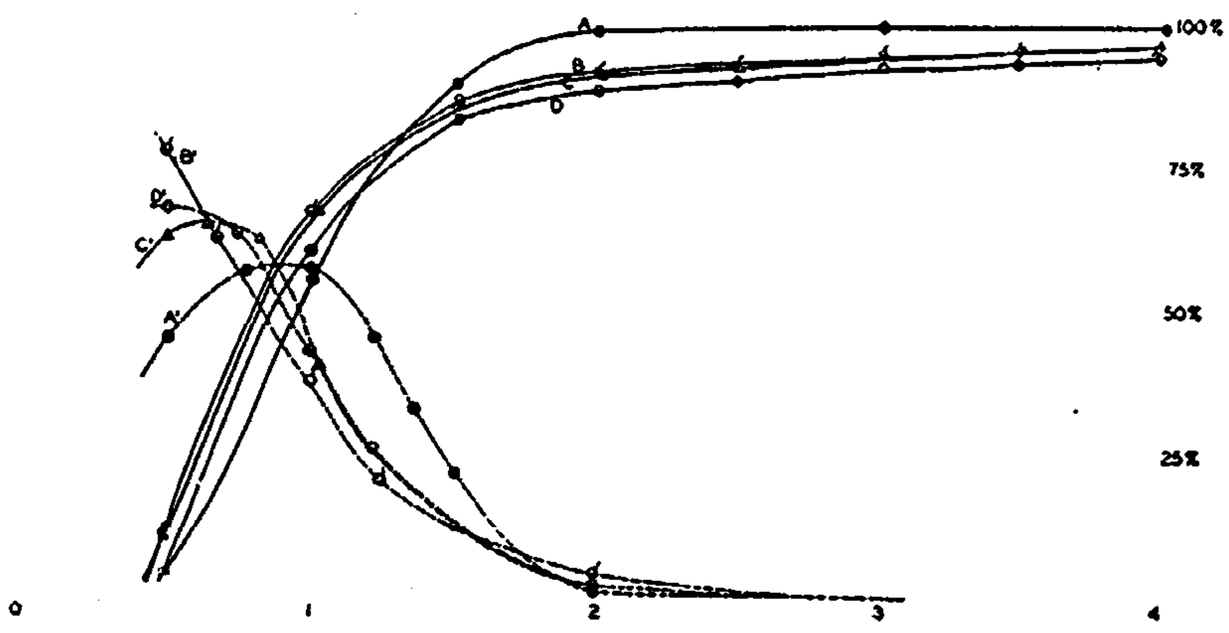

FIG. 7. OCTANE-WATER EMULSIONS (TWO MONTHS OLD)
●, AA′, 0.01 *M* sodium oleate; ⌕, BB′, 0.10 *M* sodium oleate + 0.01 *M* sodium hydroxide; △, CC′, 0.05 *M* sodium oleate; ○, DD′, 0.10 *M* sodium oleate.

Figure 7 shows the influence of the amount of the emulsifier as compared for emulsions of the same age and when the state of equilibrium has been definitely established, namely, two months after the initial preparation. It is obvious that with an increase in the concentration of the emulsifier a higher maximum level for the per cent of small size droplets is obtained.

D′ > C′ > A′ for 0.005 *M* (measured only for a one-month old emulsion). In addition, the most stable emulsion in this series of increasing stability with the concentration of the emulsifier is the emulsion corresponding to 0.10 *M* sodium oleate plus 0.01 *M* sodium hydroxide; in other words, an emulsion in which hydrolysis has been retarded.

STANOLAX–WATER EMULSION

For the first time in the history of emulsion investigation, emulsions four and five years old have been investigated with regard to their stability, using the method of following the changes in the distribution of sizes in emulsion systems as a means for detecting small rates of changes in their

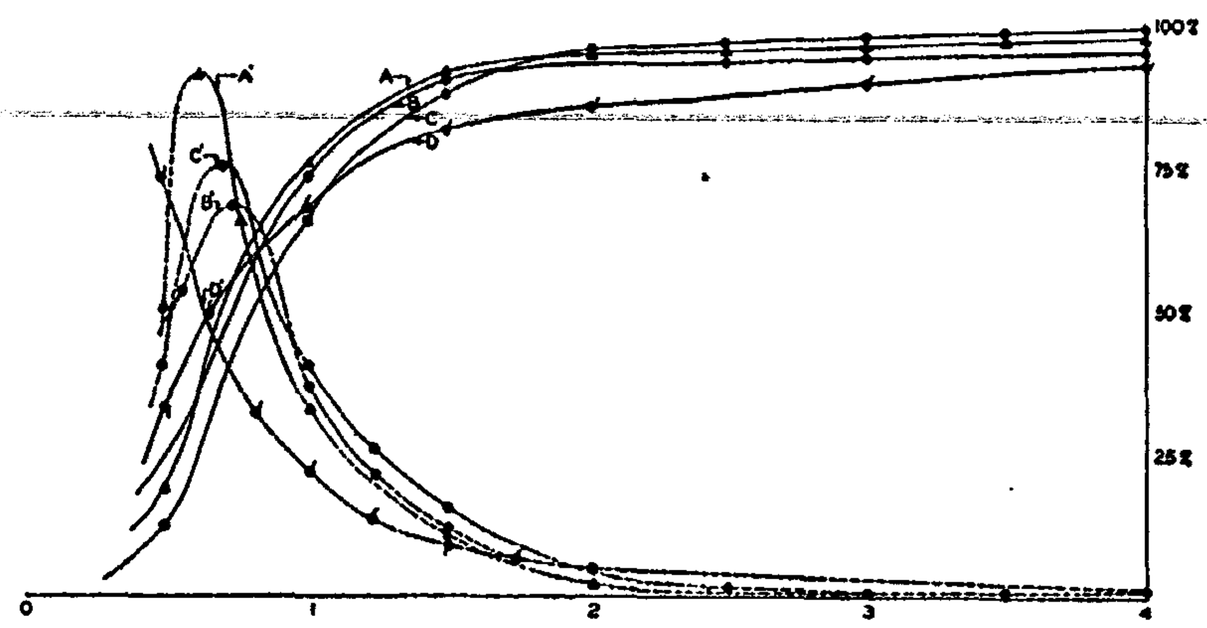

FIG. 8. STANOLAX-WATER EMULSIONS

△, AA′, 0.10 *M* sodium oleate, seven days old; ○, BB′, 0.10 *M* sodium oleate + 0.05 *M* oleic acid, five years old; ●, CC′, 0.10 *M* sodium oleate, forty-one days old; ⌕, DD′, 0.10 *M* sodium oleate, four years old.

permanency. The emulsions investigated were prepared by Harkins and Beeman four and five years prior to undertaking the present investigation.

As may be seen from figure 8, curves B′ and D′ still retain the same shape as those for freshly prepared emulsions under the same conditions. But in comparing them with A′ and C′, the level of maximum size globules is displaced towards the lower one for old age emulsions. The emulsion for curve B′, containing oleic acid to prove the influence of electrolytes, showed a hydrolysis similar to that of a freshly prepared emulsion, while the emulsion (four years old) for curve D′, without the addition of an acid, had a shape typical of permanent emulsions without hydrolysis.

Figure 9 summarizes the results of the investigation on stanolax-water emulsions by varying the concentration of the emulsifier. The influence of the amount of the emulsifier used is pronounced in this case also, that is,

in the same direction as was the case with the fluid octane oil which is less viscous than the heavy paraffin oil stanolax. The stability, as well as the larger per cent of small droplets in the dispersed phase of the emulsion, increases with an increase in the amount of the emulsifier used, provided emulsions are compared under strictly identical conditions, seven-day old emulsions being compared.

Furthermore, as in figure 8, for 0.10 *M* sodium oleate concentration, the younger emulsion A′ has its maximum level at a higher per cent of small droplets than the older emulsion C′, but for 0.05 *M* sodium oleate concentration, B′ lies below A′. The first case is the reverse of what takes place

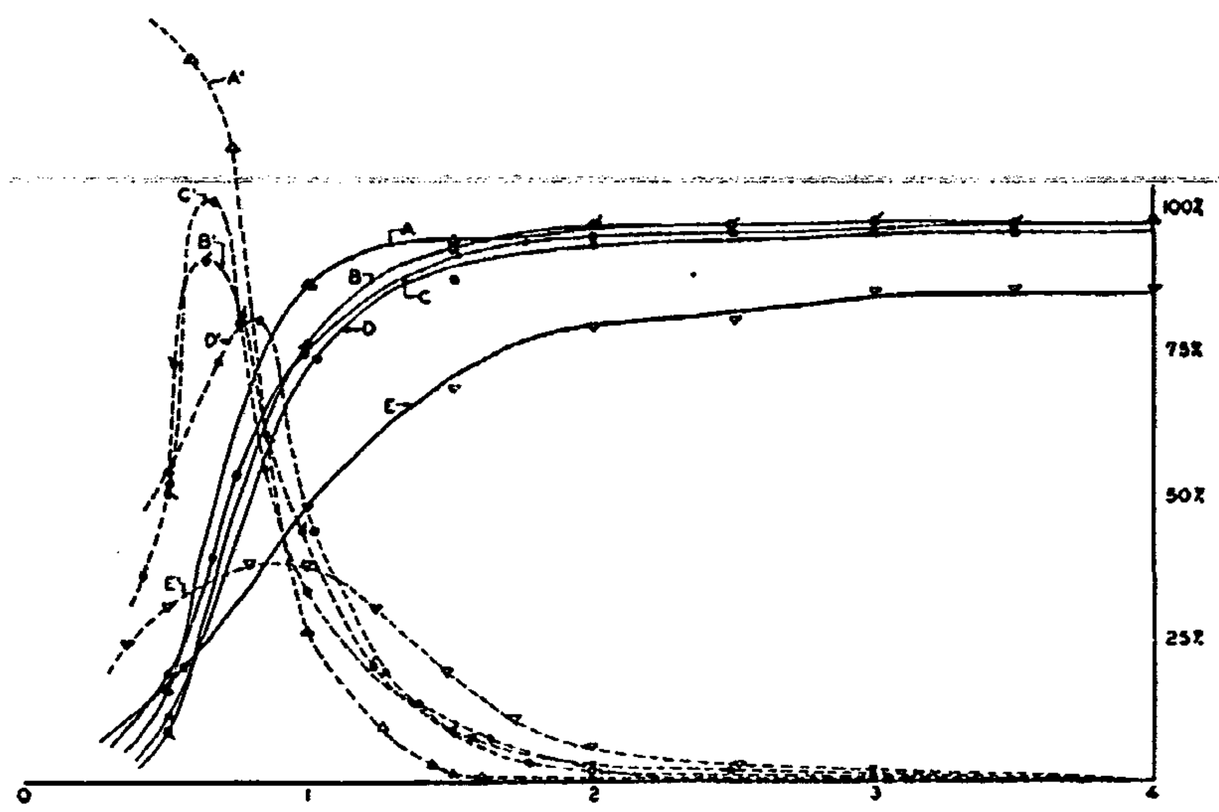

FIG. 9. STANOLAX-WATER EMULSIONS

△, AA′, 0.05 *M* sodium oleate, twelve days old; ⌕, BB′, 0.05 *M* sodium oleate, seven days old; ○, CC′, 0.10 *M* sodium oleate, seven days old; ■, DD′, 0.005 *M* sodium oleate, four days old; ▽, EE′, 0.005 *M* sodium oleate, twelve days old.

in the case of octane emulsions. Perhaps when a high concentration of the emulsifier is used with a viscous oil the equilibrium is established in a different manner, owing to the difference in diffusion, and the influence of hydrolysis does not change it with time. The low concentration of the emulsifier 0.005 *M* sodium oleate in the stanolax oil emulsions indicates a behavior similar to that in the case of octane emulsions.

CONCLUSIONS

A statistical method, using a microprojection equipment, was employed to obtain the number distribution curves for octane–water and stanolax–water emulsions with sodium oleate as the emulsifier.

The influence of various factors, such as concentration of the emulsifier, age of the emulsion, and presence or absence of hydrolysis in the systems concerned with reference to the distribution of sizes in both kinds of emulsion systems, was studied. From the experimental data, integral distribution curves were drawn. The results could only be interpreted by deriving mathematically the differential curves for the corresponding integral curves.

The shape and the level of the per cent of maximum small size globules on the derivative curves reflects the presence or absence of hydrolysis, high or low concentration of the emulsifier, and actual age of the emulsion. This method was proposed for measuring the stability of emulsions, and the latter was proved for the first time in the literature for stable emulsions four to five years old.

I desire to express my deep appreciation and most sincere thanks to Professor W. D. Harkins for his valuable suggestions and kind coöperation in this work.

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PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS. VI

Some Applications and Limitations of the Specific Heat Method as a "Non-comparative Criterion of Purity"

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Received July 19, 1934

Part III (8) of this series of papers contains a discussion of the enormous rise in the values of heat content and specific heat of a solid at constant pressure, $(\Delta H)_s$ and $(Cp)_s$, respectively, just below its melting (freezing) point owing to the presence of impurity. In Part V (9) it was pointed out that only a small amount of impurity is necessary to raise the value of $(Cp)_s$ above that of $(Cp)_l$, the specific heat of the liquid, at the freezing point, and it was shown that if $(Cp)_s > (Cp)_l$, we may at once suspect the presence of impurity in the sample. The purpose of the present communication is to point out certain possibilities which must be kept in mind in applying such heat content and specific heat data as a "non-comparative (10) criterion of purity."

Although there is a high probability that a given compound is quite pure if the value of $(Cp)_s$ increases almost linearly with temperature and so as not to exceed that of $(Cp)_l$ at the freezing point, actual exceptions and apparent exceptions exist. The actual exceptions comprise all the cases of impure samples where the change from the liquid to the solid state takes place completely at constant temperature, e.g., a eutectic mixture. The apparent exceptions are comprised of cases in which the change from the liquid to the solid state takes place over a temperature range but where this temperature range lies completely above the highest temperature for which the data for the heat content, and therefore for the specific heat, of the solid have been determined experimentally. This can best be seen by reference to a diagram.

In figure 1 the dotted lines and the upper full line represent the heat contents in calories per gram, ΔH, of pure benzene in the liquid and solid states

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at various temperatures near the freezing point, 5.5°C.; ΔH for the pure liquid at 5.5°C. is taken as zero. The full lines represent the heat contents of a 1-g. sample of benzene containing 1.48 mole per cent of naphthalene, i.e., enough to lower its freezing point 1°C. (See paper III of this series, samples I and V, respectively.) The eutectic temperature of this binary system is −3.5°C., i.e., 8°C. below the freezing point of the sample being considered, and the eutectic composition is about 13 mole per cent, 19.7 weight per cent, of naphthalene (12). The total heat change for 1 g. of the impure sample during its complete solidification can be calculated on

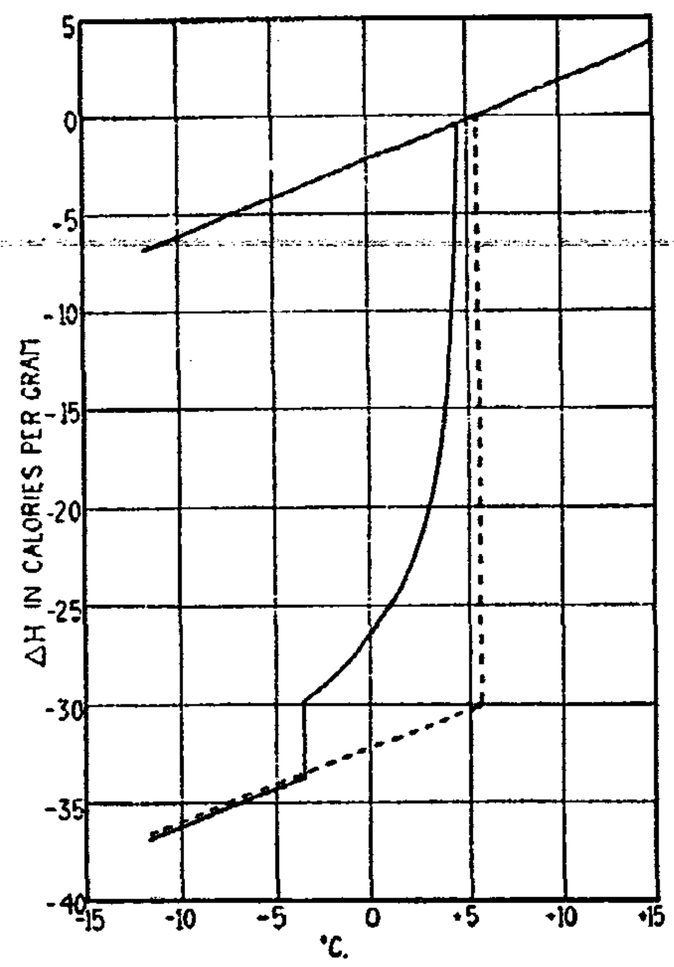

FIG. 1. HEAT CONTENT–TEMPERATURE CURVE FOR A PURE AND FOR AN IMPURE SAMPLE OF BENZENE

the basis of Washburn and Read's values and on their conclusion that the system behaves ideally. One gram of eutectic liquid would give up about (0.197 × 36.4 + 0.803 × 30.1) or 31.35 calories during solidification, that is, about 1.25 calories per gram more than pure benzene. For the particular sample in question the amount of benzene crystals which would separate on cooling to −3.5° is 0.88 g. per gram of sample (8), so that there remains 0.12 g. of eutectic solution. This gives up 0.12 × 1.25 or about 0.15 calorie per gram more on solidification than the same amount of pure benzene. Thus it is obvious that the heat content of the sample completely solidified at the eutectic temperature is 0.15 calorie per gram lower than that for

benzene. This is represented in figure 1 by the sharp drop in the heat content curve at −3.5°.[2] Below this temperature the curve would be expected to run practically parallel to that for pure benzene since the slope, i.e., the specific heat, will not be much different, the specific heat of crystalline mixtures being an additive property (7). The uppermost curve in figure 1, i.e., that for the liquid and supercooled liquid states, can be considered as the same for the pure and slightly impure benzene.

From figure 1 it is obvious that if the heat data for the impure sample in question did not include any values for the temperature range −3.5° to +4.5°C., the data would be interpreted as proving that the sample was highly pure, since the specific heat of the solid would be almost linear with respect to the temperature and apparently $(Cp)_s < (Cp)_l$ at the melting point. This would also be true in case the benzene contained any concentration of naphthalene as impurity up to 20 per cent by weight and indeed, since the same condition would exist on the other side of the eutectic, it would be impossible to distinguish by means of this heat data alone between a pure compound and a sample containing as high as 30 to 40 weight per cent of naphthalene.

The case of cerotic acid reported by Garner and King (4) probably falls in this category. These authors pointed out that although the sample was a mixture of at least two acids, probably $C_{26}H_{52}O_2$ and $C_{28}H_{56}O_2$, as shown by x-ray analysis (3), the curves for the specific heat up to within 6°C. of the freezing point failed to show the usual abnormalities indicative of the presence of impurities. It seems probable therefore that the eutectic temperature for the mixture falls within 6°C. of the freezing point. Indeed this is in accord with the fact that an equimolecular mixture of the straight chain acids $C_nH_{2n}O_2$ and $C_{n+2}H_{2n+4}O_2$ has a melting point only 6.1°C. below the freezing point of the C_n acid when n = 16; 5.5°C. when n = 18; 4.4°C. when n = 20; 4.3°C. when n = 22; and 4.2°C. when n = 24 (3). For the mixture of the C_{26} and C_{28} acids, therefore, the melting point would be expected to be about 4°C. below the freezing point of the C_{26} acid.[3]

Let us finally point out a possible misinterpretation of the heat content and specific heat data when the data for the range just below the melting point are complete. *The curve for the sample of benzene containing 1.48 mole per cent of naphthalene as impurity, given in figure 1, might be mistaken for that for a nearly pure compound with a transition point at −3.5°C., the*

[2] In actual practice this drop does not take place at a constant temperature since, as in the case of the pure substance, even a trace of impurity causes the solidification to take place over a range.

[3] The fact that the heat of fusion for this sample as obtained by Garner and King (4) is much lower than that of either the pure C_{26} or C_{28} acid, indicates, if we assume that the sample contained no other impurity, that this binary system is not ideal.

β-form being stable below that temperature and the α-form above.[4] It is therefore at once obvious that such a heat content curve with a break below the melting point cannot safely be accepted as definite proof of a transition point unless the curve just below the *melting* point (instead of below the supposed transition point) indicates that the sample is highly pure.

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[4] The heat of fusion of the α-form would then be taken as the difference in the heat content of the liquid at +4.5°C. and that of the "solid form" obtained by extrapolating the curve for the solid from just above −3.5°C. up to +4.5°C. The heat of transition would be taken as the difference between the heat content of the "solid α" and the "solid β" at +4.5°C. by extrapolation of the corresponding curves up to +4.5°C.

THE DROP-WEIGHT METHOD FOR THE DETERMINATION OF ELECTROCAPILLARY CURVES

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Received August 8, 1934

Electrocapillary curves for non-aqueous solutions are of interest in assessing the rôle of the solvent in the double layer at a metal–solution interphase, but in an attempt to extend previous electrocapillary work to such solutions, it was found that the accuracy of a capillary electrometer was very much diminished, since the liquid no longer wets the glass perfectly and the angle of contact between the mercury and the glass is less than 180° by an uncertain and variable amount. In bad cases it is impossible to determine an electrocapillary curve at all in this way. It is therefore a matter of importance to examine other methods for the determination of electrocapillary curves, methods that may not suffer from this defect, and can be used to obtain electrocapillary data for non-aqueous solutions.

The drop-weight method was first used by Kučera (4) and has since been employed in electrocapillary work for special purposes in a limited number of cases, but only the following facts regarding its applicability and accuracy have emerged. (a) Kučera found that, if throughout the course of an electrocapillary curve, the dropping rate is kept constant and slow, the drop-weight–potential curve is roughly parallel to the corresponding electrocapillary curve. The only data for electrocapillary curves available at that time were those of Paschen (5), so that, by modern standards of accuracy, this rough agreement is not very significant. (b) In dilute aerated solutions a spurious maximum occurs on the positive branch of the drop-weight–potential curve, owing to the reduction of the oxygen present in the solution (Heyrowský (3)), but this can be avoided by using air-free solutions. In any case the effect only becomes large if the solution is very dilute. (c) When the interphase between the mercury and the solution is non-polarizable, the drop-weight method is particularly liable to lead to false results, but this is now well understood (see Craxford (2)) and need not be discussed here, since this paper is concerned only with the polarized interphase.

Thus before confidence can be placed in electrocapillary curves obtained by the drop-weight method, it is necessary to develop a reliable drop-

weight technique for electrocapillary problems, and to compare curves obtained by it with the corresponding curves obtained by the use of an accurate capillary electrometer. Such a comparison is necessary, since a detailed application of the mathematical theory of the drop-weight method is impracticable, and it is therefore unjustifiable to assume, without experimental proof, that the surface tension is linearly proportional to the drop-weight over the whole of the electrocapillary curve. The requisite experimental proof of this assumption is given in this paper.

EXPERIMENTAL DETAILS

Two forms of apparatus were used for the determination of drop-weight electrocapillary curves under air-free conditions, and they are sufficiently described by the diagrams (figures 1 and 2). The construction of the capillary, at the tip of which the mercury drops are formed, is however a rather more subtle matter. Kučera drew out a piece of ordinary thermometer tubing, and broke it off cleanly under water. The radius of the tip, which was the narrowest part of the capillary, was of the order of 0.002 cm., but with this arrangement Kučera was unable to extend his electrocapillary curves to potentials appreciably more negative than the electrocapillary maximum, on account of active electrolysis. Preliminary trials with such capillaries gave rather uneven curves, probably due to small changes in the effective radius of the capillary tip, arising from the very slow but unavoidable electrolysis that always takes place when a mercury surface is polarized. Such changes would become unimportant if the capillary tip were larger, and this would also effect a considerable saving of time, because for each measurement, a large number, fifty to one hundred, of the very small drops have to be counted out in order that their total weight may be large enough to minimize errors in weighing. Using wider capillary tips, only relatively few, ten to twenty, drops need be collected and weighed together each time. Hence the method used by Bennewitz and Delijannis (1) was tested, because this involves a capillary with a radius of about 0.1 cm., which is constricted above the tip so as to reduce the rate of flow by the desired amount. This gives smooth and reproducible curves only at the more positive potentials, in fact, at those potentials used by Bennewitz and Delijannis. As the mercury becomes more negative, very small amounts of gas form high up in the capillary and collect in the constriction, so breaking the thread of mercury. This insulates the drop of mercury that happens to be forming at that time, and thereby alters its potential, and hence its surface tension. The gas bubble is then swept down by the flowing mercury into the wider parts of the capillary, where it disperses to the walls and rises up into the constriction once more. This cycle is repeated many times before the bubble becomes large enough to be finally swept out of the capillary. While these proc-

esses are occurring the drop-weight is clearly unreproducible and useless. This difficulty has however been eliminated by the type of capillary shown in the figures, where a large bulb, A, containing about 10 cc. of mercury, is interposed between the capillary tip and the constriction B. The top of the tube C is connected to a mercury reservoir by means of a rubber tube. This arrangement effectively prevents the collection of gas in the constriction, and its use enables electrocapillary curves to be prolonged almost

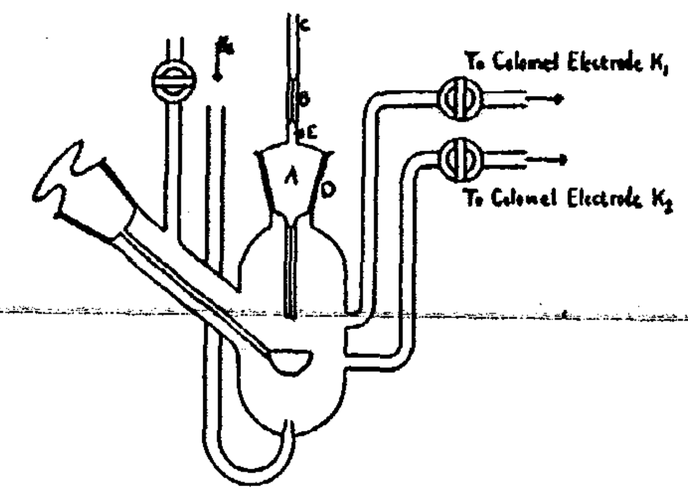

FIG. 1. APPARATUS USED FOR THE DETERMINATION OF DROP-WEIGHT ELECTROCAPILLARY CURVES

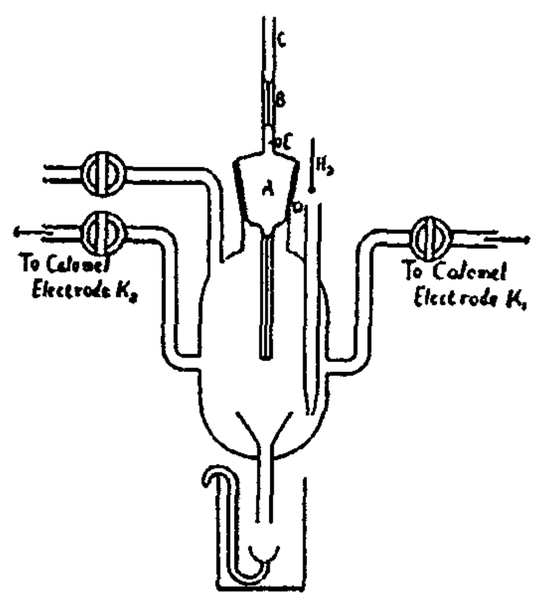

FIG. 2. APPARATUS USED FOR THE DETERMINATION OF DROP-WEIGHT ELECTROCAPILLARY CURVES

as far into the negative region of potential as with an ordinary capillary electrometer. The interposed bulb also prevents foreign bodies or other impurities derived from the rubber tube from reaching the capillary tip, and so vitiating the surface tension measurements, because in the course of each series of experiments the volume of mercury that drops through the capillary is considerably less than the volume contained in the bulb A.

For each series of measurements, the apparatus is thoroughly cleaned,

filled with the necessary solution, a cork inserted at D instead of the capillary, and the air removed by bubbling oxygen-free hydrogen for several hours. Meanwhile the bulb A of the capillary is filled with pure mercury, and connected by means of a rubber tube to the mercury reservoir, taking care to enclose no air bubbles in the connection. The mercury used was purified and redistilled *in vacuo*, and the rubber tube was freed from sulfur compounds by boiling first in caustic soda solution, and then several times in distilled water. After being dried, it was shaken out several times with pure mercury before use. When mercury has begun to drop from the capillary, the latter is inserted into D in place of the cork, and after standing for half an hour for everything to come to a steady state, measurements may be commenced. The whole apparatus is fixed to a very heavy stand on a brick pillar, built in a basement laboratory, to avoid vibration, which Kučera showed to have a very large effect on the drop-weight. For each measurement the dropping mercury is polarized to the required amount by applying a suitable potential difference between the contact E and the polarizing electrode K_1, and hydrogen is bubbled through the solution for about ten minutes, and is then turned off. The potential of the dropping mercury is then measured against the calomel electrode K_2. The potential usually fluctuates slightly according to the state of the drop, but clearly, it is the value just before the drop breaks away and falls, that is connected with its surface tension. There is no difficulty in measuring this potential, but in any case the fluctuation is small. The height of the mercury reservoir is then adjusted until the dropping rate becomes equal to any desired value, which must be kept fixed for each series of measurements. This rate must be a slow one, of the order of one drop every six or more seconds. The collecting spoon is then moved under the capillary, and twenty drops counted out and removed. The potential is again measured. The drops are poured into a 5-cc. crucible, washed twice with distilled water, and dried with strips of filter paper. The crucible is then placed in a vacuum desiccator, and its contents weighed next day. If, after each series of measurements, the capillary is washed thoroughly, it will continue to give satisfactory results for a long period of time.

RESULTS

Table 1 contains the results of such measurements for *N* potassium nitrate solution. Column 2 contains the weights of twenty drops, and column 3 the surface tension for the same potential, measured by means of an accurate capillary electrometer. The ratio of the surface tension at the maximum to the maximum drop-weight is 305.1, and this factor is then used to convert each of the drop-weight values to surface tensions, by multiplication, and the result is given in column 4. The agreement between columns 3 and 4 throughout the whole of the range of potential

employed shows that the drop-weight method is accurately applicable to the determination of electrocapillary curves. At any potential the surface tension, as given by this method, is always well within 1 dyne per centimeter of the value given by the capillary electrometer, and hence the surface tension is correct to within 0.2 per cent.

TABLE 1

The electrocapillary curve for N potassium nitrate at 15°C.

POTENTIAL (N. CAL.)	DROP-WEIGHT (20 DROPS)	SURFACE TENSION MEASURED BY CAPILLARY ELECTROMETER	SURFACE TENSION CALCULATED FROM DROP-WEIGHT
	grams	*dynes per cm.*	*dynes per cm.*
−0.011	1.2390	378.3	377.9
−0.046	1.2548	382.2	382.7
−0.073	1.2673	386.8	386.7
−0.145	1.2956	395.7	395.3
−0.178	1.3077	399.2	398.8
−0.211	1.3185	402.6	402.3
−0.247	1.3306	406.0	406.0
−0.286	1.3430	409.3	409.8
−0.326	1.3530	412.3	412.8
−0.361	1.3611	414.8	415.2
−0.392	1.3667	416.4	417.0
−0.433	1.3732	418.5	419.0
−0.470	1.3764	419.8	420.0
−0.516	1.3791	420.8	420.7
−0.545	1.3807	421.2	421.2
−0.578	1.3810	421.3	421.3
−0.613	1.3803	420.9	421.1
−0.649	1.3789	420.2	420.7
−0.679	1.3752	419.2	419.6
−0.714	1.3710	417.6	418.2
−0.760	1.3625	415.2	415.7
−0.816	1.3504	411.7	411.9
−0.863	1.3388	407.9	408.4
−0.907	1.3257	404.0	404.3
−0.959	1.3093	399.2	399.3
−1.008	1.2928	394.0	394.4
−1.048	1.2736	389.4	388.6
−1.107	1.2529	382.3	382.2
−1.167	1.2288	374.4	374.8

SUMMARY

A technique for the determination of electrocapillary curves by the drop-weight method has been developed, and the resulting curves are shown to coincide to within 0.2 per cent with the corresponding curves obtained in the usual way with a capillary electrometer.

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THE PHYSICAL CHEMISTRY OF FLOTATION. V

Flotation of Graphite and Sulfur by Collectors of the Xanthate Type and its Bearing on the Theory of Adsorption

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Received August 20, 1934

Gaudin (3) states that graphite and sulfur are intensely water-repellent and that to float them it is often sufficient to add a "frother" such as pine oil. Though other oils are sometimes added, Gaudin does not attribute their beneficial effect to their functioning as collectors. Nor does he attribute any collecting power to the frothers, but assumes that the natural floatability of these two minerals is sufficient to account for their flotation. Xanthates, it is claimed, exercise no collecting function toward sulfur and graphite, and their addition would be merely wasteful.

We have found, however, that concentrations of frothers considerably in excess of those required to produce a good froth are necessary to induce good flotation of graphite. With certain other frothers in neutral solutions, no substantial flotation is obtained whatever their concentration, and it has been concluded that graphite, like most other minerals, requires a collector for satisfactory flotation. In those cases where a reagent, usually regarded purely as a frother, is alone sufficient to induce good flotation, it has been shown that the reagent is itself a collector for the graphite. Contrary to the generally accepted view, it has been found that collectors of the xanthate type (xanthates, dithiocarbamates, dithiophosphates, etc.) are excellent collectors for both graphite and sulfur. Sulfur occupies a different position from graphite since it usually floats readily without any collector. Under some conditions, however, the floatability is considerably enhanced by collectors of the xanthate type, and it has been shown, moreover, that they are abstracted from solution by the sulfur.[1]

The response of graphite and sulfur to collectors of the xanthate type is of considerable theoretical significance. It does not seem possible to connect the response of a mineral with the possession of any particular type of lattice structure by the mineral. Sulfur and cleiophane, cerussite and

[1] In an earlier paper (6) we made the statement that sulfur is not influenced by xanthates. This incorrect view was due to our not having experimented with sufficiently high concentrations of ethyl xanthate.

anglesite, graphite, galena and chalcopyrite, copper and gold represent among them several different types of crystal lattice, but they all adsorb xanthates from solution, and, what is more significant, all lead to the same maximum angle of contact for each xanthate at a line of triple contact air–solid–xanthate solution. The last-mentioned fact indicates that, following the adsorption of the xanthate, the external or effective surface is the same in all cases, and that it consists entirely of the non-polar groups of the orientated adsorbed xanthate molecules.

It would be premature to conclude that the nature of the forces binding the xanthate molecules to these vastly different surfaces is the same for all of them. Nevertheless there emerges from these observations sufficient evidence to prove that certain of the proposed theories of adsorption cannot be of general application.

Taggart (5) claims that chemical (soluble) collectors function by forming a substantially insoluble orientated water-repellent film on the surface of the mineral to be floated. He has endeavored to show that this film is formed by double decomposition between the soluble collector and the surface of the mineral. In cases where the solubility of the mineral is so low as to render such action improbable, as, for example, galena, it is assumed that a previous oxidation has already changed the mineral surface into some compound of suitable solubility. Though it has been shown that the surface of galena may become oxidized and that the oxidized film may react with ethyl xanthate by double decomposition, it has not, in our opinion, been shown that unchanged galena cannot adsorb ethyl xanthate. Indeed, the procedure for floating anglesite in practice, namely, to add sodium sulfide as well as xanthate, points to the conclusion that lead sulfide itself adsorbs ethyl xanthate more readily than does lead sulfate. This may be demonstrated by air–mineral contact tests, as will be shown in a future publication.

At the surfaces of sulfur and graphite there can be no chemical reaction with xanthate of the type postulated by Taggart. The double decomposition theory cannot therefore be of general application, even if it be true in certain cases. The constancy of the contact angle, whatever the adsorbing solid, suggests, however, that the forces causing adsorption of xanthates are similar for all solids, and that any theory of the action of xanthates should explain their action on graphite as well as on galena.

While it is contended that the simple chemical theory of adsorption should logically be abandoned, certain observations that lent support to it should not be forgotten, though the reason for them is obscure. The readiness with which a sulfide mineral adsorbs a collector of the xanthate type increases as the solubility of the compound formed between the base metal of the mineral and the collector decreases. It should be pointed out however, that since the solubilities of the heavy metal xanthates run

strictly parallel with the solubilities of their sulfides, this generalization might be expressed in an alternative form, namely, that the readiness with which a sulfide mineral adsorbs a collector of the xanthate type increases as the solubility of the mineral decreases.

It is dissatisfying to reject one theory of adsorption without substituting for it another theory that is in agreement with experimental facts. It is therefore proposed to consider the nature of the forces at the surfaces of solids with a view to deciding whether sufficient is known concerning them to provide an explanation for the adsorption of collectors. It is generally agreed that surrounding each of the atoms or ions of a solid there exist strong forces which are responsible for the cohesion that opposes cleavage or grinding, and which lead to high melting and vaporization temperatures. At the surface these forces are available for attracting other ions, atoms, or groups of atoms, but until recently very little was known of their magnitude. De Boer and Custers (2) have, however, made an attempt to calculate the energy of adsorption of phenol on sodium chloride, dividing the binding forces into two types, the van der Waals forces and the electrostatic forces. It was shown by them that molecules with a high dipole moment are preëminently adsorbed electrostatically by the ions of the crystal lattice, whereas the van der Waals forces are operative for the nonpolar portion of the adsorbed molecules. The soluble flotation reagents known as collectors possess either a high dipole moment or a high degree of dissociation. Most of the adsorption of common collectors on solids possessing an ionic lattice structure must therefore be attributed to electrostatic forces emanating from the surface ions, acting either on the dipoles or the dissociated ions of the collector.

For solids of the graphite type, in which the electrons are shared equally between the atoms of the crystal lattice, different considerations must apply, and in this case it is difficult to reconcile the interior structure with an apparently undiminished ability to adsorb the xanthate type of collector. At the surface of such solids there must be a different arrangement of the electrons and a development of more polar characteristics.[2] The structure of graphite is such that the surface consists of a hexagonal pattern of carbon atoms with alternate carbon atoms having available one electron for sharing with any atom or group also capable of supplying an unshared electron. Before it can adsorb xanthate or during the adsorption, a rearrangement of electrons is necessary. Of the carbon atoms carrying an unshared electron every second one would be able (if spatial

[2] Adams and Jessup (1) have shown by means of contact angle measurements on original crystalline surfaces and on surfaces produced by scraping, that the surface forces differ according to the method of producing the surface. Surface rearrangements are therefore sometimes necessary for thermodynamic equilibrium, but the rate of rearrangement may be infinitesimally small.

considerations permitted) to adsorb a xanthate ion, while the other similar atoms would accept the electron available from these atoms on which adsorption occurs.

It has been found that the adsorption of ethyl xanthate by graphite does not change the pH value of the solution; it follows that xanthic acid[3] alone is not adsorbed, for if it were, the solution would develop alkalinity. It has been shown, too, that the xanthate adsorbed on graphite may be approximately determined by an iodine titration; it cannot therefore be present as dixanthogen. Since xanthic acid is a strong acid, it is probable that undissociated potassium xanthate is not adsorbed. We are therefore led independently to the conclusion that the xanthate ion is adsorbed. Graphite can supply no ion to replace the xanthate ions adsorbed, and unless a positive ion (potassium ion) is also adsorbed, the graphite must become strongly negatively charged following the adsorption. There probably exists a surrounding layer of potassium ions.

It is well to consider the difference between this conception of the adsorption of xanthate ions and Taggart's conception of chemical action, since the external appearance of the solid with its adsorption film is identical according to the two theories. Nothing is known of the crystal structure of lead xanthate, but it must certainly be very different from that of lead sulfide. The interior forces of the lead xanthate lattice must differ from those of the lead sulfide lattice, and the surface forces also must differ. These differences are manifested in the different solubilities in water and alcohol, and in the great ease with which air displaces water at the surface of the former. Consequently, the forces available to bind a xanthate ion to the surface of lead sulfide (by adsorption) must differ from those available to bind the same ion to the surface of lead xanthate (by crystal growth). The concentration of xanthate ions in equilibrium with two such different surfaces must therefore differ. Hence, in an earlier paper (4) Taggart was led to express tentatively the view that "the solubility of the substance as a surface coating is somewhat less than that of the same substance independently put into solution." This statement must be interpreted as meaning that lead sulfide binds a xanthate ion to its surface more firmly than does lead xanthate. We have found it useful to retain the conception of an "adsorption solubility product" of lead xanthate at such a surface. Provided that it is not confused with the true solubility product of lead xanthate, there can be no confusion due to its use. It is merely implied that the concentration of the lead ion in solution influences the adsorption of xanthate ions at a lead sulfide surface in a manner qualitatively similar to but differing quantitatively from the manner in which it is known to influence the deposition of sulfide ions at the surface.

[3] Barsky (7) has suggested that xanthic acid may be adsorbed by galena.

Taggart's suggestion that there must first be formed a film of sulfate (or other sulfoxide) before adsorption can occur, leads to an alternative picture, with an intermediate layer of lead sulfate between the lead sulfide and the xanthate film. (If this intermediate film be not retained in the final model, the supposed conversion to sulfate loses its significance. For if a xanthate ion *can* ultimately be attached to the sulfide lattice it is clearly unnecessary to postulate a sulfate layer at any stage of the process.) Here again the forces binding the xanthate ion to the surface differ from those binding it to a lead xanthate lattice, and the surface cannot be identical with a surface of pure lead xanthate.

EXPERIMENTAL METHODS

A. Contact angle measurements

These have been carried out by the methods described in the third paper of this series (8). The sulfur specimens were cut from a solid obtained by allowing fused flowers of sulfur to cool. The usual methods of polishing are satisfactory for sulfur, but not for graphite. None of the methods tried gave a polish as good as can be obtained on specimens of the sulfide minerals or metals, and the use of linen as a final polishing medium was useless. Magnesium oxide as abrasive on a plane lead or aluminum plate proved moderately satisfactory.

B. Flotation tests

Grinding was accomplished under water with a porcelain pestle and mortar, and the pulp was deslimed by shaking with water in the test tube and pouring off the mineral that did not settle within fifteen seconds. The flotation tests were carried out in rubber stoppered test tubes (size 6 in. x 1 in). About 2 g. of ground material with 30 cc. of water were introduced and the reagents added. The tube was then shaken vigorously. If a frother is present an excellent froth can be produced in this way, and if the mineral is in a condition susceptible to flotation from 50 per cent to 100 per cent of it will float in a well-mineralized froth that does not collapse on standing. Even when the mineral is not in a condition susceptible to flotation, a few particles usually float in an incomplete film on the surface. Unless the particles in the surface showed crowding this small tendency to float was ignored. Though the method is incapable of giving results that could be applied without modification in practice, it is a more rapid and more easily controlled medium for studying the effects of reagents than an ordinary flotation machine. The major differences between the test tube and the flotation machine lie in the method of aeration, and in the pulp density.

C. Consumption of xanthate

The xanthate was estimated before and after the abstraction tests by titration against standard iodine. The precautions necessary because of the low concentrations of xanthate and the consequent use of $N/1000$ iodine will be described elsewhere.

EXPERIMENTAL RESULTS

Graphite

Flotation in the absence of reagents. Ground graphite will float in an incomplete film if it is fed carefully on to the surface of water. If, however, it be once submerged, only a small proportion of the particles will float again. Washing with ether, to remove any adherent oil, has little effect on the flotation of graphite, nor does heating to a red heat, with or without subsequent quenching in water. It does not seem to matter whether the graphite is ground dry or under water.

Effect of the recognized frothers. Under the conditions of these test tube tests, 10 mg. of terpineol (one of the major constituents of pine oil) per liter gives a fairly stable froth in water, but between 25 and 50 mg. of terpineol per liter is required to produce satisfactory flotation of graphite. With isoamyl alcohol 30 mg. per liter gives a fairly stable froth in water, but between 200 and 500 mg. per liter is required to produce a good flotation of graphite. Neither of these frothers induces satisfactory contact in contact angle tests, though solutions of high concentration lead to slight and irregular contact.

Acetone, though a frother, is not, in neutral solution, a collector for graphite. One gram of acetone per liter gives a froth of low stability, and with 200 g. per liter the froth is still not very stable. Whatever its concentration, however, acetone is without influence on the floatability of graphite. If a suitable collector is present as well (e.g., 5 mg. of potassium amyl xanthate per liter), the acetone exerts the usual function of a frother in facilitating the formation of a stable mineralized froth; about 10 g. per liter is necessary for this purpose. Ethyl alcohol and cyclohexanol are frothers that behave in a manner similar to acetone.

In alkaline solutions all of these frothers give stable froths at lower concentration and all of them lead to flotation of graphite. Whereas in the absence of a collector 2 g. of acetone per liter gives appreciable flotation at pH = 12, and 10 g. per liter gives good flotation, in the presence of 10 mg. per liter of potassium amyl xanthate 250 to 500 mg. per liter of acetone gives good flotation. In general it has been found that the addition of amyl xanthate permits of the flotation (especially of the larger particles) with considerably lower concentrations of "frother" than would otherwise be possible, and this is true whether alkaline or neutral solutions are used.

Effect of collectors of the xanthate type. Ethyl xanthate, if at sufficiently high concentration, is a good collector for graphite in test tube flotation tests. In these tests isoamyl alcohol (30 mg. per liter) was used as the frother. About 25 mg. of ethyl xanthate per liter definitely gives some flotation, but higher concentrations are required to give a permanent mineralized froth. Contact angles varied from approximately 30° for a concentration of 5 mg. per liter to 60° for concentrations greater than 200 mg. per liter. Copper sulfate did not improve either contact or flotation at the lower concentrations of xanthate; it is not an activating agent for graphite.

A concentration of 5 mg. of potassium amyl xanthate per liter gives good flotation of graphite; again 30 mg. of isoamyl alcohol per liter was used as frother. Contact angles varied from 57° for a concentration of 5 mg. per liter of potassium amyl xanthate to 80° for a concentration of 500 mg. per liter. Cyanide (1 g. of sodium cyanide per liter) is without influence on flotation or on contact, but after a short conditioning period strong alkali (pH = 13) prevents flotation, probably because it slowly saponifies the xanthate. If a solution containing 5 mg. of potassium amyl xanthate per liter is kept at pH = 13 for an hour before use, it fails to induce flotation of graphite.

Of the dithiocarbamates the butyl compound is more effective than the ethyl. Potassium dibutyl dithiocarbamate (10 mg. per liter), with isoamyl alcohol (30 mg. per liter) as frother, induces excellent flotation of graphite. Solutions containing 5, 50, and 500 mg. per liter induced contact angles of 58°, 65°, and 74°, respectively. Sodium diethyl dithiophosphate must be at a high concentration to cause flotation. As the concentration is increased, flotation first becomes possible at about 500 mg. per liter, but 10 g. per liter gives excellent flotation. The latter concentration leads to a contact angle of 60°.

Thus, graphite generally responds to collectors of the xanthate type (containing the CS_2 group) in the same order as the sulfide minerals, which are least susceptible to the dithiophosphates, most susceptible to the dithiocarbamates, and of intermediate susceptibility to the xanthates. Like those on sulfide minerals, the collector films on graphite are very stable. Amyl xanthate cannot be recovered from the surface by washing with hot water or alcohol.

Consumption of xanthate. Graphite rapidly abstracts ethyl xanthate and amyl xanthate from their solutions. Within ten minutes 2 g. of dry ground graphite completely removed the amyl xanthate from 20 cc. of a 20 mg. per liter solution. Within half an hour 2 g. removed 69 per cent of the amyl xanthate from 40 cc. of a 500 mg. per liter solution, and 50 per cent from a second similar solution. The pH value remained unchanged

at 6.8; had xanthic acid been abstracted the pH value would have changed to between 10 and 11. Similar results were obtained for ethyl xanthate.

It is impossible to recover the adsorbed xanthate by digestion of the graphite with hot water or hot alcohol. That the xanthate has been adsorbed unchanged on the surface of graphite is, however, suggested by the results of a titration of a suspension of the conditioned graphite against $N/1000$ iodine. The reaction is a slow one, several hours' contact with the iodine solution being necessary, and an accurate titration is impossible. However, at least 80 per cent of the adsorbed ethyl xanthate can be evaluated in this way. In a control test, graphite that had not been treated with xanthate consumed less iodine than corresponds to 10 per cent of this amount.

Sulfur

Sulfur differs from graphite in that it is inherently much more readily floatable. Sulfur that has been ground very coarsely under water does

TABLE 1

Abstraction of amyl xanthate by two grams of sulfur

NO.	CONCENTRATION OF XANTHATE		IODINE EQUIVALENT OF XANTHATE ABSTRACTED	XANTHATE ABSTRACTED
	Initial	Final		
	mg. per liter	*mg. per liter*	*cc.*	*mg.*
1	312	268	3.4	0.70
2	156	108	3.7	0.77
3	94	50	3.4	0.70
4	31	0	2.5	>0.5

not float completely on shaking it up with water or dilute solutions of the frothers already mentioned, but if it be allowed to slide slowly on to the surface a heavy film flotation can usually be obtained. However, by using coarse sulfur and low concentrations of frothers, it can be demonstrated that the xanthate type of collector, if present in sufficiently high concentration, enhances the floatability of sulfur. The adsorption of the collector by sulfur may also be studied by measuring the contact angle at its surface in the presence of a solution of the collector. Thus 500 mg. of potassium di-*n*-butyl dithiocarbamate per liter led to an angle of contact of 78°. Amyl xanthate did not, however, induce the customary angle of contact.

We cannot confirm a statement by Christmann (7) that whereas sulfur is not wetted by water, pine oil causes it to be readily wetted by water. We find that the floatability of sulfur is considerably increased by the addition of pine oil. If sufficient pine oil is added to give large undissolved globules, the sulfur, being wetted by pine oil in preference to water, goes

into the pine oil phase, or into the interface. The combined sulfur-pine oil aggregate is readily wetted by air and floats readily, unless sufficient sulfur is present to make its density greater than that of water. Christmann's conclusion that the polar group of the pine oil is orientated outwards at the surface of sulfur is therefore unjustified.

The adsorption of collectors by finely divided sulfur has been determined by measuring the abstraction of xanthate from solution. Table 1 demonstrates that the amount of amyl xanthate removed is independent of the initial concentration of the xanthate, and that the whole of the xanthate may be removed from sufficiently dilute solutions. Two grams of flowers of sulphur and 16 cc. of xanthate solution were used for each test, three hours' contact being allowed between sulfur and solution. The sulfur was then washed until the washings were free from xanthate and the unconsumed xanthate determined by titration against $N/1000$ iodine. In order that the sulfur should be wetted by the xanthate solution, it was first wetted by 1 cc. of acetone. In a control test without sulfur, but with acetone, there was no appreciable loss of xanthate.

This work was carried out for the following companies: Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Company of Australasia Ltd., Mount Lyell Mining and Railway Co. Ltd., and the Burma Corporation Ltd. The authors with to express their thanks to Mr. H. Hey, under whose general direction they have worked, and to Professor E. J. Hartung, who has generously provided laboratory accommodation in the Chemistry Department of the University of Melbourne.

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THE EFFECT OF ELECTROLYTES UPON THE RATE OF HYDROLYSIS OF DIETHYL ACETAL[1,2]

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Received August 23, 1934

The kinetic method for the determination of the dissociation constant of benzoic acid in potassium chloride solutions has been shown to yield results in agreement with the electrometric method (7, 10).

In order to determine the dissociation constants of acids in solutions of other salts, it is necessary to calibrate the reaction for these salt solutions. This involves a study of the primary kinetic salt effect of the reaction. The present paper extends the study of Kilpatrick and Chase to eight solvent salts. The results are not only of value for the determination of hydrogen-ion concentrations, but in themselves they are of interest as a study of primary kinetic salt effect in a reaction of the zero kinetic type, $A^0 + B^- \rightarrow$ products.

The rate-determining step may be regarded as the formation of the complex as postulated by Brönsted (2, 3) or the decomposition of the intermediate complex in equilibrium with the reactants (1). In either case the equation which expresses the kinetic salt effect for this type of reaction is

$$\ln k_{H_3O^+} = \ln k^0_{H_3O^+} + (\beta + \beta' - \beta'')C \qquad (1)$$

where $k_{H_3O^+}$ represents the velocity constant for molar hydrogen ion at the concentration C of the uni-univalent salt, and $k^0_{H_3O^+}$ is the velocity constant for molar hydrogen ion at zero electrolyte concentration. β is the salting-out constant for acetal in the equation,

$$\ln f_0 = \beta C \qquad (2)$$

[1] An abstract of this paper was presented at the Eighty-sixth Meeting of the American Chemical Society, held at Chicago, Illinois, September, 1933.

[2] Abstracted from the dissertation of Leonard C. Riesch which was presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[3] George Lieb Harrison Fellow in Chemistry, 1933–1934.

and β' and β'' are the salting-out terms for the ions in the expression,

$$\ln f = -\alpha\sqrt{C} + \beta' \text{ (or } \beta'')C \tag{3}$$

where β, β', and β'' depend upon the specific electrolyte.

Equation 2 has been shown to hold over wide ranges of concentration in certain cases (11). Equation 3 would not be expected to hold over a wide range of concentration.

An examination of the results in the literature indicates that the magnitude of the electrolyte effect varies greatly. Two typical examples are given in figure 1, in which $\frac{\log k_{H_3O^+} - \log k^0_{H_3O^+}}{C}$ is plotted against the electrolyte concentration C.

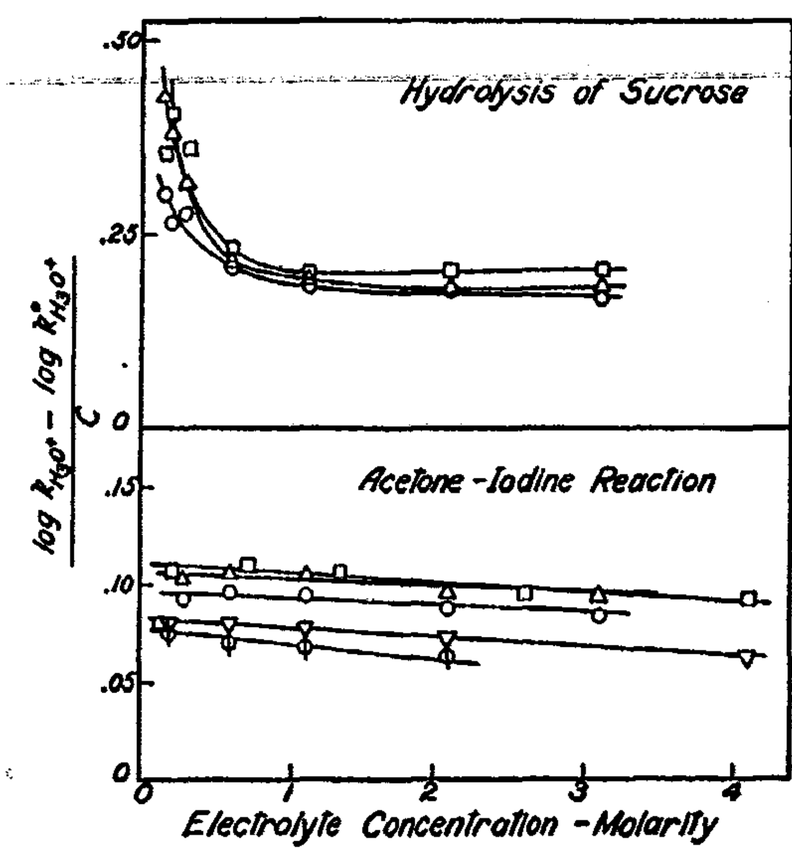

FIG. 1. THE VARIATION OF THE B VALUES WITH ELECTROLYTE CONCENTRATION
○, KCl; △, NaCl; □, LiCl; Φ, KNO_3; ▽, $NaNO_3$

The points represent the values of B, which equals 2.3 $(\beta + \beta' - \beta'')$, at the various concentrations. It is to be noted that in the case of the acetone-iodine reaction B is small and fairly constant, while in the case of the hydrolysis of sucrose B decreases until an electrolyte concentration of approximately one molar is reached, after which B remains almost constant.

For small values of B and low concentrations, equation 1 reduces to the form,

$$k_{H_3O^+} = k^0_{H_3O^+} + \lambda C \tag{4}$$

This equation has been subjected to many experimental tests in dilute solution and has been shown to hold within the accuracy of the measurements (4).

In the case of diethyl acetal the B value is large, and equation 4 cannot be expected to hold, but through the range of concentration where equation 3 is valid, log $k_{H_3O^+}$ should be a linear function of the concentration. A few experiments reported by Brönsted and Wynne-Jones (6) apparently show this to be the case.

Brönsted and Grove (5) have studied the primary salt effect in the hydrolysis of dimethyl acetal, and find that while the magnitude of the effect depends upon the particular electrolyte, equation 1 holds up to a concentration of 0.2 molar. The results reported herein indicate that equation 1 does not hold very exactly even in dilute solutions, but that B becomes fairly constant at high concentrations.

EXPERIMENTAL PART

The course of the reaction was followed dilatometrically, the apparatus and the method of calculation being the same as that used by Kilpatrick and Chase (10).

The acetal was purified by fractional distillation after treatment with anhydrous potassium carbonate, the fraction boiling between 102.5–103°C. (760 mm.) being used. It was essential that the acetal be free from acidic impurities. Frequent tests for acidic impurities were made by adding 0.5 cc. of acetal to 50 cc. of carbon dioxide-free water containing bromothymol blue. During the course of the work it was found necessary to keep the acetal in tightly stoppered bottles to prevent the formation of acetic acid. Apparently a trace of moisture and acid result in the hydrolysis of the acetal to acetaldehyde, which on oxidation yields acetic acid thereby increasing the amount of acid present and the rate of hydrolysis. The salts were purified when necessary. The sulfonates were recrystallized several times from alcohol after decolorization with activated charcoal.

An inspection of table 1 indicates that there is apparently a slight increase in $k_{H_3O^+}$ with increasing concentration, and a difference between the acids; however, this is probably within the experimental error of the measurements. We have therefore taken $k^0_{H_3O^+}$ as 2.469.

Table 2 gives the results with lithium chloride solutions. The magnitude of the electrolyte effect is thirteen-fold at three molar, and even at 0.2 molar it is 27 per cent. Table 3 summarizes the $k_{H_3O^+}$ values for the other salts. The specific effect of the various salts is evident. The $k_{H_3O^+}$ values vary over 100 per cent at some concentrations. Table 4 gives the B values calculated as for figure 1. From this table it is evident that the B values are much greater than those given in figure 1 for other reactions,

TABLE 1

Results at low electrolyte concentration

ACID	CONCENTRATION	k (OBSERVED)	$k/C_{acid} = k_{H_3O^+}$
	moles per liter		
HCl	0.00502	0.01221	2.432
HCl	0.010096	0.02478	2.454
HCl	0.01004	0.02456	2.445
HCl	0.01004	0.02447	2.439
HCl	0.01506	0.03736	2.480
HCl	0.02008	0.05021	2.501
HNO_3	0.00510	0.01244	2.439
	0.01020	0.02507	2.458
	0.01020	0.02569	2.520
	0.01530	0.03776	2.468
	0.02040	0.05066	2.484
$HClO_4$	0.00510	0.01246	2.443
	0.01020	0.02559	2.508
	0.01020	0.02497	2.447
	0.01530	0.03803	2.485
	0.02040	0.05104	2.502

TABLE 2

Electrolyte effect at 0°C. in lithium chloride solutions

HCl	LiCl	k (OBSERVED)	$k/C_{acid} = k_{H_3O^+}$
moles per liter	*moles per liter*		
0.010096	0.040	0.02620	2.60
0.010096	0.090	0.02819	2.80
0.010096	0.140	0.02967	2.95
0.010096	0.190	0.03164	3.13
0.010096	0.240	0.03296	3.27
0.010096	0.290	0.03432	3.40
0.010096	0.390	0.03781	3.75
0.010096	0.490	0.04182	4.14
0.010096	0.590	0.04564	4.52
0.010096	0.790	0.05406	5.35
0.005048	0.995	0.03185	6.31
0.005048	1.495	0.04782	9.47
0.005048	1.995	0.07310	14.48
0.003029	2.497	0.06588	21.75
0.002019	2.998	0.06892	34.13

and that equation 1 is only approximately in agreement with experiment even in dilute solution.

The value of B apparently decreases with concentration and becomes fairly constant at the higher concentrations. If the assumption that equation 2 holds is correct, the change in B must be due to the fact that equation 3 does not express the change of the activity coefficient of the

TABLE 3

$k_{H_3O^+}$ at 0°C. for various electrolytes

ELECTROLYTE CONCENTRATION	NaCl	KCl	$NaClO_4$	$C_6H_5SO_3Na$	$p\text{-}C_6H_4CH_3SO_3Na$	$LiNO_3$	$NaNO_3$	KNO_3
moles per liter								
0.05	2.58		2.61	2.55	2.58			
0.10	2.76	2.79	2.84	2.63	2.68	2.77	2.72	2.74
0.15			3.04	2.73	2.74			
0.20	3.08	3.11	3.21	2.81	2.82	3.05	3.01	2.89
0.30	3.43		3.60	2.89	2.93	3.30	3.19	3.09
0.40	3.73	3.73	4.04	3.06	3.06	3.55	3.50	3.31
0.50	4.08		4.52	3.19	3.23	3.85	3.76	3.51
0.60	4.48	4.37	5.01	3.35	3.40	4.14	3.95	3.73
0.70				3.47	3.49			
0.80	5.27	5.08	5.98	3.65	3.63	4.80	4.43	4.08
0.90				3.75	3.75			4.27
1.00	6.16	5.74	7.08	3.97	3.80	5.51	4.99	4.49
1.10								4.62
1.20								4.88
1.25	7.47			4.45				
1.50	9.09	7.95	10.44	5.04		7.85	6.51	
1.75	10.83		12.43	5.62				
2.00	13.06	10.96	15.15			10.98	8.32	
2.25	15.69		18.49					
2.50	18.90	14.34	22.43			15.06	10.60	
3.00	27.64	19.42	31.50			21.08	12.97	

ions with increasing electrolyte concentration. The more exact form of equation 3 is

$$-\log f = \frac{A\sqrt{C}}{1 + \kappa b} + \beta' C \tag{5}$$

where b is the mean ionic diameter of the given ion and the ions in the solution. Other equations of this type have been used by other investigators (13), but in all cases for this type of reaction the resulting equation for the salt effect has the same form as equation 1.

TABLE 4

$$\frac{\log k_{H_3O^+} - \log k^{\circ}_{H_3O^+}}{C} = B$$

ELECTROLYTE CONCENTRATION	$NaClO_4$	LiCl	NaCl	KCl	$LiNO_3$	$NaNO_3$	KNO_3	p-$C_6H_4(CH_3)SO_3Na$	$C_6H_5SO_3Na$
moles per liter									
0.05	0.50	0.46	0.40[0.49]				(0.54)	0.40	0.30
0.10	0.61[0.54]	0.55	0.49(0.53)[0.50]	0.49 0.46	0.51	0.43[0.38]	0.46[0.41]	0.36	0.28
0.15	0.60	0.52	(0.53)					0.31	0.29
0.20	0.57[0.52]	0.51	0.49(0.56)[0.45]	0.48 0.46	0.46	0.43[0.35]	0.35(0.46)[0.36]	0.29	0.28
0.25		0.49							
0.30	0.54	0.47	0.48		0.42	0.37	0.33	0.25	0.23
0.40	0.53	0.46	0.45	0.44 0.45	0.39	0.38	0.32	0.24	0.23
0.50	0.53	0.45	0.44		0.39	0.37	0.31	0.23	0.22
0.60	0.51	0.44	0.43	0.41 0.44	0.37	0.34	0.30	0.23	0.22
0.70								0.22	0.21
0.80	0.48	0.42	0.41	0.39	0.36	0.32	0.27	0.21	0.21
0.90							0.26	0.20	0.20
1.00	0.46	0.41	0.40	0.37 0.39	0.35	0.31	0.26	0.19	0.21
1.10							0.25		
1.20							0.25		
1.25			0.38						0.20
1.50	0.42	0.39	0.38	0.34 0.35	0.33	0.28			0.21
1.75	0.40		0.37						0.20
2.00	0.39	0.38	0.36	0.32 0.32	0.32	0.26			
2.25	0.38		0.36						
2.50	0.38	0.38	0.35	0.31 0.31	0.31	0.25			
3.00	0.37	0.38	0.35	0.30 0.31	0.31	0.24			

The values in ( ) are from the data for diethyl acetal given by Brönsted and Wynne-Jones; those in [ ] are for dimethyl acetal from the data of Brönsted and Grove; those in ‾ are from Kilpatrick and Chase for diethyl acetal.

The temperature coefficient

The acetal reaction is so sensitive to hydrogen ion that $k_{H_3O^+}$ cannot be determined accurately by direct measurement above 0°C. The method employed was the two-thermostat method of Rice and Kilpatrick (12). Portions of the same solution were placed in two similar dilatometers in

TABLE 5

Electrolyte effect on the temperature coefficient

HCl (APPROX.)	SALT	k_{35}/k_{25}	E	DEVIATION FROM 22,323
moles per liter	*moles per liter*		*calories*	*calories*
0.0001	—	3.372	22,199	124
0.0002	—	3.402	22,360	37
		KCl		
0.00015	0.10	3.423	22,474	151
0.000125	0.50	3.420	22,458	138
0.0001	1.00	3.447	22,600	277
0.00004	2.00	3.493	22,843	520
0.00004	2.00	3.550	23,139	816
0.00004	3.00	3.449	22,611	288
0.00004	3.00	3.407	22,388	65
0.00004	3.00	3.275	21,666	657
		NaCl		
0.00007	1.00	3.385	22,270	53
0.00004	2.00	3.516	22,963	640
0.00004	2.00	3.323	21,934	389
0.00004	3.00	3.206	21,277	1,046
		$C_6H_5SO_3Na$		
0.0001	1.00	3.326	21,949	374
		KNO_3		
0.00005	3.00	3.325	21,942	381
Average.....		3.395	22,323	±370

thermostats at 35°C. and 25°C., respectively. The temperature interval was determined by a calibrated resistance thermometer, and the thermostats were controlled to ± 0.005°C. Equivalent portions of acetal were added to each and $k_{obsd.}$ was calculated in the usual manner. The quotient k_{35}/k_{25} yielded the temperature coefficient directly. Table 5 gives the results and the energy of activation calculated from the Arrhenius equation.

Apparently the value of the energy of activation remains constant in the presence of neutral salts within the experimental error of measurement.

DISCUSSION

As already stated the results cannot be expressed by equation 1. Upon examination the deviations are found to be hyperbolic functions of the concentration. Equations which express the experimental results within 2 per cent are given below.

$NaClO_4$ $\log k = 0.392 + 0.62C - (\sqrt{0.0576 + 0.104C^2} - 0.24)$
$LiCl$ $\log k = 0.392 + 0.58C - (\sqrt{0.00292 + 0.0482C^2} - 0.054)$
$NaCl$ $\log k = 0.392 + 0.55C - (\sqrt{0.010 + 0.0535C^2} - 0.10)$
KCl $\log k = 0.392 + 0.53C - (\sqrt{0.0256 + 0.0787C^2} - 0.16)$
$LiNO_3$ $\log k = 0.392 + 0.50C - (\sqrt{0.0049 + 0.0438C^2} - 0.07)$
$NaNO_3$ $\log k = 0.392 + 0.45C - (\sqrt{0.0225 + 0.0639C^2} - 0.15)$
KNO_3 $\log k = 0.392 + 0.43C - (\sqrt{0.0144 + 0.0697C^2} - 0.12)$
$C_6H_5SO_3Na$ or p-$C_6H_4(CH_3)SO_3Na$ $\log k = 0.392 + 0.40C - (\sqrt{0.000225 + 0.0418C^2} - 0.015)$

TABLE 6

Correlation between velocity constant and acidity function

KCl IN MOLES PER LITER	$\log k$	H_0	$\log k + H_0$
0.00	0.389	1.05	1.44
1.00	0.759	0.88	1.64
2.00	1.040	0.75	1.79
3.00	1.288	0.60	1.88

Hammett (8, 9) has recently tried to show a relationship between the velocity constant of a reaction and the acidity function. He finds that the rate of the inversion of sucrose, and the rate of the hydrolysis of ethyl acetate and cyanamide in salt solution, can be expressed by the equation:

$$\log k + H_0 = \log k_2$$

where k is the velocity constant of the reaction, H_0, the acidity function, is equal to $-\log a_{H^+} f_B/f_{HB}$, and k_2 is a constant. In order to test the relationship for the acetal reaction, our values of $\log k$ and the corresponding H_0 values for potassium chloride solutions determined by Hammett are given in table 6.

The last column shows that $\log k_2$ is not constant. In the case of the inversion of sucrose by trichloroacetic acid Hammett interprets the lack of constancy as indicating general acid catalysis. In the case of the acetal reaction it might seem that catalysis by acids stronger than H_3O^+ exists.

The order of the effect of the anions is $ClO_4 > Cl > NO_3 > RSO_3$, which might favor this view. However, the fact that changing the concentration of the hydrogen ion does not change the value of $k_{H_3O^+}$ argues against this view. If molecule catalysis were present an increase in the concentration of H_3O^+ should alter the ratio of acid molecule to hydrogen ion and $k_{H_3O^+}$, calculated on the assumption that the hydrogen ion is the sole catalyst, should vary. Further evidence against the view that acids other than H_3O^+ catalyze this reaction will be presented in a later paper.

SUMMARY

1. The primary kinetic salt effect of nine salts has been determined for the hydrolysis of diethyl acetal catalyzed by strong acids in aqueous solution.

2. The temperature coefficient has been determined, and the heat of activation was found to be independent of the electrolyte concentration within the experimental error of measurement.

3. The reaction has been calibrated to determine the hydrogen-ion concentration of buffer solutions.

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NEW BOOKS

Raumchemie der festen Stoffe. By W. BILTZ. 24 x 16 cm. x + 338 pp. Leipzig: Leopold Voss, 1934. Price: unbound, 22.5 RM; bound, 24 RM.

The present volume has been produced by Professor Biltz and a number of collaborators, and is a very illuminating account of the information which may be gained from a study of molecular volumes of large numbers of substances. The approach to the subject is perhaps somewhat old-fashioned in the sense that tabular information concerning atomic and ionic radii as determined by crystal analysis has not been given, although references to crystallographic literature are very full and up-to-date.

The first part of the book gives tabular information on molecular volumes and densities of solids corrected back to absolute zero, and the references to original work set out in detail at the end of each table number several hundred. Although the writers in most instances refer to the type of crystal structure of a particular compound and to the determination of its atomic arrangement, this is as far as the author goes in presenting the more modern physical results. The book is of a distinctly different type than Hassel's recent *Krystallchemie* and covers a much greater range of substances in a more general way. The considerations of radius-ratio and the additive laws for atomic volumes and atomic radii do not perhaps receive quite so much attention as some readers may wish.

The book seems to fall between the entirely tabular type and that of a treatise, with the consequence that the lack of a substance index of any kind makes it a little difficult to use as a detailed work of reference. There is no question, however, that it is an extremely valuable compilation, and the excellent diagrams summarize the more important conclusions arrived at. The end-cover contains a detachable sheet of atomic and ionic volumes set out in the form of the periodic table; this should prove very valuable for quick reference.

J. T. RANDALL.

Thermionic Emission. By A. L. REIMANN. 23 x 15 cm.; xi + 324 pp. London: Chapman and Hall, 1934. Price: 21s.

The subject of thermionics is one which has attracted a good deal of interest during the last thirty years, but it is only very recently that a more complete understanding of the mechanism of electron emission by heated bodies has come about. The application of modern quantum statistics to the problems of metallic conduction and the properties of semiconductors has given us a much clearer insight into the fundamentals of thermionic emission by clean metals and oxide cathodes, respectively. Dr. Reimann's book, whilst preserving an admirable balance between theory and experiment, has not neglected to give considerable space to the pioneer work of Richardson, H. A. Wilson, and others, which did so much to set the subject on its feet. The outlook of the book is entirely fundamental and physical, and the author has wisely left accounts of the obvious practical applications of his subject to others. The techniques of preparing the various thermionic emitters for accurate physical measurement are dealt with in a very clear way; to the practising physicist as well as to the theoretician and student the book is certain to be as valuable as it is timely.

The main items of the book deal with electron emission from clean metals, from contaminated metals, and from oxide cathodes; in addition there are chapters on the emission of ions and modern general theory of electron emission. To the reader not so interested in the detailed presentation of the subject there is an introductory general survey of sixty-seven pages, which should be of great value to physical chemists. Perhaps in a later edition Dr. Reimann might even extend and simplify this chapter a little, as many of the conceptions and arguments may be a little difficult for the non-specialist to grasp on a first reading. A section of the work which may be of more special interest to readers of this journal is concerned with the electron emission from contaminated metals such as cesium on tungsten (W–Th), barium on oxygenated tungsten (W–O–Ba) etc. The book contains considerable information not available elsewhere on this aspect of thermionics; it is well produced and printed, and it possesses the rare virtues of being well-written and indexed.

J. T. RANDALL.

Strahlentherapie in kolloidchemischer Betrachung. By R. E. LIESEGANG. 25.5 x 18.5 cm. 46 pp., being pp. 871 to 914 of the Textbook of Medical Colloid Therapy, by Drs. L. Lichtwitz and R. E. Liesegang and Prof. Dr. Karl Spiro. Dresden: Verlagsbuchhandlung Theodor Steinkopff, 1934. Price: 3.00 RM.

This small monograph consists largely of tabulated results of various related publications, dealing with the effects of radiation (light, ultra-violet, x-rays and gamma rays) upon living tissue, considered from the aspect of colloid chemistry. In a short preliminary note the view is advanced that the evolution of species and the non-survival of prehistoric species may be due to the change of type of the radiation incident on the surface of the earth. The action of radiation of different wavelengths upon purely inorganic colloids is first considered on the basis of tabulated findings of various investigators, and the results are briefly discussed from the aspect of molecular charge and photochemical action. Further tabular data are given in respect to the action of radiation on various proteins, which come into question in physiological processes, the "heat point" theory of Dessauer being introduced. Similarly the effects of radiation upon ferments and their action is discussed, followed by a section on the action upon bacterial cultures. This leads to sections of more direct interest to the practical medical radiologist as to the effects of radiation upon the blood, protozoa, egg and ovarian tissues, and isolated organs. Finally the effects upon living skin and carcinomatous tissues are tabulated and briefly discussed.

The monograph, being largely in tabular form, will be of assistance even to those not reading German, but the subject matter is of limited interest, being practically addressed to the few medical radiologists carrying on intense radiation treatment of cancer and other diseases, rather than to those interested in the underlying biochemical phenomena.

B. J. LEGGETT.

Das Wasserstoffisotop. By R. FRERICHS. Ergebnisse der exakten Naturwissenschaften, Sonderabdruck aus Band XIII (not sold separately). 23 x 15.5 cm.; pp. 258–309. Berlin: Julius Springer, 1934. Price: unbound, 28 RM; bound, 29.40 RM.

This small monograph gives a good account of the investigations on heavy hydrogen which had been carried out to the first part of 1934. Considerable attention is devoted to the method of separation. The physical properties are next considered, including nuclear properties and disintegration by the D-nucleus. Something is said of the isotope H^3. The molecules HD and D_2 and the equilibrium between them are dealt with. The rest of the material is mainly concerned with the physical

and chemical properties of heavy water. The article is illustrated and provided with a bibliography of 186 items, which may perhaps illustrate the active interest in the new isotope shown in such a short period of time.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium, Teil A, Lieferung 2. 26 x 18 cm.; vi + 285–450 pp. Berlin: Verlag Chemie, 1934. Price: 34 RM. Subscription price: 22.50 R.M.

The volume deals with the electrochemical properties of aluminum, with its reactions with non-metals, metals, compounds of non-metals (including corrosion) and metals, solutions, and organic compounds; with the hydrolysis of aluminum salts; and with the qualitative and quantitative analysis of aluminum, and the methods of testing the corrodibility of the metal. The subjects are treated very thoroughly and with references to the literature. The volume maintains the high standard of the work in general and includes a good deal of information of physicochemical interest.

J. R. PARTINGTON.

Einführung in die Lehre von den Kolloiden. By H. BECHHOLD. 23.5 x 16 cm.; 160 pp. Leipzig: Steinkopff, 1934. Price: 10 RM.

This small volume contains a series of chapters dealing with various properties of colloid systems and written by different authors; the introductory chapter was written by Dr. Bechhold. Dr. Hock deals with the methods by which colloid particles can be identified in properties with macro-molecules as well as their assemblage in sols and gels. Two chapters were contributed by Dr. Heymann on interfaces and the electrical properties of colloid systems. The preparation and purification of colloids are discussed by Drs. Schwarz and Erbe, whilst two chapters on the optical properties and x-ray examination of colloid systems were written by Drs. Hauser and Brill.

Whilst the book scarcely attains the ideal aimed at by the editor, viz., a complete survey of the present position of colloid chemistry and physics, it is nevertheless very readable and would serve as a general introduction to those who wish to take up the subject. The chapters on the optical properties and x-ray examination are especially to be commended.

E. K. RIDEAL.

The Atom. By J. TUTIN. 14 x 22 cm.; 103 pp. London: Longmans, Green and Co., 1934. Price: 6s.

The conception of the Rutherford-Bohr atom has paved the way for advances in many branches of science; it has also satisfied one of the tests of a useful theory in its ability to predict new facts. Therefore some surprise is occasioned when the claim is made that an "inverted" atom, with the electrons in the nucleus and the massive particles circulating in orbits outside, would serve equally well to explain the facts.

Dr. Tutin makes such a claim in his book, and goes further in stating that his "alternative" atom explains in a simple way many important phenomena of physics and chemistry which are so familiar that they are accepted as though no explanation were necessary. Prominent among these explanations is the distinction between metal and non-metal, a distinction which, though forming the basis of the study of chemistry, finds no expression in the orthodox picture of the atom. In Dr. Tutin's theory, however, atoms of metals are provided with free electrons external to the nucleus.

The most radical change which the new theory suggests is in the mechanism of valency. This, in the orthodox view, is a concern of electrons, and therefore should be able to be correlated with spectral emission. To provide a similar mechanism for both valency and spectral emission implies that those atoms which are chemically most active should be most easily excited optically. That this is not true is well-known. Oxygen, one of the most active chemically, yields a spectrum only with difficulty; the inert gases are notably easy to excite spectrally and yet are assumed, because of their chemical inertness, to have their electrons in very rigid configurations.

It appears to the reviewer that on these grounds any alternative atom merits close examination.

Let us see how Dr. Tutin finds an alternative. He notes that it is unsatisfactory to have (1) an electronic mechanism for both valency and spectral emission, (2) no distinction between metal and non-metal. He overcomes the latter by allotting free electrons to metals, i.e., by furnishing a mechanism associated with ease of spectral emission. But do the properties of elements warrant a close parallelism between ease of spectral emission and metallic nature? Dr. Tutin's argument seems to suggest so, and yet his scheme does not show it (radon with twenty-two free electrons should surely be a metal). Has he not removed one difficulty only to raise another?

The "inverted" atom of Dr. Tutin is not so simple to grasp as the name suggests. It is not merely a "mirror image" of the Rutherford-Bohr one. The nucleus consists of electrons only, and their number is given by the atomic number of the element; but around the nucleus we may have isolated protons or electrons, or combinations of these in one or more of six possible groupings. (The stability of the nucleus is not discussed, but "since extranuclear electrons are repelled by the nucleus, they can only be tied to the atom by attaching themselves to groups of protons.") At the outset, therefore, the author has made *ad hoc* assumptions flexible enough one would imagine to allow him to "explain" anything. It could be justified only if it gave a neat and consistent picture of the elements of the Periodic Table. But a glance at the structures suggested reveals no such consistency. There is little resemblance between the structures of related elements, e.g., the halogens, nor even between the structures of the inert gases.

The weakest point in Dr. Tutin's essay is in his treatment of isotopes. This is all but shelved by his assumption that single protons may be used as constructional units and placed near the nucleus where they play no part in atomic union. The difference between an atom and its isotope, however, does not concern protons only, but an equivalent number of electrons. What happens to these? Dr. Tutin does not say, but in the solitary example discussed by Li^6 and Li^7, it appears that Li^7 has a free electron whilst Li^6 has not. According to his theory the former should conduct electricity, whereas the latter should not. Dr. Tutin does not make the prediction, although there are grounds for believing that it may soon be possible to test it experimentally.

The impression given by the book is that it is immature in that it deals superficially with a vast number of properties without adequate discussion of any one of them; and that the space devoted to justifying the Law of Causation would have been better used to meet the objections likely to be raised by the champions of the Rutherford-Bohr atom. It is difficult to say for whom the book was written. The general student is not competent to weigh the evidence produced; the specialist would not be satisfied with vague claims of what the theory involves, but would need a much more detailed discussion of each point raised.

JOHN A. CRANSTON.

Journal of the Institute of Metals. Volume LV (Proceedings). 304 pp. 17 plates. Edited by G. Shaw Scott, M.Sc., F.C.I.S. London: The Institute of Metals, 36 Victoria Street, Westminster, S.W.1. Price: £1.11s.6d. plus 6d. postage inland, 9d. postage overseas.

The latest volume issued by the Institute of Metals is essentially a record of the papers presented at the Manchester Autumn Meeting and of the discussions on these papers. A special contribution is the Autumn Lecture, which deals with the work of Walter Rosenhain, a distinguished past president of the Institute, who died in 1934. A complete record of his published work forms a valuable appendix to the lecture; the list covers five closely printed pages. A great part of the present volume consists of a very practical series of communications, together with a general discussion, on the improvement of white bearing metals—a subject of much interest to engineers at the present time.

Resonance Radiation and Excited Atoms. By A. C. G. MITCHELL and M. W. ZEMANSKY. 338 pp., 84 figures, and 56 tables. New York: The Macmillan Co., 1934.

The book is an exhaustive treatise on this special topic in molecular physics. In Chapter I such parts of modern spectroscopy are introduced as are needed in the further development of the subject. The sources of resonance radiation, the resonance lamps, are described and hyperfine structure of line spectra and resonance radiation are covered. Physical and chemical effects connected with resonance radiation are dealt with in Chapter II. Some of the topics included are: stepwise radiations, sensitized fluorescence, interaction of excited atoms with molecules and attendant chemical effects. The principle of microscopic reversibility or of detailed balancing or complete equilibrium is fully discussed in a most satisfactory manner. In Chapter III the authors cover the topic of absorption of light and the determination of the life time of the resonance state. Some of the sections are: the absorption coefficient of a gas, the emission and diffusion of resonance radiation, absorption within a resonance line as compared with the absorption of its edges, the magneto rotation and dispersion of the edges. Chapter IV contains an account of the collision processes involving excited atoms, the broadening of spectral lines, and the quenching of resonance radiation, while Chapter V concerns the phenomenon of polarization of this type of radiation. An appendix contains several pertinent derivations of formulas and tables of functions. Each chapter ends with a complete bibliography of the subject matter dealt with, giving in alphabetical order references to the original literature. The style is simple and the story is unfolded in a direct and forceful manner. All students of modern atomic, molecular, and chemical physics will welcome this volume, as it brings together the complete literature of an interesting and important development of modern spectroscopy.

GEORGE GLOCKLER.

The Sub-Atom. By WILLIAM M. VENABLE. 148 pp.; 11 figures. Baltimore: The Williams and Wilkins Co., 1933.

The author tries to establish a different theory of matter than is held by modern chemists and physicists. He does not like the Bohr-Rutherford model of the atom with its positive massive center and its planetary electrons. He says: "Atoms are revealed as composite bodies made up of aggregations of ions each with a positive charge $+e$, accompanied with its negative charge $-e$. These smaller ions each with its electron are designated sub-atoms." The book is the product of an active mind trying to change every concept with which it comes in contact. The alpha particle has mass 2 and not 4 and a charge $+e$ and not $2e$. The modern concept of light emis-

sion and absorption by atoms is no good. Hydrogen spectra found as impurity in spectroscopic investigation are not due to such impurity at all, but arise from the fact that hydrogen is contained in all other heavier elements as a sub-element. One wonders why the author condescends to use any current concept at all. He probably could not think of replacements or he would have done so. To anyone even only superficially acquainted with modern chemical physics, the book is very annoying. However, from another point of view, it is interesting reading. It stimulates one's interest in reviewing the arguments which have led to our modern concepts of atomic and molecular structure.

GEORGE GLOCKLER.

Theoretical Physics. Vol. II. Electromagnetism and Optics. (Maxwell-Lorentz). By W. WILSON. 315 pp.; 78 diagrams. New York: E. P. Dutton and Co., 1933.

In this second volume the author continues his treatment of theoretical physics based on notes from lectures to university students. He covers electrostatics (Chapter I), polarization in dielectric media (Chapters II and III), magnetostatics (IV), electromagnetism (V and VI), thermoelectric currents (VII), Maxwell theory (VIII), and electron theory (IX and X). The very nature of the subject demands the mathematical treatment the author accords it. In his preface he points out the special form of the electromagnetic field equations in which an unusual notation brings out a four-dimensional appearance suggestive of relativity theory. This material covers 234 pages, leaving only about 80 pages for five chapters on optics. These cover geometric optics (XI), physical optics, interference and diffraction (XII), Huygens' principle (XIII), propagation of light in crystalline media, polarized light (XIV), and general questions concerning the propagation of light (XV). Some of the chapters have a bibliography appended, where the interested reader can find the best known references concerning the material discussed. This seems particularly fortunate in the latter chapters, for the treatment there is certainly concise and not one word is wasted. This treatise on theoretical physics should appeal particularly to chemists as a reference-set where they can expect to find precise statements concerning the various topics discussed.

GEORGE GLOCKLER.

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