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Page 208. In figure 1 the vertical line through G should be extended down to meet the horizontal line joining the batteries. Another cell (total of 4 volts) should be in the grid circuit.

ON THE U-TUBE METHOD OF MEASURING ELECTROPHORESIS

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There is a general impression that electrophoretic data obtained by the U-tube method are not as reliable as those obtained from the observation of individual particles by the aid of the microscope. This impression no doubt has its origin in the fact that in the latter method due allowance is made, by means of the Smoluchowski theoretical treatment, for the influence of the electrosmotic flow of the medium upon the electrophoretic velocity of the suspended particles, whilst in the U-tube case no correction for electrosmosis is applied. Nevertheless the values obtained by the U-tube method are of the anticipated order of magnitude, although it does not appear that any measurements have been carried out hitherto to demonstrate that the electrophoretic velocity directly observed in the U-tube is identical (within the legitimate experimental error) with the velocity obtained by the microscopic cell method. In the present paper a few measurements are recorded which serve to substantiate the belief that the results obtained by the two methods are in fact in satisfactory agreement. This finding, whilst satisfactory in itself, nevertheless raises a problem which cannot at present be accounted for on theoretical grounds. Briefly the point is as follows.

As is well known, in the microscope cell arrangement, which consists essentially of a *closed* cell entirely filled with the suspension, the direction and magnitude of electrophoretic motion of any individual particle depends upon its position at the moment of observation. In general all the suspended particles are sensibly affected by the electrosmotic flow of the medium, which moves in one direction near the walls and in the reverse direction in the central region of the cell. The consequence is that the electrophoretic velocity of a suspended particle near the wall is too small or too great depending upon the sign of the electric charge on the particle, medium, and wall, respectively, whilst at the center a similar erroneous result is obtained but in the opposite sense. There is but one position within such a cell at which the observed electrophoretic velocity is effectively independent of the electrosmotic flow. Ordinarily the suspended particles have the same sign as that on the glass wall of the cell, both being opposite to that on the liquid medium. In such a case the suspended particles near the wall may actually be carried in a direction opposite to that which would be expected from the sign of their electrophoretically effective charge. All this behavior is apparently well accounted for by Smoluchowski's theoretical treatment.

In the U-tube method no attempt is made to follow the motion of an individual particle. Instead, the rate of ascent or descent of the meniscus is measured, the meniscus being the area of separation of the turbid (or colored) suspension from the transparent medium which occupies the remaining portion (usually the upper portion) of the two limbs of the U-tube. Naturally care is taken to keep the applied potential gradient constant by having the same electrical conductivity maintained throughout the tube proper.

It would be reasonable to expect that in the U-tube arrangement electrosmotic flow of the liquid medium would take place just as it does in the microscope cell. If this is so one would not expect to find, as one does in fact find, a permanent and sharp meniscus or boundary, since the existence of such a boundary implies, or seems to imply, that *all* the particles, independent of their distance from the wall of the tube, are travelling in the same direction with the *same* velocity.

This difficulty was explained, or rather explained away, by the suggestion that in a U-tube of ordinary dimensions the electrosmotic effect though present had not time to bring about any observable disturbance during the time usually taken for a set of moving boundary readings (about thirty minutes). This, however, seems to be ruled out by the observations of Gilford (2), who used a tube of ordinary dimensions and observed microscopically the movements of individual particles,—the tube being *entirely* filled with the suspension, however. The same behavior was observed as in the microscopic cell, i.e., the direction and magnitude of the velocity of individual particles was a function of their distance from the wall, this effect being naturally attributed to electrosmotic streaming of the medium, and furthermore such disturbances set in as soon as the external field was applied. Again, from an expression given by Lamb (3) it can be calculated that surface disturbances would reach the center of a tube of radius of the order 0.5 cm. in approximately six seconds. The difficulty of accounting for the existence of a sharp boundary between suspension and supernatant liquid remains.

In the ordinary U-tube arrangement the surface of liquid in each limb is free, and consequently electrosmotic movement of the medium would be expected to produce a head in one of the limbs. This effect, though not ordinarily observable, has in fact been observed by the use of a U-tube with constricted end (4). In the microscope method, as well as in Gilford's arrangement of a single vertical tube, there is no "free" surface.

The experiment has therefore been tried by the present writers in which a closed U-tube completely filled with liquid was employed. Again precisely the same result was obtained as with the ordinary open U-tube arrangement. Further, as it was just conceivable that the apparent automatic elimination of the electrosmotic flow might be connected with the fact that the suspension occupied the bent portion of the U-tube, measurements were carried out in which the suspension occupied a position in the vertical limbs with medium both above and below. Here four boundaries can be observed. Once more the same results were obtained as before.

We are not in a position to offer any explanation of the apparent elimination of the electrosmotic effect in the U-tube measurements as ordinarily carried out. Nevertheless, our measurements, which are briefly recorded in tables 1 and 2, justify us in regarding the observed velocities obtained by this method as reliable, in that they agree with the results obtained by the microscopic cell method.

ELECTROSMOSIS MEASUREMENTS

Electrosmotic velocity of water and citrate solutions against quartz and various types of glass

The apparatus was of the moving bubble type. The main electrodes, which consisted of two 3.5 N calomel electrodes, were connected by bridges (3.5 N potassium chloride in 5 per cent agar-agar gel) with the U-tube (1.5 cm. diameter) which contained the plug. On either side of the plug was a platinized platinum auxiliary electrode used to determine, and to keep constant, the P.D. across the plug. The indicator capillary connected the two limbs of the U-tube, the whole apparatus being completely filled with solution. The quartz of the plug was crushed in an iron mortar and, after obtaining particles which passed an 88-mesh sieve but were retained by a 100-mesh sieve, was thoroughly cleaned.

The mobility under unit potential gradient is given by:

$$v = \frac{V}{H} \cdot k$$

where V = volume of liquid transported in unit time, H = P.D. across plug, and k = "cell constant" of plug, i.e., the ratio of the effective length to the effective cross section.

The value of k was determined by filling the U-tube with $N/10$ potassium chloride and determining the conductivity across the plug by the bridge method. The conductivity measurements were reproducible to within 5 per cent on reforming the plug. The electrodes used in the determinations of k were the auxiliary electrodes of the electrosmosis experiments.

It will be seen that the magnitude of these mobilities is of the same order as the electrophoretic mobilities measured.

ELECTROPHORESIS MEASUREMENTS

Initial curvature of the boundary

A glass U-tube of the Burton type, having a bore of 0.6 cm., was set up and into this was introduced water, as supernatant liquid, and a 0.4 per cent tristearin emulsion. The latter was electrolyte-free in order that the electrosmotic effects should be great. The electrodes were a lead anode and a lead monoxide cathode, to prevent gas formation.

TABLE 1

Electrosmotic mobility of sodium citrate solutions against quartz

CONCENTRATION OF SODIUM CITRATE	P.D. ACROSS PLUG	CURRENT	TIME FOR BUBBLE TO TRAVERSE 14.7 CM.	MOBILITY
millimoles per liter	*volts*	*milliamperes*	*seconds*	*cm./sec./volt/cm.*
0	204	0.1	102	71.0×10^{-5}
1	142.5	1.1	232	44.4×10^{-5}
2	142.5	2.1	277	38.5×10^{-5}
4	142.5	4.5	306	35.5×10^{-5}
10	112	6.4	202*	23.7×10^{-5}

* Over a distance of 5 cm.

TABLE 2

Electrosmotic mobility of water against various types of glass

GLASS	MOBILITY
	cm./sec./volt/cm.
Soda glass	66.8×10^{-5}
Jena glass	70.0×10^{-5}
Pyrex	59.5×10^{-5}

A P.D. of 60 volts was applied, the boundaries being observed through a telescope. After two minutes, a distinct curvature of the boundaries was observable, the rising boundary becoming convex and the falling one concave. Thereafter each meniscus retained its shape. It is not improbable that this initial change in the boundary is an electrosmotic effect, especially in the light of the result obtained from Lamb's equation.

Electrophoresis of gelatin

Abramson (1) has measured, by the microscopic method, the electrophoretic mobility of silica particles covered with gelatin in acetate buffers. The following determination of the mobility, in acetate buffers, of kieselguhr particles covered by gelatin was made, using the U-tube method.

This U-tube was fitted with side-arms carrying the current-bearing electrodes. The anode was of zinc and the cathode of lead coated with lead peroxide, thus eliminating gas formation and the accompanying disturbances. Small platinum electrodes in the main U-tube were used to determine the potential gradient.

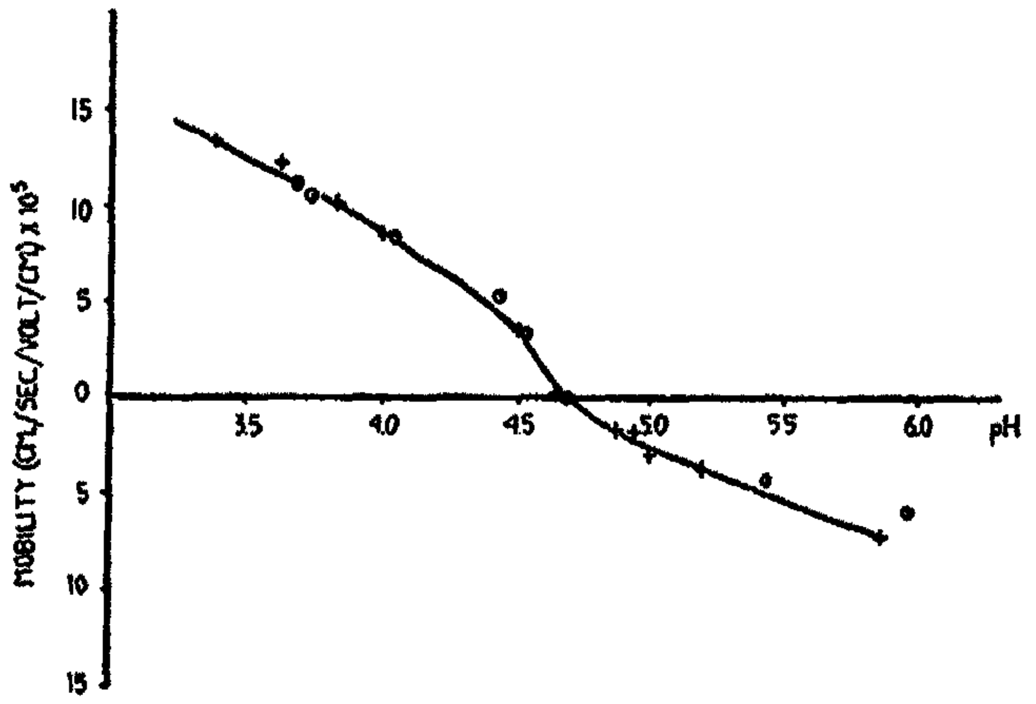

Fig. 1. Electrophoretic mobility of gelatin in $N/150$ acetate
+, Abramson; ⊙, Roberts and Carruthers

TABLE 3

Electrophoretic mobility of gelatin in N/150 sodium acetate

pH	MOBILITY
	cm./sec./volt/cm.
5.96	6.1 $\times 10^{-5}$ towards anode
5.43	4.5 $\times 10^{-5}$ towards anode
4.68	No movement
4.53	3.14 $\times 10^{-5}$ towards cathode
4.43	5.2 $\times 10^{-5}$ towards cathode
4.05	8.4 $\times 10^{-5}$ towards cathode
3.73	10.5 $\times 10^{-5}$ towards cathode
3.68	11.1 $\times 10^{-5}$ towards cathode

The gelatin used was Digestive Ferments Co.'s "Bacto-Gelatin." The concentration of the sol was similar to that used by Abramson (0.4 per cent). To this sol was added 4 g. of finely divided, purified kieselguhr, and the whole well stirred and allowed to stand overnight.

In the preliminary work an attempt was made to use, as supernatant liquid, a buffer of the same ionic concentration as the buffered suspension, but containing no gelatin. However, the buffering properties of the gelatin were sufficiently great to alter the pH appreciably, and to avoid any error due to this or to the fact that the rising boundary would be moving in a medium of different viscosity to that of the falling boundary, it was found convenient to employ as supernatant liquid a gelatin sol, identical in concentration and buffered in the same manner as the kieselguhr suspension.

The buffer employed was *N*/150 sodium acetate. Over the pH range examined the ionic strength of the sol was maintained constant. This was effected by making the sol *N*/150 with respect to sodium acetate and adding increasing amounts of acetic acid. To each 100 cc. of dispersion 2 g. of sucrose was added to increase the specific gravity. It was observed that after adding the electrolyte to the dispersion there was a noticeable rate of settling in the U-tube. As the mean of an upward and a downward movement was taken in each case, the error due to this must be very small.

pH determinations were carried out in every case by means of the hydrogen electrode.

The results obtained are given in table 3 and plotted with those of Abramson in figure 1.

It must be concluded from the very fair agreement obtained, that in the U-tube apparatus corrections for electrosmosis are unnecessary and that the values of the mobilities obtained by this method are very close to the absolute values.

SUMMARY

It is shown that measurements carried out by the U-tube method, without any correction for the electrosmotic flow of the medium, agree satisfactorily with those obtained by the microscopic cell method where such correction is necessarily introduced.

No attempt is made at present, however, to solve the theoretical difficulty inherent in this finding.

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THE VISCOSITY OF SODIUM AMALGAMS

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Paranjpe and Joshi have suggested that the properties of liquid sodium amalgams may be most readily accounted for by assuming that the solution is colloidal. They (8) enumerate a large number of phenomena which may be easily explained on the colloidal hypothesis. The case for the idea that dilute amalgams are true solutions has been stated by one of us (1) and further comments in favor of the colloidal point of view presented by Joshi (3).

Two questions arise from this discussion which can be treated to some extent independently. The first is the question of the number of variables required to define a sodium amalgam. If Paranjpe and Joshi are correct in their assumption that temperature, pressure, and concentration are not sufficient to define completely the properties of an amalgam but that the method of preparation and the previous history are also important, then practically all physical measurements on sodium amalgams are of little value, as attention has usually not been directed to these last conditions. In order to evaluate the enormous amount of data on sodium amalgams this question must be answered, and it is a question which can be answered by relatively simple experiments.

The second question has to do with the structure of a liquid sodium amalgam. If the answer to the first question should turn out to be that properties depend not only on temperature, pressure, and composition but also on the physical history of the amalgam, then the presumption would be that the structure is colloidal. If, on the other hand, the answer should turn out to be that the properties of amalgams are completely determined by the temperature, pressure, and composition, then the strongest evidence for the colloidal point of view will have been removed.

Paranjpe and Joshi report results of two types of experiments which indicate that the properties of amalgams change with time. They describe briefly the results of Barave on the change of viscosity with time. This work was later reported in a note (7). Barave finds that the viscosity decreases from 10 to 20 per cent if amalgams are kept for two or three days without agitation. It is also reported that a scum or "cream" forms on the amalgam which disappears on shaking, only to re-form on standing.

The viscosity is restored to its original high value by shaking. These results are sufficiently striking to warrant serious consideration of the colloidal hypothesis. Since previous workers in this field have reported no scum formation when the apparatus was free from oxygen and water (1, 5, 6), it seemed worth while to attempt to repeat the experiments of Barave under a variety of conditions in order to determine whether or not the change in viscosity with time and the formation of a scum is a general property of sodium amalgams.

EXPERIMENTAL

In order to avoid contamination of the amalgam all experiments were carried out in glass apparatus free from stopcocks or rubber connections. The glass was heated and evacuated with a mercury diffusion pump at the beginning of each experiment, until the pressure was about 10^{-6} mm. as measured by a McLeod gauge. Amalgams were prepared by the method used by Paranjpe and Joshi, namely, the electrolytic procedure described by Richards (9) and by the distillation method of Lewis and Kraus (6). The mercury was purified by repeated washing with nitric acid in an apparatus of the type described by Hildebrand (2), and the sodium carbonate used in the electrolysis was recrystallized. The amalgam prepared by electrolysis was introduced directly into the viscometer and the latter then sealed off, eliminating stopcocks.

The data reported by Paranjpe and Joshi give no idea of the dimensions of the capillary or the time of flow. We, therefore, constructed a number of viscometers of such dimensions as to have always a velocity of flow well below that which would give turbulence. Since Barave's experiments indicate that the viscosity is restored to its original value by shaking, it seemed possible that flow through the capillary would have the same effect to some extent and therefore that a small head of amalgam would be desirable if one were to repeat his experiments. Several viscometers were, therefore, constructed with the two bulbs of the viscometer as close together as possible while still having one bulb directly over the other. A capillary 12–19 cm. long with a bore ranging from 0.03–0.05 mm. extended well below the lower bulb and was connected to it by a vertical tube of 6-mm. diameter. This type of viscometer, however, was not free from an objection. At the end of a determination the apparatus was inverted and the amalgam allowed to flow back into the original bulb where it remained without agitation until the beginning of another run. At the beginning of a run the instrument had to be turned into a vertical position. This agitation might be equivalent to the vigorous shaking after which Barave found the viscosity returned to the high value. We therefore constructed the apparatus shown in figure 1 which permitted the amalgam to be held for any desired length of time in the upper bulb and then, without agitation of the amalgam which was to flow through the capillary, the viscometer could be started by simply raising the glass plunger from the lower part of the viscometer. This avoided any possible objection on the ground that the amalgam was unnecessarily agitated before beginning a determination. The plunger was raised by means of a glass float in the

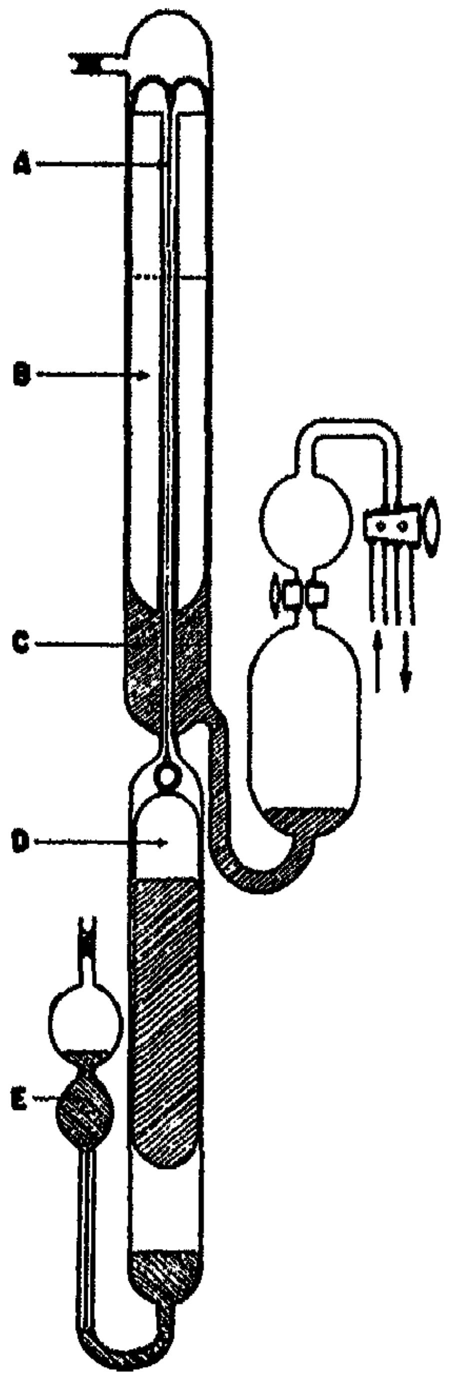

Fig. 1. Vacuum viscometer. A, nickel wire; B, float; C, mercury; D, plunger; E, amalgam, 10 cc. Vertical dimensions have been multiplied by 1/8 and horizontal dimensions by 1/4.

upper part of the apparatus, which was in turn raised by admitting mercury to the upper chamber, a nickel wire connecting this float with the glass plunger. At the conclusion of a run the mercury was removed from the upper chamber by evacuation of the bulb and the amalgam returned to the upper bulb of the viscometer. All measurements were carried out in a glass thermostat at 25 ±0.01°C.

EXPERIMENTAL RESULTS

Our results may be summarized very briefly. We have found no indication of any variation of the viscosity of sodium amalgams with time, and not the slightest trace of scum formation on standing. When working with the most concentrated amalgams we did observe large crystals floating on the surface of the amalgam, but these had no effect on the viscosity unless small crystals were present in such large amounts as clearly to plug the capillary. The amalgam would then drain away from them and leave a mass of crystals in the capillary. We expected to find the best evidence of a change in viscosity with time when the amalgams were nearly saturated, but the data recorded in table 1 give no evidence of such an effect.

TABLE 1

Viscosities of dilute sodium amalgams

METHOD OF PREPARATION	MOLE FRACTION OF SODIUM	TIME SINCE PREPARATION	TIME AT REST BETWEEN RUNS	TIME OF FLOW	VISCOSITY RELATIVE TO MERCURY
		hours	*hours*	*seconds*	
Electrolytic	0.0289	2.5	1.25	254	1.134
		3	<0.2	253	
		12.5	9.5	254	
		12.75	<0.1	254	
		37	23.5	254	
		37.25	<0.2	253.5	
Distillation	0.0513	1.5	1	296	1.439
		2	<0.2	294.5	
		97.5	95.5	295.5	
		169.5	72	295.5	
		171	<0.2	295	
Mercury added to the above amalgam, shaken and stirred		173.5	1	296.5	
		176.5	3	296.2	
		294	117	296.5	
Same amalgam, shaken and stirred		294.5	<0.1	296.2	
		390	95.5	296.5	
		1449	1059	300	(See text)

In addition to the data reported in table 1, similar results were obtained on seven amalgams using the simple type of apparatus first described above. The time between runs varied from twenty minutes to sixty-five days.

The last datum recorded in table 1 was obtained by adjusting the amalgam level so that the upper surface was at the point in the capillary at which the initial time was usually taken. The plunger was then raised as rapidly as possible and the time determined as usual. Obviously a little time was lost in raising the plunger and in establishing a constant rate of flow of the amalgam. The purpose of this experiment was to reduce all stirring to an absolute minimum before starting a measurement. As will be observed, there is no indication of a decrease in viscosity.

We have observed some of these viscometers for more than two years and can report that the surface is as clear and clean to-day as the day they were prepared and as clean as any surface of pure mercury as far as one can detect by observation.

DISCUSSION OF RESULTS

Our experimental results are in complete disagreement with those reported by Paranjpe and Joshi. From our experiments one would conclude that the properties of sodium amalgam are uniquely determined by the temperature, pressure, and concentration. In favor of Barave's experiments, however, it must be pointed out that he observed certain reproducible phenomena which we have not found, and hence our results may be disposed of by saying that negative results do not disprove one good set of positive experiments. It must be emphasized, however, that the variation in viscosity observed by Barave was very large, and that with many kinds of apparatus and different methods of preparing amalgams we were unable to find this effect. Our results indicate that it would not be profitable for us to search further to reproduce the results of Barave. It is to be hoped that the experiments of Barave will be repeated and, if his results be confirmed, that sufficiently explicit directions be given to permit repetition of the experiments in other laboratories.

With regard to the question of whether sodium amalgam is colloidal or not, it would seem rather unprofitable to consider this question further until the experimental facts are clearly established. We have corresponded with Joshi regarding this problem, and I think we agreed that the viscosity behavior and scum formation were among the strongest arguments in favor of the colloid hypothesis.

It has been reported by Köhler (4) that silver and copper amalgams form amalgams which change in viscosity with the time. These experiments, however, have no bearing on the properties of liquid amalgams, as the amalgams used by Köhler contained much more than enough copper or silver to produce a saturated amalgam. The solubility of copper is given by Richards (10) as 0.0024 per cent at 15°C. and the solubility of silver is given by Tamman and Stassfurth (11) as 0.08 per cent at 20°C. The amalgams investigated by Köhler ranged in concentration from 0.3 to 1.0 per cent and therefore must have contained a great deal of the solid phase.

In order to find if possible a variation in the viscosity of liquid silver amalgams with time we prepared four amalgams by a variety of methods.

In no case did we obtain a variation on standing of as much as 0.25 per cent, which was our experimental accuracy in measuring the time. Only when the amalgams had not been carefully filtered did we observe a decrease of the viscosity with time.

CONCLUSIONS

1. The viscosity of liquid sodium and silver amalgams is found to be independent of time.
2. No scum forms on sodium amalgams when kept in glass containers which have been properly baked and evacuated.
3. These experiments lessen the probability that sodium amalgams are colloidal.

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THE DETERMINATION OF SURFACE CONDUCTANCE FROM MEASUREMENTS ON SUSPENSIONS OF SPHERICAL PARTICLES

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As the particle size of a suspension of an insulating material is decreased, the surface conductance at the particle–water interphases plays an increasingly important rôle in determining the electric conductance of the suspension, and with particles a fraction of a micron in diameter, suspensions can readily be prepared in which the suspended particles add more to the conductance than the same volume of the suspending fluid. We have, for example, prepared suspensions of kaolin with a particle size of about 0.25 micron in diameter, whose conductance was more than twice that of the fluid obtained after removal of the suspended material by centrifugation.

The use of suspensions presents many advantages in the measurement of surface conductance. It is important for the theoretical discussion that we can determine the electrokinetic potential at the interphase directly on the suspension used for the conductance measurements by a determination of the cataphoretic velocity of the suspended particles. So far, suspensions of particles down to 0.25 micron in diameter have been studied. Measurements on still finer suspensions would be interesting, since here the thickness of the diffuse double layer should become apparent in the results. We need, however, a more powerful centrifuge to be able to separate these particles from the suspending fluid. In the following, a preliminary study of the method is presented.

Largely because the subject of surface conductance had its origin in Smoluchowski's (9) theoretical treatment of the diffuse double layer, it has been tacitly assumed in experimental studies of the subject that the aqueous interphase can with sufficient accuracy be represented as a pure conductance. Actually, this is not always the case. Each element of interphase is also the seat of a reactance (4), so the interphase should be represented by a complex admittance[1] which, per square centimeter of interphase, may be expressed as $\sigma_s + jC_s\omega$, where σ_s may be termed the

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[1] The admittance is the reciprocal of the impedance.

surface conductivity and C_s the surface capacity. $\omega = 2\pi n$, where n is the frequency. Since $C_s\omega$ is not necessarily negligible compared to σ_s an error may be introduced by deriving σ_s from pure conductance measurements, but these should be replaced by measurements of complex admittance; that is, both the conductance and the dielectric constant of the systems under investigation should be determined. This has been the method used, although since the influence of C_s has been negligible in our measurements only the conductances need be considered. A general study of complex surface admittance will be presented elsewhere. The remark may be added that since C_s varies with the frequency, σ_s will contain (3) a term dependent upon the same mechanism which produces C_s, and therefore in such cases where the influence of C_s is appreciable not only is it impossible to measure σ_s without considering C_s, but also the theoretical discussion of the former must involve the latter.

Most of the present measurements were made on suspensions of glass spherules prepared from powdered Pyrex glass which was blown through a blow torch (2). The material was obtained through the courtesy of Dr. L. D. Bishop of the Bureau of Standards. The glass was washed, over an extended period, in distilled water and thereafter equilibrated with the solutions to be used. Two series of experiments have been made, one with solutions of potassium chloride of strength varying from 0.0001 to 0.01 mole per 1000 cc., another less complete with solutions of hydrochloric acid.

The conductance and dielectric constant were measured at frequencies between 1/2 and 100 K.C. with a bridge, using a substitution method. The electrolytic cell containing the suspension is compared with a cell filled with a solution of potassium chloride, the difference in dielectric constant being compensated for by a parallel condenser, while equality of resistance can be obtained by varying the distance between the electrodes in the comparison cell. The resistance of the potassium chloride is measured by comparison with a low inductance resistance box, this measurement being made at low frequency. The influence of electrode polarization, though negligible in the present measurements, could be eliminated by measuring at different electrode distances.

The electrolytic cell containing the suspension has the form of a test tube, with the electrodes sealed into its upper portion. After the measurement on the suspension has been made, the cell is placed in the centrifuge and the suspended matter separated. The liquid between the electrodes now is the suspending fluid, and thus without removing the suspension from the conductivity cell the conductance of the suspending fluid can be measured. This procedure is convenient when working with dilute solutions for which contact with the carbon dioxide of the air must be prevented. The measurements were made at a temperature of 21.4°C.

The value of the surface conductance is calculated by making use of a formula derived by Maxwell (6). This formula gives the conductance (K) of a suspension of spherical particles each of which is composed of a sphere (radius a and specific conductance K_2) surrounded by a concentric spherical shell (thickness t and specific conductance K_3). The formula reads:

$$\frac{\dfrac{K}{K_1} - 1}{\dfrac{K}{K_1} + 2} = \rho \frac{\dfrac{\bar{K}_2}{K_1} - 1}{\dfrac{\bar{K}_2}{K_1} + 2} \tag{1}$$

with

$$\bar{K}_2 = K_3 \frac{(2K_3 + K_2)(a + t)^3 - 2(K_3 - K_2)a^3}{(2K_3 + K_2)(a + t)^3 + (K_3 - K_2)a^3} \tag{2}$$

and where K_1 is the specific conductance of the suspending fluid and ρ is the volume concentration of the suspension.[2] For the present case, we use $K_2 = 0$ and, assuming the thickness t of the region from which the surface conductance is derived as small compared to the diameter of the suspended particles, we can take

$$(a + t)^3 = a^3 + 3ta^2$$

and consequently

$$\bar{K}_2 = \frac{2tK_3}{a} \tag{3}$$

Defining the surface conductivity σ_s by $\sigma_s = tK_3$ we obtain from equations 1 and 3

$$\sigma_s = \frac{\left(\dfrac{K}{K_1} - 1\right) + \dfrac{\rho}{2}\left(\dfrac{K}{K_1} + 2\right)}{\rho\left(\dfrac{K}{K_1} + 2\right) - \left(\dfrac{K}{K_1} - 1\right)} K_1 \cdot a \tag{4}$$

For the determination of the volume concentration ρ, two methods have been used. One depends on measurements of the specific density of the suspension (δ) and of the suspending fluid (δ_0), the value of the volume concentration being calculated from

$$\rho\delta_1 + (1 - \rho)\delta_0 = \delta$$

where δ_1 is the specific density of the glass spherules, measured with a pycnometer.

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[2] The same formula is used for calculating the complex surface admittance, replacing conductances in the formula by the corresponding complex admittances.

The second method for determining ρ is indirect but more convenient. It consists in adding solid potassium chloride to the suspension, enough so that the influence of the surface conductance on the conductance of the suspension is inappreciable, and thereafter the conductances of the suspension (K) and suspending fluid (K_1) are measured and the volume concentration ρ_1 of this suspension calculated by Maxwell's formula (equation 1 with $\bar{K}_2 = 0$):

$$\frac{1 - \dfrac{K}{K_1}}{\dfrac{K}{K_1} + 2} = \frac{\rho_1}{2}$$

The volume concentration ρ of the original suspension is thereafter obtained by introducing a slight correction for the volume change due to the addition of the salt.

In table 1 is shown a comparison of the two methods.

The diameter of the spherules was determined by counting the number of spherules present in a known volume of a suspension of known volume concentration. The counting was carried out with a ruled chamber such as is used for counting blood cells or bacteria. The value obtained for the diameter was $2a = 1.7\mu$.

The results are given in table 2. The surface conductances are practically independent of the frequency between 1/2 and 100 K.C.,[3] showing, however, a slight decrease as the frequency is decreased (4). In the case of the dilute solutions, when the suspended glass is added to the solution of the electrolyte with which it is being equilibrated, one observes a rise in conductance, rapid at first and gradually slowing down. This happens even after prolonged washing of the glass with the electrolyte and is probably due to the solution of the glass. For this reason, when the measurements were made there was an appreciable quantity of foreign electrolytes (besides the hydrogen and hydroxide ions) present, amounting in the most dilute solutions to about 10 per cent in equivalent conductance. The concentrations of potassium chloride and hydrochloric acid given in the second column of table 2 are those required to account for the actually observed conductances of the suspending fluid.

The following measurements were made to determine whether the values obtained for the surface conductance show any dependence on the size of the suspended particles. These measurements were made on kaolin spherules, obtained through the courtesy of Dr. F. S. Brackett of Research Associates Incorporated. Two different particle sizes were used, with diameters of $2a = 0.6\mu$ and $2a = 3.4\mu$, respectively, and the suspen-

[3] At higher frequencies σ_s shows a marked increase (5).

sions were made up in a solution of sodium carbonate. The results are shown in table 3. A somewhat smaller value for σ_s is obtained for the

TABLE 1

Comparison of percentage volume concentrations, determined by (1) specific density and (2) electrical conductance

SUSPENDED MATERIAL	VOLUME CONCENTRATION IN PER CENT FROM	
	Specific density	Conductivity
Pyrex spheres	34.2	34.2
Pyrex spheres	28.4	28.7 28.0
Kaolin spheres	10.2 9.9	10.2 10.2

TABLE 2

Measurements on suspensions of glass spherules (diameter 2a = 1.7μ) in solutions of potassium chloride and hydrochloric acid

SUSPENDING FLUID	CONCENTRATION IN MICROMOLES PER 1000 CC.	VOLUME CONCENTRATION PER CENT p	CONDUCTIVITY (OHMS^{-1} CM.$^{-1}$)		ELECTROPHORETIC POTENTIAL (IN MV.) ζ	SURFACE CONDUCTIVITY (OHMS^{-1})	
			Suspension K	Suspending fluid K_1		Observed	Calculated
KCl	169	33.0	18.42×10^{-6}	23.14×10^{-6}	−74	0.45×10^{-9}	0.21×10^{-9}
KCl	470	21.9	50.35×10^{-6}	64.10×10^{-6}	−74	0.58×10^{-9}	0.35×10^{-9}
KCl	930	27.7	86.7×10^{-6}	126.8×10^{-6}	−78	0.58×10^{-9}	0.54×10^{-9}
KCl	1900	26.5	172.2×10^{-6}	251.6×10^{-6}	−73	0.86×10^{-9}	0.68×10^{-9}
KCl	7900	28.4	$675. \times 10^{-6}$	1042×10^{-6}	−70	1.8×10^{-9}	1.25×10^{-9}
HCl	90	25.8	27.80×10^{-6}	35.95×10^{-6}	−42	0.42×10^{-9}	0.21×10^{-9}

TABLE 3

Measurements on suspensions of kaolin spherules in sodium carbonate

DIAMETER OF SPHERULE (10^{-4} CM.)	VOLUME CONCENTRATION PER CENT p	CONDUCTIVITY (OHMS^{-1} CM.$^{-1}$)		SURFACE CONDUCTIVITY (OHMS^{-1}) σ_s (obsd.)
		Suspension K	Suspending fluid K_1	
0.6	12.65	46.3×10^{-6}	51.0×10^{-6}	0.30×10^{-9}
3.4	37.0	29.7×10^{-6}	51.0×10^{-6}	0.40×10^{-9}

smaller sized spherules, but the difference is not outside the present limit of experimental error.

For the experiments with glass spherules, the measured surface conductances were compared with the theoretical values derived on the assumption that the surface conductance represents the conductance of the ions of the diffuse double layer. Including the electrosmotic term, the surface conductance for an electrolyte completely dissociated into two monovalent ions, is given (1, 8) by:

$$\sigma_s = \frac{D^{3/2}(KT)^{3/2}\sqrt{n}}{2\sqrt{2}\,\pi^{3/2}\eta\epsilon}\left[e^{-\frac{\epsilon\zeta}{2KT}} + e^{\frac{\epsilon\zeta}{2KT}} - 2\right] + \sqrt{\frac{DKTn}{2\pi}}\left[u_1e^{-\frac{\epsilon\zeta}{2KT}} + u_2e^{\frac{\epsilon\zeta}{2KT}} - (u_1 + u_2)\right]$$

where K is Boltzmann's constant, T the absolute temperature, ϵ the electronic charge, ζ the electrokinetic potential, and n the number of cations or anions per cubic centimeter. For D, the dielectric constant, and for η, the coefficient of viscosity, of the diffuse double layer, we have used the values for water ($D = 79.9$; $\eta = 0.0098$). The quantities u_1 and u_2 are the ionic mobilities of the cations and anions respectively. For these values we have used those obtained at infinite dilution.

The electrokinetic potential, ζ, has been determined by measuring the electrophoretic velocity of the suspended particles by the moving boundary method. In carrying out this determination the suspension used for the conductance measurement was diluted with the suspending fluid, a suspension of about 1 per cent volume concentration being most suitable. The dilution did not appear to change the electrophoretic velocity, as far as could be learned by changing the degree of dilution from several per cent to a fraction of 1 per cent. The suspending fluid also formed the electrical connection between the suspension and the electrodes of the cataphoresis cell. The gravimetric movement of the boundary amounted to from 5 to 10 per cent of the electrophoretic velocities and was compensated for by taking readings with the boundary moving in both directions and averaging. Since the conductance of the suspension and suspending fluid differ by only 1 or 2 per cent, the electric field can be taken as uniform between the electrodes. The value of ζ is calculated from

$$v = \frac{\zeta D}{4\pi\eta}$$

where v is the electrophoretic velocity per unit field strength.

The theoretical values of σ_s given in table 2 are calculated on the basis of the concentrations of electrolytes given in the first and second columns. As remarked above, for the dilute solutions, these concentrations represent only approximately the composition of the suspending fluid, being actually the equivalent values derived from the observed conductances. For the present, however, this method of calculation is of sufficient accuracy. It should be pointed out that in the case of the potassium chloride solutions the influence of the hydrogen ion is negligible, since these solutions are slightly alkaline. The observed values of σ_s are of the order of 50 per cent higher than the theoretical ones, a deviation in the same direction, although smaller, as found in other recent experimental studies of this subject (7, 10).

The present measurements should be considered as preliminary, and there will be some question as to how great the errors are until a more complete study has been made. It should also be recognized that the present theory for the conductance of the diffuse double layer contains a certain amount of simplification and approximation. This leaves considerable uncertainty as to the exact extent to which the observed surface conductance exceeds that contributed by the diffuse double layer, although the reality of an excess must be allowed. As has already been noted, there is a slight decrease of the surface conductance with decreasing frequency and the excess conductance would therefore be smaller (and might disappear) at zero frequency. The most likely explanation of an excess conductance would be that it is due to the participation of the solid surface in the transport of the current. The presence of the surface capacity (4) itself shows that there is a transport of current at the interphase besides that considered in the present theory of the diffuse double layer. The fact that the surface capacity varies with the frequency requires this surface capacity to be associated with a conductance, the value of which can in certain cases be calculated theoretically when the surface capacity is known as a function of the frequency (3). We find that the observed change of the surface conductance with frequency can be completely accounted for in this way, while it still remains to be seen if all the excess conductance can be thus explained. The detailed discussion of this problem will be dealt with elsewhere in a general study of surface admittance.

SUMMARY

A method is described for determining surface conductance from observations on suspensions of spherical particles. Suspensions of glass and kaolin of diameters from 0.6 to 3.4μ in solutions of potassium chloride, hydrochloric acid and sodium carbonate have been studied at frequencies from 1/2 to 100 K.C. and the experimental surface conductances compared with the values calculated from a consideration of the diffuse double layer. The observed surface conductance can be accounted for on this basis only in part, the difference increasing as the frequency is increased (4). The existence of an additional type of current transport besides that offered by the diffuse double layer is also shown by the presence of surface capacitance (4), indicating a current transport (probably at the solid surface)

which is associated with polarization. There is a theoretical connection between the surface conductance and the surface capacitance (3) by which one can account for the frequency variation of the surface conductance.

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HYDROGEN BRIDGES IN ICE AND LIQUID WATER

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It was shown by W. H. Bragg (3) in 1922 that the x-ray diffraction data obtained from ice by Dennison (4) were in agreement with a structure in which each oxygen is equidistant from four others tetrahedrally arranged around it.[1] This distribution of oxygens has since been verified by further work (1). Bragg proposed that, in agreement with the theory of "hydrogen bridges" (or "hydrogen bonds") proposed independently by the writer (5) and by Latimer and Rodebush (9), there is a hydrogen midway between each pair of adjacent oxygen atoms. Although the hydrogens do not contribute appreciably to the x-ray scattering, this seemed to be the most reasonable distribution, considering the symmetry of the arrangement of oxygens and the probable forces between the atoms.

That neighboring atoms in liquid water must be held together in very nearly the same way as in ice is indicated by the slight change of density, dielectric constant (2, 11), and various other properties on melting, by the low heat of fusion compared with the heat of vaporization, and by x-ray data obtained in this laboratory (8) and elsewhere (2) showing that on the average each oxygen in liquid water has about four neighboring oxygens at a distance only slightly greater than the O–O distance in the solid.

One is thus led to postulate hydrogen bridges throughout the liquid; many of these, however, being bent or stretched and some broken, at any instant, as a result of the heat motions. The bending of many of these bridges when ice melts permits a slightly closer packing, hence a greater density. As the temperature rises, more and more of the bridges are broken and stretched, the average interoxygen distance becomes larger, and the density decreases.

In several respects this picture has not been entirely satisfactory. The low conductivity of pure water compared with water containing hydrogen ions (and also negative ions, of course) seems quite inexplicable. Moreover the high dielectric constant in both the liquid and solid, down to temperatures considerably below zero (for low frequencies), seemed to be evidence for the existence of molecular units, some of which are quite free to orient themselves in an electrostatic field.

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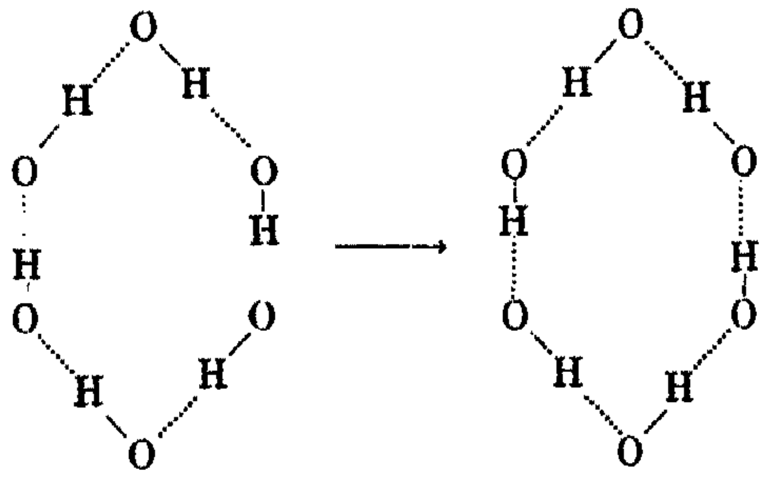
[1] A tetrahedral arrangement of four oxygens around each oxygen was predicted by the writer on the basis of the theory of hydrogen bridges.

Largely because of these two arguments the writer[3] suggested that the hydrogen of each hydrogen bridge in solid and liquid H_2O may be closer to one oxygen neighbor than to the other, in such a way that each oxygen keeps but two close hydrogen neighbors, all oxygens in ice and most of them in water also having two other hydrogen neighbors at a somewhat greater distance. As Pauling (10) has recently shown, this picture makes possible a calculation of the entropy of ice more nearly in agreement with experiment than that calculated on the assumption of rotating molecules. The additional assumption that the potential energy hump in the center of each hydrogen bridge in the structure is small is sufficient to account for both the conductivity and dielectric constant behavior, as will now be shown.

Although the shifting of a single hydrogen in a hydrogen bridge in ice or water from the vicinity of one oxygen to the vicinity of the other might be quite difficult, owing to the size of the energy hump, such a shift is much facilitated if at the same time another hydrogen nucleus approaches the first oxygen (thereby making its effective charge less negative) and a hydrogen previously close to the second oxygen moves away from it (making its effective charge more negative). Jumps in unison of all of the hydrogens in a ring, in such a way that after the jumps, as before, each oxygen has but two close hydrogen neighbors, may therefore occur quite frequently, just as a result of the ordinary heat energy.



The presence of an external electrostatic field favors such jumping in all cases in which the resultant electric moment in the direction of the field is increased, hindering those jumps decreasing the electric moment in that direction. (For a 6-bridge ring the resultant moment change is

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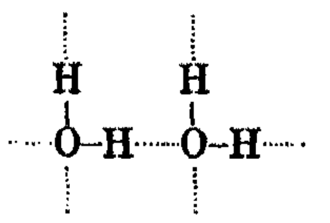
[3] In a preliminary edition of his book on "Chemistry, the Science of Atoms and their Interactions," in 1933. Essentially the same picture, as regards each atom's immediate neighbors, has been proposed by Bernal and Fowler (2).

slight; this is not so, however, for many larger, less symmetrical rings.) Qualitatively the effect is much the same as if the substance contained a small percentage of rotatable molecular dipoles, and the large dielectric constant in both solid and liquid is accounted for (cf. reference 2).

At temperatures which are too low, the temperature energy is insufficient to make even these synchronized shifts possible, and the dielectric constant decreases to a very small value. The shifts in a ring do not occur instantaneously as soon as the field is applied, as the vibrations of the atoms must be suitably timed and must have sufficient energy. Because of this time lag the dielectric constant values are less for high frequencies than for low frequencies, at any given temperature. When the temperature energy available is sufficiently large, the synchronized jumps of the hydrogens in a ring become synchronized oscillations about their mean positions. The effect of the field on this portion of the structure then becomes practically negligible. This accounts for the diminution of dielectric constant as the temperature rises, at temperatures slightly below zero, for low frequencies.

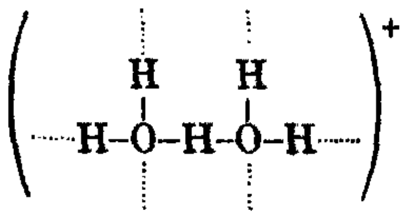
Each hydrogen nucleus in pure water may be considered, roughly, as bridging between an OH^- ion and an H_2O molecule. The bridge is obviously unsymmetrical, the hydrogen in question being held close to the OH^- (so producing an H_2O molecule):



$$\cdots\overset{\text{H}}{\text{O}}{-}\text{H}\cdots\overset{\text{H}}{\text{O}}{-}\text{H}\cdots$$

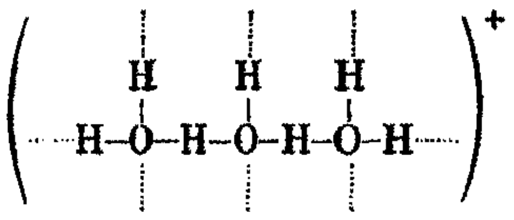
A jump of this hydrogen nucleus to the other end of the bridge, giving OH^- and H_3O^+, practically never takes place (cf. figure 2); hence the extremely low conductivity of pure water.

If an acid is dissolved in water the hydrogen nuclei produced by dissociation undoubtedly also serve to bridge between oxygens, each such nucleus connecting two H_2O molecules. With less repulsion between the oxygens one would expect a shorter O–O distance than in the case just considered. The hydrogen would be expected to oscillate symmetrically about the midpoint. We may represent this situation thus:



$$\left(\cdots\text{H}{-}\overset{\text{H}}{\text{O}}{-}\text{H}{-}\overset{\text{H}}{\text{O}}{-}\text{H}\cdots\right)^+$$

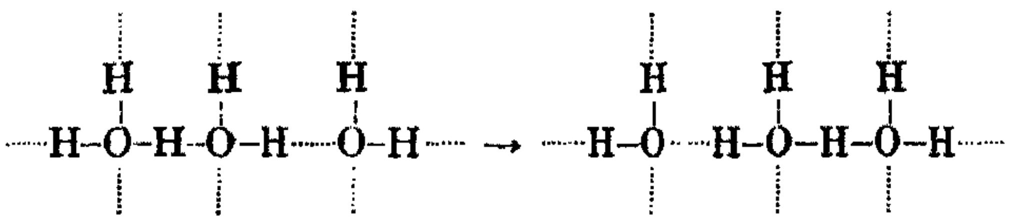
There is no *a priori* reason for eliminating the possibility of $H_7O_3^+$ and larger ions, containing two or more practically symmetrical bridges:



$$\left(\cdots H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H\cdots\right)^+$$

The larger such ions however, the less the stability of the symmetrical bridges; it seems likely that $H_5O_2^+$ is the usual limit.

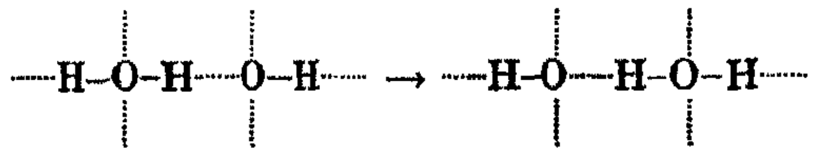
The effective charge on each of the $H_5O_2^+$ oxygens is less negative than that on an H_2O oxygen. In view of this fact, we should expect such shifts as the following to occur readily:



$$\cdots H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H\cdots\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H\cdots \rightarrow \cdots H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}\cdots H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H-\overset{\overset{\vdots}{H}}{\underset{\vdots}{O}}-H\cdots \qquad (1)$$

In this process the charge shifts with but little actual motion of the atoms. In a potential gradient between two electrodes, shifts of this sort which move the positive charge toward the negative electrode are favored in preference to shifts in the opposite direction. As these shifts would be very rapid this theory accounts for the high mobility of hydrogen ion in water. (The chain mechanism postulated here differs but little from that proposed by the writer (6) in 1931. With the symmetrical bridges assumed at that time however, there was no obvious reason for the low conductivity of pure water, as noted above.)

In an OH^- ion the effective charge on the oxygen atom is more negative than on the oxygen atom in a water molecule, hence the O–H distance in this ion is less than in water. In water solution such an ion, unlike H^+, would probably not form aggregates such as $(H—O—H—O—H)^-$ because the larger Coulomb repulsion between the oxygens and larger Coulomb attraction between the central hydrogen and each oxygen would tend to make the central hydrogen bridge an unsymmetrical one. The oxygen atom in an OH^- ion would be expected to tend to surround itself with four unsymmetrical hydrogen bridges, like that in a water molecule or $H_5O_2^+$ ion. Shifts such as



$$—H-\overset{\vdots}{\underset{\vdots}{O}}-H\cdots\overset{\vdots}{\underset{\vdots}{O}}-H\cdots \rightarrow \cdots H-\overset{\vdots}{\underset{\vdots}{O}}—H-\overset{\vdots}{\underset{\vdots}{O}}-H\cdots \qquad (2)$$

would be expected to occur, although not so readily, on account of the greater O–O repulsion, as shifts of the type of equation 1. It is thus reasonable that the mobility of the hydroxide ion is greater than that of other ions which cannot exchange atoms with the solvent in this way, and still is less than that of hydrogen ion.

In attempting to make the treatment of hydrogen bridges in ice and water more quantitative, we shall first consider a hypothetical bridge in which the energy of interaction between neighboring hydrogen and oxygen atoms is the same as in the OH molecule in its normal state. (Many of the calculations have also been carried out using the constants for a higher energy state, with results only slightly different from those to be described.) For this interaction we assume a modified Morse function, of the type recently applied successfully by the writer (7) to the calculation of molecular constants for diatomic molecules. This is of the form

$$U\,(\text{in } 10^{-12}\text{ ergs}) = e^{-a(r-r_{12})} - C'e^{-a'(r-r_e)} \tag{3}$$

in which a, a', r_{12} and C' are constants determined from band spectrum data. In this case $a = 6.0$, $a' = 1.29$, $r_{12} = 1.125$ (assumed to be the same as calculated for the $^2\Sigma^+$ state) and $C' = 11.83$. The equilibrium distance r_e is 0.969. For the method of calculating the other constants from a, r_{12}, r_e and the vibration frequency ω_e, the writer's first paper (7) on diatomic molecules may be consulted.

Taking the oxygen to oxygen distance as 2.75 A.U. (its value in ice), the potential energy, for a hydrogen moving along the O–O centerline, changes as shown in the top curve of figure 1. It is seen that there are two minima, about 1.10 A.U. from the oxygens, with an energy hump between them of about 0.15×10^{-12} erg. It may be noted that $\frac{1}{2}\,kT$, the average molecular energy per degree of freedom, is only about 0.02×10^{-12} erg at room temperature. If the O–O distance is taken as 2.70 A.U., the experimental value for hydrogen bridges in H_3BO_3, $AlHO_2$ and some other compounds, the size of the central hump is very much diminished and the shorter O–H distance is increased to 1.13 A.U. For a distance between oxygens of 2.55 A.U., such as observed in $NaHCO_3$ and KH_2PO_4, there is but one minimum, at the center.

From these results one must conclude that, if our assumption regarding the variation of the O–H interaction energy with distance is even approximately correct, the hydrogen bridges in ice and liquid water cannot be symmetrical, with the hydrogens oscillating about points midway between the oxygens. Each hydrogen must remain considerably closer to one oxygen neighbor than to the other.

It is obvious that the energy is lowest—the stability greatest—if each oxygen in ice or liquid water has two close hydrogen neighbors. The effective charge on the oxygen of an H_3O^+ ion is less negative and that on the oxygen of an OH^- ion is more negative than that on an oxygen of an

H_2O molecule. The attraction between the oxygen of an H_3O^+ ion and each of its hydrogens is therefore less than that between an H_2O oxygen and each of its hydrogens; likewise the attraction between the two atoms of an OH^- ion is greater. Calculation shows that a very slight difference in effective charge on the two oxygens joined by a hydrogen bridge suffices to eliminate the double hump in the potential energy curve, leaving only a single minimum on the side of the oxygen with the more negative effective charge. Adding to the O–H interaction energy represented by the uppermost curve of figure 1 a term $\alpha e^2/d_{H-O}$, to take account of a decreased Coulomb attraction between the hydrogen atom and one of the oxygens, unsymmetrical single-minimum curves (see the two lowest curves of figure 2) are obtained for all values of α greater than 1/20 (for d_{O-O} = 2.75 A.U.). If at the same time another term of the same form but opposite sign to

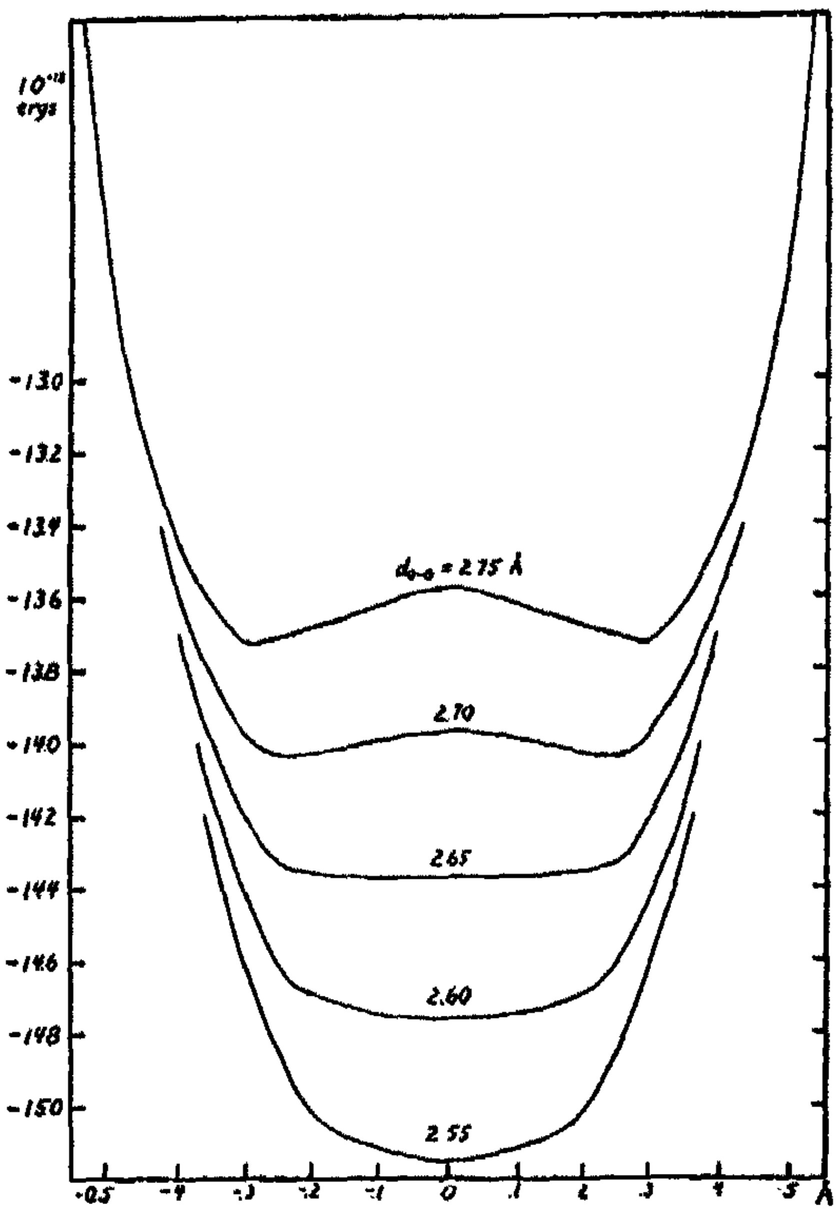


FIG. 1. Potential energy curves for hydrogen bridges with various fixed oxygen-oxygen distances, assuming the O–H interactions to vary with distance as in the OH molecule.

represent an increased attraction between the hydrogen and O_2 is included, the central hump is eliminated with still smaller values of α. One must conclude then that a shift of one hydrogen of an H_2O molecule to a neighboring molecule to give H_3O^+ and OH^- ions could not occur.

If one decreases the effective negative charge equally on both oxygens of a hydrogen bridge, the central hump tends to disappear, both because of a decrease in the O-O distance (figure 1) and because of the decreased Coulomb attraction between the hydrogen and each oxygen (see the two upper curves of figure 2). This furnishes the justification for the assumption that the hydrogen ion consists of a relatively strong, symmetrical bridge joining two H_2O groups. Reversing the argument, a hydrogen bridge connecting two OH^- ions would be weaker, longer, and more un-

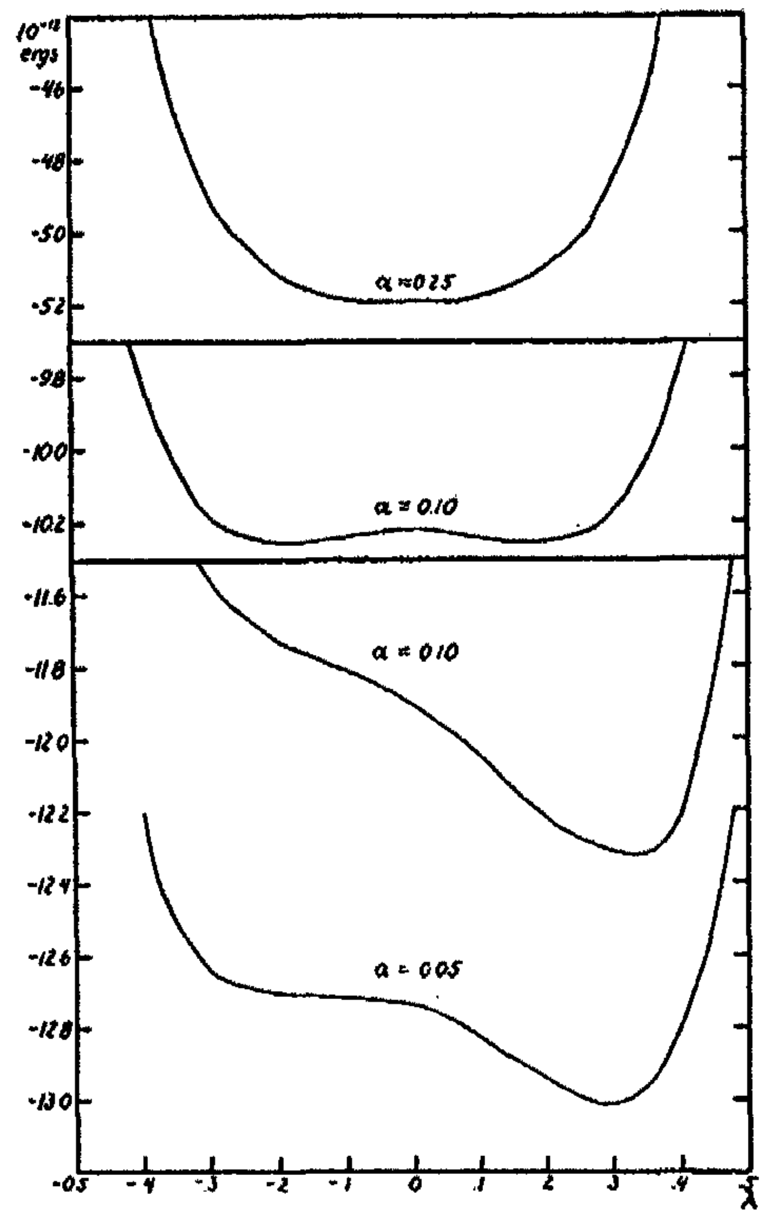
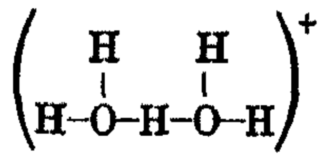


FIG. 2. Potential energy curves for hydrogen bridges having d_{O-O} fixed at 2.75 A.U. To the O-H interaction energy as in the OH molecule a Coulomb term $\alpha e^2/d_{O_1-H}$ is added for each of the two lowest curves. For the two others terms of this form are added for both O_1-H and O_2-H interactions.

symmetrical than the bridges in pure water (connecting, in effect, OH^- ions and H_2O molecules).

As will be shown elsewhere, the F–F distance in the FHF bridge can be calculated with reasonable accuracy, using constants obtained entirely from other sources. To a large extent this distance depends on the interpenetration repulsion between the two fluorine atoms, assumed to be representable by an exponential term, $e^{-a(r-r_{12})}$. Because of inaccurate knowledge of the best value of r_{12} to use for the repulsion between two oxygen atoms, of the effective charges on the oxygen and hydrogen atoms, and of the magnitudes of the van der Waals constants, the corresponding calculation for OHO bridges cannot at present be carried out satisfactorily. It is instructive however to calculate the value of r_{12} which is necessary to give equilibrium for different O–O distances, neglecting the van der Waals terms (which are small) and the Coulomb terms (which do not change rapidly with the distance). Taking $a = 4.78$ as for neon and fluorine, one obtains $r_{12} = 2.80$ for $d_{oo} = 2.75$ A.U. and $d_{o_{I}H} = 1.10$ A.U. For O–O and O_I–H distances of 2.70 A.U. and 1.13 A.U., respectively, $r_{oo} = 2.78$ A.U. For $d_{oo} = 2.55$ A.U., with the hydrogen in the middle, $r_{oo} = 2.70$ A.U. It is seen that a small decrease in the "basic radius" ($r_o = r_{oo}/2$) suffices to change an unsymmetrical bridge (two minima in the potential curve) into a symmetrical one (only one minimum, in the middle). This "radius" is a measure of the extension in space of the outermost electrons in the atom *in the direction of the other oxygen*. Its value depends on the tightness with which these electrons are held by the kernel and on what is on the other side—on the polarizability of the atom and on the magnitudes and directions of the forces tending to polarize it.

Increased polarization resulting in a decreased basic radius for the oxygen at each end of a hydrogen bridge—and so a decreased O–O distance—may result from an increase in the number of close hydrogens or from their replacement by atoms of a sufficiently electronegative element such as carbon or phosphorus. In either case a single minimum potential curve is favored. This line of reasoning furnishes an additional argument for the structure



$$\left(\mathrm{H{-}\overset{\overset{\textstyle H}{|}}{O}{-}H{-}\overset{\overset{\textstyle H}{|}}{O}{-}H}\right)^{+}$$

with a strong central bridge, for the hydrogen ion in water solution. It also accounts for the small O–O distances observed in sodium bicarbonate and potassium dihydrogen phosphate.

SUMMARY

Evidence for the existence of hydrogen bridges in liquid and solid water and against their being symmetrical is reviewed. With sufficiently small energy barriers in the center of each OHO bridge, synchronized jumps over them of all of the hydrogens in a ring of hydrogen bridges are possible. The resulting partial freedom of orientation of the dipoles accounts satisfactorily for the dielectric constant data for ice and liquid water. Reasons are given for considering hydrogen ion in water to be $(H_2OHOH_2)^+$, consisting of a relatively strong, symmetrical hydrogen bridge connecting two H_2O groups. By very slight contemporaneous shifts of two hydrogen nuclei, such an ion can, in effect, add OH_2 at one end and lose H_2O at the other, thus shifting the position in the solution of the excess positive charge. This picture thus accounts for the high mobility of the hydrogen ion in water solution.

Potential energy curves for OHO bridges are calculated for different O-O distances, taking the O-H interactions as in the OH molecule. For the smaller distances there is a single potential minimum; for the larger distances, such as observed in liquid and solid water, it is double. The central hump is eliminated if the Coulomb attraction between the hydrogen and one or both of the oxygens is slightly greater than in the OH molecule.

The hydroxide ion is probably OH^- rather than $(HOHOH)^-$, the greater repulsion between the oxygen atoms making a symmetrical bridge less likely than in the case of the positive ion. The shift H—O—H . . . . O—H to H—O . . . . H—O—H should occur, but less readily than the corresponding shift in the case of hydrogen ion, hence the mobility should be less, as observed.

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THE DIFFUSION OF COPPER SULFATE IN AQUEOUS SOLUTIONS OF SULFURIC ACID

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For an electrochemical problem now being investigated in this laboratory, it was necessary to know the diffusion constant of copper sulfate in aqueous solution in the presence of varying amounts of sulfuric acid. A search of the literature showed that the plaints of other investigators as to the meagerness and uncertainty of the diffusion data would have been justified in the case of copper sulfate also. We have therefore determined the diffusion constant of copper sulfate in aqueous solutions of sulfuric acid, and the results are recorded here.

The method was that originally developed by Northrup and Anson (4) and since that time used extensively by McBain and his associates (3); since it has already been discussed adequately in the literature, no lengthy description is needed. In brief, it consists in enclosing in a glass cell of known volume a solution of the material whose diffusion constant is desired; the base of the cell is a sintered glass diaphragm whose pores are sufficiently small to prevent streaming of the solution as a whole, and at the same time are large enough to permit diffusion to take place unhindered. The cell is suspended with the diaphragm just dipping below the surface of an equal volume of pure solvent, and after allowing diffusion to proceed for a suitable length of time, the amount of solute that has diffused through the diaphragm is determined; from this it is possible to compute the diffusion constant, provided the cell has previously been calibrated with a substance of known diffusion constant.

It has been found desirable, after filling the cell with solution, to carry out a preliminary diffusion to ensure a more or less linear drop of concentration in the diaphragm before transferring the cell to the sample of solvent into which the final diffusion is to take place. Under these conditions, it can easily be shown, on the assumption that Fick's diffusion law is obeyed, that to a first approximation

$$\begin{aligned} c' &= \frac{c_0}{2}\left(1 + e^{-2kAt/lV}\right) \\ c'' &= \frac{c_0}{2}\left(1 - e^{-2kAt/lV}\right) \end{aligned} \qquad (1)$$

where c_0 is the initial concentration inside the cell in equivalents per liter, c' and c'' are the concentrations of the inner and outer solutions after the diffusion has proceeded for t seconds, A and l are the effective cross-sectional area and thickness of the diaphragm, and V is the volume of both the inner and outer solutions. Hence

$$\beta kt = \log (c' + c'') - \log (c' - c'') \tag{2}$$

where β, the "cell constant," is $2A/2.3026\,lV$, and can be determined once and for all for the cell by diffusion measurements with a substance of known k.

The use of equations 1 and 2 involves the assumption (in addition to that implicit in Fick's law) that the concentrations of the inner and outer solutions are changing so slowly that a steady state is set up in the diaphragm, i.e., that there is a linear drop of concentration throughout the diaphragm at all stages of the experiment. Actually, as Barnes (1) has shown, this is not necessarily the case, but he finds from a rigorous solution of the problem, that to a high order of approximation the only change introduced in equations 1 and 2 is that β becomes $(2A/2.3026lV) \times (1 - \lambda/6)$, where λ is the ratio of the volume of the liquid in the diaphragm to that in the cell. Since this revised cell constant depends only on the geometry of the apparatus and is determined automatically by the calibration, no error is introduced by this cause in equation 2.

The assumption of Fick's law, however, implying that k is independent of c, is a more serious matter. If k does depend on the concentration, the concentration gradient $\partial c/\partial x$ will vary from top to bottom of the diffusion layer even when a steady state has been attained in the diaphragm. However, on the assumption that $k = k_0\ (1 - \alpha c)$, which fortunately covers the case of copper sulfate, it is easy to allow for this. At any cross section of the diaphragm, the total amount diffusing in a time dt is $-kA(\partial c/\partial x)dt$, which, for a steady state in the diaphragm, is constant from the upper surface of the diffusion layer ($x = 0$) to the lower surface ($x = l$). Assume an "effective" diffusion constant k', independent of c, which will cause the same amount of solute to diffuse for the same total drop in concentration across the diaphragm. Then

$$-k'A\,\frac{(c'' - c')}{l}\cdot dt = -kA\cdot\frac{\partial c}{\partial x}\cdot dt \tag{3}$$

Simplifying, multiplying through by dx, and integrating between the limits $x = 0$ and $x = l$,

$$k'(c' - c'') = -\int_0^l k\cdot\frac{\partial c}{\partial x}\cdot dx = k_0 \int_{c''}^{c'} (1 - \alpha c)\,dc \tag{4}$$

Hence

$$k' = k_0 - k_0\alpha(c' + c'')/2$$

but $(c' + c'')$ is constant throughout the experiment. Therefore the "effective" diffusion constant, k', computed by equation 2 is the true (differential) diffusion constant for the average of the inside and outside concentrations, or (what is the same thing) for one-half the initial inside concentration.

The cells used were similar to those employed by McBain,—of Jena glass with G4 pore size and of about 100-cc. capacity. Their volumes were determined by weighing the cell with liquid just to the top of the diaphragm, and then weighing again when full; the volumes so determined could be checked to 0.1 cc. The liquid in the outer compartments (small beakers of 125-cc. capacity) was measured by specially calibrated pipets. During a measurement, each cell with its attendant beaker was suspended in an individual glass air bath immersed in a water thermostat electrically controlled to ±0.02°C. The cells and beakers were carried by a bridge which had no connection with the thermostat and which was supported on sponge rubber blocks to minimize vibration; each cell was hung from a wire suspension to ensure that the diaphragm was horizontal, and this suspension and the support for the beaker forming the outside compartment were attached to ebonite rods to avoid any transfer of heat from the outside air to the solutions.[1] The top of each air bath was closed with a slotted fiber disk covered with absorbent cotton, and as an additional precaution against evaporation from the outside compartment, a few cubic centimeters of a solution roughly isotonic with that in the outer compartment were placed in the bottom of each air bath.

The cell constants were determined by calibration at 20°C. with $N/10$ potassium chloride solution, whose diffusion constant has been found by Cohen and Bruins (2) to be 1.448 cm.^{2} per day = 1.676×10^{-5} cm.^{2} per second; successive calibrations for a cell gave values of β differing in general by less than one fifth of 1 per cent.

The acid copper sulfate solutions with which the cells were initially filled were made up from recrystallized B.D.H. analytical reagent copper sulfate, a stock solution of C.P. sulfuric acid, and boiled conductivity water; the sulfuric acid solution which was to be placed in the outer compartment was always made up to the same volume concentration of acid as the solution to be used in the cell. After a preliminary diffusion to set up a steady

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[1] We have found that to obtain consistent results it was necessary to eliminate vibration as far as possible, and also to control temperature somewhat more carefully than has been suggested by other investigators; a fluctuating temperature produces a pumping action of the solution in the cell which tends to break up the diffusion layer in the diaphragm.

state in the diaphragm (usually with copper sulfate solutions this required ten to twelve hours), the cell and beaker (now containing a fresh sample of

TABLE 1

Data for run No. 176

Acid concentration = 3.6 equivalents per liter; T = 18.00°C.;
t = 125.62 hours = 4.522×10^5 sec.

CELL	β	c'	c''	$k \times 10^6$
Cell II	0.0777	0.5208	0.1016	4.89
Cell III	0.0826	0.5162	0.1072	4.90
Cell IV	0.0549	0.5496	0.0763	4.88
Cell V	0.0654	0.5379	0.0883	4.87

TABLE 2

Values of k_0 and of $k_0\alpha$

Equivalent H_2SO_4 per liter	0	0.005	0.10	0.10	0.10	0.5	1.0	3.6	7.6
T°C	18	18	10	18	25	18	18	18	18
$10^6 \cdot k_0$	6.28	6.28	4.97	6.28	7.81	6.24	6.01	5.02	3.66
$10^6 \cdot k_0\alpha$	2.56	2.56	2.00	1.60	2.70	0.94	0.82	0.32	0.12

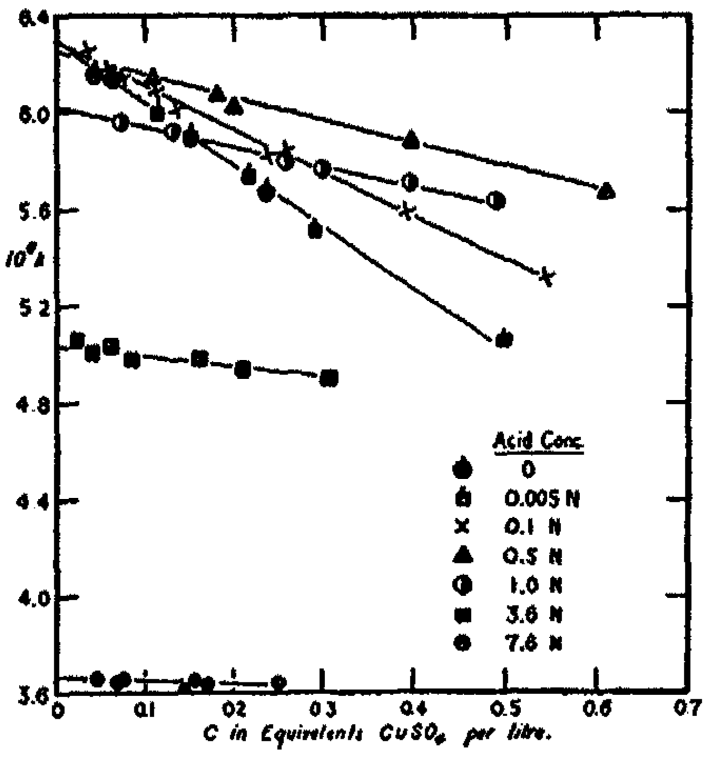

FIG. 1. The diffusion of copper sulfate in aqueous solutions of sulfuric acid at 18°C.

the acid solution) were left in the thermostat for from five to eight days; at the end of this time, the cell was removed from the beaker, and both solutions were analyzed electrolytically for copper. As an example, the data for one such run, selected at random, are summarized in table 1. Thus from the table, the diffusion constant of copper sulfate in a solution containing in 1 liter 3.6 equivalents of sulfuric acid and 0.31 equivalent of copper sulfate is 4.89×10^{-6} cm.^{2} per second.

The results of a large number of such measurements, all at 18°C., are shown in figure 1; each point is the average of four measurements similar to those recorded in table 1. It is evident from the graph that for a given acid concentration and for the range of copper concentrations used, k is a linear function of c to a close approximation. Table 2 gives the values of k_0 and of $k_0\alpha$ for various strengths of acid, and also for various temperatures for one acid concentration.

It is evident from the table that for solutions extremely dilute in copper sulfate the diffusion constant decreases in a more or less linear manner with increasing acid concentration. Since the forces retarding diffusion are usually assumed to be proportional to the viscosity, one would expect that the product $k_0\eta$ for a given temperature would be roughly constant, and this is very approximately the case.[2] In the more concentrated solutions, however, increase in acid concentration tends to decrease the dependence of k on the copper concentration, and at the moment there does not seem to be any plausible explanation of this.

We have also carried out a few experiments to measure any diffusion of the sulfuric acid during an experiment. Naturally this will only be prominent if the acid concentration is relatively small, and the difficulties of analysis (barium sulfate precipitation in the presence of a copper salt) are considerable. However, our results show, as might be expected, a definite diffusion of the acid from the outer solution to the inner, i.e., against the copper sulfate; thus in one experiment ($c_0 = 1.6312$, $c' = 1.3200$, $c'' = 0.3122$ equivalent of copper sulfate per liter) with 0.1 N sulfuric acid as solvent, it was found after one hundred and ninety-two hours diffusion that the inner solution was 0.014 equivalent of sulfuric acid per liter stronger than the outer. On the other hand, with relatively high concentrations of acid (1 N or more), there is evidence of a slight but definite diffusion of acid with the copper; this effect is now being investigated in this laboratory.

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[2] The product $k_0\eta$ increases about 15 per cent when the acid concentration increases from 0.1 N to 7.6 N.

A PRELIMINARY STUDY OF THE ABSORPTION SPECTRA OF CEPHALIN, LECITHIN, AND SELECTED ANTIGENS[1]

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Additional data on the antigens which are used in the complement-fixation and precipitation tests for syphilis are essential for comparative purposes and for determining the relationship between the antigenicity of these substances and their physical and chemical characteristics and, ultimately, in a comprehensive search for the antigenic substance which is responsible for the serological reactions of syphilis. Hence, a quantitative spectrophotometric study of cephalin and lecithin from beef brain in different stages of purification and of beef-heart antigens prepared in this laboratory for routine use in the serological tests for syphilis, and for experimental purposes, has been undertaken; the preliminary work is here reported.

The observations recorded are based on a study of the absorption spectra of these materials in the visible and ultra-violet ranges between λ 6800 and 2150 A.U.

Absorption spectrum curves in the visible region were obtained with a Hilger-Nutting spectrophotometer with a Pointolite lamp of 150-candle power as light source. The wave-length drum of the spectrophotometer was calibrated by means of a mercury arc and by helium, nitrogen, and hydrogen-discharge-tube spectra. The position of the prism was checked before making each set of readings by adjusting the position of the yellow line of helium, λ 5876 A.U. For the determination of the density values in the regions where the materials were particularly transparent, a neutral filter was used, and the cells containing the absorbing substance and the control were interchanged. In all cases at each wave length, density values obtained with the spectrophotometer and used in the calculation of the extinction coefficients are based upon at least five determinations.

The absorption spectrograms for the ultra-violet region were obtained with a Hilger E 316 quartz spectrograph used in conjunction with a Hilger sector photometer. The wave-length scale of the quartz spectrograph was calibrated with mercury-arc, aluminum-spark, helium-tube, and hydro-

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[1] Presented at the meeting of the Society of American Bacteriologists, held in New York, December 28, 1935.

gen-discharge-tube spectra. The light source was a tungsten-steel condensed spark.

The accuracy of the spectrophotometric technic was tested in the visible region by comparison of curves obtained for copper sulfate ($CuSO_4 \cdot 5H_2O$) and potassium dichromate solutions in different cell depths with the standard curves for these substances published by Mecke and Ley (3), Houstoun (2), Grünbaum (1), and others. In the ultra-violet region the spectroscopic procedure was tested by a comparison of curves for potassium dichromate with the standard curves for this substance recorded by von Halban and Siedentopf (6), Rössler (5), and others. The agreement between all the standard curves and ours was very close.

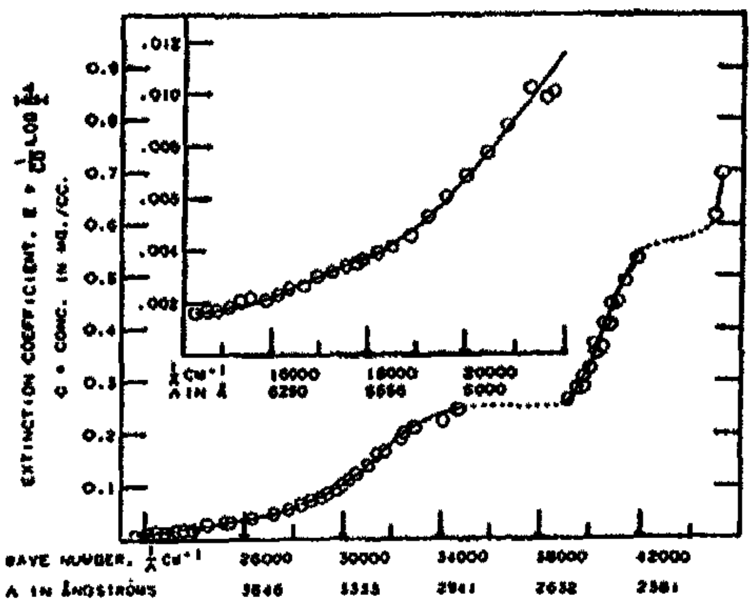

FIG. 1. Visible and ultra-violet absorption spectrum curves of purified cephalin from beef brain

All the solutions studied were apparently clear, yet faint Tyndall light, manifesting scattering of light, was observed; but the correction of the absorption curves for this effect has not yet been determined.

Purified cephalin, for which published data are given by Wadsworth, Maltaner, and Maltaner (8, 9), and lecithin, not highly purified, were investigated by this method. The antigens studied were those used in the routine complement-fixation tests for syphilis, which are modifications of the Bordet-Ruelens and of the Neymann-Gager type, and those prepared for precipitation tests by a new method (7).

The absorption spectrum curve for purified cephalin is presented in figure 1. Wave lengths in Ångström units and wave numbers, $\frac{1}{\lambda}$ cm.$^{-1}$, are plotted against extinction coefficient,

$$E = \frac{1}{cd} \log \frac{I_0}{I}$$

where *c* is the concentration in milligrams per cubic centimeter, *d* is the depth of the cell—in this case, 1 cm.—I_0 is the intensity of incident light, and *I* is the intensity of light after passing through the solution.

The curve for cephalin is fairly smooth in the visible region, with a slight change in slope between λ 6250 and 5550 A.U., but in the ultra-violet range it indicates two regions where inflections occur: one between λ 2850 and 2550 A.U., *E* about 0.25, near where the proteins are known to absorb radiation, and a second between λ 2400 and 2220 A.U., where *E* is about 0.55.

A previous very limited study of lecithin, not highly purified, yielded an absorption curve in the visible region of the spectrum which was smooth and indicated very little absorption between λ 7000 and 5000 A.U., where the absorption began to increase. Spectrograms for the ultra-violet region gave evidence of selective absorption between λ 2800 and 2500 A.U. and between λ 2400 and 2230 A.U. These two regions occur about where selective absorption was indicated by the ultra-violet absorption curves for cephalin.

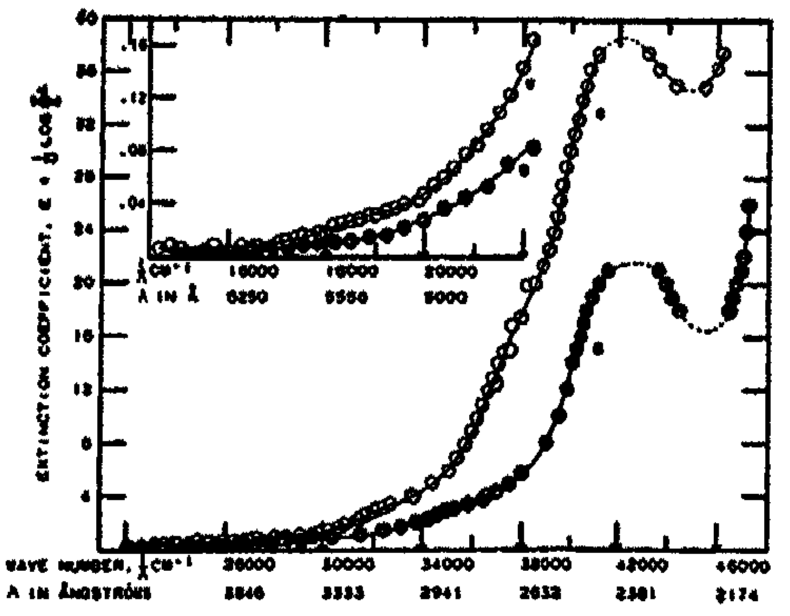

FIG. 2. Comparison of the visible and ultra-violet absorption spectrum curves of beef-heart antigens for complement-fixation tests prepared by modified methods of Bordet and Ruelens (curve B) and Neymann-Gager (curve W).

The absorption curves for one sample each of a modified Bordet-Ruelens and of a modification of a Neymann-Gager antigen are presented in figure 2. In the preparation of the Bordet-Ruelens antigen, the acetone-extracted tissue was further thoroughly extracted with anhydrous ether. The vacuum-dried tissue was then extracted with absolute alcohol at room temperature for ten days. The filtered extract is the antigen used for curve B. The modification of the Neymann-Gager antigen, which is represented by curve W, employs air-dried tissue, preliminary extraction with anhydrous ether, and final extraction by boiling with absolute alcohol.

Curve W represents a substance which is less transparent in both the visible and ultra-violet ranges of the spectrum than that represented by curve B. Both curves are fairly smooth in the visible region, with a slight inflection within the range from λ 5450 to 5300 A.U. in curve W. The latter also shows inflections within the range of about λ 3350 to 2950 A.U. and λ 2850 to 2530 A.U., where curve B is smooth. Both curves have definite absorption bands farther in the ultra-violet. The maximum of this band for curve W is at λ 2375 A.U., where the extinction coefficient ($E = \frac{1}{d} \log \frac{I_0}{I}$) is 38.4±; the minimum, at λ 2235 A.U., where E is 34.5±. The maximum of the band in curve B lies about 40 A.U. farther towards the shorter wave lengths—that is, at λ 2335 A.U., where the extinction coefficient is 21.8±; the minimum at λ 2190 A.U., where E is 16.5±.

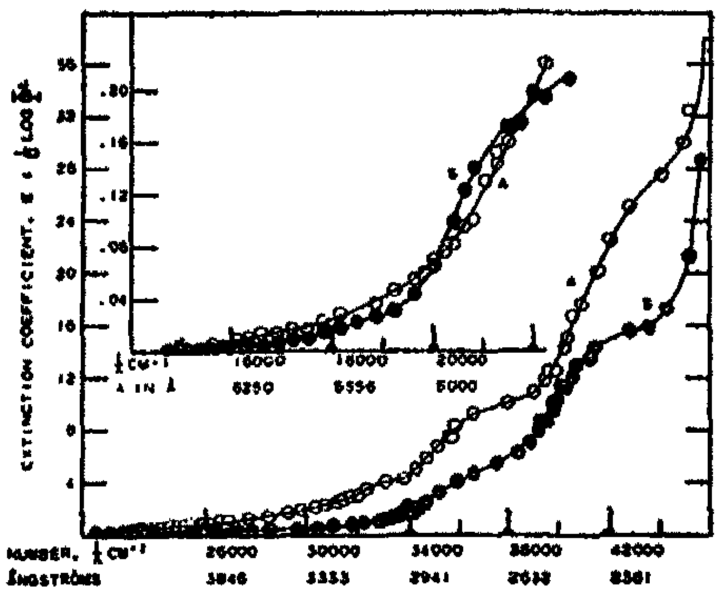

FIG. 3. Comparison of the visible and ultra-violet absorption spectrum curves of beef-heart antigens for precipitation tests prepared from tissue infused with water (curve A) and with 20 per cent sodium chloride solution (curve S).

The hydrogen-ion concentration values, determined colorimetrically, were the same for all the antigens for which absorption curves are presented.

The antigen represented by curve A in figure 3 was prepared for use in a precipitation test. It was a 95 per cent alcoholic extract of beef-heart tissue which had been subjected to an aqueous infusion at 55°C., previous to acetone treatment and subsequent drying. The antigen represented by curve S was a 95 per cent alcoholic extract of tissue similarly treated, except that the infusion was carried out with a 20 per cent sodium chloride solution in place of water.

A comparison of their absorption curves in the visible range of the spectrum shows that the antigen which is prepared from tissue treated with sodium chloride solution shows an inflection in its curve S in the range of λ 4950 to 4600 A.U. whereas the curve A for the antigen prepared from tissue infused with water shows no inflection in this range. Both curves indicate little absorption in the range λ 6800 to 5500 A.U., in which curve A represents slightly higher values of extinction coefficient than curve S. This work has been further substantiated by determining the curves for two other antigens of the same type, prepared in the same way as the antigens represented by curves A and S.

In the ultra-violet range between λ 4160 and 3900 A.U., curve S shows indications of selective absorption, whereas curve A is smooth. This difference is more clearly indicated in figure 4. Both curves have inflections in the ranges from λ 2800 to 2600 A.U. and from λ 2500 to 2300 A.U., approximately. Curve A has a slight inflection near λ 3000 A.U. and represents a less transparent substance than does curve S throughout the ultra-violet range of the spectrum. In order to illustrate more clearly than is indicated in figure 3 the contrast in the curves in the range between λ 4160 and 3900 A.U., this portion of the curves has been drawn to a much more open scale and is presented in figure 4. The flat portion of curve S is contrasted with the smooth portion of curve A in this range.

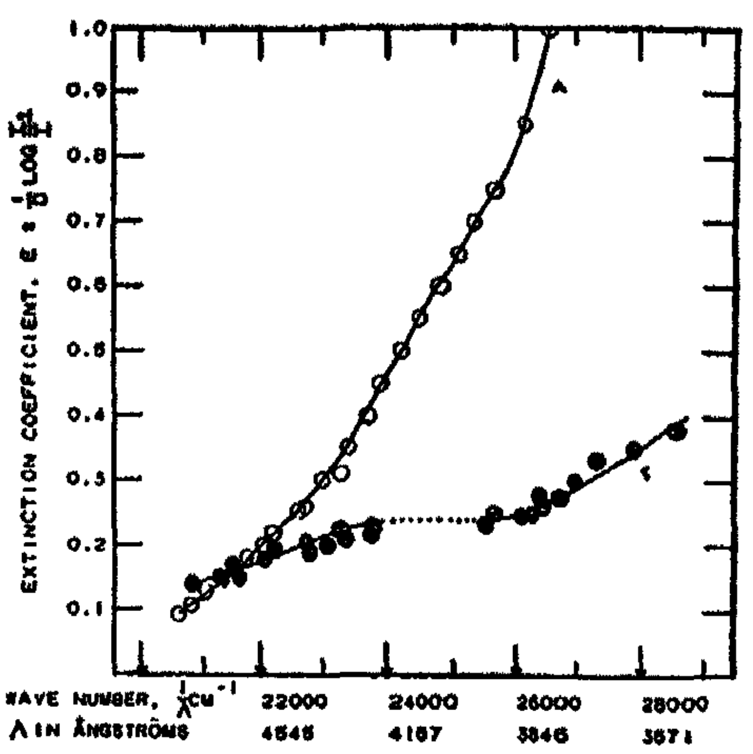

FIG. 4. Comparison of absorption spectrum curves of beef-heart antigens A and S within the range λ 4800 to 3700 A.U.

Curves for each of the two types of antigens—complement fixing and precipitating—which have already been shown in figures 2 and 3, have been plotted together for comparative purposes and are presented in figure 5.

There are a number of points of difference between the curves W and S for the complement-fixation and precipitation antigens, respectively, but the most outstanding difference is within the range from λ 2500 to 2300 A.U., where the curve W shows a definite absorption band (*E* value for maximum, 38.4±), whereas curve S has merely an inflection and indicates less absorption, with values for *E* between 10 and 15.8 within this range. Curves for several other antigens showed definite bands for the complement fixation, and inflections only for the precipitation types. Curve W indicates selective absorption in the ultra-violet ranges from λ 3350 to 2950 A.U. and from λ 2850 to 2530 A.U , and is fairly smooth in the visible region of the spectrum. Curve S has slight inflections between λ 2800 and 2600 A.U. and λ 2500 and 2300 A.U. in the ultra-violet and a definite inflection in the visible region from λ 4950 to 4600 A.U., where the curve W is smooth and indicates less absorption.

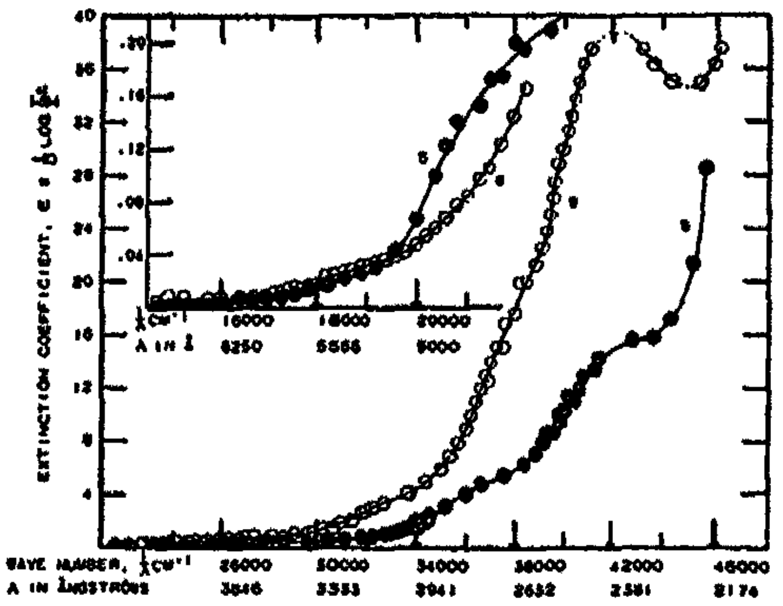

FIG. 5. Comparison of the visible and ultra-violet absorption spectrum curves of a modified Neymann-Gager antigen (curve W) and one for precipitation tests prepared from tissue infused with 20 per cent sodium chloride solution (curve S).

It seems well to record here a supplementary note regarding the fluorescence of these materials and also of the results of tests for the effects of exposure to ultra-violet radiation. All of the substances for which absorption curves have been shown fluoresced when irradiated with ultra-violet light from either a carbon arc or a quartz mercury-vapor arc through a Corning red-purple corex filter. Solutions of cephalin are generally characterized by fluorescence, according to Parnas (4). The sample studied fluoresced with a brilliant blue light, the band extending from about λ 6300 to 4200 A.U., the maximum intensity being between λ 5300 and 5200 A.U.; all the antigens fluoresced with a bluish-green light. There was no significant change in the coagulative activity of cephalin which had been exposed to the ultra-violet light of the tungsten-steel condensed spark for the time required to make spectrograms, nor in the degree of fixation of complement obtained in antigen or antibody titrations performed with syphilitic sera and the antigens represented by curves B and W.

SUMMARY

From this preliminary spectroscopic study of cephalin, lecithin, and beef-heart antigens, it is noted that selective absorption in two ranges of the ultra-violet regions of the spectrum, about λ 2850 to 2500 A.U. and λ2550 to 2200 A.U., is common to all and that the first range is near that in which the proteins are known to absorb. Differences between the absorption curves for the complement-fixation and precipitation antigens and between two samples of each type have also been recorded.

Little consideration has as yet been given to the identification of the substances which may be responsible for the selective absorption indicated by the curves shown.

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A STUDY OF THE LAWS GOVERNING THE CATION-EXCHANGING PROPERTIES OF A PRECIPITATED ALUMINUM SILICATE

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INTRODUCTION

Upon undertaking (1) the research here described, it was the intention of the author to study the quantitative variation in certain properties, especially that of cation exchange, as a function of the composition of a precipitated aluminum silicate. However, this proved to require considerable preliminary work, since it was found that the factors upon which the cation-exchange capacity depended were not sufficiently known. That is to say, the cation-exchange capacity depends on so many variables that it was found necessary to study a particular case first.

It was decided to prepare an aluminum silicate under known conditions, then to measure a series of properties for it. In this paper the theoretical aspects of the aluminum silicate considered as a colloidal particle will be taken up first. This will be followed by the experimental results.

THEORETICAL

Let us first consider the picture of the suspended particle (2). We may suppose the particle to consist of an interlacing of aluminum and silicon by oxygen atoms in a more or less random manner.[1] Further, the particle contains a number of hydroxyl groups attached either to silicon or aluminum atoms. We may assume that these hydroxyl groups are capable of splitting off hydrogen ions or of taking up hydrogen ions. That is to say, a negative or positive charge may be produced at a given point on the surface of the particle, according to whether we have respectively an ionization by the splitting off of a hydrogen ion or the acceptance of such an ion from the solution. To a varying degree according to the conditions, these two processes take place in each particle. This may be represented schematically in some such way:

$$\mathrm{M(OH)}_n = \mathrm{M(OH)}_{n-p-q}\cdot(\mathrm{OH}^-)_p\,(\mathrm{O}^-)_q + (q-p)\,\mathrm{H}^+$$

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[1] That this arrangement is random is indicated by the fact that no lines were found on a Röntgen photograph of our precipitate.

Where $M(OH)_n$ represents the unionized particle with n OH groups, and $M(OH)_{n-p-q}\cdot(OH_2^-)_p(O^-)_q$ the ionized form after splitting off q H^+ ions and taking up p of the same, it is to be expected that the dissociation as represented in the above equation will in the main be a function of the pH of the solution in which the particle is suspended. Under the working conditions used the main process has been one of splitting off hydrogen ions, owing to the fact that the pH is considerably on the basic side of the isoelectric point. Because of this splitting off of hydrogen ions, the particle will be negatively charged. Consequently, the cations in the solution will tend to form an ionic atmosphere around it. In our particular case, these cations will be sodium ions. In the ionic atmosphere, the number of cations in excess of anions will be exactly enough to bring about electroneutrality of the particle and the surrounding solution. A further assumption which we permit ourselves to make is that no metallic cations can occupy positions analogous to hydrogen in the OH groups, i.e., form covalent complexes of the type O·Na with either alumina or silica.

With the above assumptions in mind, the cation-exchange capacity of the aluminum silicate for Na^+ or other cation may be taken as a measure of the algebraic sum of the charges on the particle. In this algebraic sum, the charge of all ions, contained in the particle in the form of sterically hindered ions, will be included. And any positive charges on the surface of the particle, which may have resulted from taking up hydrogen ions, are to be made a part of the summation.

With this as a picture it is obvious that the cation-exchange capacity must vary inversely to exactly the same extent as the particles take up or give off hydrogen ions. By adding acid or base to the suspension containing salts of known concentration and making electrometric titration curves, one obtains a measure of the hydrogen ions taken up or given off as a function of the pH. In order to calculate this function it is only necessary to make a similar titration using a salt solution of the same composition as that in which the precipitate is suspended. The difference between the amount of acid or base, as the case may be, used to bring the suspension in a salt solution to a certain pH and that required to bring the salt solution alone to the same pH, gives the value of the hydrogen ions taken up or given off respectively by the precipitate. Thus from the two titration curves it is possible to calculate the change in cation-exchange capacity with pH.

It is to be expected from thermodynamic considerations and is shown to be the case for zeolites by Rothmund (4) and Kornfeld, and for soil silicates by Riehms (3) that for constant composition of the cation-exchanging substance the dependence of the pH on the concentration of the salt in suspension will be logarithmic. If we decrease the pH by one unit the concentration must increase by tenfold for a univalent ion, by a hundred-fold for a divalent ion, by a thousandfold for a trivalent ion, etc. From this and the titration curves for the various cations, we may compute the functional relations between the cation-exchange capacity, the pH, and the cation concentration.

EXPERIMENTAL

Preparation of the "aluminum silicate"[2]

A specially prepared silica was used in preparation of the aluminum silicate. A typical example of the method used will be given. A Kahlbaum preparation (250 g.) of silicon tetrachloride was hydrolyzed by dropping it from a separatory funnel into water (2 liters), keeping the mixture at a low temperature by surrounding the reaction vessel with cold water. Ten repeated washings and filterings with hot distilled water, at intervals of twelve or more hours, were found to give a sample of silica which was free from chloride ion and which upon treatment with hydrofluoric acid left a residue less than one hundredth of 1 per cent.

The aluminum silicate was prepared by dissolving the silica so obtained in a 3.8 N solution of sodium hydroxide, so that the molar concentration of silica was 1.9. This mixture was added to a boiling solution of aluminum nitrate (0.1111 N) containing methyl red, until a permanent yellow had just been obtained. About 60 cc. of the sodium silicate mixture was necessary for every 500 cc. of aluminum nitrate solution. The precipitate was boiled with continual stirring for half an hour. After cooling, the mixture was diluted ten or more times, and a series of decantings performed until no appreciable residue was found in the supernatant liquid, i.e., less than 2 mg. per 100 cc. The suspension thus formed was diluted so that the residue on evaporation and drying at 150°C. was nearly 0.01 g. per gram of suspension. In this form it was used for experimentation.

Method of treatment with silver nitrate

The method of experimentation was as follows: A known volume of suspension was centrifuged. The resulting gelatinous mass, from which supernatant liquid can be poured without loss of the disperse phase, was added to a known weight of silver nitrate solution and in many cases of sodium nitrate solution. The mixture was rotated slowly (about one revolution per minute) for a varying period up to twenty hours, which is necessary if complete equilibrium is desired. However, it was found that for many purposes one or two hours was sufficient. This suspension was again centrifuged, and the weight and silver content of the decant determined. These processes were repeated a varying number of times, accord-

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[2] It is to be noted that the product obtained here is not aluminum silicate, but rather a complex of alumina and silica possessing OH groups at various points. For the sake of simplicity, this complex will be referred to as aluminum silicate.

ing to the specific purpose of the experiment. After decanting for the last time, the gel was analyzed for silver and a check made of the total silver found as compared with that used. In all cases except the one noted below, the Volhard volumetric method was used in the analysis for silver.

Calculation of amount of silver taken up by the aluminum silicate

The following formula is used in the calculation of the silver taken up by the precipitate,

$$\mathrm{Ag}_s = \frac{C_{\mathrm{Ag}} G_{\mathrm{Ag}} C(G_{\mathrm{Ag}} + G_{\mathrm{Na}} + G_{\mathrm{H_2O}})}{\alpha[1 - C/1000 \times (M_{\mathrm{Ag}} - M_{\mathrm{Na}})]}$$

where

Ag_s = millimoles of silver taken up per gram of original precipitate dried at 150°C.,

C_{Ag} = concentration of silver nitrate solution (moles per 1000 g. of solution) added,

G_{Ag} = grams of silver nitrate solution added,

C = concentration of silver nitrate in soution decanted (moles per 1000 g. of solution),

G_{Na} = grams of sodium nitrate solution added,

$G_{\mathrm{H_2O}}$ = grams of water in the gel (or sometimes the suspension, if used instead),

α = grams of precipitate used (dry weight at 150°C.),

M_{Ag} = atomic weight of silver, and

M_{Na} = atomic weight of sodium.

Time required to reach equilibrium

Table 1 shows the effect of time of treatment upon the amount of silver taken up by the precipitate. There were roughly 100 cc. in the final suspension and a dry weight of precipitate of about 1 g. In the second column is found the number of millimoles of silver (Ag_s) taken up by 1 g. of precipitate (dry weight at 150°C.). In the third and fourth columns are found the respective concentrations of silver and sodium in the decanted solution, expressed in moles per 1000 g. of solution. The parentheses around the numbers in the column giving the sodium concentrations indicate that these numbers are obtained by indirect calculation. All numbers without such parentheses have been obtained by direct experimental measurements. The last column gives the value of the check, ρ, of the experimental accuracy in the determination for silver. This is defined by

$$\rho = \frac{\text{Number of moles of silver found} - \text{number of moles of silver used}}{\text{Number of moles of silver used}}$$

It was found that four of the above-mentioned treatments of the gel from 100 cc. of suspension with 100 cc. of 1 *N* silver nitrate were sufficient to saturate the precipitate with silver. The maximum amount of silver which can be introduced into the precipitate by repeated treatments with solutions of silver nitrate is called the cation-exchange capacity with respect to silver, and is given in millimoles of silver per gram of "sodium" precipitate dried at 150°C.

TABLE 1

Time required to reach equilibrium

TIME OF TREATMENT WITH SILVER NITRATE	Ag_s	Ag_l	Na_l	$\rho \times 10^4$
5 min.	1.63	0.0833	(0.0084)	−2
1 hr.	1.72	0.0843	(0.0088)	−3.2
20 hrs.	1.80	0.0824	(0.0084)	−2
45 hrs.	1.79			

Ag_s = silver taken up by the aluminum silicate (millimoles per gram). Ag_l, Na_l = concentrations of silver and sodium respectively in the solution. ρ = check of experimental accuracy.

TABLE 2

Comparison of silver taken up with sodium given off

SAMPLE	$NaNO_3$ 1ST DECANT	$NaNO_3$ 2ND DECANT	$NaNO_3$ 3RD DECANT	$NaNO_3$ 4TH DECANT	$NaNO_3$ 5TH DECANT	$NaNO_3$ 6TH DECANT	$NaNO_3$ TOTAL	Ag FOUND	$\rho \times 10^3$
1	1.54	0.17	0.06	0.01	0.00	0.00	(1.78)	1.76	−1.5
2	1.55	0.17	0.06	0.01	0.00	0.00	(1.79)	1.76	−1.7

Demonstration that the process is an exchange of silver with sodium

Table 2 gives the sodium nitrate found in the successive decants of an experiment consisting of six treatments of a gel from 100 cc. of suspension with 100 cc. of 1 *N* silver nitrate solution. The silver was precipitated from the decants as silver chloride and the sodium nitrate in the filtrates estimated by evaporation and conversion to sodium chloride upon repeated evaporation with concentrated hydrochloric acid. The total sodium is then compared with the amount of silver which has entered the precipitate, as determined by the titration of the final gel for silver. The value for silver in the precipitate, 1.76 millimoles per gram, agrees favorably with the values, 1.78 and 1.79 millimoles per gram of precipitate, obtained for sodium in the decants, and shows that the process is a true exchange of silver for sodium. We may conclude from this that the amount of nitrate ion entering the precipitate during an experiment is negligibly small.

From the method of preparation of the suspension, i.e., removal of all foreign salts by repeated decanting, it is to be expected that the nitrate-ion content in the precipitate should be negligibly small. A colorimetric test showed that the amount of nitrate ion was of the order of 0.005 millimole per gram. Since the nitrate ion does not form complexes either with silica or alumina, and since there is a large *negative* charge on the particle, it is probable that this small amount of nitrate ion has been retained in the interior of the precipitated particles and is thereby prevented from escaping because of steric hindrance.

Part of the sodium sterically hindered

The question arises here as to whether all the sodium contained in the precipitate can be exchanged or not. In this connection a determination of the cation-exchange capacity gave 1.79 millimoles per gram, while an analysis made at the same time on the same sample gave 2.01 millimoles per gram. It then appears that there is a small amount of sodium, i.e., 2.01 – 1.79 or 0.22 millimole per gram not exchangeable for silver. It may be noted that this non-exchangeable sodium in the precipitate must be considered as forming such a part of the interior structure as to be thereby prevented from exchanging because of steric hindrance.

Cation-exchange capacity as a function of the age of the aluminum silicate

We will now discuss the cation-exchange capacity as a function of the age of the aluminum silicate. Experiments on the freshly prepared suspension of table 2 gave the value 2.11 millimoles per gram, while the experiments of table 2, which were performed from three to four months later, gave 1.76 millimols per gram. This change was checked by an analysis of the supernatant liquid from the suspension after standing for this period. This gave for sodium in the liquid phase 0.38 millimole per gram of precipitate in the suspension, which agrees well with the difference $2.11 - 1.76 = 0.35$. At this point it is of interest to note that the dry residue (red heat) found in the supernatant liquid was 5.9 per cent of the dry weight (150°C.) of the total precipitate. The relative amounts of the various constituents are given in table 3. It will be seen that the relative amounts of Al_2O_3 and SiO_2 are rather closely the same in the two cases, but that there is considerably more Na_2O in the residue from the supernatant liquid than in the precipitate itself. The ratio by weight of silica to alumina in the case of the precipitate is 2.8 to 1, while in the case of the residue from the supernatant liquid it is 3.1 to 1. It is of interest to compare this fact of a nearly unchanged ratio of silica to alumina with the theory of Mattson, who maintains that the weathering always proceeds in such a way that the isoelectric point is approached. From Mattson's work one would expect a considerably larger ratio of silica in the supernatant liquid than in the precipitate itself. According to Mattson's principle of the isoelectric weathering, a precipitate is most stable at the pH corresponding to the isoelectric point. The isoelectric point of our suspension is a little greater than 4, as shown by figure 2. However, on bringing the suspension to the isoelectric point by adding the calculated amount of nitric acid, it was found that about 10 per cent of the alumina and about 1 per cent of the silica were dissolved. This fact indicates that the isoelectric point is not the pH at which the suspension is most stable. This leads one to the conclusion that the factors governing the stability of the alumina–silica complex are not mainly electrostatic, but also depend considerably on the chemical constitution of the system.

TABLE 3

Relative amounts of the various constituents

CONSTITUENT	PRECIPITATE	DRY RESIDUE FROM THE SUPERNATANT LIQUID
	per cent	*per cent*
SiO_2	60.33	60.2
Al_2O_3	21.64	19.6
Na_2O	4.11	20.2
H_2O	13.92	

Measurement of the equilibrium relations for silver–sodium

Having considered the question of the cation-exchange *capacity* of the aluminum silicate with respect to the exchange of silver and sodium, a word now will be said with regard to the equilibrium states in which only part of the exchangeable sodium has been exchanged for silver. Table 4 gives a summary of some experimental results. The quantities present are the same as those of table 1. In figure 1 the logarithm of the ratio of the concentrations of sodium to silver in the liquid phase, $\log \left[\frac{(Na)}{(Ag)}\right]_l$, is plotted against the logarithm of the ratio sodium to silver taken up by the precipitate, $\log \left[\frac{(Na)}{(Ag)}\right]_s$, as calculated from the values of the saturation capacity obtained experimentally. Two straight lines are found, one for the freshly prepared suspension, another for the suspension from twelve to sixteen weeks old. Several points of intermediate age are also found. It will be noted that, in the case of the suspension from twelve to sixteen weeks old, the points are much more diffusely scattered than is the case for the freshly prepared precipitate.

TABLE 4

Measurement of equilibrium relations for silver-sodium

EXPERIMENT	SAMPLE	Ag_s	Ag_l	Na_l	$\rho \times 10^3$	TIME OF ROTATION
						hours
1	2	1.80	0.0824	(0.0093)*	−2	20
2	1	1.81	0.0816	(0.0071)	−1.1	20
2	2	1.52	0.0380	(0.0384)	−0.8	20
2	3	1.58	0.0317	(0.0170)	−0.8	20
3	1	1.97	0.0762	(0.0165)	−1.5	20
3	2	1.80	0.0388	(0.0688)	−2.7	20
3	3	1.18	0.0404	(0.511)	−3.7	20
3	4	1.12	0.0409	(0.510)	−2.9	20
3	5	0.29	0.0508	(5.10)	−5.4	20
3	6	0.30	0.0509	(5.00)	−6.7	20
4	1	1.83	0.02281	(0.0237)		15
4	1	2.12	0.1472	(0.0313)	−1.4	20
4	2	1.87	0.02447	(0.0239)		15
4	2	2.10	0.1498	(0.0298)	−0.1	20
6	1	(1.54)	0.910	0.0105		2
6	1	(1.71)	0.990	0.0012		15
6	1	1.75	0.997	0.0004	−2.7	20
6	2	(1.54)	0.909	0.0105		2
6	2	(1.71)	0.990	0.0012		15
6	2	1.75	0.999	0.0004	−4.8	20
6	3	(1.54)	0.908	0.0104		2
6	3	(1.71)	0.991	0.0013		15
6	3	1.77	1.000	0.0005	−3.5	20
7	1	(1.54)	0.911	0.0104		2
7	1	(1.71)	0.991	0.0012		15
7	1	(1.77)	0.998	0.0004		20
7	1	(1.78)	0.999	0.0001	−3.5	20
7	2	(1.55)	0.912	0.0105		2
7	2	(1.72)	0.990	0.0012		15
7	2	(1.78)	0.999	0.0004		20
7	2	(1.79)	1.000	0.0001	−4.5	20
8	1	0.19	0.1121	(3.589)	−1	
8	2	0.20	0.1117	(3.582)	−2	20
8	3	0.48	0.1452	(0.926)	−1	20
8	4	0.52	0.1446	(0.995)	−3	20
8	5	1.42	0.1528	(0.0104)	−0.5	20
8	6	1.44	0.1529	(0.0105)	−3	20
9	2	1.30	0.533	(0.432)		20
9	3	0.74	0.0866	(0.765)		20
9	5	0.14	0.0673	(0.873)		20
9	6	0.13	0.0673	(0.872)		20

Ag_s = millimoles of silver in the precipitate per gram of sodium precipitate used. Ag_l = concentration of silver in the liquid phase. Na_l = concentration of sodium in the liquid phase.

* All numbers in parenthesis are not directly measured.

Titration of the aluminum silicate

Several samples of the suspension were prepared. One contained only water[3] as suspending agent. The others contained various added electrolytes, sodium nitrate, sodium chloride, potassium chloride, silver nitrate, calcium nitrate, barium nitrate, and lanthanum nitrate, each of a concentration of 0.1 *N*. The pH values of these samples were determined. The results of these determinations are shown in table 5. A number of titration curves with the addition of 0.1 *N* nitric acid and sodium hydroxide solutions were made on each of these samples of the suspension (see table 6). The titrations of the suspension containing silver nitrate were performed with the glass electrode. In that case neither hydrogen nor quinhydrone electrodes can be used, the hydrogen electrode because of the presence of the NO_3^- ion, and the quinhydrone electrode because of the reduction of silver nitrate to metallic silver. In all the other cases the quinhydrone

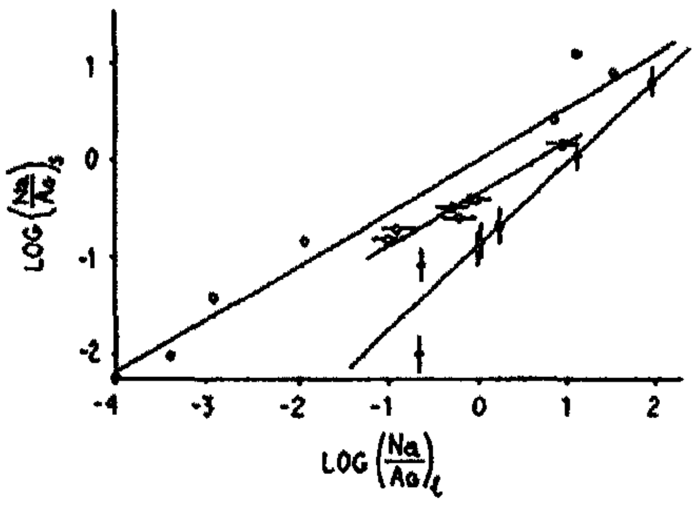

FIG. 1

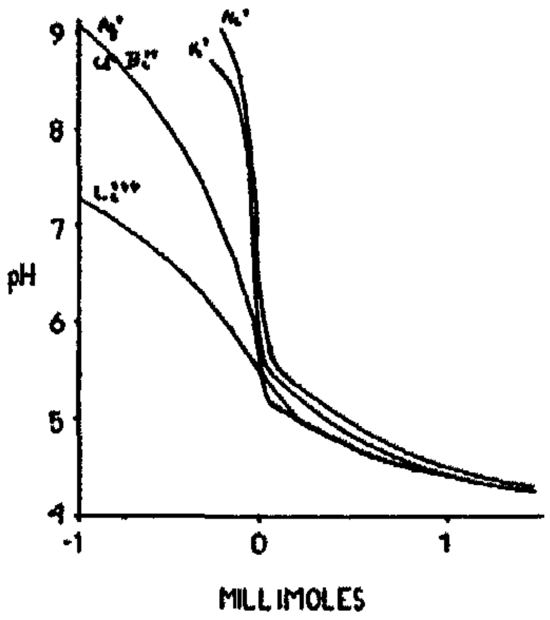

FIG. 2

FIG. 1. Equilibrium relations for the exchange of silver and sodium. The logarithm of the ratio of the concentration of sodium to silver in the liquid phase, $\log\left[\frac{Na}{Ag}\right]_l$ is plotted as abscissa against the logarithm of the ratio of the same elements in the solid phase, $\log\left[\frac{Na}{Ag}\right]_s$, as ordinate. ϕ represents points for the freshly prepared suspension; o represents points for the suspension from twelve to sixteen weeks old; -o- represents points for the suspension of intermediate age.

FIG. 2. Titration curves for the aluminum silicate suspension containing various ions in one-tenth normal solutions. The pH is plotted against the amount of 0.1 *N* nitric acid or 0.1 *N* sodium hydroxide added expressed in millimoles per gram of precipitate dried at 150°C.

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[3] Sodium is present in the equilibrium concentration of about 0.004 *N*, after centrifuging and decanting the suspension from twelve to sixteen weeks old.

electrode was used. Comparison was made between the glass and the quinhydrone electrode for the case of the suspension containing sodium chloride, and a pH value of 6.36 was found for the quinhydrone electrode compared with 6.37 found for the glass electrode. Table 6 gives the pH as a function of the amount of acid added to each suspension. The first column gives the salt used, the second the amount of acid added in millimoles per gram of precipitate (dried at 150° C.), and the last the corresponding pH. In all cases 0.840 g. of precipitate, 0.0843 N nitric acid, and an original volume of 100 cc. were used.

It was found that the reproducibility of the experiments was poor on the basic side of the pH range. As an example of the dependence of minor factors on the resulting pH in this region, the following example is cited. Using a sample of suspension containing 0.1 N sodium chloride, if 2 cc. of 0.1115 N sodium hydroxide is added all at once the resulting pH is 8.58, but if it is added in amounts of 0.5 cc. at intervals of ten minutes, the value obtained is 8.74.

TABLE 5

*Values of pH in untitrated suspensions**

SUSPENSION CONTAINED IN	pH
Water	7.7 (hydrogen electrode)
	7.68 (quinhydrone electrode)
	7.73 (glass electrode)
	7.69† (quinhydrone electrode)
	7.71† (glass electrode)
$NaNO_3$ (0.1 N)	6.39
NaCl (0.1 N)	6.36
KCl (0.1 N)	6.35
$AgNO_3$ (0.1 N)	5.98
$Ca(NO_3)_2$ (0.1 N)	5.99
$Ba(NO_3)_2$ (0.1 N)	6.00
$La(NO_3)_3$ (0.1 N)	5.58

* All numbers not specifically noted were obtained by use of the quinhydrone electrode.

† These values were obtained after the suspension had been "purified" by centrifuging, adding water to same volume as before, and allowing to stand one hour.

Figure 2 shows the results which are considered to be best for the different ions in the 0.1 N solution. The pH is plotted against the amount of nitric acid and of sodium hydroxide added (both in millimoles per gram of precipitate). Examining these curves it will be noted that the lower the pH the less the specific effect due to each ion. This is to be expected, since the more acid the suspension the lower the net electrical charge and hence the specific effects, which are assumed to be in part electrostatic, will be

TABLE 6

Titration of the suspension with nitric acid (0.0843 N) using quinhydrone electrode

In all cases, weight of precipitate = 0.840 g. and original volume = 100 cc.

SALT	ACID ADDED IN MILLIMOLES PER GRAM	pH*	MEAN
No salt	0.00	7.70†	
	0.10	6.96	
	0.20	6.48	
	0.50	5.66	
	1.00	3.85	
	1.51	3.32	
$NaNO_3$ (0.1*N*)	0.00	6.69	
	0.10	6.02	
	0.20	5.73	
	0.50	5.08	
	1.00	4.49	
	1.51	4.23	
NaCl (0.1 *N*)	0.00	6.38	
		6.36	6.37
		6.36	
		6.39	
	0.10	5.89	
		5.89	5.89
		5.89	
		5.86	
	0.20	5.53	
		5.51	5.50
		5.48	
		5.47	
	0.50	4.96	
		4.98	
		4.93	4.94
		4.90	
	1.00	4.57	
		4.57	
		4.52	4.57
		4.60	
NaCl (0.1 *N*)—*Concluded*	1.51	4.32	
		4.30	4.30
		4.30	
		4.29	
KCl (0.1 *N*)	0.00	6.34	
		6.38	6.35
		6.35	
		6.34	
	0.10	5.77	
		5.78	5.78
		5.80	
		5.76	
	0.20	5.42	
		5.41	5.40
		5.39	
		5.39	
	0.50	4.83	
		4.84	4.83
		4.84	
		4.80	
	1.00	4.42	
		4.42	
		4.44	4.43
		4.46	
	1.51	4.25	
		4.26	
		4.25	4.26
		4.27	
$AgNO_3$ (0.1 *N*)	0.00	5.98	
	0.10	5.43	
	0.20	5.14	

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* Each number shows an individual experiment. Thus in many cases it can be seen how much the values varied upon repetition.

† This value is the mean of the values obtained from the glass and quinhydrone electrodes.

TABLE 6—*Concluded*

SALT	ACID ADDED IN MILLIMOLES PER GRAM	pH*	MEAN	SALT	ACID ADDED IN MILLIMOLES PER GRAM	pH*	MEAN
$AgNO_3$ (0.1 *N*)—*Concluded*	0.50	4.69		$Ba(NO_3)_2$ (0.1 *N*)—*Concluded*	0.20	5.12	
	1.00	4.41			0.50	5.67	
	1.51	4.24			1.00	4.38	
					1.51	4.21	
$Ca(NO_3)_2$ (0.1 *N*)	0.00	5.99					
	0.10	5.39		$La(NO_3)_3$ (0.1 *N*)	0.00	5.58	
	0.20	5.10			0.10	5.27	
	0.50	4.67			0.20	5.05	
	1.00	4.24			0.50	4.69	
					1.00	4.38	
$Ba(NO_3)_2$ (0.1 *N*)	0.00	5.99			1.51	4.21	
	0.10	5.42					

reduced. It will also be noted that nearly the same curve is found for the sodium and potassium ions and likewise one for silver, calcium, and barium ions. It is not understood why silver ion follows the curve for the divalent ions calcium and barium, but it must be supposed that there are specific effects which lead to this result.

From the curves of figure 2 we may calculate, on the basis of the considerations and postulates made in the theoretical section, the relations between the cation-exchange capacity and the pH. From the experimental results the value of the amount of exchangeable sodium ions in the untitrated suspension, to which neither acid nor base have been added, is 1.78 millimoles per gram. This value was found by treating the suspension with silver nitrate. Figure 3 shows the results of these calculations. The cation-exchange capacity, *S*, is plotted against the pH for 0.1 *N* solutions of the various cations in the suspension.

To check this relation between the pH and the cation-exchange capacity, calculated from the titration experiments, the amount of sodium ions exchangeable with silver ions has been measured at pH 5.10 in 0.1 *N* sodium chloride, and found to be 1.38 millimoles per gram. According to the curve in figure 3, we see that at pH 5.10 the value 1.37 is found and, conversely, at the cation-exchange capacity of 1.38 millimoles per gram the pH 5.08 is given. This agreement is very close and perhaps is better than should be expected.

Reversibility of titration

The question of the reversibility of these titrations is of interest. In order to determine this, the suspensions containing 0.1 *N* sodium and potassium chlorides respectively were titrated back after first having been titrated forward with acid and base, respectively. Figure 4 shows the

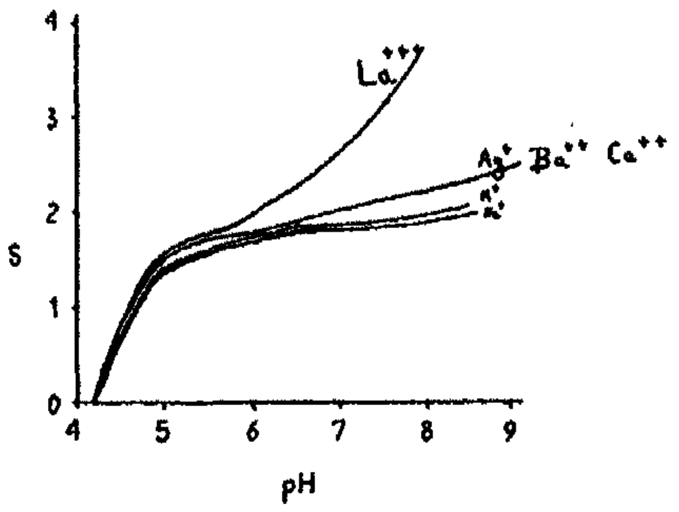

FIG. 3

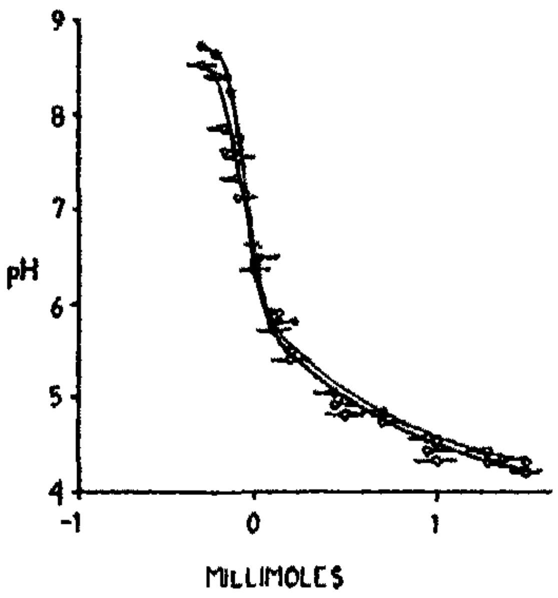

FIG. 4

FIG. 3. Relation between the cation-exchange capacity, *S*, and pH for one-tenth normal solutions of the various cations in the suspension.

FIG. 4. Titration of the aluminum silicate suspension in tenth normal solutions of potassium chloride and sodium chloride, showing back titration points. ○ represents the forward titration for sodium; -○- represents the forward titration points for potassium; -○ represents the back titration points for sodium; ○- represents the back titration points for potassium. In one case, where there may be ambiguity, the back titration points for Na⁺ and K⁺, after the addition of base, are shown by |-○ and ○-| , respectively.

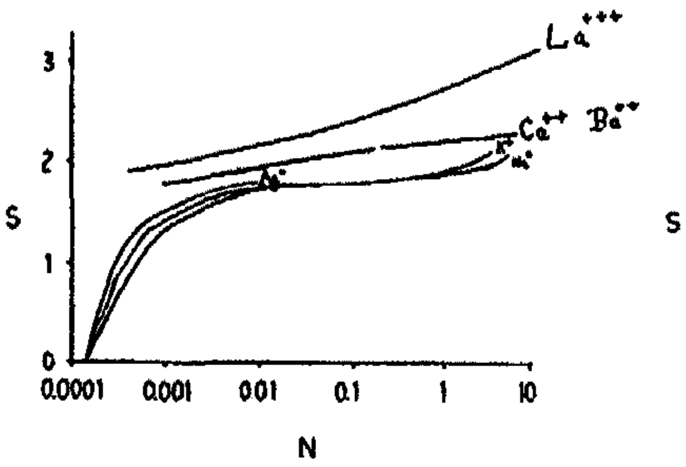

FIG. 5

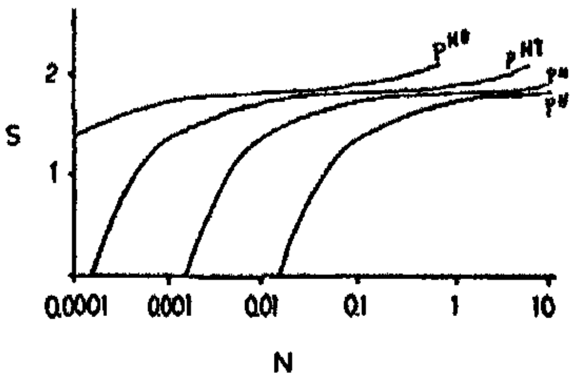

FIG. 6

FIG. 5. The relation between the cation-exchange capacity, *S*, and the salt concentration, *N*, at pH = 7

FIG. 6. The relation between the cation-exchange capacity, *S*, and the salt concentration, *N*, in the case of sodium ion at several pH values.

results of these experiments. It will be noted that there is a certain degree of irreversibility in the curves on the basic side of the pH range, but that the irreversibility is negligible on the acid side. From this fact and the difficulty in obtaining reproducibility on the basic side, we may conclude that the precipitate is unstable in such solutions. Considering further the results of the breaking down of the precipitate and its solubility in acid solutions near the isoelectric point, it seems that the pH of maximum stability must lie at neutrality or at a somewhat lower pH. Comparable results have been obtained by Riehms on clays.

It has been thought of interest to calculate the relation between the cation-exchange capacity, *S*, and the cation concentration, *N*, for a given pH, say 7 (see theoretical part). The results of these calculations are shown in figure 5. The cation-exchange capacity is plotted against the logarithm of the cation concentration. The values of the logarithms are not expressly given in figure 5, which shows only the values of the concentrations from which the logarithms were calculated. Figure 6 gives the same relation for sodium ion at several pH values.

SUMMARY

The theoretical aspects of the colloidal aluminum silicate particle are discussed. It is shown that the cation-exchange capacity will depend upon the pH of the suspending solution and upon the nature and concentration of salts present in the solution.

Experimentally, a single type of aluminum silicate was prepared. The conditions of preparation of this aluminum silicate are given in detail. The method of experimentation for the direct measurement of silver taken up by the aluminum silicate is explained. It is demonstrated that the process is a mole-for-mole exchange of silver for sodium, and that a small part of the sodium is non-exchangeable by silver. It is pointed out that the cation-exchange capacity depends on the age of the sample. The equilibrium relations where only part of the silver has been exchanged have been measured and discussed. pH determinations and titration curves were made on the suspension containing a number of salts in tenth normal solution. Calculations based on the theoretical picture were made and discussed.

The author wishes to express his sincerest appreciation to Prof. N. Bjerrum and to the American Scandinavian Foundation for making possible the carrying out of the above research.

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CATHODE POLARIZATION AS A FUNCTION OF THE CURRENT DENSITY IN FUSED SALTS

18-114

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Cathode polarization in fused salts has been studied very little up to the present time. There is one paper by Aten and others (1), but Aten was interested only in the relation between the cathode potential and the current density in connection with the character of cathode deposits obtained from fused salts. Our method of experimenting was the same in principle as that used by Aten. The fused salt in a porcelain crucible was placed in an electric furnace with the carbon electrodes—cathode and anode—passing through the opening in the cover of the furnace. The potential was measured between an auxiliary electrode and the cathode at various current densities. The auxiliary electrode was constructed in the following way. The fused metal being plated was placed at the bottom of a quartz test tube with capillary jet at the side which was closely pressed to the cathode. The test tube was filled with fused electrolyte through the capillary jet; thus a lead or cadmium electrode was obtained. The contact of liquid metal in the test tube with the wires connected to the potentiometer was made by means of an iron wire. This wire was enclosed in a porcelain capillary in order to prevent contact of the iron wire with the fused electrolyte. We measured the resistance of the cathode in order to make the necessary correction. In this measurement the cathode was at the same temperature condition as that during the investigation at cathode polarization. The highest possible error was 0.01–0.02 Ω in the determination of cathode resistance.

In the case of lead chloride the curve $E_{\text{cath}} = f$ (current density) has the form shown in figure 1. It is seen that the potential of the cathode is more positive than the potential of the auxiliary electrode at comparatively low current densities. The cathode potential becomes less and less positive by increasing the current density and finally equals the potential of the auxiliary electrode (figure 1, point *A*). The current density at point *A* is equal to 0.2–0.15 ampere per square centimeter. Thus electrolysis of fused lead chloride at significant current densities can take place when the difference of the potentials between the electrodes is less than the E.M.F. of the system Pb($PbCl_2$ fused) Cl_2. The effect indicated was previously noticed by R. Lorenz (3), who explains the phenomenon as a depolarizing action. This is confirmed by the fact that we were able by saturating the fused lead chloride with metallic lead to reduce the current density, at which the curve $E_{cath} = f$ (current density) crosses the axis of the ordinates, from 0.2 amp. to 0.015 amp. It is known that lead chloride can "dissolve" a significant quantity of metallic lead. R. Lorenz supposed that in this case an emulsion of the lead is formed in the fused salt. However, Eitel and Lange (2) showed that the metal is not in colloidal form, but in true solution. The solution of the metal in the fused salt is explained by these authors by the formation of compounds of metallic lead with lead chloride.

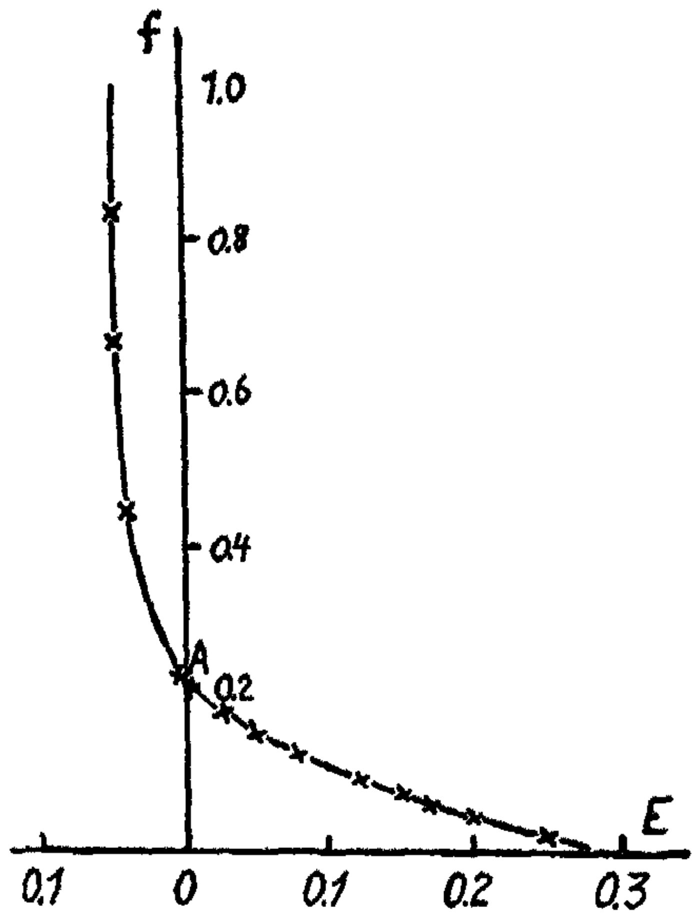

FIG. 1

The part of the curve that lies in the region of the positive values of potential can be explained by assuming that during the dissolution of metallic lead in the fused salt monovalent lead ions are formed. Consequently it is possible that in the case of absence of metal in fused salt during electrolysis the discharge of Pb^{++} ions to Pb^{+} ions took place at the cathode. The potential of the cathode may be expressed in the following form:

$$E = a - \frac{RT}{F} \ln \frac{C_{Pb^{+}}}{C_{Pb^{++}}} \qquad (1)$$

where a is constant, and $C_{Pb^{+}}$ and $C_{Pb^{++}}$ are the concentrations of the mono- and bi-valent ions near the cathode.

Reasoning by analogy from the case of concentration polarization in water solutions, C_{Pb^+} and $C_{Pb^{++}}$, and placing their values in equation 1 we have

$$E = a - \frac{RT}{F} \ln \frac{K_1D - C_0}{C_0^1 - K_2D}$$

Here K_1 and K_2 are constants at a given temperature; C_0 and C_0^1 are the concentrations of the ions Pb^+ and Pb^{++} in the mass of the electrolyte. C_0 is insignificant (the fused salt was not in contact with the metal). Dividing the numerator and the denominator of the logarithmic fraction by C_0^1 and combining all constants in a, we shall finally have:

$$E = a - \frac{RT}{F} \ln \frac{D}{1 - KD} \tag{2}$$

The value of the constant a is determined by the condition that the difference of the potentials between cathode and auxiliary electrode is zero at a certain current density, D_0 (point A, figure 1).

$$a = \frac{RT}{F} \ln \frac{D_0}{1 - KD_0}$$

Putting the value of a in equation 2 we shall have:

$$E = \frac{RT}{F} \ln \frac{D_0 (1 - KD)}{(1 - KD_0) D} \tag{3}$$

The results of the experiments with fused lead chloride at 600°C. and the values of the constant K are shown in table 1.

The part of the curve $E = f$ (current density) was studied for fused lead chloride in the region of the negative values of potential in experiments 2, 4, and 5 at 550°C. The results of these experiments are shown in table 2.

In a given case the relation $E = f$ (current density) may follow an equation of the form $E = a - b \ln D$. The coefficient b has the following values:

exp.	2	4	5
b	0.0348	0.0391	0.0417

From the figures given it is seen that the coefficient b is approximately equal to the quantity $RT/2F$, which has the value 0.0354 at 550°C.

The relation obtained can be explained by supposing that in the region of the negative values of the potential the process $Pb^{++} + 2\Theta \rightarrow Pb$ on the cathode plays the coördinal rôle. In this case we can suppose that atoms of the metal which are formed at the cathode remain near it in the dissolved state and then these atoms condense in droplets with a certain definite speed (the fused metal did not wet the carbon cathode). In connection with the above view, we can write the following expression for the potential of the cathode:

$$E = a - \frac{RT}{2F} \ln \frac{C_{Pb}}{C_{Pb^{++}}}$$

TABLE 1

Results of experiments with fused lead chloride at 600°C.

E	EXPERIMENT 1		EXPERIMENT 2		EXPERIMENT 3		EXPERIMENT 4	
	D	K	D	K	D	K	D	K
volts	amp./sq. cm.		amp./sq. cm.		amp./sq. cm.		amp./sq. cm.	
0.000	0.150		0.153		0.170		0.200	
0.025	0.130	4.00	0.130	3.50	0.150	3.84	0.180	3.54
0.050	0.107	3.74	0.110	3.95	0.137	4.32	0.157	3.44
0.075	0.090	3.96	0.093	3.97	0.120	4.40	0.140	2.92
0.100	0.073	3.76	0.087	4.00	0.107	4.74	0.117	3.64
0.125	0.063	4.40	0.067	4.40	0.097	4.78	0.100	3.73
0.150	0.050	4.40	0.060	4.80	0.083	4.21	0.087	3.90
0.175	0.040	4.50	0.050	5.05	0.067	3.40	0.073	3.99
0.200	0.033	4.70	0.040	5.02	0.043	4.84	0.057	3.97
0.250	0.020	4.90	0.023	5.05	0.023	4.34	0.030	3.69

TABLE 2

Results of experiments with fused lead chloride at 550°C.

EXPERIMENT 2		EXPERIMENT 4		EXPERIMENT 5	
E	D	E	D	E	D
volts	amp./sq. cm.	volts	amp./sq. cm.	volts	amp./sq. cm.
0.009	0.160	0.001	0.225	0.015	0.614
0.011	0.186	0.014	0.279	0.029	0.837
0.017	0.213	0.029	0.446	0.033	1.000
0.027	0.264	0.048	0.670	0.035	1.115
0.033	0.422	0.052	0.837	0.044	1.228
0.044	0.527			0.048	1.396
0.052	0.580			0.052	1.507
0.060	0.738				

C_{Pb} is the concentration of the atoms of lead which are in the dissolved state near the cathode. Regarding the value $C_{Pb^{++}}$ as constant, we shall have:

$$E = a - \frac{RT}{2F} \ln C_{Pb} \qquad (4)$$

Assuming at each current density an equality between the speed of discharge of the ions Pb^{++} and the speed of condensation of the dissolved metallic atoms, we shall have:

$$KD = C_{\mathrm{Pb}} - C_0 \tag{5}$$

where C_0 is the value of a concentration corresponding to equilibrium at a given temperature. Placing the magnitude C_{Pb} in the expression of potential and making some simplification, we shall finally have:

$$E = a - \frac{RT}{2F} \ln (1 + K_1 D) \tag{6}$$

If the constant K_1 is great enough, equation 6 may be written thus:

$$E = a - \frac{RT}{2F} \ln D \tag{7}$$

The curve $E = f$ (current density) in fused cadmium chloride is similar to the corresponding curves for lead chloride, only here the curve intersects the axis of the ordinates at greater current density (experiment 6). Saturating the fused cadmium chloride with metallic cadmium (experiment 7) we succeeded in reducing the value of this current density almost to zero; thus the total curve lies in the region of negative values of the potential.

TABLE 3

Results of experiments with cadmium chloride

EXPERIMENT 6		EXPERIMENT 7			
E	*D*	*E*	*D*	*E*	*D*
volts	*amp./sq. cm.*	*volts*	*amp./sq. cm.*	*volts*	*amp./sq. cm.*
+0.120	0.006	−0.016	0.002	−0.084	0.044
+0.113	0.024	−0.022	0.006	−0.104	0.048
+0.081	0.045	−0.033	0.010	−0.117	0.066
+0.060	0.084	−0.048	0.014	−0.132	0.088
+0.033	0.253	−0.053	0.018	−0.141	0.110
+0.026	0.353	−0.067	0.026	−0.150	0.132
+0.004	0.446	−0.073	0.034	−0.157	0.170
−0.027	0.670				

The results of experiments 6 and 7 can be seen in table 3. In cadmium chloride the dependence $E = f(D)$ also seems to follow an equation of the form $E = a - b \ln D$. The coefficient b is equal to 0.0435 (experiment 6) and to 0.0348 (experiment 7), i.e., to $RT/2F$. In the region of the negative values of the cathode potential (experiment 7) the existence of the indicated relation can be explained in a similar way to that of chloride. The relation

$$E = a - \frac{RT}{2F} \ln D$$

for cadmium chloride, which is not saturated with metallic cadmium (experiment 6), can be explained by supposing that by dissolving the metallic cadmium in its chloride salt the formation of the ions Cd^+ does not take place; thus on the cathode the process $Cd^{++} + 2\ominus \rightarrow Cd$ takes place. In connection with this, at all current densities the velocity of formation of the cadmium atoms will equal the velocity of their diffusion in the mass of the electrolyte. Thus we can write:

$$KD = C_{Cd} - C_0$$

where C_0 is the concentration of the cadmium atoms in the mass of the electrolyte. Determining the concentration of the cadmium atoms near the cathode, C_{Cd}, we obtain

$$C_{Cd} = KD + C_0$$

If C_0 is very small (the fused salt was not in contact with the metal), we shall finally have:

$$E = a - \frac{RT}{2F} \ln D$$

RÉSUMÉ

The cathode polarization in fused salts of lead chloride and cadmium chloride has been experimentally studied. The part of the curve $E = f(D)$, lying in the region of the positive values of the potential, is explained by the slowness of the diffusion process of Pb^+ ions or cadmium atoms from the cathode in the mass of the electrolyte.

In the region of the negative values of the potential the relation $E = f(D)$ can be expressed by the equation

$$E = a - \frac{RT}{2F} \ln D$$

We have explained the equation of this form by the slowness of condensation of the lead or cadmium atoms which are formed at the cathode in the liquid.

In conclusion we desire to express our thanks to Prof. A. N. Frumkin for his attention to this work.

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OXIDATION PROCESSES AT THE CATHODE

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The nature of the cathodal deposits in the electrolytic deposition of metals depends upon the conditions of the electrolysis. The same metal may deposit itself either in a solid smooth layer or in the form of crystals which grow into dendrites. At times the electrolysis is accompanied by the formation of a spongy mass on the cathode; sometimes the deposit takes the form of an entirely black porous powder.

With high current densities the deposition of metals takes place from dilute solutions in the form of porous, black, highly dispersed powders. Although this phenomenon has been known for a long time and a considerable amount of work has been done in this field, the problem is still not entirely cleared up.

The deposition of a black powder-like deposit on the cathode has been reported by many authors. As far back as in 1848 Poggendorf (12) reported the deposition of silver-black. Somewhat later Mylius and Fromm (8) described the formation of black deposits of platinum, zinc, cadmium, and lead. Later similar deposits were obtained for a number of other metals. We may now state definitely that under certain conditions black deposits can be obtained with almost all metals which form deposits on the cathode in electrolysis.

In a study of the cathodal processes in the electrolysis of copper salt solutions, one of the authors (6) found a definite relation between the concentration, the current density, and the time of the appearance of the black deposit. The observed regularity in the time when the deposit changes its appearance is undoubtedly connected with its structural and chemical composition. The authors have now studied in detail the structure and composition of the black deposits, using the röntgenographic method.

Black deposits of copper, zinc, cadmium, and silver, which settled out from dilute solutions of various salts at high current densities, were obtained. The reagents used were of "C.P. for analysis" grade. The experiments were carried out at room temperature. A 100-cc. beaker was used for a bath. The anode was a spiral of the metal and was placed at the wall of the beaker, surrounding on all sides the cylindrical platinum cathode in the center of the beaker. This arrangement gave a uniform current density on the cathode (= 1 amp. per square centimeter). The porous black deposit of the metal (about 2 mm. thick), which settled out during the electrolysis, was quickly removed with the cathode to a beaker of hot distilled water and at once taken off from the electrode with a glass rod. The cathode was put back into the solution and the experiment was repeated until a sufficient quantity of deposit was collected. This was washed with hot water, dried between sheets of filter paper, and packed in a slightly damp state into straws for analysis by Debye's method.

The x-rays were obtained from Hadding's ionic tube with a copper anode and filtered through a nickel-filter; after filtration only the K_α rays with an average wave length of $\lambda_\alpha = 1.539$ A.U. remained. The röntgenogram data were calculated as the average values of four objective measurements. The error in the calculation of the parameters did not exceed 0.003-0.005 A.U.

It is characteristic of almost all the röntgenograms made that additional diffraction rings were present, and it was established that these were due to oxides. The relative intensities of the diffraction rings of the metals and their oxides were not always the same. The difference depends upon the chemical nature of the metal as well as upon the nature of the electrolyte from which the metal was deposited.

In general, the presence of oxides in electrolytic deposits is a well established fact (1, 3, 5), but the causes of their appearance are not fully investigated. Applying the relative intensity of the diffraction rings of the metals and their oxides as a criterion, we have determined the approximate content of oxides in various deposits. *The copper deposits* were studied most extensively. They consisted of metallic copper and of cuprous oxide. In none of the röntgenograms was cupric oxide discovered. Both copper and cuprous oxide were in a high state of dispersion, since the rings of the röntgenograms were slightly diffuse. Copper deposits were obtained from solutions of the nitrate, sulfate, and chloride and also the baked deposit from the nitrate. The results are given in table 1.

Table 1 shows that the deposits contain a considerable quantity of cuprous oxide. Foerster and Seidel (3), who first observed cuprous oxide in deposits of copper, gave an explanation for its formation. When cupric sulfate is electrolyzed under certain conditions, the cupric ion at the cathode is reduced to cuprous ion and cuprous sulfate is formed; the latter is hydrolyzed and cuprous oxide formed. R. Luther (7) supports this scheme. The results of our investigations, however, do not harmonize with this point of view. The comparison of the cuprous oxide contents of various deposits leads us to believe that the cuprous oxide is formed as a result of oxidation, which is effected mainly by the anion. The higher the oxidizing power of the anion, the greater the oxide content in the precipitate. Besides this factor, other oxidizing factors are also taking part, as is shown by the presence of cuprous oxide in the deposits resulting from the chloride solution. Evidently the cupric cation and the hydroxyl ions of the solvent are also capable of exerting an oxidizing effect. It is possible that a hydrolysis process is also taking place, according to Foerster's scheme, but it seems to play a secondary rôle.

It is very interesting to note that both copper and cuprous oxide in the precipitates have greatly increased parameters of the crystalline grating. These increases vary with a certain regularity, the lower the oxide content in the precipitate the greater being the increase in parameter. At the same time the percentage increase in the parameters of copper and cuprous oxide of the same precipitate is almost the same. The increase in parameter is evidently due to the penetration of hydrogen into the crystalline grating, with the formation of so-called solid solutions of the second order,—hydrogen dissolved in copper and in cuprous oxide. Electrolysis at high current densities occurs in conditions which are exceptionally favorable for the formation of solid solutions of hydrogen. The deposits settle out in a highly dispersed state. Parallel with the settling out, a discharge of the hydrogen ions takes place at the cathode and every crystalline particle of precipitate contains hydrogen on its surface during the whole process of growth. The higher the concentration of hydrogen on the growing particle, the greater is the quantity of hydrogen which will imbed itself into the crystalline grating and the greater the increase in the parameter. Simultaneously with this, secondary oxidizing factors are active at the cathode, affecting the particles of the precipitate as well as the hydrogen on their surface. Evidently, the more active the oxidizing factors are, the less hydrogen will be dissolved in the precipitate and the more oxides will be present.

TABLE 1

Results of the röntgenographic investigations

KIND OF COPPER DEPOSIT	Cu_2O			Cu		
	Approximate per cent in precipitate	Parameter of the grating	Per cent increase of parameter	Approximate per cent in precipitate	Parameter of the grating	Per cent increase of parameter
	per cent	*A.U.*		*per cent*	*A.U.*	
Precipitate from the nitrate.........	40–45	4.279	0.45	55–60	3.627	0.47
Precipitate from the sulfate.........	25–30	4.290	0.70	70–75	3.636	0.72
Precipitate from the chloride........	10–15	4.300	0.94	85–90	3.642	0.90
Baked deposit from the nitrate......	40–45	4.266	0.14	55–60	3.621	0.30

Copper and cuprous oxide crystallize in the cubic system. The normal parameters are: for copper $a = 3.61$ A.U.; for cuprous oxide $a = 4.26$ A.U.

From this point of view it is clear that the greatest increase in the parameters of copper and cuprous oxide should be observed with the chloride solution, since in this case the oxidation processes are the weakest. The reverse should be found with the nitrate solution.

Thus, the secondary oxidation processes at the cathode, connected with the oxidizing activity of the ions, affords a satisfactory explanation of the changes in the size of the parameters of the gratings of copper and cuprous oxide observed in our investigations.

The fact that the increase in parameter is observed not only in copper but also in cuprous oxide is of significance, since it proves that the oxidation of the metal by the anion is taking place during the whole process of precipitation of the metal and not only after the current is cut off.

In order to bring out the effect of heat on the deposition, one of the copper precipitates obtained from the nitrate was baked. This changed the color from dark-brown to the ordinary red color of copper. The diffraction rings of copper and cuprous oxide on the röntgenograms became very sharp, which indicates a decrease in dispersion. The size of the parameters of the grating decreased, especially for cuprous oxide, the parameter of which almost reached the normal size. At the same time the loss of hydrogen by the copper precipitate was small, in spite of the fact that in baking the metal was brought to a red heat. Evidently the copper grating is holding on very firmly to the dissolved hydrogen.

The zinc deposits studied were obtained from nitrate and from chloride solutions.

The precipitate obtained by the electrolysis of the nitrate was almost completely oxidized, while the electrolysis of the chloride gave a metal with an insignificant admixture of zinc oxide. This fact is analogous to the regularity observed in the precipitates of copper and confirms the oxidizing rôle of the anion. The solvent, evidently, plays a secondary rôle as an oxidizing factor.

The results with the zinc precipitates are an additional confirmation of the inapplicability of the hydrolytic view for the general explanation of the origin of the oxides present in the cathodal precipitates.

It is worthy of notice that while the precipitate from cupric nitrate contained 40–45 per cent of cuprous oxide, the precipitate from zinc nitrate contains almost completely oxidized zinc. This shows that the oxide content depends upon the degree of oxidizability of the metal.

Unlike copper, the deposited zinc has normal parameters of its crystalline grating. Evidently, zinc by its chemical nature is not capable of absorbing hydrogen. On the other hand, zinc oxide has a much enlarged parameter, more than 1.5 per cent, which shows a considerable quantity of dissolved hydrogen. *The cadmium deposit* was precipitated by electrolysis of the nitrate solution. Similar to the deposits from the nitrates of copper and zinc, it contained only 40–50 per cent of metal. Unfortunately the röntgenogram was not definite as to the nature of the admixtures. Altogether we were able to measure seventeen diffraction rings, of which nine were those of cadmium; the other eight were rings of an unknown structure, definitely neither of cadmium oxide nor of cadmium hydroxide, the gratings of which are known. We assume that the admixture is Cd_2O, the structure of which is not known and which has been very little investigated. This assumption is strengthened by the fact that the deposit of copper, which is capable of forming two kinds of oxide, always contained only the lower oxide,—cuprous oxide. The metallic cadmium in the deposit has a considerably widened grating. The increase in the parameter is 1.08 per cent, which indicates a great absorption of hydrogen.

The silver deposit was also obtained from the nitrate solution. The deposit does not contain any oxide, the röntgenogram containing only the silver rings. The grating differed very little from the normal, and the increase hardly exceeds the possible experimental errors, hence silver dissolves hardly any hydrogen.

TABLE 2

Comparison of copper, zinc, cadmium, and silver

ORDER IN THE ELECTROMOTIVE SERIES	THEIR NORMAL POTENTIALS BY THE NORMAL HYDROGEN ELECTRODE	THE OXIDE CONTENT IN THE DEPOSIT FORMED FROM THE NITRATE
	volts	*per cent*
Zinc	−0.76	97–98
Cadmium	−0.40	50–55
Copper	+0.34	40–45
Silver	+0.80	No oxide

The deposits from the nitrates were obtained from all the metals under investigation—copper, zinc, cadmium, and silver. If we place the oxide content of the deposits in the order of the metals in the electromotive series, as in table 2, a definite regularity is seen. The oxide content diminishes with the diminished oxidizability of the metal. This confirms the idea expressed above.

Along with the oxidizing action there is also at the cathode a reducing action, due to the hydrogen set free. Its importance in the general process depends upon the deposition potential of the metal and upon the pH of the solution.

The sum of all the factors enumerated above determines the character of the secondary chemical process and the composition of the cathodal deposits in each particular case.

Thanks to the high dispersion state of the deposited metals, the changes brought about by the secondary chemical processes become exceptionally augmented. The nature of the secondary processes, however, is not a function of the current densities, the same process but to a different degree taking place at both high and low current densities. Therefore all the conclusions reached for deposits formed at high current densities hold good also for electrolysis in ordinary conditions. Oxidation taking place during deposition causes heterogeneity of the deposit and has considerable influence on its physical structure.

SPONGY DEPOSITS

The above study led us to the idea that oxidation is also a possible cause of growth of the so-called spongy deposits on the cathode. The oxide content of deposits from nitrate solutions increases in the direction silver, copper, cadmium, zinc, i.e., it depends on the oxidation tendency of the metals. The tendency for spongy deposit formation, all other conditions being equal, follows the same order. The greater tendency of zinc for spongy deposit formation, as compared with cadmium, was reported as far back as 1897 by Mylius and Funk (10). Of the four metals mentioned, zinc has the greatest oxidation tendency and it is exactly in the electrolysis of this metal that spongy formations cause the greatest difficulties. In the earlier investigations, the zinc spongy formation was considered to be due to the action of hydrogen (4) and even the formation of a hypothetical hydride, ZnH_2 (14). Later, however, it was noted that the spongy mass is obtained in cases favorable for the formation of oxide. Mylius and Fromm (9) noticed the appearance of a spongy layer at the surface of a solution, where the air can exert its oxidizing effect, while inside a crystalline deposit is formed. It was also noted that the addition of hydrogen peroxide, oxygen-containing turpentine, or other oxidizing agents to the electrolyte favors sponge formation. Foerster and Günther (2) and Sebborn (13) point out the influence of hydroxide ions on the formation of sponge, connecting this with formation of zinc hydroxide.

Although black pulverized metals are deposited at very high current densities and sponge formation occurs, mainly, at low densities, both phenomena are accompanied by the formation of oxides at the cathode. This was also well established with copper. Foerster and Seidel (3) and Kistiakovsky, Bymakov, and Krotov (5) show the presence of cuprous oxide in the deposits obtained at high as well as at very low densities. Some medium densities favor the deposition of pure metal.

Sponge formation was studied with zinc and cadmium. The electrodes consisted of the metal under investigation; the anode had the form of a rod, the cathode of a rectangular 3 cm. plate. The electrolyte was a solution of the sulfate. In the case of cadmium 0.01 per cent gelatin and 0.1 per cent H acid were added to the solution to avoid dendrite formation.

The zinc sulfate solution used was without additions. The experiments were carried out at room temperature.

The electrolysis of cadmium sulfate was carried out at current densities of 0.01 amp. per square centimeter. The electrolyte solution contained 10 per cent cadmium sulfate. The metal deposited at first in a compact smooth layer all over the surface of the cathode. Soon, however, a narrow strip of a gray spongy mass was clearly visible on the cathode at the very surface of the electrolyte solution. As time went on this mass spread downwards, gradually covering a larger and larger area of the cathode.

After an interval of about seven hours the sponge occupied about a quarter of the surface of the electrode. Towards the end of the experiment, which lasted about fifteen hours, the sponge covered considerably more than half the surface. The electrode was thoroughly washed and samples of the spongy and of the compact deposits were taken for the röntgenographical study. Experiments carried out under similar conditions, but with various additions to the electrolyte solution, showed that acidification of the solution always retards the appearance of spongy deposit. This deposition is also retarded by the addition of reducing substances. Thus the addition to the solution of even a relatively small amount of formaldehyde (0.2 per cent CH_2O) considerably retards the appearance, as well as the rate of growth of the spongy mass over the electrode. A reduction in the current density, similar to the one described in the literature (4, 11) for zinc, increases the tendency of spongy deposit formation for cadmium.

The electrolysis of zinc sulfate was carried out under similar conditions at a current density of 0.02 amp. per square centimeter. At this current density a sufficiently thick layer of solid zinc was obtained alongside with the spongy deposit.

The results of the x-ray study show that both spongy deposits—zinc and cadmium—contain oxides. The zinc deposit contains zinc oxide, and the cadmium, presumably Cd_2O. The additional rings on the last röntgenogram are identical with those which were found by us in the cadmium deposit obtained at high current densities. Although both spongy deposits contain oxides, the solid layers of zinc and cadmium consist of the pure metals.

The oxidation could be considered as due mainly to the anion of the salt, although other factors are not excluded. The fact that the sponge appears at first at the surface of the solution shows that oxidation is also effected by atmospheric oxygen. This contradicts the view that the appearance of oxides on the cathode is due to the hydrolysis of the salts. The conditions for hydrolysis are the same at the surface of the solution as within it. Neither does the hydrolytic interpretation of the presence of oxides explain the effect of hydrogen peroxide, oxygen-containing turpentine, and other oxidizing agents in favoring the sponge formation, nor does it explain the effect of reducing substances (CH_2O) in greatly retarding the process. It is also not clear why in the spongy deposits as well as in the black deposits obtained at high current densities only oxides are found, but not even traces of hydroxides, while the latter should undoubtedly be present if the process were accompanied by hydrolysis. All these isolated facts are completely explained by assuming that the process at the cathode consists of two opposite tendencies, reducing and oxidizing. The factors strengthening the latter tendency favor the formation of porous black and spongy deposits. The strengthening of the reducing tendencies, on the contrary, hinders this process. An increase in the concentration of hydrogen ions of the electrolyte, causing an increase in the amount of hydrogen liberated during electrolysis, should diminish the tendency to sponge formation. An increase in the current density has a similar effect. However, a great increase in the density augmenting the reducing processes causes at the same time a great increase in the state of dispersion of the deposited metal. Under certain conditions a point might be reached when the metal will deposit in a state of very high dispersion. This increases its oxidation capacities to such a degree that conditions favorable for oxide formation are again created and a porous structure again appears, which causes the formation of black powder-like deposits.

SUMMARY

An x-ray study of the powder-like cathodal deposits of copper, zinc, cadmium, and silver formed from aqueous solutions of various salts by the electrolysis at high current densities was carried out, and the formation of spongy deposits during the electrolysis of solutions of cadmium and zinc sulfate was investigated.

1. The powder-like deposits are dispersed and contain oxides, which are formed as a result of secondary oxidation processes at the cathode.
2. The approximate oxide content of the deposits, determined by a comparison of the intensity of the diffraction rings, depends mainly upon the oxidizing capacities of the anion of the salt.
3. The oxide content depends also upon the readiness of the deposited metal to become oxidized, i.e., upon its position in the electromotive series.
4. Some metals and their oxides—copper, cadmium, cuprous oxide, and zinc oxide—which enter into the composition of the deposits have greatly enlarged parameters of the crystal gratings, evidently due to the absorption of hydrogen. Zinc and silver have normal parameters.
5. The appearance of a porous structure at very low and at too high current densities is explained.

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THE POSTPRECIPITATION OF ZINC SULFIDE WITH MERCURIC SULFIDE[1]

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The induced precipitation of zinc sulfide by cupric sulfide has been investigated by Kolthoff and Pearson (6). These authors pointed out that the phenomenon is not a case of coprecipitation, but one of postprecipitation. In the present study it is shown that mercuric sulfide has a much greater promoting effect on the postprecipitation of zinc sulfide than has copper sulfide. The results are not only of quantitative but also of qualitative significance. It will be shown that all or most of the zinc may be found in the precipitate of the second group when mercury is present, the acidity not too high, and filtration made not too quickly after passage of hydrogen sulfide. In addition, the mechanism of the promoted precipitation of zinc sulfide by mercuric sulfide has been studied more in detail and investigated as a function of the age and treatment of the mercuric sulfide. For a great number of details and experimental results the reader is referred to the thesis of the junior author (see footnote 1). A review of the entire subject has been published recently (5).

MATERIALS USED

All materials used were recrystallized from C.P. quality reagents and tested for purity.

When working with mercuric chloride in the presence of hydrochloric acid a white precipitate of $2HgS \cdot HgCl_2$ was first formed on passage of hydrogen sulfide, being transformed to black mercuric sulfide with more hydrogen sulfide. In order to exclude the formation of this intermediary compound, experiments were also made with solutions of mercuric perchlorate instead of mercuric chloride in sulfuric acid medium.

The hydrogen sulfide was prepared in an ordinary Kipp generator from commercial stick iron sulfide and commercial hydrochloric acid. The iron sulfide contains a considerable amount of free iron, which leads to a dilution of evolved hydrogen sulfide with hydrogen. It was found that the varia-

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[1] From the experimental part of a thesis submitted by Romund Moltzau to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

tion in partial pressure of the hydrogen sulfide with the strength of the acid present in the generator and the varying composition of the iron sulfide were responsible to a great extent for the difficulty experienced in obtaining reproducible results in the postprecipitation of zinc sulfide. Poor reproducibility has been noted by many workers in this field (1, 3, 6). The gas from the generator was first passed through a solution of sodium bicarbonate and then through water before entering the precipitation flasks.

PROCEDURE

Method of precipitation with hydrogen sulfide

The precipitations were carried out in 250-ml. Erlenmeyer flasks of Pyrex glass. The washed gas was led into the precipitation flasks through flexible connections allowing mechanical shaking of the solutions during continued passage of hydrogen sulfide. The electrically operated shaker employed provided a decided movement of the solutions without splashing onto the stoppers by imparting a rotary motion in the horizontal plane. Care was taken to realize as far as possible a uniform flow of gas in comparable experiments. Unless otherwise stipulated the following general procedure was observed. Before precipitation the air was expelled from the system by rapid passage of hydrogen sulfide for a period of two minutes. The gas was then bubbled through the solutions for a few minutes (usually three) accompanied by gentle shaking by hand. Thereafter continuous passage of gas was maintained over the solutions during the subsequent period of mechanical shaking.

Method of analysis

In general the following method of analysis was employed. The contents of the precipitation flasks were filtered and the precipitates immediately washed four times with cold water. The filtrates containing the washings were then boiled until free of hydrogen sulfide and, in case only small amounts of zinc were present, were evaporated to appropriate volumes. The solutions after cooling were titrated with 1/40 M potassium ferrocyanide solution, using diphenylamine as an internal oxidation–reduction indicator in the presence of a small amount of potassium ferricyanide. The method followed was that recommended by Kolthoff and Pearson (7).

In cases where large amounts of hydrochloric acid were present in the filtrate, most or all of it was removed by evaporation and the residue, if heated to dryness, was taken up in 10 ml. of 4 N sulfuric acid and diluted to an appropriate volume. In many cases the precipitates were extracted with hot or cold 3 N hydrochloric acid, in which instances the above procedure was followed before titration of the extracted zinc. Owing to the great resistance offered by the zinc in the precipitate to pass wholly into solution the precipitates were often refluxed with hydrochloric acid (3 N or more concentrated). This treatment resulted in a considerable amount of mercury passing into solution which, if not removed, interfered with the analysis. In such cases the extraction solutions were resaturated with hydrogen sulfide and filtered if a filterable precipitate was obtained. It should, therefore, be understood that the analyses of the filtrates are accurate and the analyses of the extracts of the precipitates are less accurate, though the error due to the presence of any mercuric ion which may have been left in solution is probably in no case greater than 2 per cent.

Filterability of the precipitates

The nature of the mixed precipitates obtained by passing hydrogen sulfide through a solution containing both mercuric and zinc salts at an acidity allowing the precipitation of some zinc differs widely from that of pure mercuric sulfide. The mixed precipitate is slimy and more gelatinous and is much slower to filter though its color, even if it contains a large percentage of zinc, appears quite as black as that of pure mercuric sulfide. Upon aging, the mixed precipitates, as well as pure mercuric sulfide, are filtered more readily than in the fresh state.

EXPERIMENTAL RESULTS

Postprecipitation and no coprecipitation of zinc

Effect of acidity. In the first place it was shown that the zinc is not coprecipitated with mercuric sulfide. Mixtures of mercuric chloride and zinc sulfate in varying concentrations of hydrochloric acid and mixtures of mercuric perchlorate and zinc sulfate in dilute sulfuric acid were treated with hydrogen sulfide in such a way that a small part of the mercury remained in the solution. Upon analysis of the filtrates all of the zinc originally added was recovered, thus showing that zinc is not coprecipitated with mercuric sulfide.

The results in table 1, which are substantiated by a great number of experiments at other acidities and times of shaking, show conclusively that we are dealing with a postprecipitation of zinc sulfide on the surface of mercuric sulfide.

The increase of the postprecipitation with time as a function of the concentration of sulfuric acid in the precipitation medium is given in figure 1. The ordinate gives the percentage of zinc precipitated, the abscissa the time of shaking in hours before filtration. The results reproduced in figure 2 are of analytical significance. Curve 1 gives the amount of zinc precipitated expressed in per cent when the mercuric sulfide is precipitated in various concentrations of hydrochloric acid and filtration made as quickly as possible. Curve 2 represents the percentage of zinc precipitated at different sulfuric acid concentrations with filtration after one hour of shaking under continuous passage of hydrogen sulfide. For the composition of the solutions see the heading of table 1.

In all cases in which the precipitation was carried out from sulfuric acid medium the experiments have been repeated with mercuric perchlorate instead of mercuric chloride. Although in the latter case no intermediate white precipitate is formed, no significant differences were found, although under all conditions slightly more zinc was postprecipitated by mercuric sulfide obtained from the perchlorate. The difference may be attributed to a difference in particle size of the mercuric sulfide obtained by precipitation of the chloride and perchlorate respectively.

TABLE 1

Postprecipitation of zinc sulfide with mercuric sulfide

25 ml. of 0.05 *M* $HgCl_2$, 25 ml. of 0.05 *M* $ZnSO_4$, and acid as noted below. Temperature, 25°C.

EXPERIMENT NO.	TIME SHAKEN	KIND OF ACID	ACIDITY BEFORE PRECIPITATION	ZINC PRECIPITATED
	minutes		*N*	*per cent*
1 (Blank)*	0	H_2SO_4	0.30	0
2	0	H_2SO_4	0.30	65
3	30	H_2SO_4	0.30	95
4 (Blank)*	30	H_2SO_4	0.30	0
5	0	H_2SO_4	0.80	13
6	30	H_2SO_4	0.80	68
7	0	H_2SO_4	1.05	15
8	30	H_2SO_4	1.0	47
9	30	H_2SO_4	2.0	8.0
10	60	H_2SO_4	2.0	8.6
11	60	H_2SO_4	4.0	0
12 (Blank)*	30	HCl	0.30	0
13	0	HCl	0.30	60
14	30	HCl	0.30	85
15	0	HCl	0.80	10.5
16	30	HCl	0.80	22
17	120	HCl	0.80	28
18	0	HCl	1.0	6.8
19	30	HCl	1.0	13
20	0	HCl	1.5	1.6
21	30	HCl	1.5	2.8
22	0	HCl	1.75	0.5
23	60	HCl	2.0	0

* The blanks contained 25 ml. of water in place of 25 ml. of 0.05 *M* $HgCl_2$.

Figure 3 gives the percentage of zinc postprecipitated from a medium 2 *N* in sulfuric acid after long periods of standing under an atmosphere of hydrogen sulfide at room temperature. The original mixture contained

25 ml. of 0.05 M mercuric chloride, 25 ml. of 0.05 M zinc sulfate, and 10 ml. of 12.0 N sulfuric acid, and was kept saturated with hydrogen sulfide by replenishing every twelve hours for the first four days by passage of hydrogen sulfide above the solution for five minutes. Thereafter the gas phase was replenished every two days. In the absence of mercuric sulfide no precipitate of zinc sulfide was formed after a month of standing under like conditions.

The effect of varying the ratio of mercury to zinc at relatively low acidities is shown in table 2. In table 3 the results are reported for a medium which was 2 N in sulfuric acid.

Unity in the expression of ratio represents 1.25 millimoles of mercury and zinc, respectively (25 ml. of 0.05 M solution).

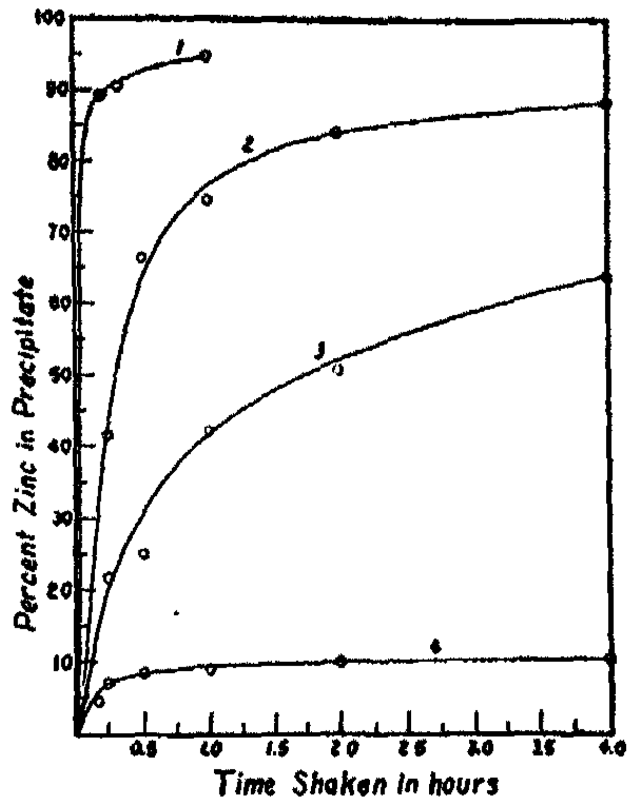

FIG. 1

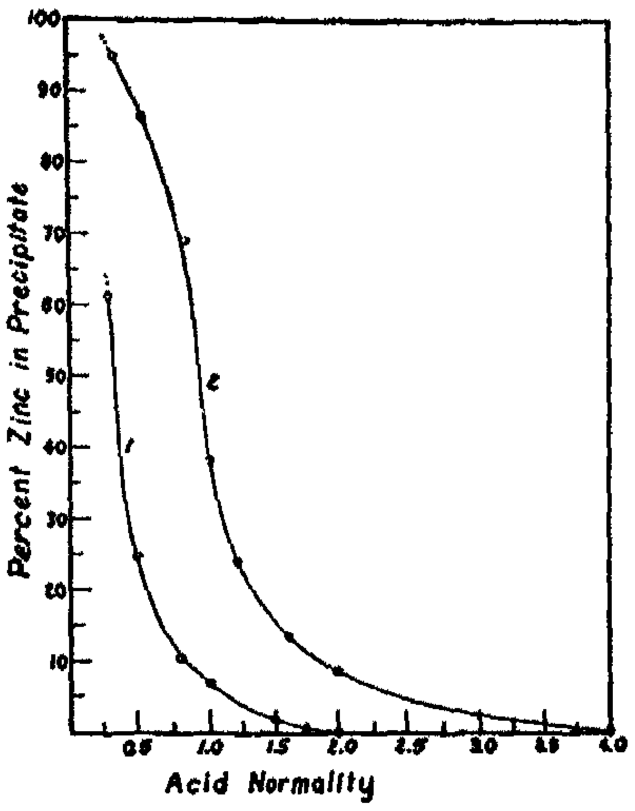

FIG. 2

FIG. 1. Time effect at various acidities. Acidity (sulfuric acid) before precipitation: curve 1, 0.35 N; curve 2, 0.77 N; curve 3, 1.31 N; curve 4, 2.0 N.

FIG. 2. Effect of acidity

In table 4 some results are given on the disappearance of zinc from a very dilute zinc solution at a high acidity after various times of standing with freshly precipitated mercuric sulfide.

Effect of partial pressure of hydrogen sulfide upon the postprecipitation of zinc sulfide

In the following experiments (see table 5) the hydrogen sulfide was diluted with carbon dioxide before entering the precipitation flasks. In the blanks a stream of pure hydrogen sulfide having the same rate of flow (about one bubble per second) as the stream of hydrogen sulfide uniting with carbon dioxide in the experiments was used. It took three to five minutes to precipitate the mercury completely using the diluted gas; less time was needed using the slow stream of pure hydrogen sulfide.

Effect of temperature

Those experiments (see table 6) in which the temperature is described as "hot" were heated over a burner until bubbles began to break the surface of the solution. They were then immediately attached to the source of hydrogen sulfide in parallel with a corresponding experiment run at room temperature. Hydrogen sulfide at room temperature was passed in above the solutions for one minute and bubbled through the solutions for three minutes in accordance with the usual method of precipitation. No further heat was applied after the initial heating and hence the flasks slowly cooled during the period of shaking, which was conducted under constant passage of the gas. Blanks were run which contained 25 ml. of water in place of the mercuric solution.

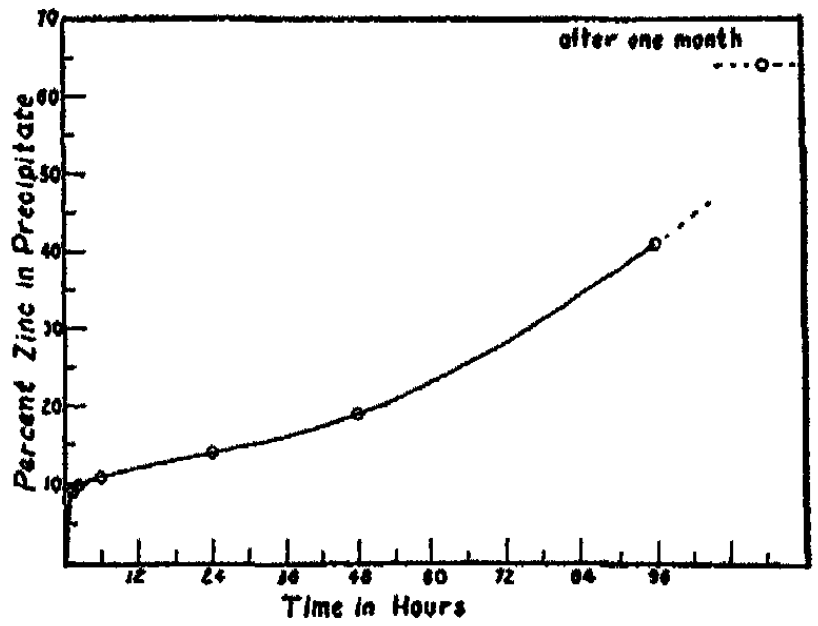

FIG. 3. Time effect at an acidity of 2.0 N in sulfuric acid

The "wall effect" mentioned in the "remarks" after experiment No. 6 is evidenced by a deposit of zinc sulfide on the walls of the flask. It is formed during the period of shaking. Avoidance of this effect is aided by the use of flasks which are well cleaned and free of scratches or rough surfaces.

Similar experiments were made in 0.35 N sulfuric acid, giving results strictly concordant with those in table 6.

Effect of aging of mercuric sulfide upon the promotion of precipitation of zinc sulfide

A series of experiments was made in which the mercuric sulfide for each individual experiment was precipitated from 25 ml. of 0.05 M mercuric chloride at an acidity of 0.73 N hydrochloric acid. The precipitate was

TABLE 2

The effect of varying the ratio of mercury to zinc at relatively low acidities

Room temperature. The total volume of solution in each experiment was approximately 55 ml.

EXPERIMENT NO.	ACIDITY BEFORE PRECIPITATION	TIME SHAKEN	RATIO Zn: Hg	ZINC IN FILTRATE IN PER CENT	ZINC IN PRECIPITATE IN PER CENT
1 (Blank)*	0.35 *N* (H_2SO_4)	0		100.0	0
2	0.35 *N* (H_2SO_4)	0	1:2	49.6	50.4
3	0.35 *N* (H_2SO_4)	0	1:1	57.6	42.4
4	0.35 *N* (H_2SO_4)	0	1:1/2	60.4	39.6
5	0.35 *N* (H_2SO_4)	10 mins.	1:2	8.3	91.7
6	0.35 *N* (H_2SO_4)	10 mins.	1:1	10.7	89.3
7	0.35 *N* (H_2SO_4)	10 mins.	1:1/2	15.9	84.1
8	0.55 *N* (H_2SO_4)	1 hr.	1:1/10	27.8	72.2
9	0.55 *N* (H_2SO_4)	1 hr.	1:1/100	81.8	18.2
10	0.55 *N* (H_2SO_4)	1 hr.	1:1/750	96.0	4.0
11	0.20 *N* (H_2SO_4)	1 hr.	1:1/10	0.0	100.0
12	0.20 *N* (H_2SO_4)	1 hr.	1:1/100	21.0	79.0
13	0.20 *N* (H_2SO_4)	1 hr.	1:1/750	54.6	45.4
14 (Blank)*	0.20 *N* (H_2SO_4)	1 hr.		98.0	2.0

* The blanks contained no mercury salt.

TABLE 3

Effect of ratio at high acidity (2 N in sulfuric acid)

Room temperature. The total volume of solution in each experiment was 60 ml.

EXPERIMENT NO.	TIME SHAKEN	RATIO Zn: Hg	ZINC IN FILTRATE IN PER CENT	ZINC IN PRECIPITATE IN PER CENT
1	2 hrs.	1:4	74.6	25.4
2	2 hrs.	1:2	81.9	18.1
3	2 hrs.	1:1	90.9	9.1
4	2 hrs.	2:1	86.8	13.2
5	2 hrs.	1/5:1	92.7	7.3
6	1 hr.	1:4	80.5	19.5
7	1 hr.	1:2	86.7	13.3
8	1 hr.	1:1	93.2	6.8
9	1 hr.	1:1/2	95.5	4.5
10	1 hr.	2:1	87.4	12.6
11	1 hr.	1/2:1	90.5	9.5
12	1 hr.	1/5:1	95.7	4.3
13	1 hr.	2/5:2	89.5	10.5
14	30 mins.	2/5:2	93.5	6.5
15	30 mins.; stood stoppered 4 days	2/5:2	81.7	18.3

allowed to age in this medium saturated with hydrogen sulfide. After the time indicated in the table as "time of aging", 25 ml. of 0.05 *M* zinc sulfate solution was added and immediately thereafter hydrogen sulfide was passed over the solution for one minute and bubbled through for two minutes. The contents of the precipitation flask were then shaken under continuous passage of hydrogen sulfide for ten minutes, filtered, the precipitate washed four times with cold water, and the filtrates analyzed for zinc. Another series was also made in which the mercuric sulfide was precipitated from mercuric chloride solution without addition of acid. After the period of aging, acid and zinc sulfate solution were added in the order named and

TABLE 4

Time effect at an acidity of 2 N in sulfuric acid employing very dilute zinc solution

Contents of flasks before precipitation: 25 ml. of 0.05 *M* $HgCl_2$, 25 ml. of 0.01 *M* $ZnSO_4$, 10 ml. of 12.0 *N* H_2SO_4 (molarity $ZnSO_4$ = 0.00417). Room temperature. Each experiment was shaken for one hour under continuous passage of hydrogen sulfide after the three-minute precipitation period and thereafter allowed to stand under an atmosphere of hydrogen sulfide for the period of time given in the table before filtration

EXPERIMENT NO.	TIME OF STANDING	ZINC IN FILTRATE IN PER CENT	ZINC IN PRECIPITATE IN PER CENT
1	0	90.0	10.0
2	0	90.8	9.2
3	1 day	89.0	11.0
4	1 day	89.4	10.6
5	3 days	90.1	9.9
6	3 days	90.7	9.3

TABLE 5

Effect of the partial pressure of hydrogen sulfide

25 ml. of 0.05 *M* $HgCl_2$, 25 ml. of 0.05 *M* $ZnSO_4$, and a volume of 4 *N* H_2SO_4 required to give the acidities indicated in the table. Room temperature

EXPERIMENT NO.	ACIDITY BEFORE PRECIPITATION	COMPOSITION OF GAS STREAM APPROXIMATE RATIO $H_2S:CO_2$	TIME SHAKEN	ZINC IN FILTRATE IN PER CENT
1	1.01 *N* in H_2SO_4	Pure H_2S	1 hr.	62.7
2	1.01 *N* in H_2SO_4	1:10	1 hr.	99.1
3	1.01 *N* in H_2SO_4	1:20	1 hr.	100.0
4	0.55 *N* in H_2SO_4	Pure H_2S	30 mins.	30.4
5	0.55 *N* in H_2SO_4	1:10	30 mins.	91.3
6	0.55 *N* in H_2SO_4	1:20	30 mins.	97.8
7	0.30 *N* in H_2SO_4	Pure H_2S	30 mins.	8.1
8	0.30 *N* in H_2SO_4	1:10	30 mins.	87.8
9	0.30 *N* in H_2SO_4	1:20	30 mins.	96.5

the experiments further conducted as described above. The results are given in table 7. The acidities listed are uncorrected for acid set free by the reaction.

Another set of experiments was carried out in which the mercuric sulfide was precipitated in 0.75 *N* hydrochloric acid at the boiling temperature. No further heating took place after precipitation, and the precipitate and supernatant liquid were allowed to cool down to room temperature. Zinc solution was added after various time intervals. The results obtained were practically identical with those in the first part of table 7, showing that the temperature at which the mercuric sulfide is precipitated from hydrochloric acid medium has no appreciable effect upon its ability to promote the precipitation of zinc sulfide. However, if the mercuric sulfide is allowed to age at higher temperatures for longer times its promoting effect upon the precipitation of zinc sulfide decreases more rapidly than when aged at room temperatures. Precipitates of mercuric sulfide obtained from mercuric perchlorate behaved qualitatively in the same way as those from mercuric chloride.

TABLE 6

Effect of temperature

25 ml. of 0.05 *M* $HgCl_2$, 25 ml. of 0.05 *M* $ZnSO_4$, and 8 ml. of 3.95 *N* H_2SO_4. Acidity before precipitation was 0.55 *N* in H_2SO_4

EXPERIMENT NO.	TIME SHAKEN	TEMPERATURE OF PRECIPITATION	ZINC in FILTRATE	REMARKS
	minutes	°*C.*	*per cent*	
1	0	Hot	85.7	The white precipitate ($2HgS \cdot HgCl_2$) persisted for one minute before becoming black
2	0	27	72.3	No white precipitate was observed
3	0	Hot	79.6	White precipitate persisted for 30 seconds. H_2S passage more rapid in experiments 3 and 4 than in 1 and 2
4	0	27	57.6	No white precipitate was observed
5	10	Hot	36.4	
6 (Blank)	30	Hot	99.5	No Hg present. Some wall effect, but the solution was entirely clear at the end of the period of shaking
7	10	Hot	38.3	
8	10	27	37.8	
9	20	Hot	22.4	
10	20	27	21.1	
11	20	Hot	19.5	
12	20	27	20.4	

A great number of experiments were carried out in which the mercuric sulfide was precipitated and aged in 3.5 N sulfuric acid before the addition of zinc solution, the final acidity being 2 N. Under these conditions a short time of aging had relatively a much greater effect upon the speed of disappearance of zinc from the solution than when precipitation was conducted at lower acidities. This may be seen from the following example:

Age of HgS (minutes)	0.5	2	5	10	60	120
Zinc in precipitate in per cent	9	7	5.5	4.5	2.4	2.0

The difference between these results and those in table 7 are attributed to the fact that in strongly acid medium little, if any, precipitation but only adsorption of zinc sulfide takes place during relatively short times of contact. At lower acidities a primary adsorption takes place with an additional precipitation of zinc sulfide. The latter, once formed, promotes its own precipitation.

TABLE 7

Effect of aging of mercuric sulfide at room temperature upon precipitation

	HgS aged in 0.73 N HCl			HgS aged in neutral medium		
Experiment No.	Acidity after addition of zinc solution	Time of aging of HgS	Zinc in the precipitate in per cent	Acidity after addition of zinc solution	Time of aging of HgS	Zinc in the precipitate in per cent
1	0.42 N in HCl	0	38	0.42 N in HCl	0	29
2	0.42 N in HCl	20 mins.	33			
3	0.42 N in HCl	30 mins.	32			
4	0.42 N in HCl	1 day	20	0.42 N in HCl	1 day	10
5	0.42 N in HCl	4 days	18	0.42 N in HCl	4 days	5
6				0.86 N in H_2SO_4	0	21
7				0.86 N in H_2SO_4	1 day	11

Extractability of the zinc from the mixed precipitate

By an extraction with 3 N hydrochloric acid at room temperature it was found impossible to remove all the zinc from the mixed precipitate. By refluxing the precipitate with 3 N hydrochloric acid complete extraction of the zinc was possible. However, with such drastic treatment relatively large amounts of mercuric sulfide go into solution as well and a subsequent separation is necessary before the zinc can be determined. Complete extraction of the zinc was made with less difficulty when the mercuric sulfide was allowed to age before it exerted its promoting effect upon the precipitation of zinc sulfide. An explanation of this behavior is given in the discussion of the results.

As an illustration a few data are reported in table 8. A great number of other examples of cold and hot extractions are reported in the thesis of

R. Moltzau (see footnote 1). In the following experiments the mercuric sulfide precipitated from neutral solution (25 ml. of 0.05 *M* mercuric chloride) was aged under the supernatant liquid saturated with hydrogen sulfide in tightly stoppered Erlenmeyer flasks. The gas in the flasks was replenished with hydrogen sulfide every two days of the period of aging. Experiments were run in pairs, one member of each pair containing the aged precipitate and the other a freshly precipitated product. After addition of the proper amount of acid and 25 ml. of 0.05 *M* zinc sulfate solution, hydrogen sulfide was again bubbled through the solution for two minutes, and thereafter the contents of the flasks were shaken under continuous passage of hydrogen sulfide for the time noted. The acidity given is that of the solution after addition of the zinc solution uncorrected for acid liberated by the reaction.

TABLE 8

Extractability of zinc with hot 3 N hydrochloric acid

EXPERIMENT NO.	ACIDITY (H_2SO_4)	TIME SHAKEN	AGE OF HgS	ZINC in FILTRATE	100 PER CENT − ZINC IN FILTRATE = ZINC IN PPT.	METHOD OF EXTRACTION	ZINC EXTRACTED	TOTAL ZINC RECOVERED
	N			*per cent*	*per cent*		*per cent*	*per cent*
Blank								
1	0.50	1 hr.	No HgS	100.0	0			
2	0.50	1 hr.	3 weeks	91.5	8.5	a	8.5	100.0
3	0.50	1 hr.	Fresh	15.6	84.4	a	81.4	97.0
4	0.66	45 mins.	2 weeks	97.6	2.4	b	2.0	99.6
5	0.66	45 mins.	Fresh	85.9	14.1	b	11.2	97.1
6	0.66	45 mins.	2 weeks	97.0	3.0	d	2.5	99.5
7	1.0	45 mins.	2 weeks	99.3	0.7	c	0.42	99.7
8	1.0	45 mins.	Fresh	91.9	8.1	c	4.7	96.6
9	1.0	2 hrs.	3 weeks	87.8	12.2	d	12.2	100.0
10	1.0	2 hrs.	Fresh	46.0	54.0	d	52.6	98.6

Method a. The precipitate was placed in a beaker with 25 ml. of hot 3 *N* hydrochloric acid. This mixture stood with occasional stirring for fifteen minutes, was filtered and the residue washed three times with cold 3 *N* hydrochloric acid and four times with cold water.

Method b. Same as method a except that the acid and the precipitate were in contact for twenty minutes rather than for fifteen minutes.

Method c. Same as methods a and b, except that period of contact was ten minutes.

Method d. The precipitate on the filter was washed ten times (5-ml. portions) with hot 3 *N* hydrochloric acid and four times with cold water.

Inhibition of postprecipitation of zinc sulfide

(*a*) *By replacing adsorbed hydrogen sulfide.* It was shown by Kolthoff and Pearson (6) that organic substances containing polar sulfur groups can replace part of the adsorbed hydrogen sulfide from the surface of cupric sulfide, thus causing an inhibition of the postprecipitation of zinc sulfide. Similar experiments were carried out in the present study with thiourea and cystine as inhibitors. In both cases it was found that the organic substance added retarded the postprecipitation of zinc sulfide with mercuric sulfide.

Experiments have also been performed in which the precipitation of mercuric sulfide was carried out in the presence of a layer of an immiscible liquid such as ether or carbon disulfide. In general a pronounced retarding effect upon the postprecipitation of zinc sulfide was found. This may be explained partly by the fact that the mercuric sulfide is more or less isolated from the aqueous solution by the second layer of organic liquid.

(*b*) *By replacing adsorbed zinc ions.* Before precipitation of zinc sulfide on the surface of mercuric sulfide occurs, an adsorption of zinc ions with the sulfide ions takes place. Ions competing with the zinc ions for adsorption with the sulfide ions will inhibit the postprecipitation of zinc sulfide.

In the first place it was shown that zinc ions are adsorbed by mercuric sulfide containing some adsorbed hydrogen sulfide.

$$\mathrm{HgS\ S^{--}} \vdots\ \mathrm{2H^{+} + Zn^{++} \rightarrow HgS\ S^{--}} \vdots\ \mathrm{Zn^{++} + 2H^{+}}$$

A fresh precipitate of mercuric sulfide from 25 ml. of 0.05 *M* mercuric chloride solution was washed with cold water until the test for sulfide and chloride in the filtrate was very faint. The precipitate was then shaken with 25 ml. of 0.005 *M* zinc sulfate and the amount of hydrogen ions liberated and zinc adsorbed was determined by titrating the filtrate with sodium hydroxide to the methyl red end point and then with ferrocyanide to determine the zinc content. In all cases the amount of acid liberated was found equivalent to the amount of zinc adsorbed.

Milliequivalents of acid liberated..........	0.029	0.025	0.022	0.016
Milliequivalents of zinc adsorbed..........	0.0285	0.0245	0.0220	0.0158

The results show conclusively that the adsorption of zinc ions is to be attributed to an exchange with hydrogen ions on the surface of the mercuric sulfide.

It was further shown that strychnine ions give a similar exchange. The strychnine was determined gravimetrically by the ferrocyanide method as recommended by Kolthoff and Lingane (4). Working with a washed mercuric sulfide precipitate, a complete exchange between the adsorbed hydrogen ions and strychnine ions was found in a solution which was 0.005 *M* in strychnine sulfate. It is suggested that a strychnine salt may be used in the determination of the amount of hydrogen sulfide adsorbed by a metal sulfide precipitate. In stronger acid medium it will be harder to replace the hydrogen ions by zinc or strychnine ions, since the effect depends upon a competition between hydrogen ions and the other ions to be adsorbed.

In weakly and strongly acid medium strychnine inhibits the postprecipitation of zinc sulfide by mercuric sulfide. A few examples of the effect in 1.4 *N* sulfuric acid are given in table 9. The air was expelled from above the solution by a two-minute passage of hydrogen sulfide followed by a three-minute period during which the gas was bubbled through the contents of the precipitation flask. Thereafter the mixture was shaken under continuous passage of hydrogen sulfide over the solution for thirty minutes. Filtration and washing were conducted as usual and the filtrates analyzed for zinc content after destroying the strychnine with bromine.

In very weakly acid medium, where the only hydrogen sulfide present was that adsorbed on the mercuric sulfide, aluminum ions were found to exert a slight replacing effect upon the adsorption of zinc ions. In more strongly acid medium, however, the aluminum did not exert an inhibiting effect upon the postprecipitation of zinc sulfide.

TABLE 9

Inhibition of postprecipitation in the presence of strychnine

25 ml. of 0.05 *M* $HgCl_2$, 10 ml. of 12.06 *N* H_2SO_4, 25 ml. of 0.025 *M* strychnine acid sulfate (or 25 ml. of 0.025 *N* H_2SO_4 in blanks), and 25 ml. of 0.05 *M* $ZnSO_4$

CONDITION	ZINC IN FILTRATE	ZINC in PRECIPITATE
	per cent	*per cent*
Strychnine present	93.7	6.3
Strychnine present	94.0	6.0
No strychnine present	84.5	15.5
No strychnine present	83.2	16.8

DISCUSSION OF THE RESULTS

1. From the analytical viewpoint it is of interest to mention that at acidities at 0.3 *N* sulfuric acid 65 per cent of the zinc was found in the mercuric sulfide precipitate when filtration was made immediately after a three-minute period of precipitation. Upon waiting for thirty minutes only 5 per cent of the zinc originally present was recovered in the filtrate. Even when precipitated from 1 *N* sulfuric acid the mercuric sulfide contains about 15 per cent of the zinc present upon rapid filtration and about 8 per cent when precipitated from 1 *N* hydrochloric acid. In order to get a quantitative separation the precipitation should be made in a solution 4 *N* with regard to sulfuric acid or 2 *N* with respect to hydrochloric acid. At the same acid concentration hydrochloric acid is more effective in retarding the precipitation of zinc sulfide than is sulfuric acid, since the activity of the hydrogen ions in the case of the former is much greater. The difference in behavior of hydrochloric and sulfuric acids is clearly

shown in figure 4. The ordinate represents the amount of zinc precipitated after shaking for thirty minutes under hydrogen sulfide (for conditions see table 1), whereas the abscissa indicates the normality of the acid.

2. The results in table 5 show that the extent of postprecipitation is decreased materially when the hydrogen sulfide pressure is diminished. Whereas 37 per cent of the zinc was postprecipitated at an acidity of 1 *N* in sulfuric acid after a one-hour period of shaking, only 0.9 per cent was postprecipitated when the gas was diluted ten times with carbon dioxide and no zinc was found in the precipitate with a twentyfold dilution (experiments 1 to 3, table 5). At lower acidities the differences are still more striking. These results are of analytical importance, since it should be possible to obtain satisfactory separations in those cases in which precipitation with hydrogen sulfide under normal pressure gives serious errors as a result of postprecipitation. The effect of the partial pressure of the gas also explains why results obtained in these postprecipitation studies frequently are irreproducible if the ratio of hydrogen sulfide to hydrogen in the gas produced in the generator varies. Moser and Behr (8) found that increased gas pressure promotes the speed and completeness of precipitation of zinc and other sulfides and made an analytical application thereof.

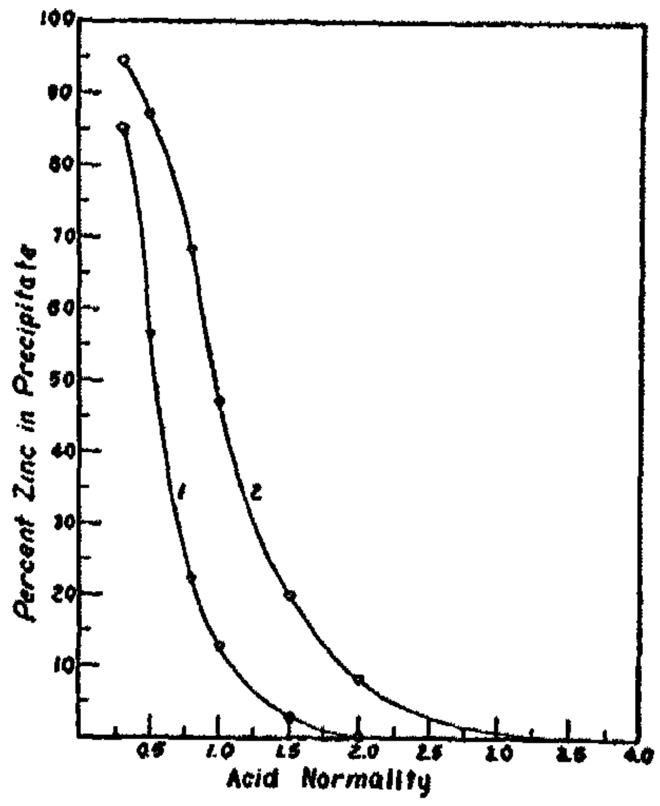

FIG. 4. Effect of acidity: effect of hydrochloric acid versus that of sulfuric acid. Curve 1, hydrochloric acid medium; curve 2, sulfuric acid medium.

3. The results in table 2 show that at relatively low acidities very small amounts of mercuric sulfide cause the precipitation of appreciable quantities of zinc sulfide (see experiments 11 and 15), the amount of zinc precipitated being far greater than corresponds to the formation of mixed sulfides

in the sense of Feigl (2). Evidently there is no one-to-one proportionality between the extent to which zinc sulfide is carried down and the amount of mercuric sulfide present. The primary reaction taking place is an adsorption of zinc sulfide on the surface of mercuric sulfide. The zinc sulfide thus formed exerts a self-promoting action on its own precipitation (3). A similar effect may be attributed to the mercuric sulfide, since it is isomorphous with zinc sulfide. When precipitation takes place at a high acidity (2 N in sulfuric acid) at a given concentration of zinc salt the amount of zinc found in the precipitate approximates, over a limited range, a one-to-one proportionality with the amount of mercuric sulfide present. From the results in table 3 it may be concluded that at high acidities during the first two hours we are dealing primarily with an adsorption of zinc sulfide on the surface of mercuric sulfide, and that postprecipitation is of secondary importance for relatively short periods of time after precipitation of the mercuric sulfide. Upon longer times of standing a slow postprecipitation of zinc sulfide occurs. In this way the shape of the curve in figure 3 is easily explained. The initial rapid rise in the curve is attributed to an adsorption of zinc sulfide, which is followed by a slow postprecipitation of zinc sulfide represented by the flatter portion of the curve. The interpretation is substantiated by the results of table 4. In these experiments the zinc sulfate concentration was five times smaller than in those reported in table 3. Comparison of experiments 1 and 2 of table 4 with 6 and 7 of table 3 shows that the same percentage of zinc present in the solution was adsorbed by the mercuric sulfide, although in the latter case the total zinc concentration was five times greater than in the former. There is a competition between the zinc and hydrogen ions for adsorption on the surface of the mercuric sulfide. At a given hydrogen-ion concentration the ratio $\left(\frac{\text{Zn}^{++}}{\text{H}^+}\right)$ adsorbed is constant. Thus when the zinc concentration is decreased five times the percentage of zinc adsorbed from the solution remains unchanged. Whereas in the experiments reported in table 3 a slow postprecipitation of zinc sulfide was found upon longer times of standing, no indication of a *precipitation* of zinc sulfide was found at a fivefold smaller concentration of zinc salt in the solution after three days of standing at an acidity of 2 N sulfuric acid. At this high acidity and low zinc concentration the solution is no longer supersaturated with regard to zinc sulfide, and no postprecipitation can take place. In this way it is possible to interpret the entire mechanism of the adsorption and postprecipitation of zinc sulfide by mercuric sulfide.

4. One of the most striking and interesting results of this study is that a postprecipitation of zinc sulfide was found in a medium which was 2 N sulfuric acid (table 3 and also figure 3). If an excess of freshly precipitated zinc sulfide was added to a solution of zinc sulfate in 2 N sulfuric acid of

the same composition as the supernatant liquid in the postprecipitation studies after the precipitation of the mercury and saturation with hydrogen sulfide, it was found that part of the zinc sulfide went into solution. In spite of this fact a slow precipitation of zinc sulfide occurs from the same medium when mercuric sulfide is present as the solid body. The apparent contradiction to the mass action law is explained by the fact that the solubility of zinc sulfide depends greatly upon the manner of its preparation and its age. The effect of aging of zinc sulfide upon its solubility is clearly demonstrated by the experiments reported in table 10.

TABLE 10

Decrease of solubility of zinc sulfide upon aging

EXPERIMENT NO.	REAGENTS	H_2SO_4 CONCENTRATION IN FINAL MIXTURE (NORMALITY)	TIME SHAKEN	Zn ORIGINALLY IN SOLUTION (MOLARITY)	FINAL Zn IN SOLUTION (MOLARITY)
Blank 1	25 ml. of 0.05 *M* $ZnSO_4$, 25 ml. of 2.0 *N* H_2SO_4	1.0	2 hrs.	0.0250	0.0250
2	Same as No. 1 plus solid ZnS (fresh)	1.0	2 hrs.	0.0250	0.0223
3	25 ml. of 0.05 *M* $HgCl_2$, 25 ml. of 0.05 *M* $ZnSO_4$, 10 ml. of 12.0 *N* H_2SO_4	2.0	2 hrs.	0.0208	0.0189
4	Same as No. 3 and No. 4 plus excess solid ZnS (fresh)	2.0	2 hrs.	0.0208	0.0358
5	60 ml. of 2.0 *N* H_2SO_4 saturated with H_2S. Excess solid ZnS (fresh)	2.0	6 hrs.	0	0.0354
6	60 ml. of 2.0 *N* H_2SO_4 saturated with H_2S plus large excess ZnS (aged)	2.0	3 hrs.	0	0.0049
7	As 6. Small excess ZnS (aged)	2.0	1.5 hrs.	0	0.0050
8	25 ml. of 0.05 *M* $ZnSO_4$, 25 ml. of water, 10 ml. of 12.0 *N* H_2SO_4, excess solid ZnS (aged)	2.0	Stood 1 month	0.0208	0.0052
Blank 9	25 ml. of 0.05 *M* $ZnSO_4$, 25 ml. of water, 10 ml. of 12.0 *N* H_2SO_4	2.0	Stood 1 month	0.0208	0.0208

The solid zinc sulfide designated as the fresh product was prepared by precipitation from a 0.1 *M* solution of zinc sulfate by the action of hydrogen sulfide. The acidity before precipitation was 0.08 *N* in sulfuric acid. After a fifteen-minute period of precipitation the sulfide was filtered off, washed several times with water and added in a moist condition to the contents of the precipitation flasks. The aged product employed was formed from a solution of zinc sulfate having an acidity before precipitation of 0.2 *N* in sulfuric acid. The precipitate was allowed to age in the mother liquor saturated with hydrogen sulfide for one month before use. As in the case of the fresh product the aged precipitate was added to the contents of the precipitation flasks in a moist condition. The work was conducted at room temperature. The acidity given is, as usual, uncorrected for acid liberated or used up by the reaction taking place. The procedure followed consisted of bubbling hydrogen sulfide through the mixture of solutions indicated for a period of three minutes after expulsion of air. Thereafter the contents of the flasks were shaken with continuous passage of hydrogen sulfide over the solutions for the time indicated in the table. In experiments 8 and 9 the solutions were kept saturated with hydrogen sulfide by frequent replenishments of the gas phase throughout the month of standing. In case solid zinc sulfide was added, addition was made after an interval of shaking sufficiently long (fifteen minutes) to insure thorough saturation of the solution with hydrogen sulfide. At the end of the period of shaking the contents of the flasks were filtered, the precipitates washed four times with cold water, and the filtrates analyzed for zinc in the usual manner.

It appears from the table that the solutions employed (0.02 *M* with respect to zinc salt, 2.0 *N* in sulfuric acid, saturated with hydrogen sulfide), while undersaturated with respect to the very small and imperfectly crystalline particles of freshly precipitated zinc sulfide, were supersaturated with respect to the aged product. The difference in solubility, in 2 *N* sulfuric acid saturated with hydrogen sulfide, of the two products is very marked, being in the neighborhood of 0.005 *M* for the aged precipitate as compared to 0.035 *M* in the case of the fresh product. Had the decrease in solubility with aging been due to only a partial change to a more insoluble form we should expect to find a greater solubility of zinc sulfide in those experiments where a large excess of the aged product was present than in those where only a small excess was present. Comparison of experiments No. 6 and No. 7, corroborated by duplicate experiments not shown in the table, shows that such is not the case. X-ray evidence gave no indication that the bulk of the precipitate changes crystal modification on aging, but did show an increase in the perfection of its crystalline state. The postprecipitation of zinc sulfide by mercuric sulfide in a medium of 2 *N* sulfuric acid is extremely slow. Apparently the zinc sulfide is precipitated in the aged, less soluble form. Even after a month of contact with mercuric sulfide equilibrium had not as yet been reached when the original zinc sulfate concentration in the mixture was 0.02 molar. If the original concentration of zinc salt was decreased to 0.004 molar no postprecipitation occurred even after long times of standing, since the solubility of well-aged zinc sulfide is greater than corresponds to this zinc concentration in 2 *N* sulfuric acid saturated with hydrogen sulfide.

5. The postprecipitation of zinc sulfide can be inhibited by making use of two different principles: (a) by the replacement of the adsorbed hydro-

gen sulfide on mercuric sulfide by an organic substance containing polar sulfur groups (a similar inhibiting effect was found by Kolthoff and Pearson (6) in working with the system copper sulfide–zinc sulfide), and (b) by a replacement of the adsorbed zinc ions by other cations. It has been shown that strychnine ions are fairly effective in this respect at various acidities (table 9). Aluminum ions, on the other hand, have only a slight replacing effect upon the zinc ions and exert no inhibiting effect upon the postprecipitation of zinc sulfide.

6. The promoting effect of mercuric sulfide upon the precipitation of zinc sulfide decreases when the mercuric sulfide is aged. Upon aging in the supernatant liquid an agglomeration of the particles occurs, resulting in a decrease of the surface and therefore, also, of the promoting effect upon the precipitation of zinc sulfide. In addition to a coarsening of the particles of mercuric sulfide, a transformation of the black, cubic form of metacinnabar into the red, trigonal form of cinnabar occurs upon aging. The speed of transformation is fairly great at low acidities and decreases with increasing acidity of the supernatant liquid. This explains why mercuric sulfide aged in neutral medium exerts less promoting effect upon the postprecipitation of zinc sulfide than that aged in acid medium for the same length of time (table 7). The speed of transformation of the black into the red form is favored very strongly by an increase in temperature. For this reason aging of the mercuric sulfide at higher temperatures decreases its promoting effect on the postprecipitation of zinc sulfide much more than aging for the same length of time at room temperature.

7. When the mixture of mercuric chloride and zinc salt is precipitated with hydrogen sulfide at higher temperatures and filtration made after the three-minute precipitation period, less zinc was found to be postprecipitated than when treated with hydrogen sulfide at room temperature (table 6). If, however, the solutions were allowed to cool down during a period of shaking under hydrogen sulfide pressure, the final result was about the same as for those experiments carried out entirely at room temperature.

8. In the experimental part of this paper it has been mentioned that zinc sulfide postprecipitated with fresh mercuric sulfide cannot be completely removed from the precipitate by a continuous extraction with 3 *N* hydrochloric acid at room temperature. Complete extraction is easier from precipitates which are formed with aged mercuric sulfide than from those formed by precipitation from solutions containing both metallic ions or from those obtained by using freshly precipitated mercuric sulfide. Apparently the zinc sulfide is intimately associated with the mercuric sulfide in the mixed precipitate, although the latter when first formed contains no zinc. The difficulty with which extraction of the zinc is made from the mixed precipitate suggests that it is present in the form of a mixed crystal.

X-ray studies reported in a previous paper (7a) indicated that a limited mixed crystal formation had occurred. The zinc sulfide then enters the black mercuric sulfide lattice after the latter has been formed. This penetration takes place most easily into freshly precipitated mercuric sulfide and only with great difficulty, if at all, in case of a well-aged product, thus accounting for the differing ease of extractability of the zinc from various types of precipitates. When dealing with fresh precipitates the penetration takes place to a maximum extent very quickly. Inasmuch as transformation to the trigonal form occurs to a large extent in all of the well-aged precipitates of mercuric sulfide, it is not possible to state definitely whether or not penetration is possible in a well-aged mercuric sulfide which has retained its cubic form. Experiments carried out with mercuric sulfide aged in strongly acid medium, in which the transformation to the red form is very slow, indicate that there may be slow penetration into well-aged products providing they consist of the metacinnabar form. It seems fairly conclusive that no penetration occurs in the case of the red hexagonal form—in other words, no mixed crystals of hexagonal habit form, although the red mercuric sulfide promotes the precipitation of zinc sulfide. It may be mentioned that the subsequent mixed crystal formation of postprecipitated zinc sulfide with mercuric sulfide is of secondary consideration with regard to the general problem of postprecipitation of zinc.

SUMMARY

1. Mercuric sulfide promotes the precipitation of zinc sulfide from acid medium. There is no coprecipitation, but the phenomenon constitutes a typical case of postprecipitation.
2. The promoting effect of mercuric sulfide upon the postprecipitation of zinc sulfide is much more pronounced than that of cupric sulfide. Even traces of mercuric sulfide have a distinct effect.
3. The postprecipitation is explained by a primary adsorption of zinc sulfide on the mercuric sulfide with subsequent precipitation of the latter. Substances replacing adsorbed hydrogen sulfide or ions competing with zinc ions in their adsorption as counter ions inhibit the postprecipitation.
4. A very slow postprecipitation occurs at an acidity as high as 2 N in sulfuric acid, although freshly precipitated zinc sulfide would dissolve at this acidity. It has been shown that at this high acidity the zinc sulfide is postprecipitated in the aged, less soluble form.
5. With aging of the mercuric sulfide its promoting effect upon the postprecipitation decreases. This is partly explained by an agglomeration of the particles, but also by a transformation of the metacinnabar to the cinnabar form. The temperature at which the mercuric sulfide is precipitated has little effect upon its ability to promote the precipitation of zinc sulfide.

6. Zinc sulfide postprecipitated with fresh mercuric sulfide cannot be completely extracted from the precipitate with 3 *N* hydrochloric acid at room temperature. The postprecipitated zinc sulfide penetrates the lattice of the cubic mercuric sulfide, giving rise to a limited mixed crystal formation.

7. The extent of postprecipitation diminishes greatly with decreasing partial pressure of hydrogen sulfide.

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THE PHYSICAL CHEMISTRY OF FLOTATION. VIII

THE PROCESS OF ACTIVATION

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Potassium ethyl xanthate, which is not normally able to induce the flotation of sphalerite (ZnS), becomes effective in the presence of a low concentration of copper sulfate. This action of a copper salt, known technically as "activation," is used for the flotation of sphalerite following the flotation of galena by xanthate alone. It is generally assumed that the sphalerite becomes coated with a thin film of copper sulfide, which can adsorb the xanthate. In support of this interpretation, it is urged that many copper-bearing minerals do adsorb xanthate from very dilute solutions. It has been demonstrated by several methods that sphalerite acquires a coating of a copper-bearing film when it is immersed in a copper sulfate solution. This coating is not removed by a water washing, but is removed by treatment with a dilute solution of sodium cyanide (12). Three molecules of cyanide per atom of copper are sufficient to prevent the activation of the sphalerite by copper sulfate, presumably because a soluble cupricyanide is formed which greatly reduces the copper-ion concentration. The minimum concentration of copper ions required to activate sphalerite is of the order 10^{-28} (12).

Many lead–zinc ores contain sufficient soluble copper to activate the sphalerite and thus to interfere with its separation from galena. Addition of sodium cyanide during grinding and conditioning of the ore usually prevents flotation of much of the sphalerite with galena, but some operators think that cyanide does not completely prevent activation. If this be true, the activation must be due to some other ion, not removable from the sphalerite surface by cyanide. Lead salts would cause activation of this type but sodium carbonate, if present, would tend to precipitate them and thus to prevent activation. The results cited later may therefore be of more than academic interest.

Berl and Schmidt (1), using a spectroscopic method to determine the amount of heavy metal ions removed by adsorption, have demonstrated that galena and sphalerite both adsorb copper and that sphalerite also adsorbs lead from solutions of their soluble salts. Ravitz and Wall (8), who used an iodometric method to measure the amount of copper removed from a copper sulfate solution by sphalerite, claim that the adsorption is almost complete within a minute; that for particles of 50 microns and over, which is the size preferred in practice, the amount of copper sulfate required for maximum recovery in flotation is approximately equivalent to the amount that would be required for the formation of a unimolecular film, and that considerably greater amounts of copper up to a fixed maximum value can be adsorbed from concentrated solutions. They suggest that the maximum amount adsorbed is just sufficient to coat with a unimolecular film the surfaces of all the unit crystal blocks, whose size is set at 0.37 micron, penetration into the crystal lattice being assumed.

In some instances activation of a mineral can be effected by adding a salt of the metal of the mineral. Thus, when using methyl xanthate as collector, chalcopyrite can be activated by copper sulfate. Similarly, the addition of zinc sulfate helps in the flotation of sphalerite by amyl xanthate. This type of activation is connected with the mechanism of the adsorption of the xanthate, and has led us to the conception of an "adsorption solubility product."

Another type of activation, exemplified by the action of sodium sulfide on anglesite and cerussite, which has already been considered (14), will not be discussed here.

It has generally been assumed that activation of sphalerite by copper sulfate is due to the formation of a surface coating of cupric sulfide, formed, in accordance with the solubilities, by the action

$$ZnS + Cu^{++} = CuS + Zn^{++}$$

If one accepts the evidence of Ravitz and Wall that a unimolecular film suffices for flotation[1], one would not expect such a film to possess the surface properties of massive covellite (CuS). Experiment does, in fact, indicate that the film has not the properties of massive covellite, at least with regard to depression by sodium cyanide or caustic soda. Figure 1, constructed from earlier papers (12, 13), shows for covellite and for preactivated sphalerite the relationships between the concentrations of cyanide and the pH value necessary to prevent air-mineral contact in the presence of 25 mg. per liter of potassium ethyl xanthate. (By preactivation is meant immersion of the sphalerite specimen in a copper sulfate solution before it is placed in the xanthate solution.) Contact for either mineral is possible below or to the left but not above or to the right of its curve.

If copper sulfate is present as well as xanthate, a considerably higher concentration of cyanide is necessary to prevent contact. With 150 mg.

[1] One could not at the same time accept the suggestion of Taggart, del Giudice, and Ziehl (9) that this film must become oxidized before it can adsorb xanthate, for if it did we should have simply a unimolecular adsorbed film of copper sulfate on zinc sulfide.

of $CuSO_4 \cdot 5H_2O$ and 25 mg. of the xanthate per liter, the corresponding curve for sphalerite, also taken from an earlier paper (13), is shown in figure 2. A similar curve has been determined by Mr. A. B. Cox for stibnite which, like sphalerite, requires activation before it will respond to a neutral solution of ethyl xanthate. It will be seen that the curves for the two minerals are very similar. The corresponding curve for covellite in the presence of copper sulfate was not determined completely, but it lies very much higher than these two curves. It is apparent, therefore, that when copper sulfate activates a sulfide mineral, the coating produced is not identical with covellite. Nor is it probable that the coatings for different minerals are held equally firmly: the non-identity of the activation curves for galena and sphalerite when using sodium diethyl dithiophosphate as a collector suggests that they are not (13).

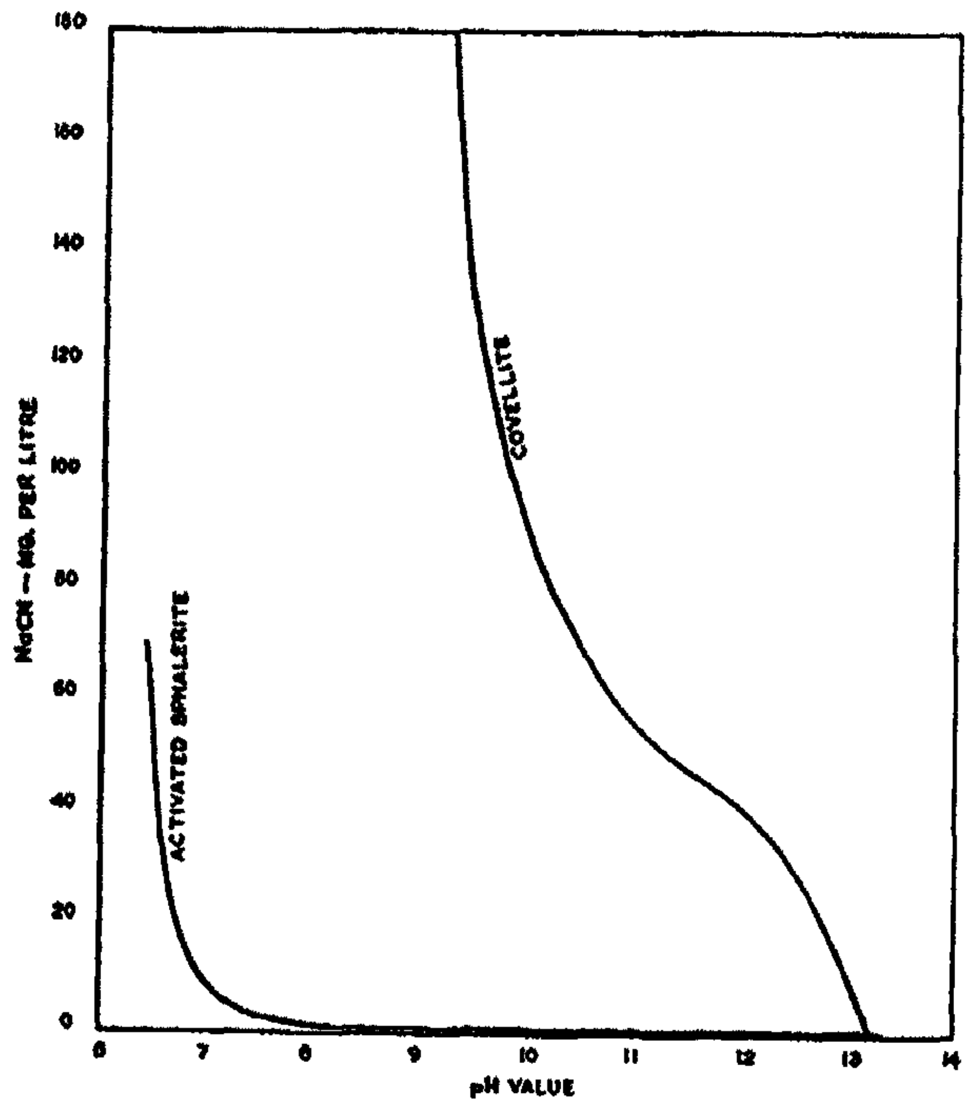

FIG. 1. Relationship between pH value and concentration of sodium cyanide necessary to prevent contact at surfaces of covellite and activated sphalerite. Potassium ethyl xanthate = 25 mg. per liter. No added copper sulfate.

For reasons which will be cited elsewhere we do not agree with the contention of Taggart, del Giudice, and Ziehl (9) that the possibility of adsorption of a *collector* is governed entirely by the solubilities of the metallic salts of that collector. However, as these authors state, there is little evidence to show whether adsorption of an *activator* is governed entirely by solubility considerations. We set out, therefore, to determine which metallic salts are effective as activators for sphalerite. If solubilities alone are responsible, immersion of a sphalerite specimen in a solution of a salt of any metal whose sulfide is less soluble than sphalerite may cause activation, but immersion in a solution of a salt of a metal whose sulfide is more soluble than sphalerite should not. In testing this view we proposed to use ethyl xanthate to indicate whether adsorption of the metal ions had occurred, the procedure being to immerse the pretreated sphalerite in a xanthate solution and to observe whether a bubble of air could effect contact with it. An assumption was made here, namely, that if the surface is filmed by the metal ions, it will respond to ethyl xanthate. When the tests were begun this seemed probable enough, for the heavy metal sulfide minerals that had been tested had all responded to ethyl xanthate. However, during the progress of the work it was found that stibnite (Sb_2S_3) does not respond to neutral ethyl xanthate solutions, but only to slightly acid solutions of ethyl xanthate. This raised doubts concerning the validity of our initial assumption. Consequently, if the treated sphalerite

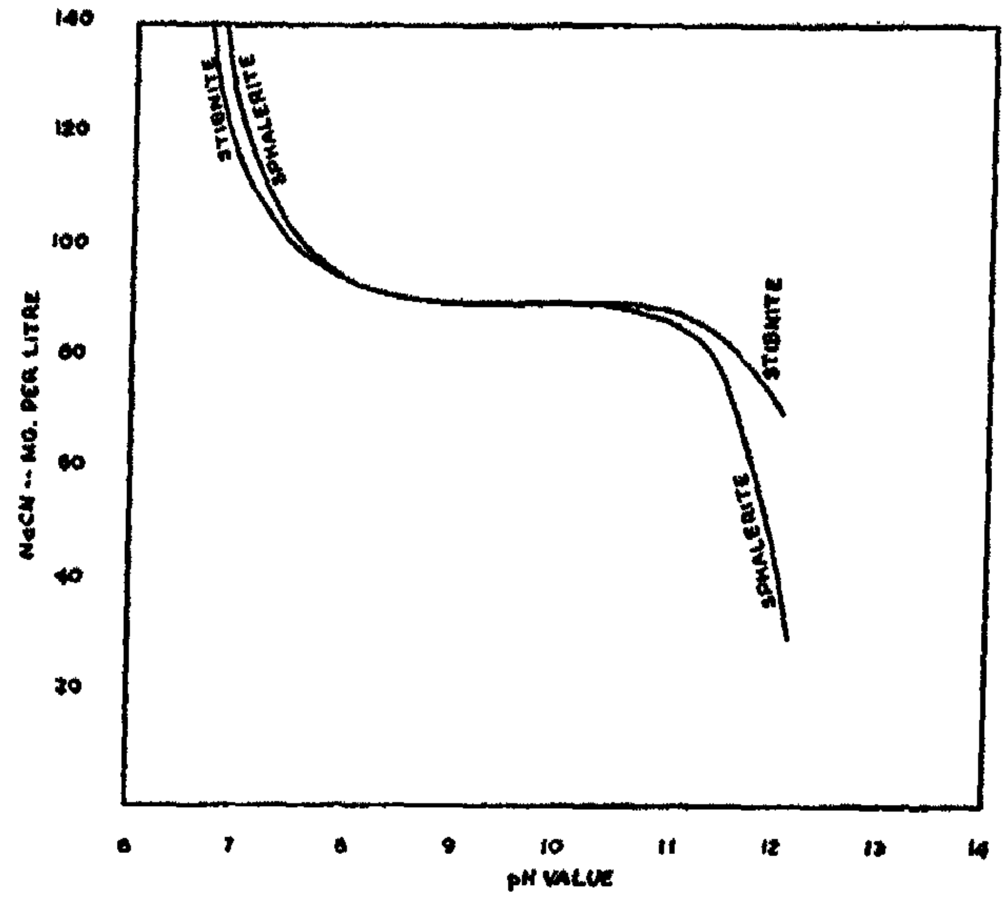

FIG. 2. Relationship between pH value and concentration of sodium cyanide necessary to prevent contact at surfaces of sphalerite and stibnite. Specimens preactivated in a solution of copper sulfate. $CuSO_4 \cdot 5H_2O$ = 150 mg. per liter; potassium ethyl xanthate = 25 mg. per liter.

specimen failed to respond to a neutral ethyl xanthate solution it was tested also in an ethyl xanthate solution at a pH value of between 4 and 5. More potent collectors could not be used, since they cause contact at a sphalerite surface in the absence of activators (13). Despite these precautions, the absence of a response to ethyl xanthate, though it suggests that adsorption of the metal ions has not taken place, does not prove it. On the other hand, if a response has been obtained, the conclusion is definite that activation has taken place.

Kolthoff (4) cites three values between 5×10^{-26} and 8×10^{-26} for the solubility product of α-zinc sulfide, and the single value 10^{-24} for β-zinc sulfide. Let us consider activation by the salt of a bivalent metal (M). If the process is dependent only upon solubilities, it follows that the filming process,

$$\mathrm{ZnS} + \mathrm{M}^{++} = \mathrm{Zn}^{++} + \mathrm{MS}$$

occurs if on the addition of the salt of M,

$$\frac{(\mathrm{M}^{++})}{(\mathrm{Zn}^{++})} > \frac{(\mathrm{MS})}{(\mathrm{ZnS})}, \text{ i.e., } > \frac{\text{Solubility product of MS}}{\text{Solubility product of ZnS}}$$

The concentration of zinc ions must be very small: we should therefore expect filming by any bivalent metal, the solubility product of whose sulfide is equal to or lower than the solubility product of zinc sulfide. For filming to occur under this mechanism it would be necessary that the term:

$$\frac{(\text{Solubility product of ZnS})}{(\mathrm{Zn}^{++})} \text{ should be greater than}$$

$$\text{(i)}\quad \frac{\text{Solubility product of MS}}{(\mathrm{M}^{++})} \text{ for bivalent metal salts}$$

$$\text{(ii)}\quad \frac{\text{Solubility product of } \mathrm{M_2S}}{(\mathrm{M}^{+})^2} \text{ for univalent metal salts}$$

$$\text{(iii)}\quad \frac{\text{Solubility product of } (\mathrm{M_2S_3})^{1/3}}{(\mathrm{M}^{++})^{2/3}} \text{ for tervalent metal salts}$$

Unfortunately, the solubility products of the metallic sulfides are not known with any degree of certainty. Table 1 sets out recorded values from various sources. Because of the decomposition of ferric sulfide it is doubtful whether the figures for it are significant. There is an enormous discrepancy between the figures cited in Landolt-Börnstein's tables for the solubilities and solubility products of heavy metal sulfides. Thus the solubility of mercuric sulfide, given as 1.2×10^{-6}, corresponds to a solubility product of the order 10^{-15}; the recorded value is 10^{-53}. For lead sulfide the corresponding figures are 10^{-9} and 10^{-29}. Though greater care

TABLE 1

Solubility product of metal sulfides

METAL	KOLTHOFF (4)	LANDOLT-BÖRNSTEIN (5)	LATIMER AND HILDEBRAND (6)	HANDBOOK OF CHEMISTRY AND PHYSICS (3)	TREADWELL-HALL (10) (CALCULATED)
Barium				Decomposes	
Strontium				Decomposes	
Calcium				Decomposes	8×10^{-4}
Magnesium				Decomposes	
Beryllium				Decomposes	
Aluminum				Decomposes	
Chromium				Decomposes	
Uranium				Decomposes	
Cerium				Decomposes	
Titanium				Decomposes	
Manganese	7×10^{-16} to 6×10^{-22}	1.4×10^{-28}	10^{-15}	1.4×10^{-15}	1.4×10^{-11}
Ferrous	4×10^{-19} to 3×10^{-22}	2×10^{-19}	10^{-19}	3.7×10^{-19}	1.1×10^{-15}
Ferric				Decomposes	(8×10^{-88})
Zinc	10^{-24} to 5×10^{-26}		10^{-23}	1.2×10^{-23}	1.1×10^{-19}
Nickel	1.1×10^{-27}	10^{-21} to 10^{-28}	10^{-24}	1.4×10^{-24}	6×10^{-21}
Cobalt	1.9×10^{-27}	3×10^{-26}		3×10^{-26}	6×10^{-21}
Thallium	7×10^{-23} to 10^{-24}	10^{-20}			
Lead	3.4×10^{-28}	10^{-29}	10^{-25}	3.4×10^{-28}	4×10^{-26}
Cadmium	7×10^{-26} to 5×10^{-29}	4×10^{-29}		3.6×10^{-29}	3.6×10^{-29}
Cuprous				2×10^{-47}	
Cupric	7×10^{-41} to 10^{-42}	8.5×10^{-45}	8×10^{-45}	8.5×10^{-45}	8.5×10^{-41}
Silver	(av.) 10^{-50}	1.6×10^{-49}	2×10^{-49}	1.6×10^{-49}	2.5×10^{-40}
Mercurous	10^{-47}				
Mercuric	3×10^{-54}	10^{-53}	1×10^{-53}	4×10^{-53} to 2×10^{-49}	4×10^{-54}
Bismuth	1.6×10^{-72} (?)				

is usually taken in the determination of solubility products, the values recorded for them are of doubtful value, for the assumptions upon which the determinations are based cannot be justified. The greatest weight must be attached to Kolthoff's figures, which were obtained from a critical study of the work of earlier writers.

Even if it were proved that solubilities alone governed activation, it is evident that the solubilities of some of the sulfides are not known with sufficient accuracy for one to be able to predict whether zinc sulfide should be activated by solutions of the corresponding heavy metal salts. The results obtained in this investigation do not, therefore, enable one to decide whether activation of sphalerite should be attributed to simple double decomposition or to "exchange adsorption" (2). There is no doubt that salts of the metals that form the least soluble sulfides activate sphalerite, nor that salts of the metals that form the most soluble sulfides do not activate it. It has not been settled, however, whether activation is governed entirely by solubility considerations for salts of metals whose sulfides are of the same order of solubility as zinc sulfide.

EXPERIMENTAL

Method I: The sphalerite specimen was polished in the usual manner (11), placed in a 10 mg. per liter solution of the heavy metal salt, and after thirty minutes, 25 mg. per liter of potassium ethyl xanthate was added. After a second period of thirty minutes the specimen was tested with a captive bubble of air to ascertain whether it had acquired a xanthate film. If contact was possible between the bubble and the surface the angle of contact was measured at intervals up to two hours. The recorded values were measured two hours after the xanthate addition; usually a steady value was reached much sooner than this.

Method II: An alternative method of activation was tried for each metal, namely, to stand the specimen for thirty minutes in a 1 g. per liter solution of the salt, then after rinsing in water, to transfer to a 1 g. per liter xanthate solution. This method possesses the advantage that there is no precipitate of heavy metal xanthate in the solution to hinder contact with the surface.

Method III: For reasons already stated, if neither of these procedures proved that activation had occurred, a third was tried, namely to test the pretreated specimen in an acidified 200 mg. per liter ethyl xanthate solution at a pH value of between 4 and 5. Control tests showed that in the absence of activators contact with sphalerite was impossible under these conditions: in solutions containing 500 mg. of potassium ethyl xanthate per liter, weak and irregular contact is obtained if the pH value is reduced to 4 by addition of hydrochloric acid, and with very high xanthate concentrations and acidities an angle of contact only two or three degrees less than 60° is obtained. This contact is not due to products of the decomposition of the xanthate in acid solutions. Nor is it due to the iron that is almost invariably contained as an impurity in the sphalerite, for resin blende, marmatite (a solid solution of iron sulfide in zinc sulfide), and cleiophane (an iron-free blende) all behave similarly. Curves obtained previously (13) suggest that sphalerite might respond, without activation, to high ethyl xanthate concentrations in acidified solutions.

Method IV: The contact tests were supplemented by direct flotation tests in stoppered cylinders. The procedure was similar to that adopted in methods I, II, and III, except that a suspension of sphalerite in water was used for the attempted activation; after additions of 20 mg. per liter of terpineol as frother, of xanthate as collector, and of acid, if there was no response in neutral solutions an attempt was made to float the mineral by shaking the stoppered tube vigorously.

PURITY OF CHEMICALS

Since even 1 mg. of copper sulfate per liter is an activator for sphalerite, it is essential that the compounds tested should be free from any substantial amounts of copper or other heavy metal salts. The purest specimens obtainable were recrystallized before use, and the xanthates were purified as described previously (11). Antimony trichloride was redistilled. Titanium trichloride was crystallized from the commercial 15 per cent solution by adding alcohol and ether, washing with ether, and then recrystallizing from alcohol by addition of ether. The water used was distilled from glass apparatus and was copper-free.

TECHNIQUE OF POLISHING

At one time during the investigation it became so difficult to obtain clean polished specimens that, had we not had several years' experience to convince us that clean specimens of sphalerite were not air-avid, we should have believed that they were. As some other investigators have apparently experienced similar difficulties, a description of the methods adopted to overcome them may not be out of place. Since one of us experienced greater difficulty than the other, and since trouble was encountered particularly in hot weather, it was suspected that the natural grease of the hands was responsible. Linen gloves lessened but did not completely eliminate the trouble, but surgical rubber gloves, when properly treated, did remove it. The gloves must be kept in such a condition that water readily wets them; this can be done by washing them with wet talc powder. Subsequently it was found that rubbing the hands with talc powder may suffice to remove the natural grease, and it is then possible to dispense with gloves.

TABLE 2

Activation of sphalerite by metallic salts

ELEMENT	SALT USED	ANGLE OF CONTACT			DIRECT FLOTATION TEST METHOD	
		Method I	Method II	Method III	Neutral solution	Acid solution
Barium	Nitrate	Nil	Nil	Nil	No flotation	No flotation
Strontium	Chloride	Nil	Nil	Nil	No flotation	No flotation
Calcium	Nitrate	Nil	Nil	Nil	No flotation	No flotation
Magnesium	Chloride	Nil	Nil	Nil	No flotation	No flotation
Beryllium	Nitrate	Nil			No flotation	No flotation
Aluminum	Potassium alum	Nil	Nil		No flotation	No flotation
Chromium	Potassium alum	Nil	Nil	Nil	No flotation	No flotation
Thorium	Nitrate	Nil	Nil		No flotation	No flotation
Uranium	Nitrate	Nil	Nil		No flotation	No flotation
Titanium	Trichloride	Nil	Irregular*	Irregular	No flotation	No flotation
Titanium	Double oxalate (K)	Nil	Irregular	Irregular	No flotation	No flotation
Manganous	Sulfate	Nil	Nil		No flotation	No flotation
Ferrous	Sulfate	Nil	Nil		No flotation	No flotation
Ferric	Ammonium alum	Nil	Nil		No flotation	No flotation
Stannous	Chloride	Nil	Nil*	Nil	No flotation	No flotation
Stannic	Double chloride (Na)	Nil	Nil	Nil	No flotation	No flotation
Arsenic	Trioxide	Nil	Nil	60°	No flotation	Good flotation
Antimony	Trichloride	Nil	Nil*	61°	No flotation	Good flotation
Nickel	Sulfate	Nil	Nil	Nil	No flotation	No flotation
Cobalt	Sulfate	Nil	Nil	61°	No flotation	Weak flotation
Thallium	Nitrate	Irregular	60		Fair flotation	Fair flotation
Cerium	Sulfate	Nil	60		Good flotation	
Lead	Nitrate	61	62		Good flotation	
Cadmium	Sulfate	61	59		Good flotation	
Cupric	Sulfate	61	60		Good flotation	
Silver	Nitrate	62	61		Good flotation	
Mercuric	Chloride	63	60		Good flotation	
Mercurous	Sulfate	61†			Good flotation	
Bismuth	Nitrate		62*		Good flotation	
Gold	Acid chloride		61		Good flotation	
Platinum	Chloroplatinic acid		Irregular	58	Fair flotation	Good flotation

* Less than 1 g. per liter because of hydrolysis. † Saturated solution.

EXPERIMENTAL RESULTS

The results of the investigation are summarized in table 2. Except for titanium the results from direct flotation tests are in agreement with those from contact tests. The contact induced by some of the salts was not of the same order as that induced by copper sulfate, for example. When using copper sulfate as activator, the xanthate caused a rapid and complete response to an air bubble, but when using a titanium salt the reaction was slow and irregular; only on rare occasions was the characteristic angle (60°) obtained, and then only over a portion of the surface. In direct flotation tests, the presence of copper sulfate results in the formation of a highly mineralized froth that is stable for days and up to 75 per cent of the sphalerite can be floated. On the other hand, titanium salts, though they cause more sphalerite particles to reach the surface than would do so in their absence, do not result in the formation of a permanent mineralized froth. With thallium nitrate as activator, it seems at first that a stable froth will form, but although much of the mineral is carried to the surface by the bubbles, the froth does not persist, and most of the mineral falls. With cobalt sulfate the flotation is still less permanent.

Owing to hydrolysis, difficulties arose in testing salts of bismuth, tin, and antimony. Activation was attempted both in solutions acidified to prevent hydrolysis and in neutral suspensions containing the hydroxide. With bismuth, sufficient of the salt remains in solution at pH = 7 to activate sphalerite, and ethyl xanthate then induces the customary contact angle and leads to excellent flotation. With antimony trichloride, however, only in slightly acid solutions is there sufficient antimony for activation; the xanthate solution also is effective only in acid solutions. Neither in acid solution nor in neutral solution was stannous chloride an activator for sphalerite. Titanium trichloride also hydrolyzes, and it was the partly decomposed solution (pH = 3.5) that was in part effective as an activator. Arsenic trioxide dissolves very slowly in water; hydrochloric acid hastens the solution process and the excess acid can be neutralized before testing.

Sphalerite reduces chloroauric acid; a precipitate of metallic gold is formed on the surface of the sphalerite when using gold chloride. It is doubtful, therefore, if the activation should be attributed to the formation of a film of gold sulfide.

Cobalt and nickel are generally believed to form fairly insoluble sulfides. The failure of hydrogen sulfide to precipitate the metals from acidified solutions of their salts is difficult to understand, for the sulfides themselves do not dissolve in dilute acid. Middleton and Ward (7) have shown, however, that the mechanism of the precipitation is complex, and that precipitation of the true sulfides does not usually occur. Attempts to activate sphalerite by a solution of nickel sulfate, made alkaline by ammonia and stabilized by ammonium chloride, were not successful.

It is surprising that neither for stannous nor for stannic salts could conditions be found that led to activation of sphalerite. We found, however, that stannic sulfide is not precipitated from a 1 g. per liter solution of the double chloride by sodium sulfide, despite the reported low solubility of stannic sulfide, 0.0002 g. per liter.

Some results for silver and mercury, cited in an earlier paper (11), seemed to indicate that if the heavy metal salt was in stoichiometric excess of the xanthate, activation was not obtained. This indication was not substantiated, for on varying the concentrations over a wider range, it was found that contact was sometimes possible with the metal salt in excess. Precipitates of the heavy metal xanthates are responsible for the difficulties, and if the surface is freed from them (by wiping with a clean linen pad) contact is possible whatever the relationship between the metal and xanthate additions. In all the tests now recorded the surfaces tested were treated in this manner to free them from precipitates, visible or invisible, that would hinder contact.

SUMMARY

1. It has been found that salts of the metals platinum, gold, bismuth, mercury, silver, copper, cadmium, lead, cerium, antimony, and arsenic "activate" sphalerite in a manner such that it responds to ethyl xanthate and floats readily. Thallium and cobalt induce a somewhat weaker response and titanium, though it does have a weak influence on the response of the mineral to an air bubble, is not a sufficiently powerful activator to cause flotation.

2. In general, the metals that are effective as activators form relatively insoluble sulfides and those that are not effective form relatively soluble sulfides.

3. It is not possible to decide whether solubility considerations alone govern the activation process. Thallium, whose sulfide is reputed to be more soluble than that of zinc, does activate sphalerite, and tin salts, which give less soluble sulfides, do not activate sphalerite. However, the reported solubility products are not to be relied upon.

One of us (E. E. W.) wishes to express her thanks to the University of Melbourne for a scholarship that has rendered the work possible. The other author wishes to acknowledge the help of the companies by which he is employed, viz., Broken Hill South Pty. Ltd., North Broken Hill Ltd., Mt. Lyell Mining & Railway Co., Zinc Corporation Ltd., Electrolytic Zinc Co. of Australasia Ltd., and the Burma Corporation Ltd. Our thanks are due also to Messrs. H. Hey and A. B. Cox for valuable help and advice.

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THE RELATIONSHIP BETWEEN CONDITIONS GOVERNING RUPTURE AND FLOW IN FLOUR DOUGHS

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INTRODUCTION

In an earlier paper (6) it was shown that there is a general correlation between the bread-making qualities of flour doughs and certain of their physical properties, chiefly relaxation time (viscosity/shear modulus) and the rate of fall of viscosity during fermentation. The importance of a further dough property, the tendency to tear when stretched, was also realized, but the discussion of the significance of this in terms of viscosity, modulus, etc., was left until further experiments had been completed. The tendency to tear varies from dough to dough, but only becomes apparent to the baker when it reaches the stage when the dough "tears" easily under bakehouse manipulation. Such doughs are called "short" and the baker speaks of varying degrees of "shortness," such as "slight shortness" or "extreme shortness." Before this stage is reached, however, the baker does not recognize this tendency to tear, although it is there and probably influences the bread-making quality of the dough. It may, for example, be an important factor in determining whether a dough bakes into a loaf having the fine vesiculated crumb generally associated with an all-Manitoba flour or the coarse and open crum from an all-English flour.

A direct measure of the tensile strength of a flour dough is at the moment impossible, partly because the value obtained depends so greatly on the conditions of stress application, and partly because the excessive flow and consequent thinning of the test piece before rupture makes a determination of the cross section impossible.

The conception of "shortness" as determined by the baker is a complex one, and probably depends partly on ductility as well as on tensile strength. Ductility represents the critical deformation of the material at the point

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[1] By mutual agreement the authors' names are given in alphabetical order and no seniority is implied.

of rupture, the tensile strength being the critical stress. The relationship between the two is complex, and it is sufficient for the present purpose to point out that ductility is a function of viscosity, shear modulus, and elastic after-effect as well as of tensile strength. When a piece of dough is extended,[2] since the stress built up in the dough is proportional to the viscosity and to the rate of extension, the tensile strength will be exceeded after quite a small elongation if the extension is rapid, whereas a slow pull will allow a big deformation before rupture occurs. Thus for a direct test carefully controlled conditions are essential, whereas the baker judges shortness partly by extending the dough at quite uncontrollable rates and stresses, and partly by observing the stretching and tearing of a mass of dough under its own weight. Shortness is therefore not a very sharply defined property, and only comparatively wide differences can be reliably observed. Such wide differences do, however, occur even within the range of commercial flours, and some quantitative measure of them is essential for a further understanding of the nature of shortness. Measurements of ductility at unknown stress but controlled rates of deformation, although fairly reproducible, do not correlate with "shortness" as determined by handling. It has been shown (15) that the size of a bubble which can be blown in a dough is only a measure of "shortness" for doughs in which this property is predominant. In more extensible doughs, the shear modulus plays an important part in determining extensibility (*vide infra*).

Although the relationships between rupture and flow conditions are not yet fully understood, certain phenomena have been observed which indicate a method by which shortness may be measured. This method depends on the relationship between the rate at which viscosity falls with increasing stress (structural viscosity)[3] and the brittleness of materials (13). If a dough were a true highly viscous fluid, it would extend until the test piece narrowed to a thread before rupture; if it were a solid, up to a limiting stress (tensile strength) it would hardly deform at all (viscosity infinite) and at this stress it would break right across. This suggests that the more a dough approximates to a true fluid, the less "short" it is likely to be.

A certain correlation between high work-hardening and shortness had been observed in the rheogram experiments,[4] and it has been known for some time that high work-hardening is generally associated with big structural viscosity, but owing to the very limited range of stress available in the rheogram method, the full implications of this were not realized, although the significance of the distribution of relaxation times in determining plastic properties had already been appreciated (14).

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[2] It is here assumed that the elastic extension is small in comparison with the non-recoverable extension.

[3] The use of this term is convenient, but does not imply agreement with the theoretical treatment of the Ostwald school.

[4] For a description of the rheogram method see references 6 and 12.

If a dough is extended until it breaks, a fibrous structure[6] can be observed with the naked eye, especially clearly in the case of a short dough. Rupture occurs as a result of the tearing apart of the fibers; the more coarse the fiber structure, the sooner the mass disintegrates, because the tearing of a single fiber makes a big rent and greatly decreases the area over which the load is distributed. Local rupture results, as Griffith (5) has emphasized, in a big conversion of potential into kinetic energy, producing a local fall in viscosity. Griffith claims that in the case of metals this effect is responsible for the fact that measured tensile strengths are always so much smaller than the theoretical ones.

The formation of gross fibers in the dough as it is deformed not only causes an increase in viscosity and shear modulus (work-hardening) but also, by producing a heterogeneity of structure, effects a progressive slipping of fibers as stress increases, which shows itself in high structural viscosity. The shear angle gets more and more distorted the grosser the fibers become. Tammann and Rejtö (*vide* Goubkin (4) consider that work-hardening in metals may be ascribed entirely to this effect, and Nádai (7) states that it is responsible for brittleness, although it is now claimed (3) that this is an exaggeration.

When the junction between two fibers slips and breaks, a rent is formed and these previously extended fibers contract, making the rent worse. It is clear that the extent of widening of the rent will depend on how much the elastic elements were extended prior to rupture. The modulus of the fibers thus affects the conditions of rupture, and in comparing the structural viscosities of doughs it is best to adjust their moisture contents such that comparisons can be made at a fixed modulus (6). It must be remembered that whereas the measurable viscosity of a heterogeneous material is probably a function of the viscosities of all its parts at the stress in question, the tensile strength depends on the resistance of the weakest part. If there is a wide distribution of viscosities amongst the elements making up the dough, this will result both in a high structural viscosity and in a tensile strength which is low for the mean viscosity. Heterogeneity, reflecting a high structural viscosity, thus always tends to favor rupture and homogeneity favors flow.

The nature of the process of fiber formation in dough is very little understood, nor is it known why some flours give doughs which are abnormally prone to it, though it would be surprising if there were no natural variation in this, such as is found in all other physical properties.

Potel (8) and Potel and Chaminade (9) have shown that mild oxidation increases shortness in dough, while reduction diminishes it. The processes may be followed by observing changes in oxidation-reduction potential.

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[6] The term "fibrous structure" really implies no more than the existence of mechanical anisotropy, but is conveniently used in this sense even in describing properties of crystals (11).

In view of the recent work of Astbury, Dickinson, and Bailey (2) one might suggest that oxidation effects some type of mild denaturation involving "the liberation or generation of peptide chains which aggregate on coagulation into parallel bundles like those found in the structure of β-keratin and similar fibres." In the case of dough, these fibers only manifest themselves when the dough is extended. Whether the process is actually reversible on subsequent reduction, or whether the reducing agent acts at different spots in the dough structure is not known.

The fiber structure of dough is also enhanced by the addition of many other materials such as the fats, which, by modifying the viscosity at certain points in the dough, tend to increase heterogeneity, and hence structural viscosity.

Astbury (1) has pointed out that the amino acid[6] cystine ($HOOC\cdot CH(NH_2)CH_2S\cdot SCH_2CH(NH_2)\cdot COOH$) can form strong cross linkages between protein chains, like the rungs in a ladder. It has been found that cystine does make unyeasted dough feel less short. Cysteine ($HOOC\cdot CH(NH_2)CH_2SH$) would be expected to be less effective in this respect, because only one end of the molecule can attach itself to the protein chain, but on the other hand, it is a reducing agent, which may account for the fact that in practice it is found to be not much less effective than cystine. Other amino acids, such as aspartic acid and *m*-aminobenzoic acid, become less effective as their polar properties diminish.[7]

The connection between structural viscosity and shortness has a profound influence on the interpretation of viscosity and modulus data in terms of baking values. The extent of elastic recovery (spring) of a short dough, as estimated at the high stresses used in handling, will not bear a normal relation to that determined at low stresses intended to correspond to those obtaining in the fermenting dough. Good spring has been shown to depend on high viscosity and low modulus, and since the latter does not alter very drastically with stress, a dough whose viscosity falls to any abnormal degree as stress is increased will also appear progressively to deteriorate in spring. This has been amply verified in the baker's experience. This means that in order to compare relaxation times (viscosity/modulus) with bakehouse data, the stresses at which they are determined should correspond with the internal stress built up in the dough during fermentation. The latter cannot yet be measured directly. This diffi-

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[6] Amino acids are found as products of proteolysis in the fermentation of flour dough, and in view of the above experiments it is tempting to suggest that changes in physical properties during fermentation may be ascribed to them. This is unlikely, however, since it has been shown (6) that these physical changes are only slightly affected by the presence of normal quantities of yeast, and Samuel (10) has demonstrated that in yeasted doughs the amino acids produced by fermentation are used up by the yeast in its metabolism (*vide infra*).

[7] Some of these experiments were suggested to us by M. Potel.

culty has not been fully overcome, but it really means that both spring as measured by relaxation time and shortness as measured by structural viscosity in the test described below, have to be taken into account in assessing the quality of a flour. The extent to which these two properties are present in a dough determines its quality, but their relationship to each other, and how this varies in different flours, is not yet fully understood.

The experiments described below are designed to test whether the effect of various materials on the shortness of doughs as judged qualitatively by handling, can be shown to be paralleled by quantitative measurements of structural viscosity. If this can be done, although shortness is realized to be an extremely complex property, we shall be in a position to say that at least big differences in shortness can be measured by means of structural viscosity. In the later part of this paper, the question of smaller differences is discussed.

EXPERIMENTAL

Dough cylinders for viscosity measurements[8] are prepared by extruding the dough through a metal "gun" at high pressure. It was noticed that when doughs showed about the same viscosity at the standard shearing stress of the order of 500 dynes per square centimeter the "shorter" doughs always came out of the gun faster and thus evidently had lower viscosities than the non-short doughs under the very high stress applied in the gun. To test this quantitatively, a flour was made short by the addition of different quantities of lard, and the viscosity (η) at 500 dynes per square centimeter under set conditions, together with the time (T) taken for a certain quantity of dough to be extruded from the "gun" under a load of 7 lb., were determined. The results, which are included in table 1, clearly indicate that over a big range of stress increasing shortness is accompanied by a rapidly increasing structural viscosity.

The time of extrusion from a gun is not a very satisfactory way of measuring viscosity, and it was of interest to determine whether the ratios of viscosities at two different stresses which could be applied in the standard technique would indicate big differences in shortness. The viscosities of a dough made without shortening agents were measured at 250 and 600 dynes per square centimeter, respectively, the ratio of these viscosities being 1.29. A similar test on a dough in which 2 per cent of lard had been incorporated showed a ratio of 1.54, 5 per cent of lard gave a ratio of 2.23, and 10 per cent of lard 2.25, although in the last case the stresses employed were no longer suitable. The structural viscosity had evidently been progressively increased by the shortening.

A test was then arranged in which other materials which were known to

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[8] The technique for measuring viscosity and modulus is described in the earlier paper (6).

affect shortness were added to flour when making doughs, varying quantities being used. The viscosity (η) and the modulus (n) at 500 dynes per square centimeter and the time of flow (T) out of the gun were measured under standard arbitrary conditions and compared in each case with a separate control. (This was done because temperature varied somewhat between the different experiments.) The results are given in table 1. η/T is taken as a measure of structural viscosity. It is clear that the effects, although perhaps not very accurately determined, are in entire

TABLE 1

Effect of certain substances on the viscosity, modulus, and structural viscosity of flour doughs

	SUBSTANCE	DOSE IN PARTS PER MILLION OF FLOUR	$\eta/\eta_{control}$	$n/n_{control}$	$T/T_{control}$	$\eta/T/(\eta/T)_{control}$
decrease shortness	Cystine	4	0.86	1.07	0.89	0.96
		20	0.79	0.88	0.98?	0.80
		1,000	0.31	0.63	0.88	0.35
		2,000	Very low	Very low	0.82	Very low
	Cysteine	4	0.86	0.99	0.82	1.05
		20	0.71	0.77	0.73	0.98
		1,000	Very low	Very low	0.13	Very low
	Aspartic acid	500	0.59	0.85	0.91	0.65
		2,000	0.36	0.52	0.65	0.57
	m-Aminobenzoic acid	500	0.61?	0.82?	0.85	0.72?
		2,000	0.64	0.76	0.77	0.84
increase shortness	Lard	40,000	0.97	1.25	0.63	1.53
		100,000	1.61	1.85	0.38	4.22
		200,000	1.48	3.10	0.10	14.8
	$FeCl_3$	High?	5.75	2.98	0.49	11.8
	HPO_3	8,000	1.71	0.93	0.40	4.3

agreement with the earlier findings, thus justifying the conclusion that for the range of variation considered the structural viscosity test gives a valid measure of shortness.

The treated and untreated doughs were compared at the same moisture contents. The addition of amino acids decreased the viscosity, modulus, and structural viscosity and in this way rendered the dough both softer and less short. The addition of extra water to a dough also lowers η, n, and η/T, and to compare the relative effects of cystine and water on structural viscosity it is necessary to make measurements at an arbitrarily chosen condition of consistency, such as a constant modulus.

A further experiment was therefore made in which doughs, with and without cystine, were compared at a modulus of 1.0×10^4 dynes per square centimeter. For the control dough $\eta = 0.85 \times 10^6$ dynes per second per square centimeter, $T = 40$ sec., and hence $\eta/T = 2.1 \times 10^4$. For the dough containing 5 parts of cystine per 100 parts of flour $\eta = 0.79 \times 10^6$, $T = 46$, and hence $\eta/T = 1.7 \times 10^4$.

Similar measurements were made at other moduli, and in each case the dough containing cystine had a slightly lower structural viscosity than the control dough. Thus a series of doughs of increasing water content and having the same moduli as the cystine doughs in table 1 would, dough for dough, have higher structural viscosities than the latter. Cystine thus makes dough less short partly by rendering it softer, as does water, and also by reducing the structural viscosity for a given consistency. To produce similar effects on consistency much larger quantities of water than of cystine are necessary. Although water and amino acids diminish shortness in a somewhat analogous way, namely through their effect on viscosity, the mechanism must be entirely different. Some tentative suggestions about the amino acid mechanism have already been discussed.

TABLE 2

Structural viscosity of doughs from some English flours

FLOUR NO.	T	η	η/T
893	54	0.6×10^6	1.1×10^4
898	45	0.7×10^6	1.5×10^4
903	38	0.6×10^6	1.6×10^4
902	40	0.65×10^6	1.6×10^4
911	35	0.6×10^6	1.7×10^4
892	43	0.8×10^6	1.9×10^4
899	32	0.7×10^6	2.2×10^4
904	21	0.55×10^6	2.6×10^4

In addition to the above tests on flours whose degree of shortness had been artificially altered, a number of flours, all milled from English wheat and which when tested in the bakehouse had shown varying degrees of natural shortness, have also been examined.

These flours were tested under carefully controlled conditions in a constant-temperature room[9] at 80°F., the temperature at which the flours had been examined in the bakehouse.

Doughs were made from each, and at intervals samples were taken on

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[9] This constant-temperature room was not available for the earlier experiments quoted in table 1.

which the values of T, η, and n were obtained. Curves were then drawn relating T, η, and n to the age of the dough, and from these, values of T and η corresponding to a modulus of 1.0×10^4 were obtained for each flour. These values, together with the ratio of η to T, are given in table 2.

Of these flours, which are arranged in table 2 in order of increasing η/T, the first two, Nos. 893 and 898, did not, according to the baker, show any signs of shortness. On the other hand, the last three, Nos. 892, 899, and 904, were all stated to be decidedly short. Of the three intermediate flours, Nos. 903 and 902 were rather short, while No. 911 was not short.

The correlation between η/T and shortness is therefore not perfect, and this may be due to one or more of the following reasons:

(1) The impossibility of differentiating by feel any but comparatively large differences in shortness.

(2) Shortness, while being mainly determined by structural viscosity and to a less extent by elastic modulus, may also be influenced by other factors which are not apparent at the moment.

(3) The shortness of a test piece of dough from which the gas has been expelled may not be the same as that of the inflated parent dough which is examined by the baker. Shortness is more easily detected by feel in an inflated dough and is possibly influenced by the vesiculated structure of the inflated dough.

(4) While T gives a rough measure of viscosity, the value obtained may be so influenced by other factors that η/T may give only an approximate value of structural viscosity.

(5) Both η and T are not constants but are dependent on the stresses used in their determination. These stresses should approximate to those operating in the dough if exact correlation with bakehouse experience is to be expected. The correct values for these stresses will only be found after considerable experience. In this connection it may be mentioned that the viscosities of the flours in table 2 were measured both at 600 and 200 dynes per square centimeter, but that the values of structural viscosities, as given by the ratio η_{200}/η_{600}, were so similar as to fail to differentiate one flour from another.

While therefore it is realized that the present methods of measuring structural viscosity and assessing shortness by feel are too imperfect to expect a close correlation between them in the case of the comparatively small differences between natural flours, there is little doubt that the two are intimately connected.

SUMMARY

1. It has been shown that the shortness (i.e., ease of tearing) of flour doughs is closely paralleled by the rate at which viscosity falls with increas-

ing stress (structural viscosity). A perfect correlation is not obtained, partly because neither property can be determined with great accuracy.

2. The effect on structural viscosity of certain substances (fats, amino acids, etc.) known to alter the shortness of dough has been measured, and the nature of the processes involved discussed.

3. The structural viscosities of doughs made from a batch of English flours have been determined, and it is found that the data are paralleled by fairly large differences in shortness as observed in the bakehouse.

4. The significance of shortness in terms of heterogeneity of dough, and its relation to tensile strength and ductility are tentatively discussed.

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SOAPS: ELECTRIC CHARGE EFFECTS AND DISPERSING ACTION

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INTRODUCTION

When a soap acts as a detergent, it functions in a number of ways. Two of its most important functions are its action as an emulsifying agent and as a deflocculating agent. By emulsification, soap suspends oily materials; by deflocculation, it suspends "inert" materials. Essentially both processes are the same in effect, for each results in the dispersion of the foreign material in the soap solution in such fashion that it can be removed with the soap solution or rinse water. While oily material is suspended almost entirely by emulsification, some solvent action by the soap solution on oils undoubtedly occurs (11, 13). However, in the relatively dilute solutions used in most washing operations, the solvent powers of soap solutions are small.

The purpose of this investigation was to consider the mechanism whereby soaps render emulsions of oily materials and suspensions of "inert" materials relatively stable. In this way it was thought possible to arrive at a more complete picture of the detergent action of soap.

THEORETICAL

In the case of oily materials emulsified by soap solutions in a washing operation, it is doubtful that water-in-oil emulsions are ever formed; only oil-in-water emulsions result. Ellis (3) and Powis (12) have shown that the stability of oil-in-water emulsions is dependent upon the value of the electric charge carried by the oil droplets. The higher the value of the charge, the more stable is the emulsion.

The oil droplets of an oil-in-water emulsion usually carry a negative charge. Since the hydrocarbon tail of the fatty-acid ion of a soap resembles the molecules of an oily material, the two should be more or less mutually soluble. If an oil droplet acquires the negative ion of a soap by dissolving this hydrocarbon tail, it also acquires the charge carried by the ion. In this way the negative charge of the oil droplet may be built up, and hence the stability of the emulsion increased.

In the case of the "inert" materials, it seems probable that a similar phenomenon would occur. Most particles, when suspended in water, assume a potential negative to that of water. The adsorption of a negative ion by such a particle serves to increase the negative potential. The magnitude of this effect on the potential increases with the valence of the ion adsorbed. For instance, the ferrocyanide ion increases the negative potential of graphite more than does the chloride ion (1).

McBain and his coworkers (8) have explained the anomalous conductivity of soap solutions by assuming the formation of colloidal micelles bearing a high electric charge-density. The formation of these micelles involves the fatty-acid ions of the soaps, and the micelles bear a negative charge. This high charge-density is analogous to a high negative valence. In view of the valence effect of ions on the electric potential, referred to above, it seems probable that, owing to the adsorption of these highly charged micelles, a soap should have a large effect on the potential of particles of inert materials suspended in a solution of the soap.

TABLE 1

Fatty acids used in the preparation of soaps

ACID	EASTMAN CATALOG NO.	MELTING POINT	SAPONIFICATION NUMBER	IODINE NUMBER
Caprylic	665			
Lauric			272.7	
Myristic	1116	53.8		
Palmitic	1213	61.9		
Stearic	402	68.5	196.3	0.54
Oleic		7.1	197.5	92.9

The effect of soap solutions on the charge of both the oil droplets of an emulsion and the particles of a suspension of an inert material can be determined by measurement of the zeta potential in an electrophoresis cell. This has been done in this investigation, and the results are reported below. An attempt has also been made to correlate the stability of the suspension of an inert material in soap solutions with the value of the zeta potential.

MATERIALS

Table 1 lists certain fatty acids from which the sodium and potassium salts were prepared according to the method of Ferguson and Richardson (4). It also includes the available constants and information as to sources of the acids.

Two oils were investigated, one a paraffin oil and the other a cottonseed oil. Neither oil contained more than 0.03 per cent free fatty acid calculated as oleic acid.

The inert material used in the majority of the electrophoresis experiments was a bleaching carbon Nuchar GL, made by the Industrial Chemical Sales Company of Chicago. It contained 1.85 per cent water-soluble ash and was grease-free. This carbon was screened to remove particles larger than 1 mm. in diameter.

APPARATUS

The electrophoresis apparatus was of the Northrop-Kunitz (9) type, and was obtained from the Arthur H. Thomas Company of Philadelphia, Pa. In order to work at elevated temperatures, a jacket was built around the apparatus and the desired temperature maintained by a thermoregulator and electric heater. Extensions were attached to the stopcock handles so that they could be manipulated from outside the jacket.

A potentiometer, used in conjunction with an assembly similar to that suggested by Gibbard (5), was employed to measure the potential drop across the electrophoresis cell.

EXPERIMENTAL PROCEDURE

The solutions were prepared directly from weighed amounts of the dry salts, including soaps, and freshly boiled distilled water which had not been allowed to cool. The solutions were brought directly to the desired temperature.

In order to prepare the emulsions, 1 cc. of the oil was shaken with 100 cc. of the water or solution. The excess oil was removed before the emulsion was used. To prepare the suspensions of inert materials, 0.1 g. of the solid was shaken with 100 g. of the solution.

When the electrophoretic velocity was to be determined, the suspension or emulsion was placed immediately in the electrophoresis cell, the velocity of the particles or globules determined with a stopwatch in the usual manner, and the potential drop across the cell measured. The microscope was focused at the level given by the equation

$$x = d\left(1/2 - \frac{1}{2\sqrt{3}}\right) \tag{1}$$

where d is the depth of the cell and x is the lower stationary level (a level at which the velocity of the liquid is zero).[1] Measurements of velocities were made only on particles from 1 to 3 micra in diameter and only on oil droplets of about 3 micra in diameter. Particles and globules of these sizes could be easily chosen in the microscopic field. The formation of a gel in the electrophoresis cell was found to cause mechanical disturbances

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[1] The cell employed in this investigation was 0.940 mm. deep, and, following the above formula, the microscope was focused 0.198 mm. up from the bottom of the cell.

which interfered with the motion of the particles. Measurement of the velocity at 60° or 75°C. avoided this difficulty. At these temperatures, none of the solutions investigated formed gels.

When the actual stability of the suspensions formed was to be determined, the solutions containing the dispersed carbon were placed in 4-oz., oil-sample bottles, stoppered, and allowed to stand sixteen hours in an air thermostat at approximately 60°C. At the end of this period, the relative stability of the suspensions could be determined by visual inspection. The maintenance of a temperature of 60°C. prevented the formation of a gel by the soaps.

All pH measurements were made with a glass electrode.

CALCULATIONS

The electrokinetic potential can be calculated from the electrophoretic velocity by the equation

$$\zeta = \frac{4\pi}{D} \cdot \eta \cdot \frac{(V)}{(X)} \qquad (2)$$

in which ζ is the electrokinetic potential, η the viscosity of the medium, V the velocity of the particle, X the potential gradient, and D the dielectric constant of the medium. All units are C.G.S.E. units.

Burton (2) has shown that, in the case of a silver sol, variation of the viscosity by changing the temperature produces a corresponding change in the velocities of the particles so that the product $\eta \frac{(V)}{(X)}$ is a constant. Gilford (6) has shown that, for a number of substances, temperature variation of the electrophoretic velocity depends only on the change of viscosity of the liquid phase. If the product $\eta \frac{(V)}{(X)}$ is constant, then the product ζD is also constant. Since D varies with the temperature, zeta must also vary. Hence, the value of zeta may be calculated from equation 2 for any temperature at which D is known.

The potentials (in millivolts) reported below are calculated to 25°C. The value of D at 25°C. was taken to be 78.5 (14). Although a comparison is made between these potentials at 25°C. and the stability of the suspensions obtained at 60°C., no discrepancy is introduced. Calculation of the potentials to 60°C. instead of 25°C. would shift all values by the same percentage, so that the relative order would remain the same; in this comparison only the relative order is considered.

Besides the potentials calculated from equation 2, the velocities actually observed, and from which the potentials were calculated, are listed. Since the velocities were obtained at various temperatures, these data cannot be compared with one another. The velocities are reported in micra per second per unit potential gradient.

RESULTS

The effect of sodium oleate on the zeta potentials of the oil droplets of two emulsions, one of a paraffin oil and the other of a refined cottonseed oil, was determined. Table 2 lists the results. The oil droplets bore an initial negative charge; this was increased by the presence of sodium oleate in the aqueous phase.

In the light of the work of Ellis (3), Powis (12), and others, these results indicate that the stabilization of oil-in-water emulsions by soap is due to the ability of soap to increase the negative charge of the oil droplets. Powis has shown that an emulsion is relatively stable if the oil/water potential difference is greater than a definite critical value of approximately 30 millivolts (plus or minus). If the potential falls below this critical value, the emulsion breaks. The extraordinarily high values of the zeta potential obtained with the emulsions made with sodium oleate listed in table 2 indicate that these emulsions are very stable. This result is in agreement with the exceptionally good emulsifying powers of soaps.

TABLE 2

Effect of sodium oleate on zeta potential of oil droplets of two oil-in-water emulsions

OIL PHASE	AQUEOUS PHASE	VELOCITY AT 28°C.	ZETA POTENTIAL
		μ/sec./volt/cm.	*millivolts*
Paraffin oil	Water only	7.1	−86
Paraffin oil	0.0036 *M* sodium oleate	12.5	−151
Cottonseed oil	Water only	6.1	−74
Cottonseed oil	0.0036 *M* sodium oleate	11.6	−140

TABLE 3

Effect of a soap solution on zeta potential of different materials

MATERIAL	WATER		SOAP SOLUTION	
	Velocity at 28°C.	Zeta potential	Velocity at 28°C.	Zeta potential
	μ/sec./volt/cm.	*millivolts*	*μ/sec./volt/cm.*	*millivolts*
A carbon black	4.5	−60	5.3	−71
A water-insoluble dye	4.6	−62	5.9	−79
Ferric oxide	2.1	−28	5.8	−78
A strain of staphylococci bacteria	2.8	−34	4.1	−49

It was next desired to determine the general effect of soaps on the charge of various inert particles. Table 3 lists the velocities and potentials observed for a number of different materials, first in distilled water and then in a dilute solution of a commercial soap. All these materials showed an increase in the negative zeta potential of the particles when placed in the soap solutions over that observed in water. The data of table 3 indicate, therefore, that these particles adsorb the negative constituents of the soap.

The remainder of the study was continued with a single material, the bleaching carbon described under "Materials". While it is known that the value of the zeta potential depends upon the history of the carbon (10), nevertheless a single carbon can be used to determine the relative effect of different salts on the potential. This was done in order to obtain the data reported below.

TABLE 4

Effect of concentration of soaps on zeta potential of carbon particles

(a) Sodium oleate at 28°C. (b) Sodium palmitate at 60°C.

CONCENTRATION	VELOCITY	ZETA POTENTIAL	CONCENTRATION	VELOCITY	ZETA POTENTIAL
moles per liter	*μ/sec./volt/cm.*	*millivolts*	*moles per liter*	*μ/sec./volt/cm.*	*millivolts*
0.0007	6.5	−78	0.0007	10.7	−73
0.0013	6.6	−80	0.0014	11.0	−74
0.0023	6.7	−81	0.0021	10.7	−73
0.0026	6.9	−83	0.0036	10.2	−69
0.0033	7.3	−88	0.0054	12.0	−81
0.0039	7.4	−89	0.0072	11.0	−74
0.0049	7.4	−89	0.107	11.2	−76
0.0056	7.2	−87			
0.0066	6.9	−83			
0.0082	6.6	−80			
0.0099	6.8	−82			

TABLE 5

Effect of various salts on zeta potential of carbon particles

COMPOUND, 0.0036 *M*	VELOCITY AT 28°C.	ZETA POTENTIAL
	μ/sec./volt/cm.	*millivolts*
Water	4.3	−52
Sodium acetate		−41*
Sodium sulfate	4.7	−57
Trisodium phosphate	5.2	−63
Potassium ferrocyanide	5.0	−60
Sodium oleate	6.9	−83

* From velocity measurement at 75°C.

Table 4 lists the data showing the effect of concentration of two different soaps on the electrophoretic velocity and zeta potential of the carbon particles. The effect of concentration over the short range investigated is small, as the data of table 4 show. Previously published data for salts

(1) show that the relationship between the potential of the suspended particle and the concentration of the dissolved salt is complex. In the range of concentration studied in this investigation, concentration is not an important factor in the value of the zeta potential, and as the data of table 4 show, no significant differences were observed. The concentrations investigated center about those used in laundry practice.

The data listed in both tables 3 and 4 are in agreement with a hypothesis that the negative ions or negatively charged ionic micelles of soaps are adsorbed by an inert surface. This, in itself, is not unexpected, for the adsorption of ions of salts by inert surfaces is a general phenomenon. However, in order for this adsorption to result in a stable suspension of the particles, the electric charge developed on the particles must be fairly high. Therefore, the magnitude of the effect of soaps on the zeta potential was compared with that of other salts.

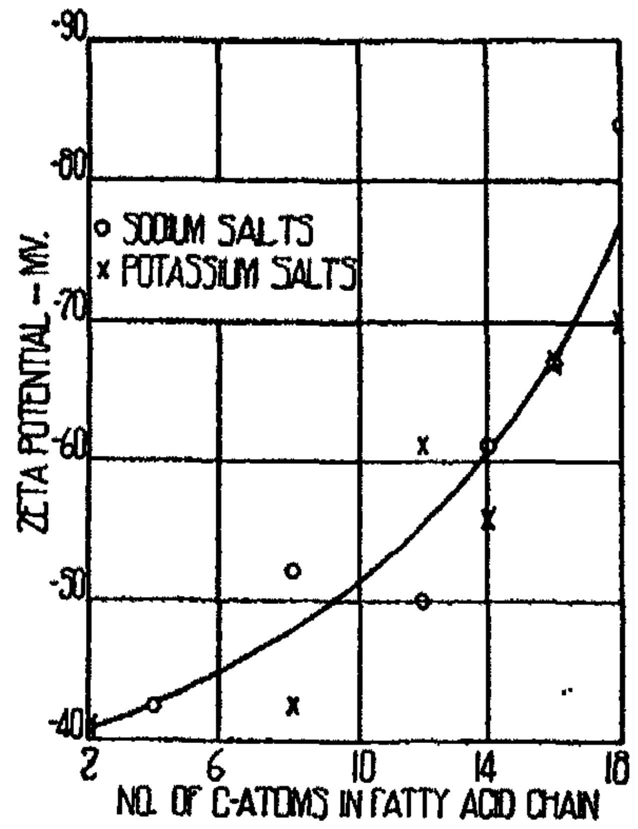

FIG. 1. Effect of increasing length of the fatty-acid chain on the zeta potential.

In table 5 is shown the effect of salts containing negative ions of different valences on the zeta potential of the carbon particles suspended in their solutions. It is evident that the increase in potential produced by sodium oleate was appreciably greater than that produced by the other salts.

In table 6 are shown the values of the zeta potential obtained when the carbon was suspended in solutions of the sodium and potassium salts of some of the saturated fatty acids. These data are plotted in figure 1, showing that the effect on the zeta potential is greater with the salts of the higher homologs (the soaps) than with the lower members of the series, and that the effect increases in a fairly regular order as the length of the carbon chain of the fatty acid increases.

Reference to table 7 shows that the alkalinity of the solutions of the sodium salts of the saturated fatty acid series increases with the length of the carbon chain of the fatty acid. It was necessary to determine whether the potentials observed for the soap solutions could be ascribed to this alkalinity. To do this, the effects of the addition of hydrochloric acid and of sodium hydroxide to solutions of sodium acetate and of sodium palmitate were determined. The data are listed in table 8.

TABLE 6

Zeta potentials obtained with sodium and potassium salts of certain fatty acids

COMPOUND, 0.0036 *M*	VELOCITY AT 75°C	ZETA POTENTIAL
	μ/sec./volt/cm.	*millivolts*
Sodium acetate	7.4	−41
Sodium butyrate	7.6	−42
Sodium caprylate	9.5	−52
Sodium laurate	9.1	−50
Sodium myristate	11.2	−61
Sodium palmitate	12.3	−67
Sodium stearate	15.4	−84
Potassium acetate	7.4	−41
Potassium caprylate	7.6	−42
Potassium laurate	11.2	−61
Potassium myristate	10.3	−56
Potassium palmitate	12.3	−67
Potassium stearate	12.7	−70

TABLE 7

pH of sodium salts of some of the fatty acids

COMPOUND, 0.0036 *M*	pH
Sodium acetate	7.8
Sodium butyrate	7.4
Sodium caprylate	7.6
Sodium laurate	8.3
Sodium myristate	10.0
Sodium palmitate	10.8
Sodium stearate	10.7

The alkalinity of the soap solutions is not sufficient to account for their large effect on the zeta potential of the carbon particles suspended in them. The sodium acetate solutions did not have as great an effect as did similar solutions of sodium palmitate with the same concentration of hydroxyl ions. One should note, however, that in order to obtain the high potential with sodium palmitate, it is necessary for the solution to be alkaline.

The effect of mixtures of fatty acids comprising the soap is shown in table 9. In this table are presented data obtained for soaps made from mixtures of oleic and stearic acids. It is apparent that there is no essential difference in the effects observed for the various mixtures. The potentials are of the same order of magnitude as those observed for pure sodium palmitate or stearate.

TABLE 8

Effect of varying the pH of solutions of sodium acetate and of sodium palmitate on the zeta potential

(a) Sodium acetate, 0.0036 *M* (b) Sodium palmitate, 0.0036 *M*

pH	REAGENT ADDED	VELOCITY AT 60°C.	ZETA POTENTIAL	pH	REAGENT ADDED	VELOCITY AT 60°C	ZETA POTENTIAL
		μ/sec./volt/cm.	*millivolts*			*μ/sec./volt/cm.*	*millivolts*
4.1	HCl	4.5	−30	2.8	HCl	3.9	−26
5.4	HCl	5.6	−38	3.8	HCl	7.0	−47
8.0		7.2	−49	4.7	HCl	7.4	−50
9.1	NaOH	7.5	−51	7.6	HCl	11.8	−80
10.0	NaOH	8.1	−55	8.5	HCl	10.1	−68
10.2	NaOH	7.5	−51	9.3	HCl	11.3	−72
11.4	NaOH	7.8	−53	10.1	HCl	11.3	−72
				10.8		10.3	−70

TABLE 9

Effect of soaps made from mixtures of oleic and stearic acids on zeta potential

STEARIC ACID IN FATTY ACID MIXTURE MAKING UP SOAP	VELOCITY AT 75°C.	POTENTIAL
per cent	*μ/sec./volt/cm.*	*millivolts*
0	13.2	−72
10	13.4	−73
20	14.9	−82
30	13.6	−75
40	14.4	−79
50	13.4	−73
60	14.2	−78
70	12.6	−69
80	13.2	−72
90	14.0	−77
100	15.4	−84

By the method described above (experimental procedure), a rough correlation was obtained between the stability of the suspension of the carbon particles in various soap and salt solutions and the zeta potential. In figure 2 is shown a comparison between the potentials observed with the sodium salts of the fatty acid series (table 6) and the relative stability of the suspension of the carbon in solutions of the sodium salts of this series. Although the method of determining the stability was very rough, the relative order of the stabilities of the suspensions formed could be ascertained easily.

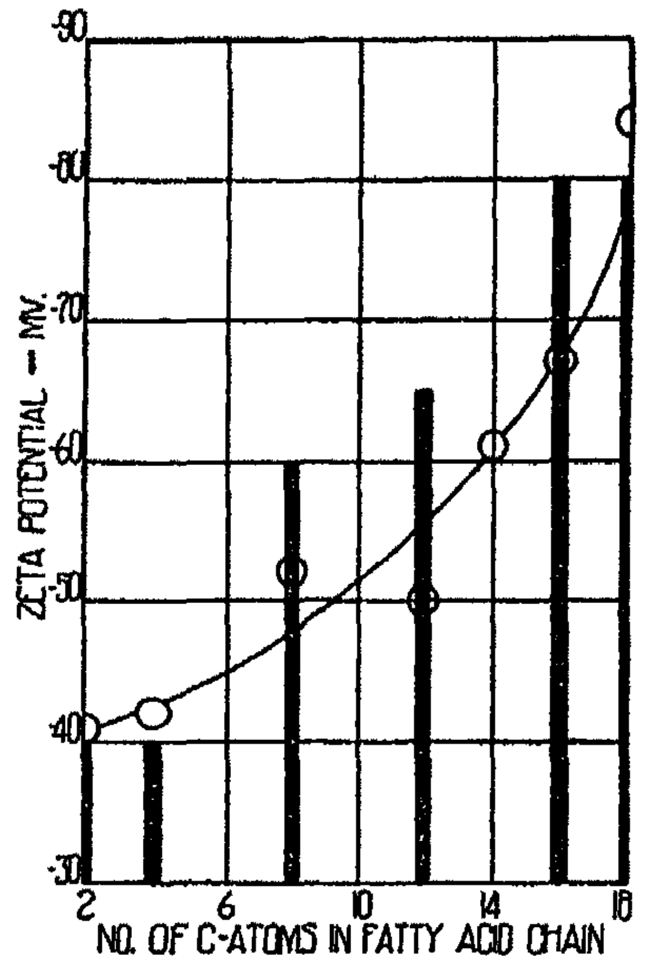

FIG. 2. A comparison of the values of the zeta potential with the stability of the suspension formed. The curve represents the values of the zeta potential for carbon particles immersed in the indicated solution. The heights of the heavy bars represent the stability of the suspension formed. The relative order of stability only is indicated.

Compared with the soaps, the inorganic salts listed in table 5 were not good suspending agents. This is in agreement with the relatively low zeta potentials observed.

DISCUSSION OF RESULTS

Emulsification of oily material and deflocculation of inert material constitute two of the primary functions of a detergent after the dirt has been removed from the surface to which it was attached. The data presented above indicate that soap solutions perform both of these important functions by essentially the same mechanism. The results indicate that both the globules of an oil-in-water emulsion and the particles of a suspension of an inert material show an increase in the values of the zeta potential when a soap is present in the aqueous phase. This increase in potential is definitely larger than that observed with other salts. While the numerical value of the zeta potential is not always very much greater in the presence of a soap, nevertheless it is possible that only a certain critical potential must be reached to form a relatively stable suspension. Powis (12) has shown this to be true of emulsions. It also appears to be true for the carbon black investigated here. The value of this critical potential probably varies with the kind of material and size of the particles, according to Stokes' law.

This increase in the zeta potential must be due to the acquisition of the negatively charged constituents of the soap, either the single ions or, more likely, the ionic micelles postulated by McBain (7). The actual mechanism of the acquisition of these negative constituents may be different in the two cases. In the case of the emulsion of an oil, mutual solubility of the hydrocarbon tail of the fatty-acid ion of the soaps and of the oil may be the means of the acquisition. When inert materials are involved, an adsorption at the surface may take place, or a process involving the capillary action of the soap solution may occur. In either case, the result is apparently the same. The high charge resulting from the acquisition of the negative constituent of the soap stabilizes the emulsion or suspension, and in this way the dirt can be removed from the vicinity of the surface to which it was attached.

The deflocculating action of soap solutions has been suggested by McBain (8) and others as a means of evaluating the detergent powers of soaps. The methods proposed consist in the determination of the actual amount of a given material that can be held in suspension by a soap solution under certain standard conditions. If, as is here suggested, the ability of the soap solution to hold the material in suspension depends upon the magnitude of the effect on the zeta potential of the particles of the suspension, then measurement of the zeta potential affords a rapid method of evaluating a detergent. The ability to emulsify can also be determined in this way. However, the method will require considerable refinement to be of practical value.

SUMMARY

The effect of soaps on the zeta potential of the oil droplets of typical oil-in-water emulsions and on the zeta potential of certain "inert" materials has been investigated. In both cases the presence of soap increased the value of the (negative) zeta potential. Very high values of the zeta potential were obtained for oil globules of emulsions, and these are considered sufficiently high to account for the stability of the emulsions. The

zeta potentials of the particles of an inert material suspended in soap solutions were appreciably higher than those obtained in solutions of other salts. In the case of the salts of the fatty-acid series, over the range investigated, the potential increases with the length of the carbon chain of the fatty acid present in the salt. It has been shown that the free alkali present in soaps is not sufficient to account for the large effect of soaps on the zeta potential. At 75°C., soaps prepared from mixtures of oleic and stearic acids have the same effect as soaps prepared from the individual fatty acids.

It has been shown that soaps producing a high negative potential on certain carbon particles also form a stable suspension of the carbon. Conversely, salts which do not alter the potential of the carbon particles to any great extent do not form stable suspensions.

This effect of increasing the zeta potential of the oil droplets of an emulsion and of the particles of a suspension is suggested as the mechanism whereby soaps act as emulsifying and deflocculating agents.

Measurement of the effect of a solution of a soap on the zeta potential of the oil droplets of an emulsion or of the particles of a suspension is suggested as a means of evaluating the detergent powers of a soap.

Our thanks are due to Professor T. F. Young of the University of Chicago for his kind interest and advice in the preparation of this material for publication.

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OPTICAL DIFFICULTIES WITH THE CYLINDRICAL CATAPHORESIS CELL

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In the cylindrical cataphoresis cell described by Mattson (1, 2) it should be of interest to know what optical precautions must be taken to obtain observations at the correct depth in the cell. This depth is that at which the velocity of the liquid due to endosmosis is zero and is calculated (2) to be (R (radius) $- R/\sqrt{2}$), or $0.293R$ measured vertically down from the top of the solution in the cell.

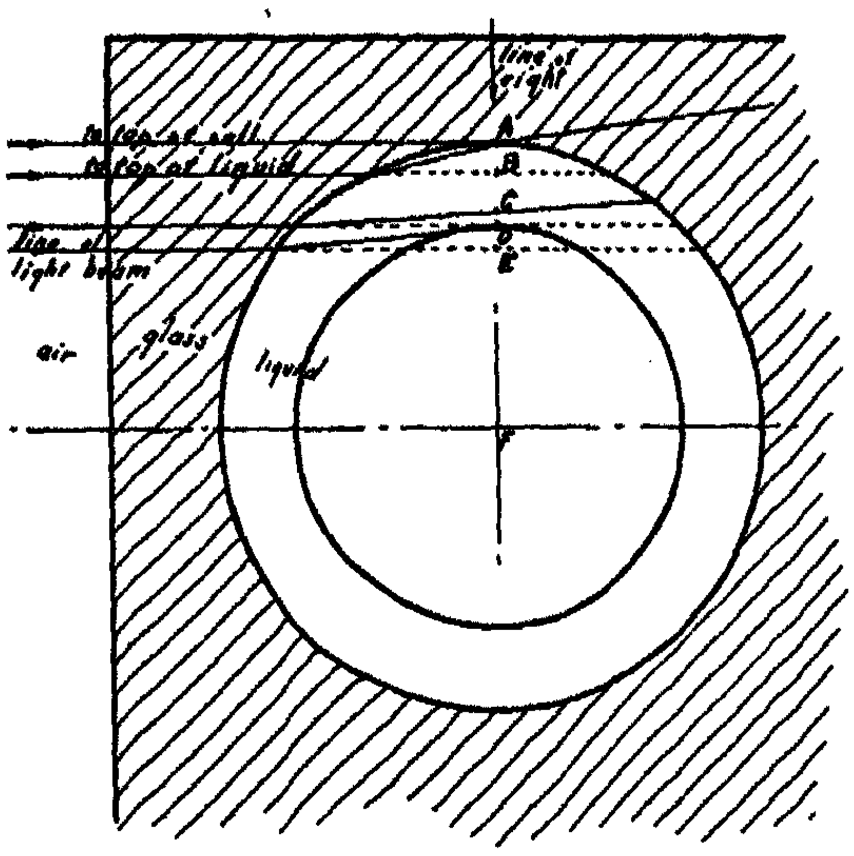

FIG. 1. Cylindrical cataphoresis cell. All depths are measured down from the top, A. D is the point or zone desired. AF is the radius of the cell. AD is ($R - R/\sqrt{2}$) or $0.293R$. AC is the depth observed when light enters the cell at the depth AD ($0.293R$). AD is the depth observed when light enters at the depth AE ($0.377R$). AB is the "blind spot," or the depths that cannot be seen until light enters at a depth greater than AB.

If the light beam enters the front of the cell at this depth and the microscope is focused on the beam in the cell, the observations made on the cataphoretic velocities of the particles do not represent the true velocities unaffected by the velocity of the liquid. The light beam does not pass from the glass to the liquid normal to the interface, and the refractive index of the glass is appreciably different from that of the water which is usually the continuous phase of the sol. Thus, the light beam is bent upward (figure 1) to a depth of 0.195*R* from the top, midway between the front and back of the cell. To obtain illumination at the correct depth, the light beam should enter the liquid at a depth of 0.377*R*.

The index of refraction of water and glass have been taken as 1.342 and 1.515, respectively, for the above calculations. If n_D for water were 1.35, owing to the salt content, the resulting discrepancy is but slightly different from that calculated. It is interesting to note that in the zone (0 to 0.114) *R*, there is a "blind spot" where the particles should not be observed, since the light beam is reflected outside the glass-water interface. It should also be noted that the front air-glass interface should be perpendicular to the light beam, or the possibility of error in the position of the light beam in the cell will be increased.

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SURFACE SPREADING AND SURFACE SOLUTION OF POSITIVELY ADSORBED SUBSTANCES

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It was observed by Miss Pockels (1) that various substances when touched to clean talc-dusted water surfaces cause streaming motions outward from the point of contamination. Although she did not then distinguish explicitly between the behavior of soluble and insoluble substances, in a later paper (2) it is clear that she considered the process of surface spreading essential to the phenomena of positive adsorption. In continuing and extending Miss Pockels' experiments, using soluble substances, we have found that all of those that lower the surface tension of water spread in the surface to form films, this surface spreading being an intermediate step in the process of solution. Thus, a fragment of hydrocinnamic acid, or a droplet of phenol, or of caprylic acid touched to a talc-dusted water surface immediately produces a circular patch cleared of talc, exactly as if an insoluble spreading oil had been applied, and on removal of the source this patch quickly contracts and disappears. A surface may be completely contaminated in this way many times and no permanent film result, showing that the momentary contamination was due to the soluble material alone. The same phenomenon occurs with camphor on water, and, as further examples, with the following substances: acetic acid, gelatin, aniline, hydrogen chloride, ethyl alcohol, abietic acid, benzamide, ammonia, ethyl acetate, potassium laurate, benzoic acid, sodium silicate, acetone, triethanolamine, hydroquinone, carbon dioxide.

This process of surface solution is extremely rapid, undoubtedly because the substances spread out into films against limitless boundaries, there rapidly achieving maximum extenuation and contact with water short of actual solution. In these films the area available for escape of individual molecules has been enormously increased. Whether solution actually occurs at a greater rate per unit area of monomolecular film than of submerged surface is not known. As expected, however, completely submerged droplets, or fragments, which have no surfaces available into which their oriented surface layers can spread, dissolve very slowly. The great difference in the rate of solution of certain partially immersed solid substances at the water surface and beneath it has been observed by Pockels

(2) and by Volmer and Mahnert (4) and by others. We have found a striking demonstration of this fact by use of a droplet of phenol, which if submerged in water will remain apparently unchanged for several hours, but if brought into the surface will spread and completely dissolve in a fraction of a second; or by observing the surface of a fine aqueous suspension of hydrocinnamic acid, in which random, spontaneous areas of spreading—"Pockels" (5)—appear, evidently caused by arrival in the surface of wandering particles previously submerged and undissolving.

Surface solution is a factor even in the dissolving of submerged fragments, because particles break off from the crystal mass as observed by Traube (3) and wander away, owing to Brownian motion and convection currents and perhaps owing to reaction of their escaping surface molecules against both particle and solution, and eventually enter the surface where they disperse by spreading. In confirmation of this, observations of clean water surfaces beneath which crystals of hydrocinnamic acid were submerged disclosed "Pockels" exactly similar to those obtained with the hydrocinnamic acid suspension previously referred to.

Many substances are dissolved in the industries by putting them on trays near the surface of water, thus utilizing the stirring action resulting from changes in density to accelerate the process of solution. In the case of materials like phenol, surface spreading is perhaps often another important, and unrecognized, factor in hastening the rate of solution. Obviously, such materials should be partly exposed above the surface.

In considering the relation between adsorption and surface tension, the mechanism of surface solution assumes theoretical importance in view of Miss Pockels' belief that solutions of all capillary-active substances are colloidal or subcolloidal in nature (2), and of Traube's ultramicroscopic evidence (3) that subcolloidal particles, or "microns", represent an intermediate stage both in the dissolving of crystals and in the growth of crystals from solution, and that they may even enjoy a stable existence in solutions of many substances.

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A COMPARISON OF THE GLASS AND QUINHYDRONE ELECTRODES FOR THE MEASUREMENT OF THE ACTIVITY OF THE HYDROGEN ION IN SUCROSE SOLUTIONS

37-309

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INTRODUCTION

In the determination of the activity of the hydrogen ion in acidified sucrose solutions by electromotive force methods, the hydrogen electrode has been used by a number of investigators, including W. C. M. Lewis and his associates (1, 3, 6), Taylor and Bomford (9), who found that the hydrogen-ion activity increases during the inversion of sucrose by acid, and by Scatchard (8), who found that the hydrogen electrode does not give reliable values of the hydrogen-ion activity in sucrose solutions.

We thought that the glass electrode (2, 5) might be used to measure accurately the activity of the hydrogen ion in sucrose solutions. We used the quinhydrone electrode for comparison.

EXPERIMENTAL PROCEDURE

Silver–silver chloride electrodes were used as standard reference electrodes. They were prepared as suggested by MacInnes and Beattie (4).

The glass electrodes were prepared as recommended by MacInnes and Belcher (5). The quinhydrone electrodes used were flat pieces of platinum, 2 x 1 cm. All of the solutions used in the measurements were 0.1 molal with respect to hydrochloric acid and 0.1 molal with respect to the other constituent, either sucrose, dextrose, or levulose. All of the measurements were carried out at 30°C.

APPARATUS

The electrical measurements made using the quinhydrone electrode were made with a Leeds and Northrup Type K potentiometer and a Leeds and Northrup high sensitivity Type R galvanometer.

The electrical measurements using the glass electrode were made with a circuit including a space charged grid tube, the G.E.F.P. 54 Pliotron. A diagram of this circuit is shown in figure 1.

The glass cell used in making measurements of E.M.F. between the silver–

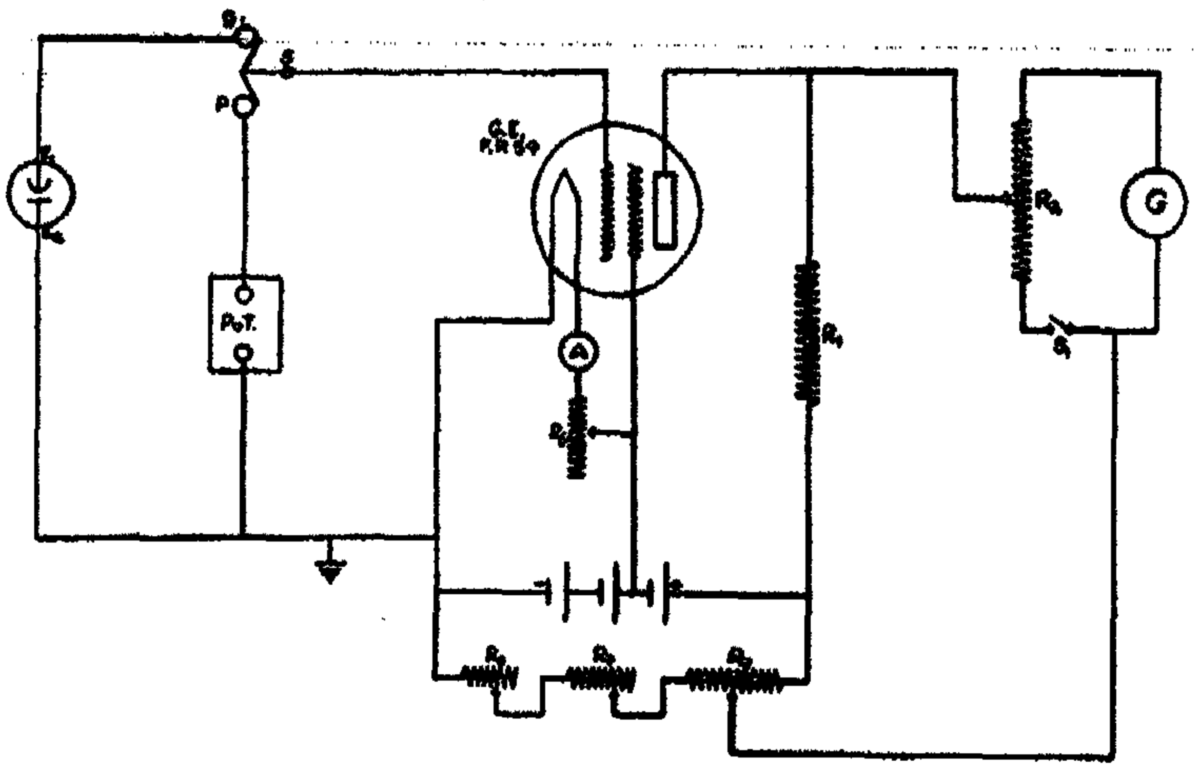

Fig. 1. Diagram of the circuit

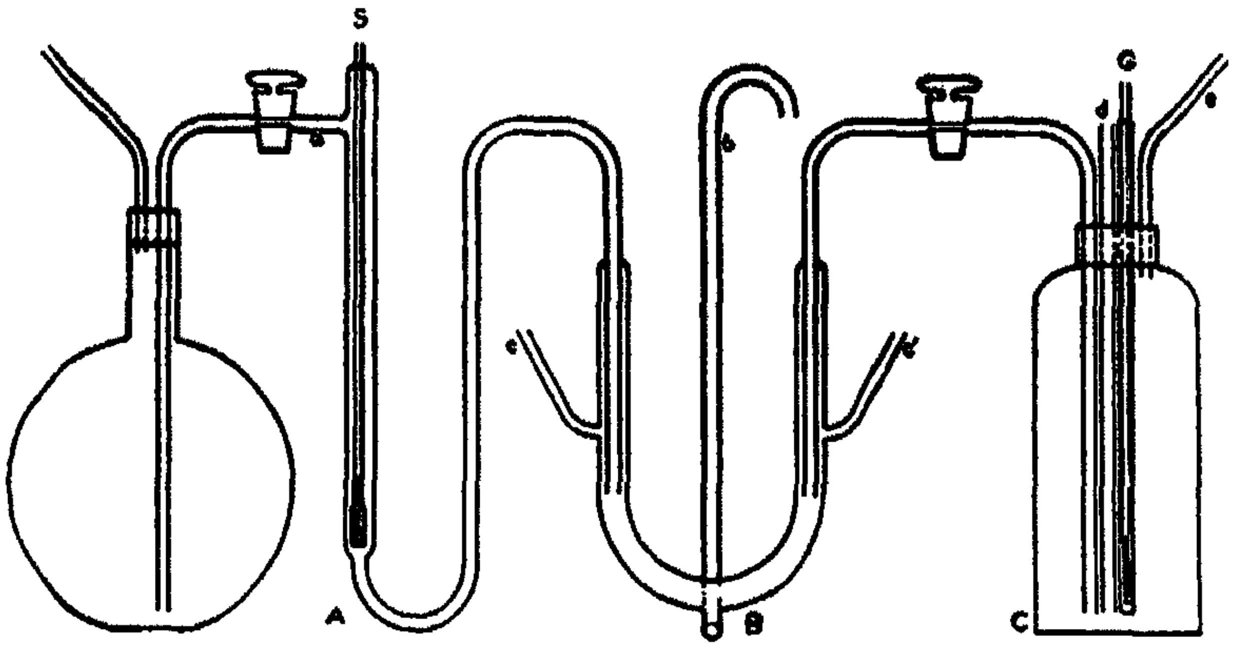

Fig. 2. Glass cell used in making measurements of E. M. F. between the silver-silver chloride half-cell and the glass electrode

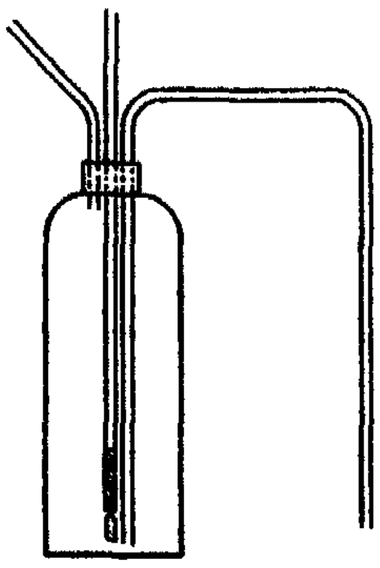

Fig. 3. The half-cell used in the experiments involving a number of electrodes

silver chloride half-cell and the glass electrode is shown in figure 2. The first series of measurements with the quinhydrone electrode was made in this cell.

The half-cell used in the experiments involving a number of electrodes is shown in figure 3.

TABLE 1

E. M. F. measurements with the cell

Pt	0.1 *M* Sucrose 0.1 *M* HCl Quinhydrone	0.1 *M* HCl	0.1 *M* HCl	Ag-AgCl

TIME		E.M.F.	TIME		E.M.F.
hrs.	*mins.*	*volts*	*hrs.*	*mins.*	*volts*
	10	0.3456	27	30	0.3446
	30	0.3455	33	30	0.3443
1	30	0.3454	43	30	0.3436
3	30	0.3454	47	30	0.3434
6	30	0.3454	53	30	0.3432
18	30	0.3448	66	30	0.3423
24	30	0.3446	72		0.3419

TABLE 2

Measurements made between pairs of platinum electrodes immersed in 0.1 molal hydrochloric acid containing quinhydrone

TIME		E. M. F. IN MILLIVOLTS									
		I	II	III	IV	V	VI	VII	VIII	IX	X
		A. F.	A. L.	A. D.	A. Ivd. S.	Ivd. S. F.	Ivd. S. D.	Ivd. S. L.	D. L.	D. F.	L. F.
hrs.	*mins.*										
	30		0.487	0.287	0.248		0.039	0.239	0.200		
1	5		0.177	0.175	0.321		−0.146	−0.144	0.002		
1	30	−0.035	0.180	0.144	0.303	−0.512	−0.159	−0.123	0.036	−0.179	−0.215
2	10	0.062	0.209	0.130	0.303	−0.364	−0.172	−0.094	0.079	−0.068	−0.147
2	30	−0.094									
3	45	0.065	0.211	0.164	0.303	−0.277	−0.149	−0.092	0.057	−0.089	−0.146
4	25	0.029									
6	45	0.380	0.224	0.213	0.304	−0.038	−0.091	−0.080	0.011	0.167	0.156
16	45	0.246									
23	45	1.465	0.173	0.115	0.164	1.166	−0.049	0.009	0.058	1.350	1.292
30	25	1.393									
42	45	2.962	0.206	0.126	−0.070	2.820	0.196	0.276	0.080	2.836	2.756

DATA

The data in table 2 represent measurements made between pairs of platinum electrodes immersed in 0.1 molal hydrochloric acid containing

TABLE 3

Measurements of E. M. F.

TIME		E. M. F. IN VOLTS				
		I	II	III	IV	V
		F. Ag	F. A.	Ivd. S. Ag	Ig. S. Ag	A. Ag
hrs.	*mins.*					
	20	0.34377	−0.00100	0.34521	0.34304	0.34476
	50	0.34409	−0.00058	0.34507	0.34491	0.34467
1	50	0.34431	−0.00033	0.34496	0.34480	0.34456
3	20	0.34429	−0.00023	0.34488	0.34473	0.34449
7	35	0.34450	0.00021	0.34469	0.34459	0.34425
21	35	0.34463	0.00120	0.34395	0.34387	0.34338
31	35	0.34494	0.00225	0.34338	0.34323	0.34260
55	35	0.34495	0.00491	0.34116	0.34104	0.33996
72		0.34516	0.00719	0.33973	0.33948	0.33790
		VI	VII	VIII	IX	X
		A. Ivd. S.	A. Ig. S.	Ig. S. Ivd. S.	Ig. S. F.	Ivd. S. F.
	20	0.00045	0.00028	0.00017	−0.00127	−0.00144
	50	0.00040	0.00024	0.00016	−0.00082	−0.00098
1	50	0.00040	0.00024	0.00016	−0.00049	−0.00065
3	20	0.00039	0.00024	0.00015	−0.00044	−0.00059
7	35	0.00044	0.00029	0.00010	−0.00009	−0.00019
21	35	0.00057	0.00049	0.00008	0.00076	0.00068
31	35	0.00078	0.00063	0.00015	0.00171	0.00156
55	35	0.00120	0.00108	0.00012	0.00391	0.00379
72		0.00183	0.00158	0.00025	0.00568	0.00543

TABLE 4

E. M. F. measurements using a glass electrode

Ag,AgCl	0.1 *M* HCl	0.1 *M* HCl	0.1 *M* HCl Glass 0.1 *M* inverting Sucrose	Ag,AgCl 0.1 *M* HCl

TIME IN HOURS	E. M. F. IN MILLIVOLTS	
	Trial I	Trial II
0.5	0.44	0.45
1.5	0.45	0.41
3.5	0.42	0.40
7.5	0.42	0.42
21.5	0.43	0.48
31.5	0.36	0.43
43.5	0.42	0.40
51.5	0.44	0.46
72.0	0.40	0.43

quinhydrone. All pairs of electrodes were connected by liquid bridges of 0.1 molal hydrochloric acid. Substances added to the cells are indicated at the top of each column. F stands for "freshly prepared electrode", D for "dextrose", L for "levulose", Ivd. S. for "inverted sucrose", and A indicates "the original acid and quinhydrone with nothing added". All substances added had concentrations of 0.1 molal.

The symbols used in table 3 are the same as those in table 2. The additional symbol Ig.S., meaning "inverting sucrose", is also used. Ag is used to indicate a Ag–AgCl electrode in 0.1 molal hydrochloric acid, in place of a quinhydrone electrode.

DISCUSSION

The data in table 1 indicate a large apparent decrease in the hydrogen-ion activity during the acid inversion of sucrose. Such a large decrease in the activity, however, appears improbable.

The data in tables 2 and 3 show that the potential of a quinhydrone electrode in old hydrochloric acid solution changes with the passage of time.

The data in tables 2 and 3 also show that the inverting sucrose, the inverted sucrose, the dextrose, and the levulose all have about the same effect upon the potential of a quinhydrone electrode. In fact they seem to affect the potential of the electrode very little.

The data in columns III, IV, and V of table 3 indicate that the potential of the quinhydrone electrodes in the old hydrochloric acid solution, the inverting sucrose, and the inverted sucrose solutions, all become less positive with respect to the silver–silver chloride half-cell as time passes. Now since the potential of the quinhydrone electrode depends solely upon the activity of the hydrogen ion and the ratio of the activity of the quinone to the activity of the hydroquinone, and since it is not probable that the activity of the hydrogen ion has changed in this closed system, it is evident that the drop in potential must be due to a decrease in the above-mentioned ratio to some value less than unity. Thus either the activity of the quinone must have decreased or the activity of the hydroquinone must have increased. Now the quinone is known to be a fairly strong oxidizing agent; it can add hydrochloric acid in a concentrated solution of hydrochloric acid. Biilmann has shown that the change in potential of the quinhydrone electrode in dilute hydrochloric acid solutions is due to some action of the hydrochloric acid on quinone. This being the case, the activity of the quinone would be reduced and the voltage of the electrode would be reduced. Since the decrease in potential for the electrodes in the inverting and inverted sucrose solutions is so very nearly the same, we can conclude that the formation of the inversion products of sucrose has little or no effect on the potential of the quinhydrone electrode. This also indicates that it makes no difference whether the inversion products are all present at once or whether they are formed in the acid solution as time goes by. Since the only other substance present is the hydrochloric acid, we must assume that it is the hydrochloric acid that is causing the change in potential of the electrode. This is also borne out by the fact that the old hydrochloric acid solution which was in contact with the quinhydrone for three days showed an even more pronounced effect upon the potential of the electrode than did the solutions which contained the inversion products of sucrose. The fact that the electrode in the inverting and inverted sucrose solutions gave a constant difference of potential during the whole seventy-two hours, wpuld indicate that the rate of change of potential of both electrodes is the same. The data in column VIII of table 3 show the truth of the above statement.

Columns VI and VII of table 3 indicate that the potential of the electrode in the old hydrochloric acid solutions becomes less positive more rapidly than does the potential of either the electrode in the inverting or that in the inverted sucrose solutions.

The data in column VIII of table 2 indicate that the rate of change of potential of the quinhydrone electrode in a solution containing levulose is the same as that for an electrode in a solution containing dextrose. Thus the data of tables 2 and 3 indicate that the products of inversion of sucrose have little or no effect, either separately or collectively, upon the potential of the electrode.

The data in column I of table 3 confirms the conclusions of Morgen, Lammert, and Campbell (7), i.e., the potential of the quinhydrone electrode can be accurately reproduced only when care is taken to clean and dry the electrode before use. In our experiments the electrode after use in the acidified quinhydrone solution was left in the solution until time for the next measurement on a fresh solution, at which time it was washed with distilled water and transferred to the freshly prepared quinhydrone solution. It may be seen that the potential of the electrode, used in the above manner, showed an increase. This would indicate that the amount of oxidation, i.e., the oxidizing agent, in the cell had increased. Now each time the electrode was placed in a fresh solution, the electrode came in contact with the air; also the solution was thoroughly shaken to dissolve the quinhydrone quickly. If oxygen from the air were absorbed on the platinum surface there is a possibility that some hydroquinone was oxidized to quinone and thus the potential of the electrode was slightly raised.

The data in table 4 show that the E.M.F. of the glass electrode with respect to the silver-silver chloride half-cell remains constant throughout the acid inversion of sucrose. Since the E.M.F. remained constant throughout the inversion, it follows that the activity of the hydrogen ion remained constant also. Thus it is seen that the hydrogen ion is a true catalyst in this reaction. The work of Taylor and Bomford (9) showed an increase in the activity of the hydrogen ion during the inversion process, but this is undoubtedly due to the hydrogenation of the sucrose, as suggested by Scatchard (8).

SUMMARY

1. The quinhydrone electrode has been used to measure the activity of the hydrogen ion in inverting sucrose solutions and has been found to give a changing potential when the electrode is left in contact with the acidified quinhydrone solution for long periods of time.

2. The glass electrode has been used to measure the activity of the hydrogen ion in inverting sucrose solutions and has been shown to give reproducible results.

3. By the use of the glass electrode it has been shown that the activity of the hydrogen ion remains constant throughout the inversion of sucrose by hydrochloric acid.

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THE ACTIVITY COEFFICIENTS OF LITHIUM CHLORIDE AND POTASSIUM IODIDE IN ETHYL ALCOHOL BY THE BOILING-POINT METHOD

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This paper presents the results obtained in an attempt to determine the activity coefficients of strong electrolytes in non-aqueous solvents by the boiling-point method. The apparatus and the technique employed are practically the same as that described in our previous paper (8).

Although the major features of the familiar Cottrell-Washburn apparatus (2, 11) have been retained, two important changes have been made. We have substituted for the troublesome gas flame a more uniform and constant source of electrical heating. Sealed into the bottom of each boiling flask is a coil of No. 30 platinum wire; these coils are of exactly the same length and resistance, thus insuring the introduction of equal amounts of heat into each flask when these are joined in series with the lighting circuit. The fine wire spiral furnishes an ideal surface for easy and rapid bubble formation which, together with the rapid flow of the liquid over the spiral, makes superheating practically impossible. The funnels, provided with slits at the bottom and several lateral openings, are placed concentric with the spirals. Under steady boiling the bubbles rising through the tube and those passing laterally through the funnel not only insure constant thermal equilibrium, but also keep the solution homogeneous by rapid agitation. Two boiling vessels are used. Instead of thermometer bulbs, the liquid from the pump flows over a test tube containing mercury in which is placed one arm of a 50-junction thermoelement. One flask containing the pure boiling solvent serves as the "cold" junction.

Bancroft and Davis (1) contend that superheating in the Cottrell apparatus is largely due to the hydrostatic pressure under which the bubbles are formed. They state that, if this superheating is removed in part by the passage of the bubbles through a mass of the solution before entering the pump, it should be further diminished in its subsequent passage through the pump. In their modification of the original Cottrell apparatus, the funnel, instead of resting upon the bottom of the flask, rests upon a constriction in the wall of the boiling flask at several inches above the bottom. In spite of the fact that they still use the gas flame for heating, they claim that the superheating of the solution and the effect due to hydrostatic pressure are completely eliminated in their apparatus. More recently, in a study of the activity coefficients of aqueous solutions of potassium chloride, Saxton and Smith (10) have devised two new forms of the Cottrell apparatus,—one for gas and one for electrical heating. Their claims for the removal of superheating are equally good.

APPARATUS AND MATERIALS

The complete apparatus, including the "K 2" potentiometer and galvanometer, were carefully shielded. A current of 6.2 amps. was maintained through the heating coils during operation.

Three thermoelements were prepared according to the specifications of White (12), one with fifty junctions and two with ten junctions each. These were standardized against a platinum resistance thermometer (Bureau of Standards, No. 292) in conjunction with a Mueller bridge and high sensitivity galvanometer. The fixed points were those of liquid oxygen, liquid ammonia, ice, the transition point of sodium sulfate decahydrate, and the boiling point of water.

Since the 50-junction element was to be used for the determination of small temperature increments near the boiling point of alcohol, it was first necessary to calibrate it for that range also. This necessitated the employment of a triangular arrangement of the three thermoelements. The two boiling flasks were filled to the working volume with pure alcohol, connected by means of the 50-junction element, and the alcohol heated to boiling. Each flask was connected in turn with the Dewar ice calorimeter by a 10-junction element. The solvent was allowed to boil in each flask until the potential of the connecting thermoelement became constant. At this point the potentials of the 10-junction elements were read, and from these potentials the apparent difference in the boiling point of the solvent in the two flasks was calculated. This potential difference, due probably to inequalities in the arms of the element, was used in correcting all subsequent thermoelement potentials.

To obtain the temperature intervals for deducing an equation relating temperature and potential at the boiling point of the alcohol, both flasks were filled to the proper volume with pure benzene; to one of these was added later successive portions of pure naphthalene. In each case the boiling was continued until the potential of the 50-junction element became constant. The potentials of the two smaller elements were read immediately and the boiling temperatures were calculated. From the boiling-point elevation thus determined we derived a potential-temperature equation for the 50-junction element in the vicinity of the boiling point of ethyl alcohol. A table was constructed by solving the equation for potentials corresponding to 0.1°C. intervals, and from these the exact temperature for any measured potential was easily interpolated.

Thiophene-free benzene, b.p. 80.17°C., absolute ethyl alcohol, b.p. 78.82°C., and naphthalene, m.p. 80.08°C., were prepared according to accepted methods. The two salts were repeatedly crystallized from pure distilled water. The potassium iodide was heated to constant weight at 140°C. just before it was used. The lithium chloride crystals were first heated in a current of dry hydrogen chloride gas until all traces of water were removed. The heating was then continued in a current of dry hydrogen to remove all traces of acid. The salts were transferred to the alcohol in the flasks without contact with the atmosphere.

The dried salts were dissolved in alcohol in the apparatus to approximate saturation at the boiling point, and the resulting solutions were used for the first measurements. The constant potential indicating thermal equilibrium, corrected by the zero reading of the element, supplied the necessary data for calculating the boiling-point elevation. Under a pressure of dry air samples of the solution were withdrawn for analysis into tared glass-stoppered flasks and weighed immediately. After a sample was removed sufficient pure alcohol was added to maintain a constant solution volume, thus making a new concentration for the next measurement. The salt content of the solution was determined volumetrically by the Volhard method. The concentrations are expressed in moles per 1000 grams of solvent.

EXPERIMENTAL RESULTS

The experimental results are collected in table 1. Here m is the molality of the salt, θ is the elevation of the boiling point, and θ/m is the molal elevation of the boiling point of the solvent. The values of θ/m for lithium chloride pass through a distinct minimum value; except for the most dilute solutions, the molal elevation of the boiling point of alcohol by potassium iodide remains practically constant throughout the whole range of concentration.

According to Raoult's law, the boiling-point elevation of a solvent by an ideal non-electrolyte should be directly proportional to the mole fraction of the solute, or to $n_2/(n_1 + n_2)$. If we assume, however, complete dissociation for a binary salt and that the ions behave as perfect solutes, the boiling-point elevation should be proportional to $2n_2/(n_1 + 2n_2)$. That is,

$$\theta = \frac{RT_b^2}{\Delta H_v} \frac{2n_2}{n_1 + 2n_2}$$

The relation between the boiling-point elevation and the molality for the two salts is shown graphically in figure 1. The broken lines represent the theoretical curves for non-electrolyte and completely dissociated salt, both assumed to be perfect solutes. Although the salts are completely ionized in the crystalline state and in solution, the relations obtained for dilute

TABLE 1

Elevation of the boiling point of ethyl alcohol by electrolytes

m	θ°	θ/m	m	θ°	θ/m	m	θ°	θ/m
(a) Lithium chloride								
0.01266	0.01535	1.2124	0.18017	0.22149	1.2293	0.41117	0.55145	1.3412
0.02328	0.02823	1.2126	0.20126	0.24871	1.2358	0.44001	0.59663	1.3559
0.04051	0.04879	1.2044	0.24234	0.30508	1.2589	0.44958	0.61244	1.3622
0.07227	0.08589	1.1884	0.27085	0.34351	1.2653	0.49303	0.68027	1.3797
0.11023	0.13108	1.1891	0.28707	0.36613	1.2756	0.57580	0.81587	1.4169
0.13115	0.15596	1.1892	0.37098	0.48366	1.3037	0.66213	0.95370	1.4404
0.15874	0.19431	1.2241						
(b) Potassium iodide								
0.01016	0.01246	1.2364	0.07003	0.08507	1.2148	0.12420	0.14984	1.2054
0.01662	0.02033	1.2232	0.07806	0.09523	1.2200	0.13796	0.16695	1.2101
0.02454	0.02956	1.2326	0.08730	0.10589	1.2130	0.14939	0.18037	1.2074
0.03822	0.04713	1.2331	0.09378	0.11467	1.2228	0.15696	0.19054	1.2139
0.05173	0.06332	1.2241	0.10657	0.12814	1.2024			
0.06010	0.07390	1.2297	0.12238	0.14754	1.2056			

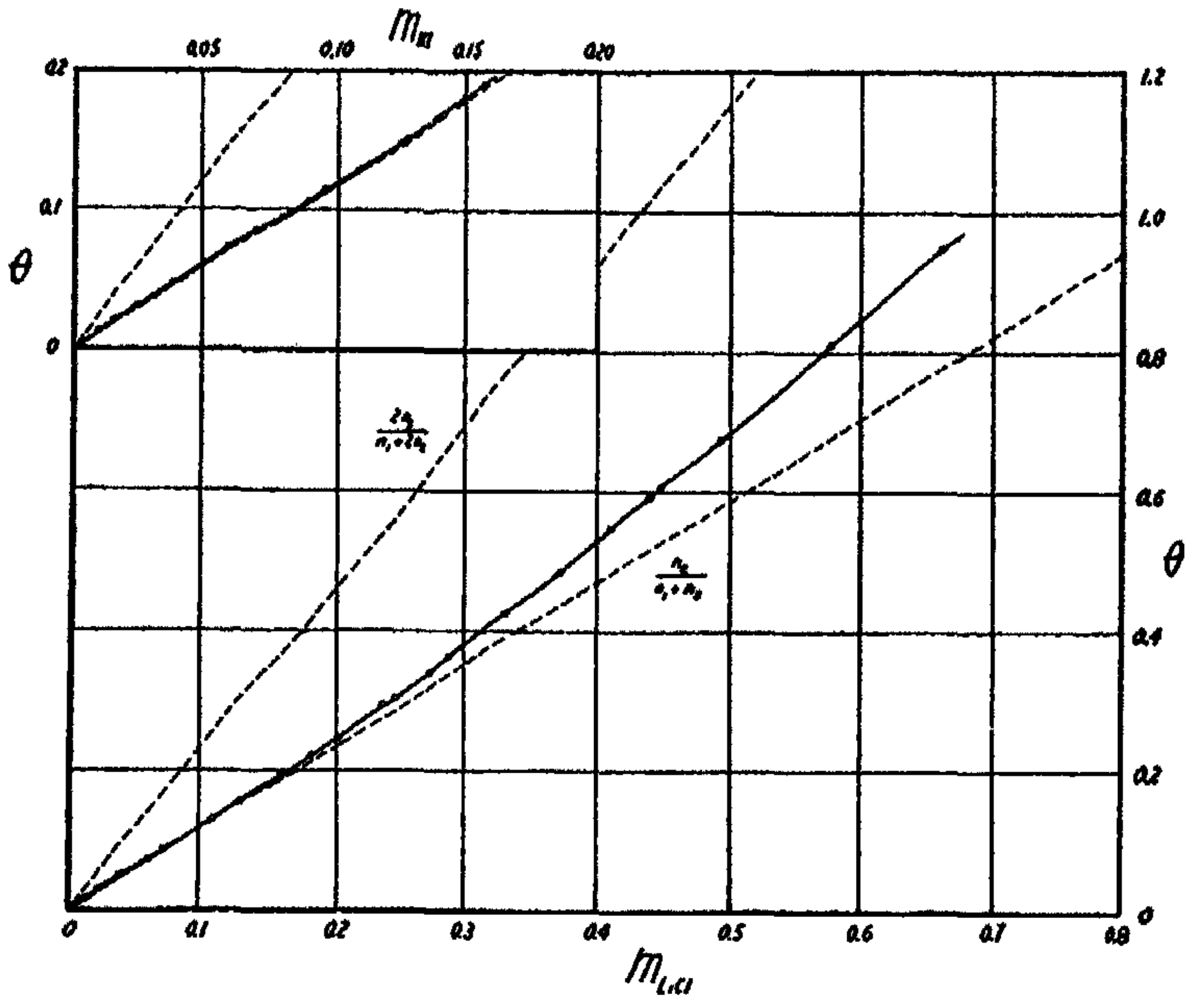

FIG. 1

solutions correspond closely with those which would be produced by undissociated solute molecules. The larger deviations from the normal boiling-point elevations in the more concentrated solutions indicate a rather decided increase in the number of free ions present. Since we have assumed that the salts are completely ionized at all concentrations, the approximation to the behavior of perfect normal undissociated solute molecules can be explained best by assuming the existence of simple or chain ions in equilibrium with paired ions or quadripoles. The formation of ion pairs and quadripoles is especially favored in solvents with low dielectric constants. The dielectric constant of ethyl alcohol (3) decreases from 28.9 at 20°C. to 20.2 at 60°C. Its unknown value at the boiling point must be still smaller.

Following the method of Lewis and Randall (5) for freezing-point work we may calculate the activity of the solvent from boiling-point elevation data. The influence of temperature on the activity of the solvent in the vicinity of the boiling point is given by the relation,

$$\mathrm{d} \ln a_1 = -\frac{\Delta H}{RT^2}\,\mathrm{d}T \tag{1}$$

If we designate by θ the elevation of the boiling point and by T_0 the boiling point of the pure solvent, the boiling point of the solution T is $T = T_0 + \theta$, and $\mathrm{d}T = \mathrm{d}\theta$. Expressing ΔH at the boiling point as a function of the temperature:

$$\Delta H = \Delta H_{T_0} + \Delta C_p\theta$$

and substituting in equation 1, we obtain

$$\mathrm{d} \ln a_1 = -\frac{[\Delta H_{T_0} + \Delta C_p\theta]}{R(T_0 + \theta)^2}\,\mathrm{d}\theta \tag{2}$$

By expanding the right-hand member, collecting terms, and neglecting terms of higher order, equation 2 becomes

$$\mathrm{d} \ln a_1 = \frac{\mathrm{d}\theta}{RT_0^2}\left[-\Delta H_{T_0} + \left(\frac{2\Delta H_{T_0}}{T_0} - \Delta C_p\right)\theta \cdots\right] \tag{3}$$

Here, $T_0 = 351.4$°K., $\Delta H_{T_0} = 9414.2$ cals. (4), and $\Delta C_p = -17.320$ cals. The molal heat capacity of alcohol at its boiling point (35.173 cals.) was calculated by means of the relation (13): $C_p = 0.5068 + 0.00286t + 0.0000054t^2$; that of the vapor (17.853 cals.) by the equation (7): $C_p = 4.5 + 0.038T$. Introducing numerical values in equation 3, we obtain

$$\mathrm{d} \ln a_1 = -0.03834\,\mathrm{d}\theta + 0.00028875\,\theta\,\mathrm{d}\theta \tag{4}$$

Upon integrating between the boiling point of the pure solvent, where $\theta = 0$, and the boiling point of the solution, and converting to common logarithms we obtain

$$\log a_1 = -0.016648\,\theta + 0.000062688\,\theta^2 \tag{5}$$

The activities of the alcohol, a_1, in the various solutions are given in table 2.

The activity of the salt, a_2, and that of the solvent, a_1, are combined in the relation

$$\mathrm{d}\ln a_2 = -\frac{N_1}{N_2}\,\mathrm{d}\ln a_1 \tag{6}$$

where N_2 and N_1 are the respective mole fractions. Combining equations 4 and 6 and substituting molalities for mole fractions, we obtain

$$\mathrm{d}\ln a_2 = \frac{21.717}{m}\,(0.03834 - 0.00028875\theta)\,\mathrm{d}\theta \tag{7}$$

For the case where θ approaches zero the last term disappears. Since we are approaching infinite dilution we may write $a_2 = m$ and equation 7 reduces first to

$$\mathrm{d}\ln m = \frac{\mathrm{d}m}{m} = \frac{21.717}{m}\,0.03834\,\mathrm{d}\theta \tag{8}$$

which by rearranging gives for the molal elevation of the boiling point of ethyl alcohol at infinite dilution,

$$\lambda = \mathrm{d}\theta/\mathrm{d}m = 1.2010^\circ \tag{8'}$$

This value is slightly lower than the value, 1.240°, given by Rosanoff and Dunphy (9).

By inserting the value of λ in equation 7 we obtain an expression for calculating the activity of any non-dissociating solute, namely,

$$\mathrm{d}\ln a_2 = \frac{\mathrm{d}\theta}{\lambda m} - \frac{0.006271}{m}\,\theta\,\mathrm{d}\theta \tag{9}$$

Since $a_2 = a_\pm^\nu$, it is evident that for any electrolyte giving ν ions per mole,

$$\mathrm{d}\ln a_\pm = \frac{\mathrm{d}\theta}{\nu\lambda m} - \frac{0.006271}{\nu m}\,\theta\,\mathrm{d}\theta \tag{10}$$

To integrate this expression Lewis and Randall (6) have invented a j-function which rapidly approaches zero at infinite dilution, that is,

$$j = 1 - \theta/\nu\lambda m.$$

Following their procedure for the freezing-point method we obtain finally for the activity coefficients of the ions of binary electrolytes in ethyl alcohol the relation,

$$\log \gamma = -0.4343 \int \frac{j}{m}\,dm - 0.4343\,j - 0.001362 \int \frac{\theta}{m}\,d\theta \quad (11)$$

To calculate the values of the activity coefficients, γ, it was first necessary to construct a large scale plot of θ against m. From this the values of θ/m, j, and j/m were calculated for round concentrations. Plots of j/m against m, and of θ/m against θ were drawn and the values of the two integrals in equation 11 were determined by means of a polar planimeter.

TABLE 2

Final data at round concentrations for ethyl alcohol solutions

m	θ°	a_1	γ	m	θ°	a_1	γ
(a) Lithium chloride							
0.01	0.01215	0.9989	0.1437	0.30	0.3860	0.9666	0.0276
0.02	0.0242	0.9978	0.1025	0.35	0.4586	0.9604	0.0258
0.05	0.0602	0.9947	0.0631	0.40	0.5345	0.9541	0.0245
0.10	0.1203	0.9894	0.0463	0.45	0.6121	0.9476	0.0235
0.15	0.1825	0.9843	0.0379	0.50	0.6909	0.9411	0.0225
0.20	0.2475	0.9784	0.0330	0.55	0.7724	0.9344	0.0218
0.25	0.3156	0.9726	0.0298	0.60	0.8541	0.9278	0.0212
				0.65	0.9376	0.9211	0.0207
(b) Potassium iodide							
0.01	0.0122	0.9989	0.1446	0.075	0.0907	0.9920	0.0539
0.02	0.0244	0.9978	0.1035	0.100	0.1207	0.9894	0.0469
0.05	0.0605	0.9947	0.0639	0.125	0.1511	0.9867	0.0420
				0.150	0.1815	0.9841	0.0382

The activity coefficients of the two salts in ethyl alcohol thus determined are collected in table 2.

In spite of the fact that we may assume that both salts are completely ionized at all concentrations, the activity coefficients of the ions of both salts are surprisingly low. While the activity of the alcohol is almost identically the same for equal concentrations of the two salts, the activity coefficients of the ions of potassium iodide are slightly higher than those of lithium chloride.

It would be interesting to calculate the activity coefficients of the ions on the basis of the Debye-Hückel theory. In the absence of knowledge of the ionic radii and of the dielectric constant of alcohol at the boiling point this is impossible.

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NOTE TO THE EDITOR

THE OPTICAL ACTIVITY OF CAMPHOR IN ALCOHOLIC SOLUTIONS

In reply to inquiries as to the light source used in the paper of the title given above (Journal of Physical Chemistry **38**, 883 (1934)), Professor Poe states, "All the readings in the paper, 'The Optical Activity of Camphor in Alcoholic Solutions,' appearing in *The Journal of Physical Chemistry*, October, 1934, were made with a Soleil-Ventzke saccharimeter, using white light from an electric light, and filtering it through a solution of potassium dichromate. The scale readings were converted into angular degrees."

NEW BOOKS

The Phenomena of Polymerisation and Condensation. A General Discussion held by the Faraday Society, September, 1935. 25 x 17 cm.; vi + 412 pp. London: Gurney & Jackson, 1936. Price: 22s. 6d.

It may be said without question that this volume is one of the most interesting published by The Faraday Society during recent years. Polymerisation and condensation products are of great fundamental and technical interest and are now receiving due attention. Professor Rideal in his introductory paper distinguishes between three types of polymers: first there are the polymers formed by linear accretion; secondly, those in which a large ring is the structural unit; thirdly, there is the condensation product formed by cross-linkage. The discussion is divided into two parts, called "general" and "special"; each of these contains highly instructive papers. Particular attention should be drawn to the two papers by Staudinger, the first of which is an extremely lucid survey of the formation of polymers of unsaturated substances. Readers coming to the subject freshly would do well to study this paper immediately after Rideal's, in order to gain some idea of the types of product and the relative ease of polymerisation in the various cases.

It is impossible to review individually all of the numerous contributions, but mention may be made of a few of special interest. Already attempts are being made to study the structure of polymers by means of x-rays; the difficulty is of course that most of them are "amorphous". Katz however shows that interesting deductions may be made by comparing the patterns with those of monomeric substances of similar type. Houwink and de Boer are making valiant theoretical attempts to link up the physical properties of polymers with atomic linkage forces, and their papers deserve close attention. Meyer has studied polymerised sulfur and poly-phosphonitrilic chloride by means of their x-ray diffraction patterns, and Melville and Gray give evidence to show that the vapor of red phosphorus is not polymerised but consists of P_4 molecules. The well-known American authorities on hydrous oxides, Weiser and Milligan, conclude that many of these are not polymerised but simply aggregates of microcrystalline particles with strong adsorptive properties. An interesting and promising application of physical methods to organic polymerisation described by Farquharson consists in following the change of magnetic susceptibility during the process.

For reference purposes the usefulness of these volumes would be improved very greatly by the addition of a subject index; the volume will no doubt serve the purpose of a handbook to many and the price is such that full documentation may be reasonably expected. The work of the editorial committee would be minimized in this respect if each author supplied a brief list of the important points dealt with in his paper.

J. T. RANDALL.

Fluorescence Analysis in Ultra-violet Light. By J. A. RADLEY and JULIUS GRANT. 5½ x 8½ in.; xi + 308 pp. 2nd edition. New York: D. Van Nostrand Co.

This second edition, appearing only three years after the publication of the first edition, signifies the interest in fluorescence analysis as also does the fact that over three hundred papers have appeared in this three-year period. The authors pointed out in their first edition that "if applied with discretion and under standard conditions, fluorescence analysis is a most valuable aid to the scientific worker, especially in routine work or sorting tests, and may usually supplement, though seldom completely replace, ordinary testing or analytical methods." The difficulty is not only that so many things fluoresce, but that the fluorescence is so often changed by the presence of other molecular species, often in very small amounts and perhaps not even suspected as being present. However, fluorescence analysis is becoming a valuable tool in the hands of those skilled in its use and cognizant of its capricious behavior, consequently an authoritative book covering this field fulfills a useful purpose.

The subject matter covered is as follows: PART I. Theory and Technique of Fluorescence Analysis. The titles of the chapters are as follows: I. Theoretical introduction; II. The production of ultra-violet light; III. Filters; IV. The measurement of the intensity of sources of ultra-violet light; V. Methods and technique of fluorescence analysis. PART II. Applications of Fluorescence Analysis. The titles of the chapters are as follows: I. Agriculture; II. Bacteriology; III. Botany; IV. Constructional materials and glass, etc.; V. Drugs; VI. Foods and food products; VII. Fuels and lubricants; VIII. Inorganic chemistry; IX. Leather and tanning; X. Legal and criminological work; XI. Medical and biological science; XII. Minerals and gems; XIII. Museum work; XIV. Organic chemistry; XV. Paints and varnishes; XVI. Paper, cellulose and allied industries; XVII. The rubber industry; XVIII. Textiles; XIX. Waters and sewage.

This is an excellent book, well written and printed, dealing with a subject of much importance and interest. It should be in every chemical library.

J. H. Mathews.

Collected Scientific Papers of Sir William Bate Hardy, F. R. S. Published under the auspices of the Colloid Committee of the Faraday Society (preface by Eric Rideal). 17.5 x 26 cm.; xi + 922 pp.; portrait; 14 plates; many figures. Cambridge, England: The University Press (New York: The MacMillan Company), 1936. Price: $18.00.

It is given to a few men to make a major impression upon the scientific thought of their times. Sir William was one of this chosen few. His contribution was all the more remarkable because of the breadth of his influence. He made major contributions to such diverse fields as zoology, morphology, cytology, physiology, biochemistry, physical chemistry, colloid chemistry, physics, and engineering. His education at Gonville and Caius College, Cambridge, was as a zoologist; following graduation he remained in the laboratories of his college, becoming a Fellow of the College in 1892 and later Demonstrator and then Lecturer in Physiology in the University of Cambridge. During this early period in his educational career (1892–1898) he published eleven papers dealing primarily with the histology, morphology, behavior, and function of the free living or "wandering cells" (i.e., the leucocytes) of crustaceans, amphibians, and mammals. It was this series of studies which led him into the field of surface phenomena. As Rideal notes in the preface of the present volume, Sir William once saw a cell divide under the microscope and he asked himself the question, "Why does a cell divide?" This question motivated Sir William's future work in that borderline field between biochemistry, physics, colloid chemistry, and physiology, and led him to investigate surface and interfacial phenomena.

In 1899 he published two classic papers in the *Journal of Physiology*. One was entitled "On the Structure of Cell Protoplasm"; the other "On the Coagulation of Proteid by Electricity." These were his beginning papers in colloid chemistry. They reflected his earlier interest in cytology, morphology, and histology. In the histological methods which he had used the tissues were fixed, hardened, dehydrated, and stained for microscopical observations. Sir William questioned whether or not such drastic treatments may not have produced from the complex colloidal matrix of the living cell structures which were in reality artifacts. So his colloid chemical studies began from the necessity of testing such a hypothesis.

Sir William was not fundamentally trained in chemistry, physics, and mathematics, but he acquired the necessary working knowledge of these fields after his formal education had been completed in the University.

His study in 1903 of the effect of the rays from radium on protein sols is one of the earlier papers on the effect of radium rays on biocolloids or living tissues. His studies of the physics and chemistry of the "boundary state" were pioneer studies in that field and early led into problems of adhesion. These problems of adhesion in turn led to his studies on the fundamentals of lubrication and the concept of the orientation of molecules, this concept antedating the later work of Harkins and Langmuir and being arrived at from an entirely different viewpoint.

To Sir William's studies on the equilibrium of the protein in the blood we owe the concept of the isoelectric point as a fundamental and characteristic property of the proteins and other colloid systems.

In the present volume all of Sir William's papers have been brought together and reprinted in chronological order. They comprise fifty-nine papers in number, beginning with a study of the histology and development of the hybroid, *Myriothela phrygia*, in 1891 and ending with the Abraham Flexner lecture "To Remind—A Biological Essay", a philosophical summing up of his life interests (delivered in 1931 but not printed until 1934). Many of the early biological papers are illustrated with plates of careful drawings, beautifully colored. The only criticism of the volume that the reviewer would offer is that it does not contain a biographical sketch. Consequently, the young reader may be left ignorant of the fact that Sir William was first and last a biologist, who used the tools of physics and chemistry to attack a fundamental biological problem.

The world of science is indebted to the Colloid Committee of the Faraday Society for making all these valuable papers accessible in one volume. The reviewer knows of no more inspiring volume to place in the hands of the young student of living processes, be he labeled botanist, zoologist, physiologist, biochemist, or biophysicist. May it assist some of these to carry on the task which Sir William laid for himself; for he says "the biologist's job is to take the findings of physics and chemistry and faithfully to apply them to the riddle of this impossible elusive living slime in its coat of many colors."

Ross Aiken Gortner.

Adsorptionstechnik. By Franz Krczil. 22 x 15.5 cm.; 132 pp. Dresden and Leipzig: Theodor Steinkopff, 1935. Price: 8.50 RM.

For one who knows adsorption mainly from the scientific laboratory it is interesting to see the enormous technical application which has developed, especially in the last twenty years. Solitary cases of technical adsorption processes are very old: the ancients used charcoal or clay to clarify wine; Lowitz in 1785 improved the quality of spirit by letting its vapor pass over charcoal; since 1794 charcoal—later boneblack—has been used in sugar refining. But it was the war and the adsorbent charcoal in the gas-masks which made the many possibilities of adsorption processes generally known.

Active carbon, bleaching clays, kieselguhr, and silica gel are the chief types of adsorbents. They are not only used to remove unwelcome impurities (coloring matters, etc.) from gases and liquids (drying and desulfurizing of gases; purification of water; refining of glycerol, of oils, resins, etc.). Valuable vapors are regained or isolated by adsorption; explosive gases such as acetylene are stabilized when adsorbed in mixture with acetone; adsorption processes are used in refrigerators.

Krzil's book is clearly and concisely written. It adheres staunchly to its title; stress is mainly laid upon the technical devices used in these processes. Theory is treated very briefly, but correctly. The question which is most important in technical application can not yet be answered from a theoretical point of view; too little is known about the causes of the specific behavior of adsorbents and adsorbed substances.

H. Freundlich.

Lehrbuch der physikalischen Chemie. By K. Jellinek. Band V, Lieferung 2. 25 x 16 cm.; pp. 289–576. Stuttgart: F. Enke, 1935. Price: 27 RM.

The present section of this well-known work deals with the photoelectric effect, positive rays, the structure of the nucleus, spectra, and radioactivity. The theory of spectra is brought into relation with the Periodic System. The discussion of spectra is based on the Bohr-Sommerfeld theory, and full deductions of mathematical equations, including the necessary analytical geometry, are given. The wave-mechanical treatment is not included. The section on nuclear physics is divided into two parts, the latest results being given separately at the end of the book. The section of spectra also includes x-ray spectra and crystal structure. The whole treatment is very clear, and the average student of physical chemistry would have no difficulty in following the author through some rather difficult parts of the subject. Presumably some account of wave-mechanical methods will be given in a later section dealing with molecule formation. The last few pages deal with the structure of molecules and stereochemistry. The general character of the book is maintained, and the present section is a very readable and intelligible account which should make an appeal to physical chemists.

J. R. Partington.

Textbook of Quantitative Inorganic Analysis. By I. M. Kolthoff and E. B. Sandell. 5¼ x 9 in.; 749 pp.; 116 figures. New York: The Macmillan Company, 1936. Price: $4.50.

This textbook of quantitative analysis from the hand of such a distinguished contributor in the field of analytical chemistry as Professor Kolthoff, who for many years has also been a successful teacher, is certain to prove immediately attractive to a great many teachers of the subject. The work covered is presented under the following heads: Stoichiometry. Gravimetric Analysis: Theoretical, Practical, Gravimetric Determinations. Volumetric Analysis: Theoretical, Practical, Volumetric Determinations. Physicochemical Methods. Analyses of Complex Materials (Brass, Steel, Silicate Rocks). It concludes with a very brief appendix containing tables of specific gravity of acids and ammonia and a table of four-place logarithms. It will be noticed that the outline above returns to the older practice of giving gravimetric determinations before volumetric.

In the opinion of this reviewer, the most noteworthy feature of the text is the highly successful manner in which theory and practice have been blended together. The sections on the mass action law and its application to strong and weak electrolytes, dissociation of water, hydrolysis of salts, buffer solutions, the solubility product principle, common ion effect, and complex ion formation are particularly lucid. It was to be expected that the chapters on the formation and properties of precipitates and coprecipitation phenomena, covering contamination of precipitates, adsorption, digestion, aging, etc., would be among the strongest in a test by Professor Kolthoff. All that need be said is that these are up to expectation. In addition to the separate sections on these highly important theoretical aspects of quantitative analysis, there occur in the appropriate places throughout the text many applications of these principles to the particular analytical procedures under consideration. On the other hand the authors have laid great stress throughout the procedures on the importance of careful and accurate laboratory technique and the avoidance of experimental errors.

A field to which the senior author has given major attention both in research and as a teacher is that of acid-base indicators, and the section devoted to this subject is admirably done, including an excellent theoretical discussion, many examples of titration curves from experimental data in accompanying tables, a fairly complete table of common indicators with their color change pH interval, methods of preparation of indicator solutions, use of mixed indicators, etc.

The section on physicochemical methods, including potentiometric and conductometric titrations, colorimetry, and spectrophotometry is a welcome addition. Several laboratory procedures on colorimetry, for the determination of ammonia, ferric iron, and silica, with the use of the Duboscq colorimeter, are included. The theory of potentiometric and conductometric titrations is very thoroughly discussed. It is strange that no analytical determinations making use of these methods are outlined, since there are many applications of both these methods which do not involve prohibitively complicated or expensive apparatus. The theory of adsorption indicators is given comprehensive treatment, and several titrations are outlined which make use of this method for obtaining end points.

The authors are apparently quite willing to take the field almost single-handed in defense of the rather nice distinction between the use of the terms "iodimetry" and "iodometry."

The volume is a distinctive addition to the library of quantitative analysis. No instructor in the subject will wish to be without it.

C. H. Schiflett.

Inorganic Chemistry. By N. Bjerrum, translated by R. P. Bell. 22 x 14 cm.; x + 317 pp. London: W. Heinemann, 1936. Price: 7s.6d.

In a foreword to this volume Professor F. G. Donnan states that this book is the finest introduction to modern chemical science that he has read. This is very high praise indeed. It will be generally agreed that no modern textbook dealing with inorganic chemistry can afford to ignore the profound influence exerted by developments in physical chemistry. In the present volume the skillful weaving of the theoretical aspects of inorganic chemistry with the very important descriptive parts of the subject calls for the highest praise, whilst the sections dealing with the modernized theory of acids and bases and the associated subject of ionization and reaction in solution make delightful reading. There is, however, one notable omission from the book. No reference is made to the crystal structure of the mineral silicates. Silicon occupies in mineral chemistry the same important position that carbon holds in organic chemistry, and the structure of the silicates is now as fully established as the molecular structure of any organic compound. Incidentally the model given in this book of the diamond crystal lattice (figure 14, p. 163) does not show the structure to the best advantage. However, whilst these are matters of opinion there can be only one opinion on the book—it is a highly reliable and most stimulating work which will be widely read by chemists. Mr. R. P. Bell has given us a fine translation, which is published in a most attractive form.

W. Wardlaw.

Die Interferenzen von Röntgen und Elektronenstrahlen. By M. von Laue. 22 x 15 cm.; 46 pp. Berlin: Julius Springer, 1935. Price: 3.60 RM.

During the autumn of 1935 Professor Laue gave a course of five lectures at Princeton, N. J., and the admirable suggestion of a wider audience has resulted in the production of this small volume. Laue's name will always be associated with that of other pioneers in the subject of x-ray interferences, and it is a matter of some interest that his latest work explains not only a newly observed x-ray diffraction effect, but also the elusive phenomenon of the Kikuchi lines in electron diffraction by single crystals.

The older theory of x-ray interference, as developed by Laue, Darwin, Ewald, and others, was entirely adequate to explain the positions of the diffraction maxima, but failed in certain little-observed respects with regard to intensities. During 1935 a new phenomenon was observed and reported by Kossel and Voges; the x-rays issuing from a single crystal anticathode act as a source of radiation within the crystal, and interference effects are observed on a photographic plate placed parallel to the crystal face. The theoretical work of Laue and Kohler joins up the older classical theory with the quantum theory in order to explain these effects, and the bridge between the two is Maxwell's law of reciprocity. The interesting thing is that the new x-ray patterns are, so far as present results go, entirely similar to the Kikuchi patterns of electron diffraction. Although unexplained details remain, the Kohler–Laue theory work provides a comprehensive theory of these effects. In spite of Professor Laue's mathematical erudition the reprinted lectures are very readable and deserve translation.

J. T. Randall.

Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikat Forschung in Berlin-Dahlem. Siebenter Band. Edited by W. Eitel. 29 x 21 cm.; 203 pp. Braunschweig: F. Vieweg, 1935.

The annual reproduction in volume form of the published work of the Kaiser Wilhelm-Institut serves two useful purposes; many of the papers appear in somewhat obscure journals and might otherwise be missed. The volume, apart from the individual merits of the papers, is more useful in indicating the trend of fundamental work on silicates in Germany. The present volume contains twenty-five papers, two of which are concerned with problems of Portland cements; another interesting paper by C. A. Becker contains much information on the physical and chemical properties of complicated glasses containing beryllium oxide. The properties of lime–soda–silica glasses containing traces of radium and thorium salts are investigated by M. Heckter, and this is followed by a long study of the system $CaO–SiO_2–MnO$ with the x-ray identification of solid solutions of pseudo-wollastonite and rhodonite. Büssen gives x-ray data on the coefficients of thermal expansion for magnesia, cristobalite, sillimanite, and carborundum. The volume closes with a very long paper by W. Weyl, giving details of numerous absorption spectra for solutions and glasses. One gets the impression that the workers on this interesting subject are tending increasingly to use physical methods for the study and interpretation of their experiments.

J. T. Randall.

Chemical Discovery and Invention in the Twentieth Century. By Sir William A. Tilden. 492 pp. New York: E. P. Dutton & Co., 1936. Price: $4.00.

The sixth edition of this meritorious and semi-popular book has been thoroughly revised by Dr. S. Glasstone of the University of Sheffield. In the preface, Glasstone states that the new material has been selected so as to fit in the structure and continuity of the earlier editions. Obsolete material has been dropped. The additional subject matter includes theories of atomic structure and molecular architecture, valency, transmutation and disintegration of the elements, heavy hydrogen and its theoretical significance, and artificial radioactivity. The new descriptive matter includes among other topics: coal and petroleum industries, synthetic rubber, plastics, fixation of nitrogen, vitamins, hormones, and plant colors.

The book is divided into four parts. I. (a) British laboratories and their uses (this section will always be of historical value). (b) Apparatus. II. Modern discoveries and theories. Clear and non-mathematical. III. Modern applications of chemistry. This includes the more recent work on vitamins, hormones, plastics, rayon, and duprene. IV. Modern progress in organic chemistry.

There are over one hundred and forty illustrations, including a dozen portraits. The author has used discrimination and good judgment in the selection and treatment of his topics. There are one or two noticeable typographical errors. For instance, I. Langmuir is called J. Langmuir (p. 241) and W. S. Harkins is called H. S. Harkins (p. 159).

The reviser states that though the book was intended originally for "non technical" readers, it contains much which would appeal to those who have some knowledge of science. Therefore it is a valuable addition to a chemistry library and can be included as collateral reading for general inorganic chemistry courses.

LILLIAN COHEN.

Molekülspektren und ihre Anwendung auf chemische Probleme. Vol. II, Text. By H. SPONER. 21 x 14 cm.; xii + 506 pp. Berlin: Springer, 1936. Price: unbound, 36 RM.; bound, 37.80 RM.

Volume I (Tables) of this work was reviewed in the December 1935 issue of this Journal. Its high standard of excellence is fully maintained in the present volume. The first two chapters deal briefly with the earlier quantum theory of atomic spectra and the quantum mechanics. Diatomic and polyatomic molecular spectra occupy the third and longest chapter in the book. Certain branches of the subject, however, are omitted and others treated very briefly, either because they have been adequately described in other well-known books of recent years or because they are of comparatively little significance for the chemical problems to which the four remaining chapters are devoted. Chapter IV deals with the determination of chemically important quantities from the analysis of band spectra, chapter V with chemical binding and valency, chapter VI with excitation of molecules by collision with electrons, atoms, molecules, and ions, and chapter VII with other chemical applications of spectroscopic results. The text is well illustrated with 87 figures, including a few spectrograms; figures 15 to 19 (pp. 51 and 54) and figure 43 (p. 118), however, would be much more useful if provided with scales of wave-length or wave-number. A further table of numerical data and a list of references of papers which appeared up to the autumn of 1935 are provided, so that the tables and text are equally up-to-date. The complete work may confidently be recommended to physical chemists and spectroscopists alike.

W. JEVONS.

X-RAY DIFFRACTION STUDIES OF CHITIN, CHITOSAN, AND DERIVATIVES[1]

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INTRODUCTION

Chitin is the compound that makes up most of the organic part of the skeletons of *Arthropoda*. In the animal kingdom, to which it is limited with very few exceptions, it occurs only in the invertebrates. In addition to forming the exoskeletons of insects, crustacea, etc., it is the major constituent of the lenses of the eyes, the tendons, and the linings of the respiratory, excretory, and digestive systems. Its rôle in forming the skeleton in invertebrates is very similar to that of cellulose in plants.

When the "encrusting" materials that occur with chitin have been removed, the pure material resembles paper pulp in appearance. Usually calcium carbonate is one of the "encrusting" substances; in the case of lobster skeletons it makes up about 75 per cent of the total weight of the shells. In the tendons, at least, we have found that this material is so finely dispersed that it does not give a crystalline diffraction pattern. The tensile strength of a fiber of chitin is remarkable. Schulze (10) records that it is 58 kg. per square millimeter compared with 35.6 for silk, 14.5 for wool, and only 50 for drawn copper.

Hot saturated sodium hydroxide hydrolyzes chitin slowly, but weaker solutions do not affect it. It is soluble in concentrated mineral acids and anhydrous formic acid, but is unattacked by others.

Meyer and Mark (8) suggested that chitin is identical with cellulose except that the secondary hydroxyl on the alpha carbon atom of the latter is substituted by an acetamide group. This structure received important support when Bergman (1) isolated chitobiose and it is now generally accepted, although Shorigin (12) has recently stated that the unit of the structure is neither glucose or mannose, but another sugar, chitose, differing in configuration. Figure 1 shows the structure proposed by Meyer and Mark compared with that of cellulose.

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[1] Presented in part before the Cellulose Division at the Ninety-first Meeting of the American Chemical Society, held in Kansas City, April, 1936. Based on a thesis submitted by Albert F. Smith to the Faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936.

From an excellent fiber pattern obtained from the tendon of *Palinurus vulg.*, Meyer and Pankow (9) found that chitin was orthorhombic and crystallized in space group V_4 or V_2. They favored the former. Their determination of structure was fairly complete except for the fixing of the side chains. These they assumed to be in the 200 plane to account for its great intensity. The size of the unit cell was $a = 9.25$, $b = 10.46$, and $c = 19.25$ A.U.; the chains are parallel to the b axis. The unit cell is shown in figure 2. Our measurements check those of Meyer and Pankow very closely.

MATERIALS AND TECHNIQUE

Chitin was obtained from the carapace of lobster, *Homarus americanus*. It was prepared by removing the carbonate with dilute nitric acid, heating for four hours with frequently changed 20 per cent sodium hydroxide, bleaching with permanganate and bisulfite, and finally dehydrating with alcohol and ether. The nitrogen content was 6.61 per cent, compared with a theoretical value of 6.89 per cent. The ash was less than 0.1 per cent.

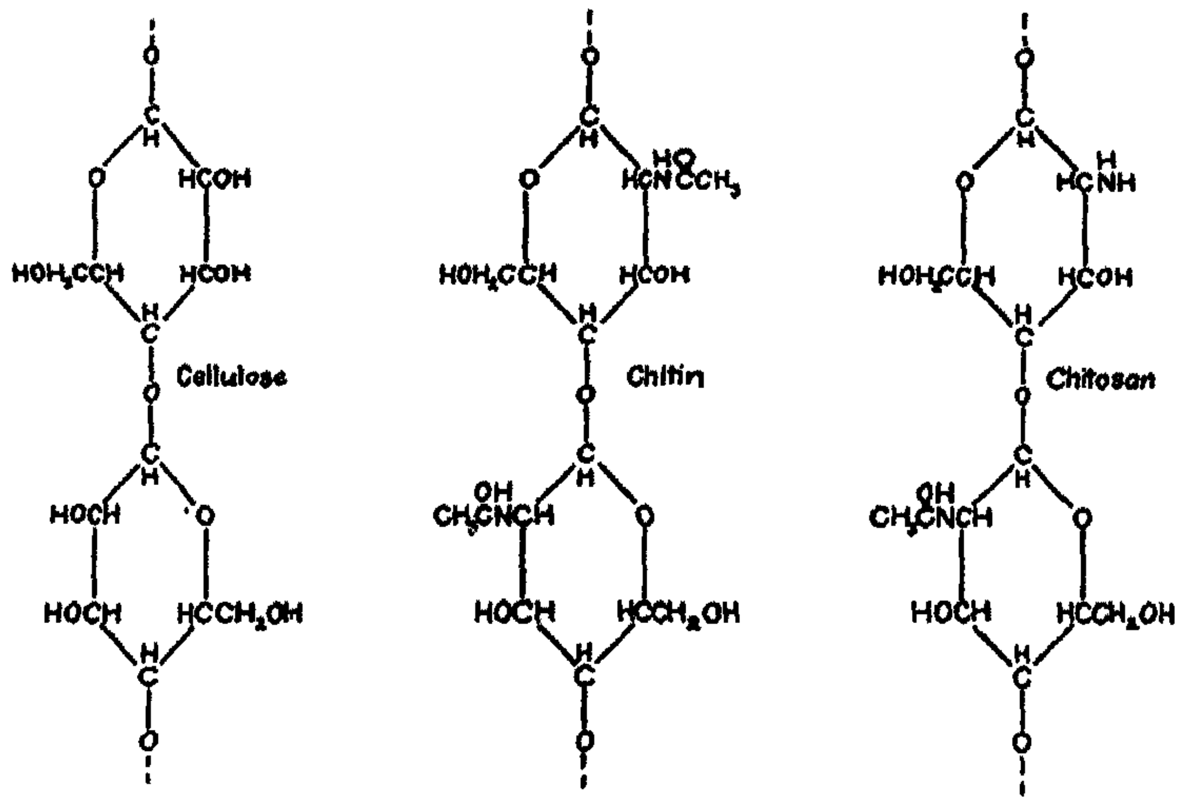


FIG. 1. Structural formulas for cellulose, chitin, and chitosan (as proposed by Löwy)

The source of x-rays was a Philips Metalix copper-target commercial diffraction tube operated at 30 kv. and 25 ma., generating principally the Cu K alpha lines. The diffraction patterns were registered on a flat film perpendicular to the beam with the sample 5.0 cm. from the film.

GENERATION AND ORIENTATION OF CHITIN

In view of the great functional and structural similarity of chitin and cellulose, it seemed possible that there might be a similarity in method of generation. Investigation of the literature revealed that Borodin (2) in a paper little known to chemists, on the slime glands of a marine worm indigenous to northern Europe, had observed tiny ellipsoidal particles that formed in the epithelial cells and were present in the cuticula. Although he apparently did not realize it at the time, his staining reactions leave little room for doubt that he observed the formation of "macromolecules" of chitin several years before similar observations were published on cellulose (4).

In search of further information concerning the structure, we found that after long soaking in absolute alcohol, which seemed to remove a wax-like binding material, a mandibular tendon from lobster could be teased apart with the aid of fine needles into uniform fibrils. These fibrils were about a micron in diameter and between crossed Nicols gave very sharp parallel extinction, indicating a high degree of orientation. They seemed to be very similar to fibrils obtained from cellulose. So far we have been unable to break these fibrils down into uniform smaller units, as has been done for cellulose.

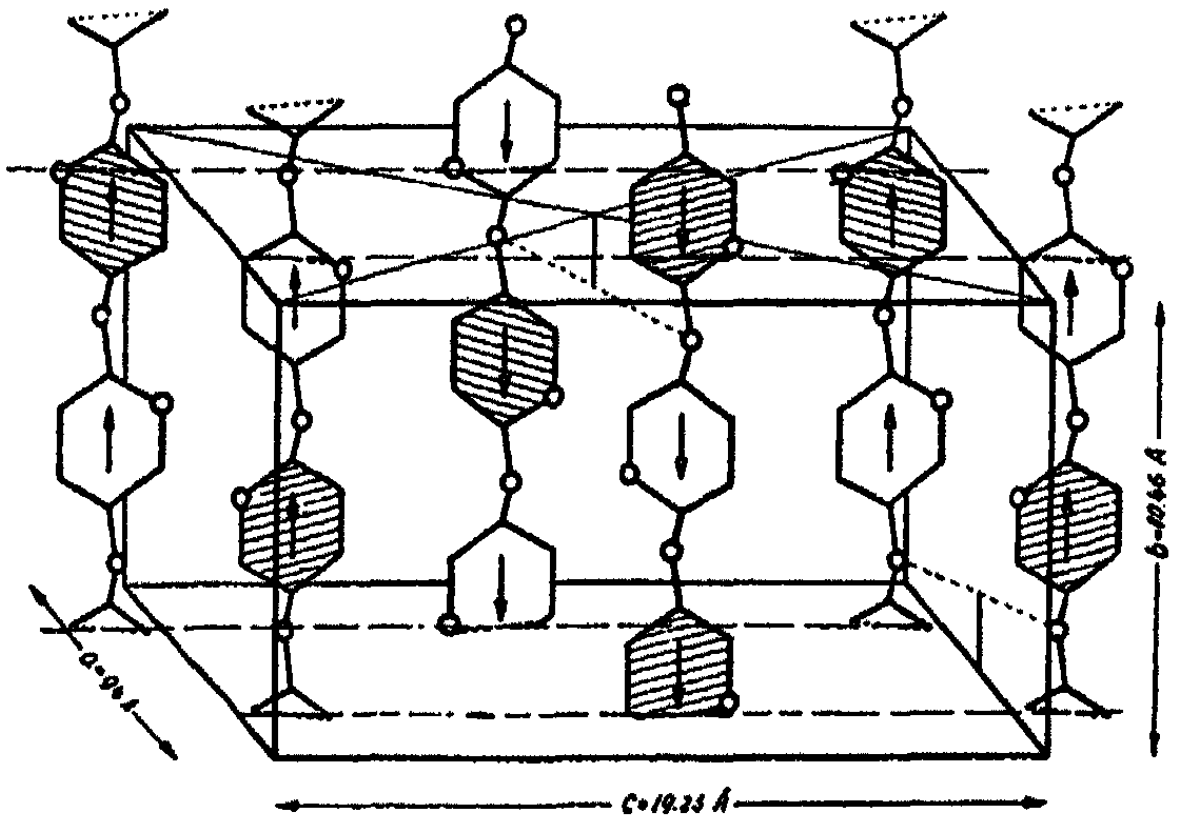


FIG. 2. Unit crystal cell of chitin (Meyer and Pankow, confirmed in present work)

From the manner of formation, chitin should be oriented. Further the orientation, in the case of sheets, should consist solely in having the carbohydrate chains parallel to the surface. If this were the case, an x-ray diffraction pattern taken with the beam perpendicular to the surface of the sheet would show the concentric rings of a random pattern. If the pattern were taken with the beam parallel to the surface, however, fibering should appear.

If an orthorhombic crystal, as chitin appears to be, is laid on a surface in such a way that the *b* axis is parallel to the surface and the crystal is allowed to rotate about its *b* axis, and also about an axis perpendicular to the surface, the locus of the face poles of any plane parallel to the *b* axis, which in chitin amounts to being parallel to the chains, may be represented on spherical projection by lines of longitude. Figure 3 shows the appearance of such a sphere viewed from a pole.

The radial lines represent the lines of longitude. The number of lines per unit area at any point represents the average number of times that the plane is in this position. If a beam of x-rays, *x*, parallel to and in the plane of the paper, is incident on the rotating crystal, the positions of the plane when satisfying the Bragg angle will be represented on the sphere by a circle or in the projection by the band *ab*. Since the intensity of any part of an interference on the diffraction pattern depends on the number of times the plane is in the position to give that reflection, and since the lines per unit area in the band *ab* indicate that number, it is possible to predict the appearance of the diffraction pattern. Since there will always be some lines per unit area in the band, there will appear a continuous ring, but since near the center of the band there occurs a maximum number, there will appear at the equatorial position on the film, the position perpendicular to the plane in which the crystal is rotating, a maximum intensity of the interference.

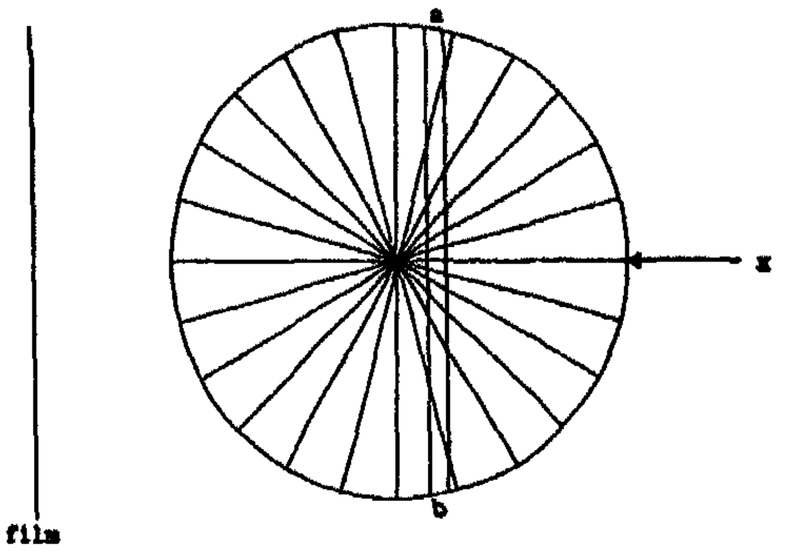
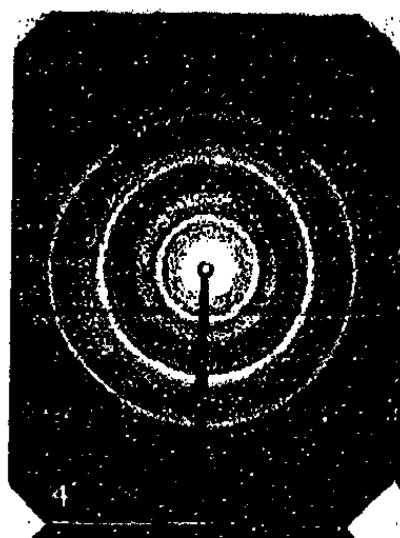
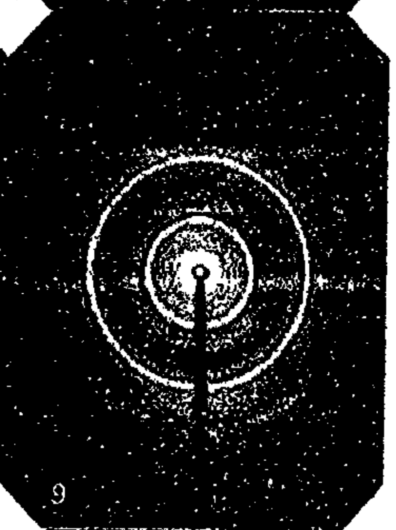
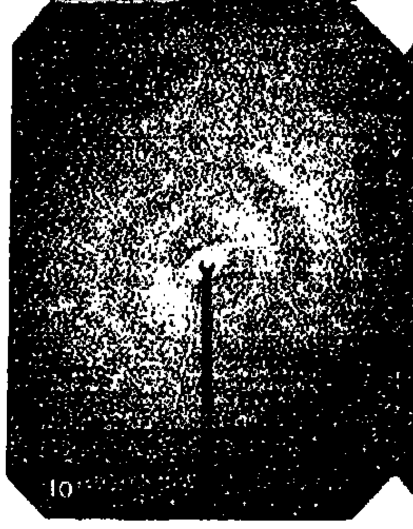


FIG. 3. Spherical projection of intensity distribution for chitin diffraction pattern

Any planes perpendicular to the *b* axis will give obviously only sharp arcs at the polar positions. Planes with inclinations to the *b* axis other than these will give intermediate appearances. If, in place of a single rotating crystal, there is substituted a large number of very small crystals whose only orientation is the *b* axis in a plane, the pattern will in no way be altered. Just such a pattern was obtained and is shown in figure 5, which is to be compared with the pattern taken with the beam perpendicular to the surface, figure 4. It was found that all naturally occurring chitin laid







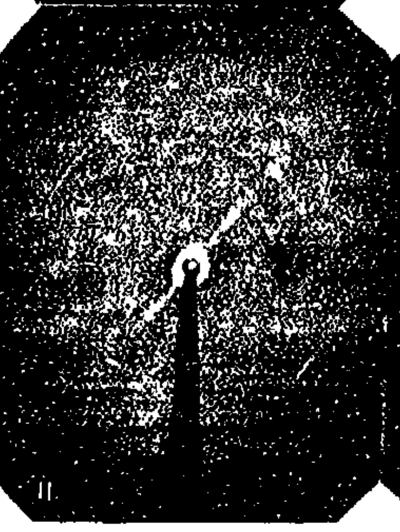


FIG. 4. Chitin sheet, x-ray beam perpendicular to surface.

FIG. 5. Chitin sheet, x-ray beam parallel to surface.

FIG. 6. Chitin fiber (mandibular tendon of lobster).

FIG. 7. Ground chitin.

FIG. 8. Chitin sheet reprecipitated from hydrochloric acid solution after one and one-quarter hours.

FIG. 9. Chitin sheet reprecipitated from hydrochloric acid solution after forty-two hours.

FIG. 10. Chitin sheet reprecipitated from lithium thiocyanate solution.

FIG. 11. Addition compound of chitin with lithium thiocyanate, formed above 200°C.

FIG. 12. Chitin swollen in lithium thiocyanate solution below 200°C.

down in sheets is oriented in this manner. In chitin fibers such as tendons, of course, the *b* axis is parallel to the axis of the fiber, just as is true in the case of cellulose.

A fiber pattern of chitin obtained from the mandibular tendon of lobster is shown in figure 6. It is entirely similar to the pattern used by Meyer and Pankow in their determination of the crystal structure. The fogging that proceeds outward from the central spot along the equatorial line indicates that parallel to the chains there exist planes of very long spacings. Since it has been possible in the case of some naturally occurring substances, such as collagen (3), to resolve these smudges into definite interferences by swelling, stretching, etc., attempts were made to do the same with chitin, but without success. It is apparent that the diffraction is taking place from planes that are so distorted as to provide a large number of spacings varying only a little in magnitude, resulting in radial smudging of the type so familiar to investigators of distortion in metals.

THE ACTION OF HYDROCHLORIC ACID ON CHITIN

It is well known that boiling concentrated hydrochloric acid eventually hydrolyzes the ether and amide linkages in chitin to give glucosamine, but many workers (6) have believed that in cold hydrochloric acid no hydrolysis occurs and hence have used the reaction to "purify" chitin. Kunike (6) used solution in acid and reprecipitation as a way of obtaining threads of chitin which he hoped to make into fabric, but the venture was not very successful. We have formed a sheet of chitin by reprecipitating it from hydrochloric acid and allowing it to dry on glass. Its tensile strength was so great that it pulled bits of glass out of the surface, but it was readily dispersed in water.

In order to discover the exact nature of the action of the acid, diffraction patterns were taken of chitin reprecipitated after various lengths of time in solution at room temperature. The patterns are shown in figures 8 and 9 along with a pattern of ground chitin for comparison (figure 7). It is necessary to compare with the pattern of a ground sample, since the intensity relationships of the interferences in the pattern taken perpendicular to the surfaces are not quite correct because of the restriction of the orientation.

In these patterns the first heavy line from the center is the interference of the 002 planes, which are parallel to the chains (the *b* axis) and approximately perpendicular to the plane of the anhydroglucose rings and the side chains. The second heavy line is the interference for the 200 planes, which are parallel to the chains and perpendicular to 002, so that they contain the rings and the side chains. The third heavy line is the combination of the interferences 030 and 031, since their spacings are so nearly the same that their interferences fall at the same point. These planes are approximately perpendicular to the chains, the 002, and the 200 planes. This applies to all of the other patterns shown in this paper. Since the intensity of a given interference depends upon the number of planes giving the reflection, any action that destroys the regularity of spacing in a given crystallographic direction will reduce the intensity of interferences from planes perpendicular or nearly perpendicular to this direction.

In the pattern of the material precipitated after one and one-quarter hours in hydrochloric acid solution (figure 8), the intensity of the interference 030, 031 is appreciably less than in the pattern of the ground chitin (figure 7). In the pattern of the material reprecipitated after 42 hours (figure 9), the intensity has decreased until the line can hardly be designated as strong. In addition to the decrease in intensity, there is a considerable broadening which indicates that the particle size in the direction of the *b* axis, that is, along the length of the chains, has been considerably reduced. The decrease in intensity indicates plainly that there has been a reduction in the length of the chains with the consequent destruction of the 030 and 031 planes. This must mean that there is occurring, even in the cold solution, a hydrolysis of the ether linkages between the anhydroglucose units. A pattern taken of material precipitated after five days in the acid shows further decrease in the intensity of the 030, 031 interference and in addition a reduction in intensity of 002. This last must result from the hydrolysis of part of the acetyl groups in the chain, causing some of the chains to draw closer together in the *c* direction, thus destroying the regularity necessary for diffraction to take place. That the 200 interference should exhibit the same intensity throughout the series is to be expected, since there is no action occurring to alter that spacing. All patterns were taken under the same conditions to permit comparison of intensities.

Since it is apparent that appreciable reduction of the chain length occurs in so short a time as one and one-quarter hours, it seems possible that Kunike's lack of success in making a satisfactory fabric may be explained on that basis. The ready dispersion of the chitin sheet formed from reprecipitated chitin and the increased difficulty of precipitation with longer time in solution is explained by greater solubility which accompanies a decrease in chain length. The generation of a few amine groups by the slow hydrolysis of the amide linkage, which is shown to occur, would also contribute toward greater solubility.

The purification of chitin by solution in hydrochloric acid and reprecipitation is obviously unsatisfactory.

Although chitin dissolves rather sharply in hydrochloric acid when the normality reaches 8.5, in sulfuric acid the normality must be considerably higher, and concentrated nitric acid has practically no effect. Apparently the solubility does not depend upon the hydrogen-ion concentration alone.

THE ACTION OF LITHIUM THIOCYANATE ON CHITIN

It has been known for some time (13) that chitin and a number of other highly polymerized substances are dispersed in hot concentrated solutions of neutral salts capable of a high degree of hydration, and that they may be reprecipitated in the form of filaments when these salt dispersions are poured into alcohol. It seemed worthwhile to investigate the process of dispersion of chitin in lithium thiocyanate.

The lithium thiocyanate solution used was saturated at about 60°C. and solidified upon cooling to room temperature. Upon heating in this solution to 95°C., chitin was rather readily dispersed into a sirupy colloidal solution.

As a precipitating medium acetone in water was found to be superior to alcohol, since the speed of the precipitation could be varied between wide limits by merely changing the proportion of acetone. By extrusion of the solution through a fine tip into a high concentration of acetone in water, threads could be made. When some tension was applied to the threads during their formation, they developed a considerable degree of orientation, as shown by their sharp parallel extinction between crossed Nicols.

Some of the jelly-like mass of chitin precipitated from the colloidal solution by dilution was placed upon a glass surface and allowed to dry. Figure 10 is the diffraction pattern obtained with the beam parallel to the surface of the sheet. It shows to a lesser degree the same type of orientation as the natural sheet. The diffraction pattern of chitin precipitated after remaining for several months in lithium thiocyanate showed no evidence of any hydrolysis.

Lithium iodide acts in the same way as lithium thiocyanate, but more slowly.

When a chitin fiber was heated to 200°C. in the lithium thiocyanate solution, we found that although there was little change in volume and the form remained the same, the diffraction pattern, figure 11, showed definite compound formation with the salt. Accurate chemical analysis was impossible, since any attempt to remove the excess salt by other than mechanical means results in destruction of the compound, but such results as were obtained showed some value less than 5 moles of lithium thiocyanate per anhydroglucose unit. This addition compound is comparable to the lithium thiocyanate–cellulose addition compounds and, as in the case of cellulose, its formation may be attributed to the ether and alcohol groups. Upon washing in water the salt is removed from the fiber, and the original chitin reappears as well oriented as originally. The interferences of the fiber pattern of the compound are given in table 1, but the determination of the crystal structure must serve as the subject of another investigation.

At temperatures below that necessary for compound formation, a fiber of chitin soaked in the lithium thiocyanate solution gives the pattern shown in figure 12. Here there is no evidence of compound formation. The interferences of planes parallel to the chains merely become smudged, showing that the regularity of their spacing is being destroyed. The interferences of planes perpendicular to the chains, 030, 031, remain sharp, indicating that the effect of the salt is to spread the chains apart without breaking them and without producing any displacement in the direction of the *b* axis. It is an example of intramicellar swelling of chitin by water alone, also proved by the diffraction pattern. If chitin is allowed to remain in the salt solution sufficiently long, the chains are spread so far apart that solution occurs.

CHITIN NITRATE

In 1906 it was established by Furth and Scholl (5) that chitin could be nitrated with fuming nitric acid to give a substance partially soluble in acetic acid. Shorigin and Hait (11) reinvestigated the substance in 1935 and found substantially the same result, but added that a considerable portion was soluble in formic acid. Since the nitrogen content of the fractions was the same, they considered that the difference in solubility arose from some other cause, probably difference in chain length.

TABLE 1

Interferences of the addition compound of chitin with lithium thiocyanate

LAYER LINE	INTENSITY*	*d* IN A.U.	LAYER LINE	INTENSITY*	*d* IN A.U.
0	4	7.30	1	1−	3.0
0	1−	6.12	2	1+	5.17
0	2	5.3	2	2	4.48
0	1−	4.46	2	1+	4.19
0	3	4.08	2	1−	3.77
0	1	3.6	2	1−	3.47
0	1−	3.14	2	1−	3.19
1	? 1−−	4.56	3	5	3.39
1	1−	3.81	3	1−	3.24
1	1−	3.38			

* An intensity of 5 indicates the greatest intensity on the pattern.

For structural studies of nitrated chitin, we prepared specimens by dissolving chitin in fuming nitric acid, allowing it to remain for one or two hours, and precipitating by stirring into water. Since the nitration of each hydroxyl group in chitin would result in an increase in weight of 20.9 per cent, the increase in weight ought to be a satisfactory way of estimating the degree of nitration, but such was not found to be the case. From the increase of weight in one experiment it was calculated that there should be 0.72 nitrate group per anhydroglucose unit, but analysis showed 1.09. The discrepancy may arise from either, or both, of two causes. Nitrogen may enter in some form other than that of the nitrate, or there may be hydrolysis or oxidation of chitin to some products that were not isolated.

The diffraction pattern of the freshly precipitated material was usually that shown in figure 13. This is a typical "amorphous" pattern, and in this case arises from the very intimate mixing of a large number of different substances with little regularity of structure. Occasionally, especially for very slow precipitation, there was obtained the pattern shown in figure 14. This pattern resembles closely that given by many resins in which the interferences are attributed to side spacings between the chains, and there is no reason to doubt that they arise from the same source in this case. The position of the rings varies from sample to sample and apparently depends on the amount of reaction that has occurred.

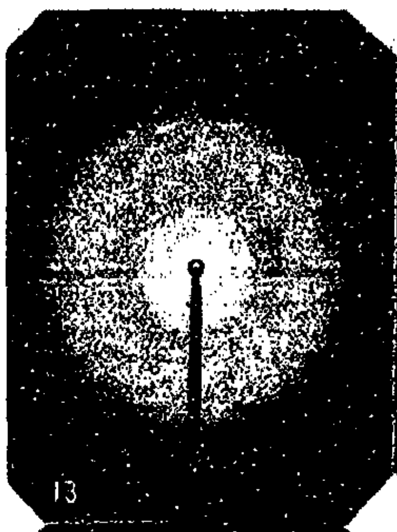
Chitin nitrate shows about the same solubility in hydrochloric acid as the original chitin, so that it is unlikely that any considerable hydrolysis of the acetyl groups has occurred. In hydrochloric acid solution there is considerable denitration, and the diffraction pattern of the reprecipitated material shows the pattern of the nitrate superimposed on the pattern of chitin. Chitin nitrate can be dispersed in lithium thiocyanate solution and reprecipitated unchanged.

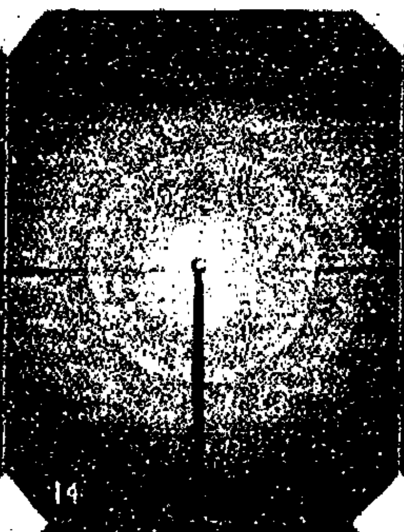
A typical diffraction pattern of the nitrate fraction soluble in acetic acid is shown in figure 15; actually the pattern varies for every sample and even for different portions of the same sample, demonstrating quite clearly that the material is, as other workers suspected, a mixture of short-chain substances resulting from the hydrolytic and oxidative action of the nitric acid. Its solubility does not arise from hydrolysis of acidamido groups to amine, since it is practically insoluble in dilute mineral acids. A considerable portion of this fraction is soluble in acetone.

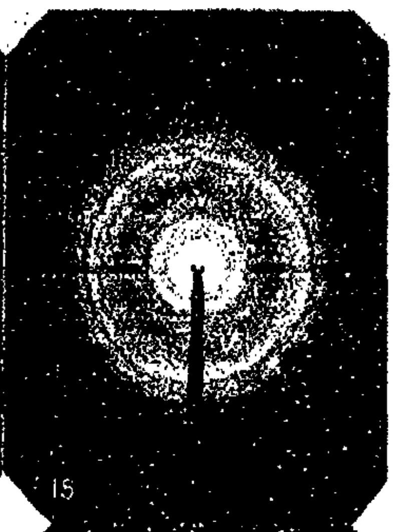
The pattern of the fraction insoluble in acetic acid but soluble in formic acid is shown in figure 16. It is more readily duplicated than in the preceding case, so that the admixed substances are apparently in fairly constant proportions. The fraction is unquestionably a mixture of compounds.

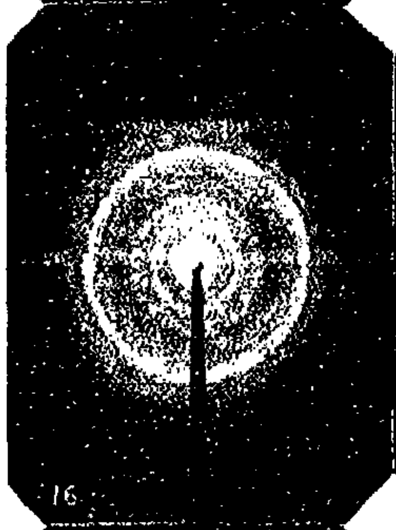
The fraction insoluble in formic acid gives a definite pattern (figure 17) and must approach the composition of a pure substance.

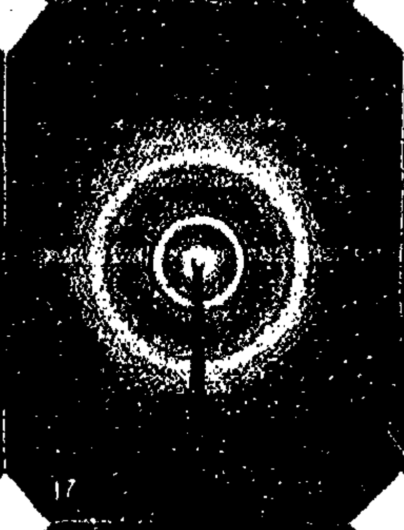
In order to determine what alteration had been made in the structure to account for the difference in solubility of the fractions, samples were denitrated by means of aqueous sodium hydrogen sulfide (11). The pattern of the denitrated formic acid-soluble fraction is shown in figure 18. The interference 030, 031 is almost entirely missing, showing definitely that the length of the chain fragments is very short. That there should be hydrolysis of the ether linkages is in harmony with the action of hydrochloric acid observed earlier. In the pattern of the denitrated insoluble fraction (figure 19), the interference 030, 031 has decreased somewhat in

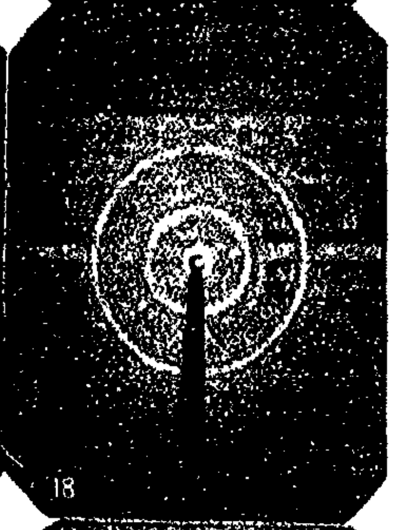












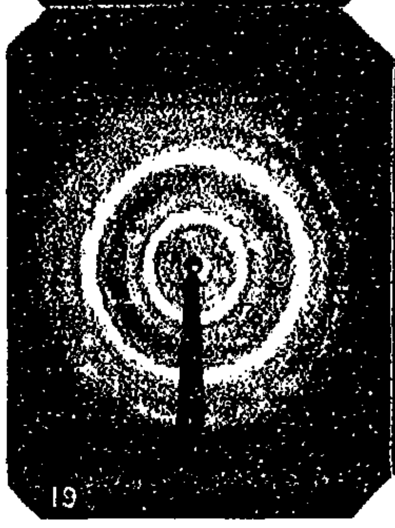


Fig. 13. Chitin nitrate freshly precipitated.
Fig. 14. Chitin nitrate very slowly precipitated.
Fig. 15. Chitin nitrate fraction soluble in acetic acid.
Fig. 16. Chitin nitrate fraction insoluble in acetic acid but soluble in formic acid.
Fig. 17. Chitin nitrate fraction insoluble in formic acid.
Fig. 18. Specimen of figure 16 denitrated.
Fig. 19. Specimen of figure 17 denitrated.
Fig. 20. Nitrated chitin fiber.
Fig. 21. Addition compound of chitin with sodium hydroxide.

intensity from that shown by the original chitin, but it is much stronger than that shown in figure 18. The chain length has been reduced from that in chitin, but to a lesser extent.

When the denitration was incomplete, the pattern of the fraction was always observed superimposed upon the pattern of the chitin. This enabled accurate measurements of the differences in the two patterns. Since the other two fractions are definitely mixtures, the measurements of the interferences observed in the case of the insoluble nitrate only are given in table 2.

Since a fiber pattern was necessary for a satisfactory approach to the analysis of the crystal structure of the nitrate, attempts were made to orient the nitrate, but none were sufficiently successful. We then attempted to nitrate a fiber of chitin without changing its orientation or physical form. This presented difficulty, since acid strong enough to nitrate the chitin also dissolved it. After many attempts the fiber whose pattern is shown in figure 20 was obtained. Nitration was accomplished by using a mixture of 5 parts fuming nitric acid (sp. gr. 1.5) and 1 part of concentrated nitric acid. The action was observed under the microscope so that it could be stopped in time to prevent solution. The fiber was extracted with formic acid to remove the short-chain fractions.

TABLE 2

Interferences observed in the case of the insoluble nitrate

SOLUBLE FRACTION		INSOLUBLE FRACTION	
d	Intensity	*d*	Intensity
11.5	4	11.5	5
7.43	3	5.89	1+
5.36	1	5.17–4.53	4
4.9	1–	3.9	1
4.48	5	3.3	3+
3.8	1	2.96	1–
3.3	3	2.6	1

The indistinctness of all interferences except those along the chain shows the incompleteness of the nitration and the correspondingly imperfect crystal structure. That considerable nitration has taken place, however, is shown by the fact that the inner equatorial spacing, 002, has moved into the position shown in the powder patterns of the nitrate.

Chitin nitrate is probably orthorhombic with $a = 9$, $b = 10.3$, and $c = 23$ A.U. The fact that the c distance has increased from the c of chitin indicates that the side-chain primary hydroxyl group does lie in the 200 plane, since the increase is just about what would be expected from the substitution of a hydroxyl by a nitrate group.

THE ACTION OF SATURATED SODIUM HYDROXIDE ON CHITIN

When a fiber of chitin was placed in hot saturated sodium hydroxide, it was found that a series of compounds was formed. A typical pattern is shown in figure 21. The patterns regularly showed definite interferences, but they were difficult to duplicate. The probable explanation is that since hydrolysis is occurring and since, as was later found, chitosan is extremely susceptible to the formation of addition compounds, most of the patterns are of mixtures of several different addition compounds formed in the course of hydrolysis.

CHITOSAN

Most authors have formed chitosan by the action on chitin of fused potassium hydroxide at 180°C. for half an hour, with resultant hydrolysis of half of the acetyl groups. Apparently identical is the product obtained upon long hydrolysis in saturated sodium hydroxide solution, since both give the same diffraction pattern and the same analysis. Löwy (7) found by an analysis of the sulfate of chitosan that it corresponded to a polymerized monoacetylglucosamine. This structure is shown in figure 1.

To follow the formation of chitosan a sheet of chitin was placed in a saturated sodium hydroxide solution held at 95°C. At intervals samples were taken out, washed free of alkali, and a diffraction pattern made with the beam perpendicular to the surface. A specimen removed after treatment for six hours produced a pattern in which interferences characteristic of chitin had disappeared except for the interference 200 which had shifted slightly but still remained (figure 22). This indicates that action occurs to destroy the regularity of spacing in the *c* direction, since it was logical to suppose that the same orientation of the chains would be maintained as long as the sample had not gone into solution. When a powder pattern (figure 23) was taken, however, it became apparent that there was some orientation greater than that exhibited by the original chitin. A pattern with the beam parallel to the surface (figure 24) confirmed the conclusion.

In order to explain these patterns satisfactorily, it was necessary to determine the crystal structure of chitosan. When a fiber of chitin was allowed to remain in hot saturated sodium hydroxide for forty hours to insure complete conversion to chitosan, and the alkali removed by washing, the fiber gave the diffraction pattern shown in figure 25. It displays a remarkable resemblance to the pattern of mercerized cellulose.

Using a mechanical apparatus which we designed for the determination of unit cell size from a single rotation pattern, we found that chitosan was orthorhombic with $a = 8.9$, $b = 10.25$, and $c = 17.0$ A.U.[2] The chains and the rings lie in the 200 planes. A description of the apparatus and the

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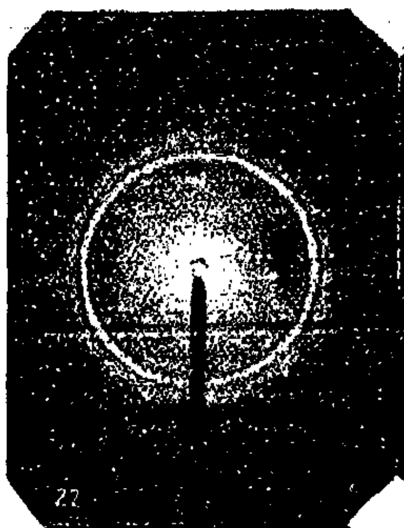
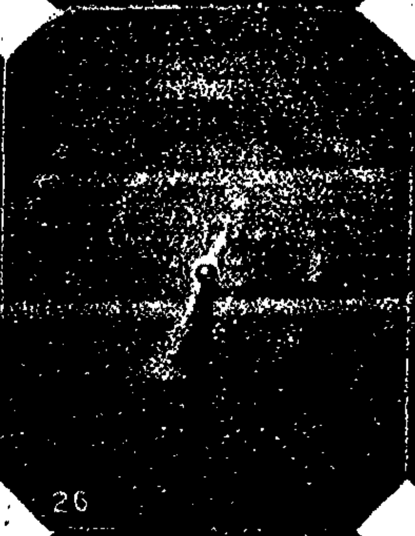
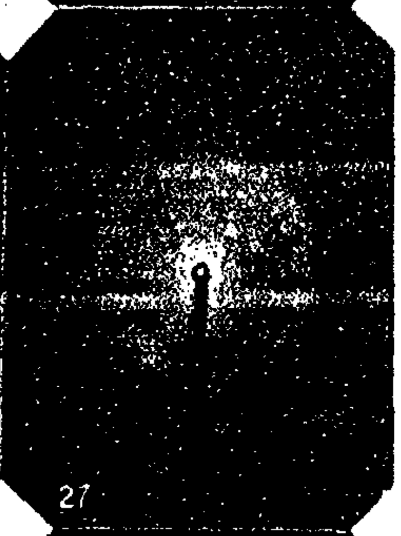
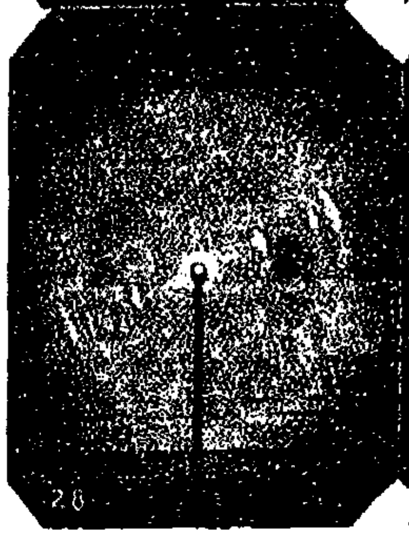
[2] A monoclinic structure with $\beta = 88°$ is not excluded as an alternative possibility.









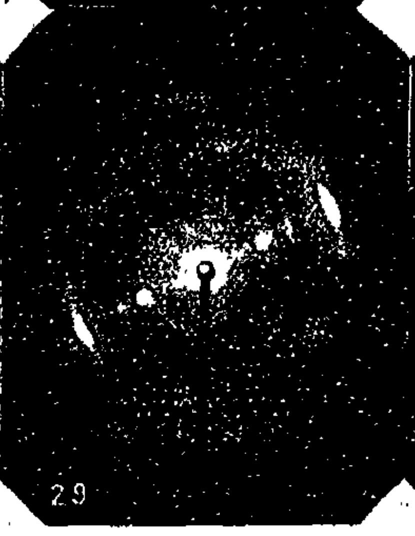


Fig. 22. Chitin after treatment with saturated sodium hydroxide solution for six hours.

Fig. 23. Chitosan sheet, x-ray beam perpendicular to surface.

Fig. 24. Chitosan sheet, x-ray beam parallel to surface.

Fig. 25. Chitosan fiber.

Figs. 26 and 27. Addition compounds of chitosan with sodium hydroxide.

Figs. 28, 29, and 30. Addition compounds of chitosan with lithium thiocyanate.

details of the crystal structure will be given in a later paper, but the spacings of the interferences, observed and calculated, are given in table 3.

From the crystal structure the orientation existing in the sheet can be deduced. In the pattern taken with the beam parallel to the surface it is seen that the interferences of planes 002 and 200 do not fall on the equatorial line, but that 002 falls on the equator while 200 occurs at the poles. Since both of these planes are parallel to the *b* axis, as shown by the fiber pattern, the only possible orientation to account for the diffraction pattern is that 002 planes must be approximately parallel to the surface. A slight variation from parallel of only a few degrees will satisfy the Bragg angle and account for the appearance of the 002 interference on figure 24. This pattern is excellent confirmation of the orthorhombic structure, since the only possible angle between these planes is 90° if the interferences are to be explained.

TABLE 3

Interferences obtained with chitosan

LAYER LINE	*hkl*	*d* ORTHORHOMBIC	INTENSITY	OBSERVED
0	002	8.5	4	8.5
0	200	4.45	5	4.46
0	202	3.94	3	4.0
0	203	3.53	1−	3.56
0	105	3.16	1−	3.12
0	006	2.83	1−	2.83
1	211	3.97	1	4.02
1	015	3.22	1−	3.25
1	310	2.84	1−	2.81
2	020	5.12	1−	5.13
2	121	4.31	3	4.35
2	123	3.5	2 (Diffuse)	3.6
2	223	2.90	1−	2.91
2	025	2.84	1−	2.78
3	130	3.20	2	3.23
3	132	3.00	3	3.02
3	230	2.71	1	2.72
4	040	2.56	1	2.50

Upon taking patterns of the chitosan fiber in a vacuum camera (3) at 15 cm. it was found that *three orders of a long spacing* of 37.5 A.U. occur; on a few patterns there was barely discernible an interference for 25 A.U., which would seem to indicate that the interferences observed were the second, third, fourth, and sixth order of a 75 A.U. spacing. These occur on the equatorial line. Their probable significance will be discussed in the paper on the crystal structure of chitosan.

ADDITION COMPOUNDS OF CHITOSAN

Chitosan is particularly susceptible to the formation of addition compounds. When a fiber soaked in concentrated sodium hydroxide was placed in a "pliofilm" cell, it gave the diffraction pattern shown in figure

26. A fiber soaked in dilute sodium hydroxide (20 per cent) gave the pattern in figure 27. Both of these patterns are of mixtures, and it is likely that chitosan forms a whole series of compounds similar to the sodium hydroxide addition compounds of cellulose. The pattern of the compound with dilute alkali is especially interesting, since in it the long spacings observed in chitosan have moved from 37.5 to 43.5 A.U., presumably to allow for the volume of the swelling agent.

With the lithium thiocyanate solution used in the work on chitin, chitosan gave a material whose pattern is shown in figure 28. If a solution diluted with two volumes of water was used, the pattern shown in figure 29 was obtained. Upon washing either of these fibers, the material giving the pattern in figure 30 was obtained. Upon further washing the original chitosan was obtained. These patterns are fairly readily duplicated, but it is possible that they are not of the pure compounds. These addition compounds of chitosan merit further investigation.

COMMENTS ON THE STRUCTURE OF CHITOSAN

Our analyses of chitosan prepared by either method have indicated only a little more than one nitrogen per biose unit instead of the two demanded by the formula of Löwy (figure 1). Since the amide linkage still exists, as shown by the presence of acetyl, the amine nitrogen appears to have been partly lost. It seems possible that Löwy's work was done on only the portion of the material retaining the amine group, since that fraction alone should form a salt.

Since the chemical information at hand reveals no reason for the hydrolysis of only one-half of the acetyl groups, and since the reaction takes place in the solid, it seems probable that there is steric hindrance to the reaction from *another* molecule. This idea is supported by the fact that since the unit along the chain is two anhydroglucose units, the acetyl groups hydrolyzed all occur on the same side of the chain.

These problems must be further investigated.

SUMMARY

1. All naturally occurring chitin displays preferred orientation of crystallites. The pattern obtained with the x-ray beam parallel to the surface of the sheet of chitin in which the chitin chains are parallel to the surface as the only orientation is derived from a consideration of the spherical projection of a rotating orthorhombic crystal.

2. Naturally occurring fibers of chitin, after treatment with absolute alcohol, may be teased apart into uniform fibrils about 1 micron in diameter.

3. Even at room temperature the ether linkages of chitin are hydrolyzed

in hydrochloric acid; concurrently, but more slowly, the amide groups also are hydrolyzed.

4. A fiber pattern of chitin is shown and discussed. Our measurements check those of Meyer and Pankow very closely.

5. At a temperature of 200°C. chitin forms a definite addition compound with lithium thiocyanate. At lower temperatures, intramicellar swelling occurs.

6. The fractions of chitin nitrate have different average lengths of the carbohydrate chain. Chitin nitrate is probably orthorhombic with $a = 9.2$, $b = 10.3$, and $c = 23$ A.U.

7. Chitin seems to form a series of addition compounds with sodium hydroxide, but the hydrolysis that occurs makes the isolation of definite compounds difficult.

8. When chitosan is formed from chitin in a sheet, it undergoes a change to a more restricted orientation. The 002 planes become parallel to the surface of the sheet.

9. Using an apparatus designed for the determination of unit cell size from a single rotation pattern, the unit cell of chitosan was determined to be orthorhombic with $a = 8.9$, $b = 10.25$, and $c = 17.0$ A.U. (or possibly monoclinic with $\beta = 88°$). A table of interferences and the indices is given, but the details of the determination and a description of the apparatus will appear in another paper.

10. Patterns are given for several addition compounds of chitosan with lithium thiocyanate and sodium hydroxide.

11. It is reported that analyses show only about one-half of the nitrogen required for Löwy's structure of chitosan, and it is suggested that there may be hydrolysis of the amine group to hydroxyl.

12. It is suggested that steric hindrance from an *adjoining* molecule may account for the hydrolysis of only half of the amide groups in chitin by alkali.

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ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. I

VERTICAL-ROD METHOD FOR THE MEASUREMENT OF CONTACT ANGLES AND PRELIMINARY STUDY OF EFFECT OF HEAT TREATMENT ON MAGNITUDE OF CONTACT ANGLES

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The angle of contact formed between solid, liquid, and gas, or between solid, liquid, and liquid is a function of the tensions existing between the phases in contact. Since the surface tension of a phase is numerically equal to its free surface energy, measurement of contact angles is of importance in connection with studies of free surface energy relations of given systems. Various methods have been employed for measuring the contact angle, as for example, the sessile-drop method, transparent-capillary-tube method, tilting-plate method, rotating-cylinder method, bubble method, drop-on-horizontal-plate method, combination drop-volume and capillary-ascension method, pressure-of-displacement method, and others. Any one of these methods will give reliable results provided it is used under properly controlled conditions. It is of greatest importance that the exact treatment history of the solid phase be known. Failure of different investigators to use solids with the same treatment history accounts largely for the divergent values for contact angles found in the literature.

It became desirable in connection with our researches to adopt some method with which measurements could be carried out rapidly. Preliminary tests indicated that readily duplicable results could be obtained by immersing the solid, in the form of a rod, vertically through a horizontal liquid interface. Other investigators had used a vertical-rod method (4, 7) or a vertical-plate method (2, 3) in investigations dealing with surface energy relations, but no simple rod method had been described which gave readily duplicable results for solid–liquid–air angles and for all types of solid–water–organic liquid interfacial angles. Such a method was developed and has been used throughout this investigation. This method will be referred to as the "vertical-rod" method.

VERTICAL-ROD METHOD FOR OBSERVING SOLID–LIQUID–AIR CONTACT ANGLES

For the measurement of solid–liquid–air contact angles the solid rod was placed vertically through the liquid surface, and a microscope in a horizontal position was focused on the system with the line of contact of the liquid with the solid approximately in the center of the field. In order to secure a true representation of the configuration of the surfaces in such a system, it was necessary that any liquid or solid through which the illuminating light ray was passed be bounded by plane surfaces and be of uniform thickness. For the case of solid–liquid–air systems in which the contact angle was less than 90° it was easy to arrange the apparatus so that observation could be made without having the light ray pass through any liquid or solid media. This was accomplished by filling to the brim with the liquid to be investigated a small rectangular glass cell having one horizontal dimension of approximately 1 cm. (figure 1a). The cell was mounted against the microscope stage and was adjusted so the surface of the liquid appeared in the field of the microscope unobstructed by the sides of the cell. The liquid surface under these circumstances was unprotected from atmospheric contamination, and it was found best to enclose this small cell in a larger rectangular cell which could be covered except for the small aperture through which the rod was inserted. The large cell had walls of clear plane polished glass.

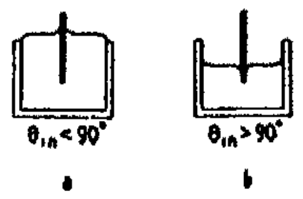

FIG. 1. Cell used for observing solid-liquid-air contact angles

In case the solid–liquid–air angle, θ_{1n}, was greater than 90° and there was a depressing of the liquid around the rod, the light beam had to pass through the liquid. For this case the cell was but partially filled with the liquid (figure 1b). The illuminating beam of light passed through the cell walls and through the body of the liquid. Since the cell walls were plane and were parallel to each other there was no distortion of the image in the microscope.

VERTICAL-ROD METHOD FOR OBSERVING SOLID–LIQUID–LIQUID CONTACT ANGLES

The arrangement of apparatus used for interfacial solid–liquid–liquid systems depended upon the characteristics of the system under investigation. When water and an organic liquid (immiscible with water) were poured into the cell and a rod inserted, a contact angle solid(rod)-water-organic liquid, θ_{n3}, represented in figure 2, a, b, c, or d, was formed. Another contact angle, solid(cell wall)–water–organic liquid, was also formed. Since the cell walls were of glass, they were more readily wetted by water than by organic liquid and the interfacial contact angle of the liquids with the cell wall, when measured through the water phase, was acute. The interfacial angle solid(rod)–water–organic liquid, θ_{n3}, could readily be viewed through a microscope in a horizontal position at the side of the cell in cases a and b, but in cases c and d the interfacial angle solid(cell wall)–water–organic liquid obscured the view. In such cases devices such as are shown in figure 2, c′ and d′, were utilized. In the diagrams *n* refers to organic liquid, 3 refers to water, the symbol θ_{n3} represents the solid(rod)–water–organic liquid angle which is expressed as measured through the water phase, and symbols d_n and d_3 represent the densities of organic liquid and water, respectively.

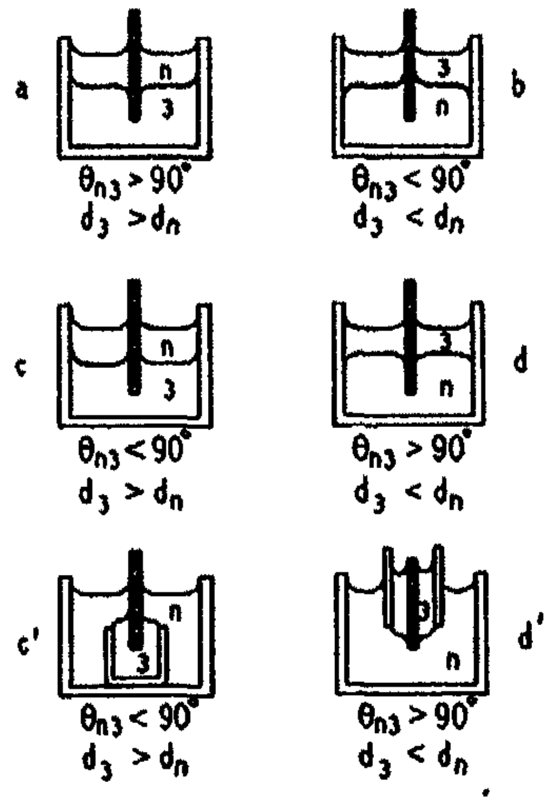

FIG. 2. Cell used for observing solid–liquid–liquid contact angles

Situation c was realized with a silica–water–benzene system. Proper conditions were attained in this case by filling the small (inner) cell to the brim with the denser liquid, and allowing the lighter liquid to flow into the larger cell until the small cell was completely submerged. This gave a liquid–liquid interface at the top of the small cell which was slightly convex upwards. When the rod was thrust vertically through the interface, the angle of contact of the interface on the solid being acute with respect to the denser liquid, the interface rose slightly and was easily brought into the field of the microscope.

Situation d was realized with a silica–water–α-bromonaphthalene system. To obtain an unobstructed view of this system a glass tube, open at both ends, was supported vertically in the larger cell, with the lower end of the tube at least a centimeter from the bottom of the cell. The lower end of this tube was ground flat, normal to its axis. The tube was about 5 cm. in length and had an inside diameter such that when the solid rod, on which the measurement was to be made, was fixed in its center there was 3 mm. or more of clear space between the rod and the inside wall of the tube. The denser of the two liquids was first run into the cell until the lower end of the open tube was completely submerged. Then by adding the lighter liquid at the top of the open tube, the liquid-liquid interface was pushed down the tube by hydrostatic pressure until it became visible at the lower end of the tube. The solid rod on which measurements were to be made was placed in the center of the tube and was then extended through the liquid-liquid interface. The interfacial contact angle thus formed was easily observed and photographed.

Method of measuring angles

The system to be examined was carefully adjusted; light from an arc was focused upon the rod so as to give good illumination of the line of contact. A microscope in a horizontal position was focused upon the points of contact at the maximum observable diameter of the rod, and photomicrographs were taken. The angles were either measured directly upon the photographic plate (lantern slide size) by means of a specially designed tangentmeter or were measured from the image projected upon a screen.

PRELIMINARY EXPERIMENTS ON EFFECT OF HEAT TREATMENT ON MAGNITUDE OF CONTACT ANGLES

Pyrex and silica rods 1 to 3 mm. in diameter were cleaned by treating with dilute nitric acid, washing with a large quantity of water, steaming, and heating to 450°C. in air for three hours. When these rods were cooled very slowly, they exhibited zero solid-water-air contact angles. When they were cooled rapidly, they gave small finite contact angles with water. Cleaned rods, 3 mm. in diameter, were drawn out to less than 1 mm. by heating either in a blast flame or in a platinum resistance coil. The solid-water-air contact angle varied from a value of zero on the 3-mm. and 1-mm. portions, i.e., maximal and minimal diameters, respectively, to over 30° on the conical section of the rod.[1] Upon examination of the conical section in polarized light, an intense strain was revealed.

Pyrex-organic liquid-air and pyrex-water-organic liquid contact angles were also investigated with such drawn-out rods, but quantitative correla-

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[1] A similar observation was made in this laboratory by Bartell and Stenzel who observed finite Pyrex-water-benzene contact angles within cone-shaped capillary tubes (unpublished observation).

tion of the free surface energy changes was impossible because of the impossibility of exactly duplicating a stressed specimen.

Freshly fused, rapidly cooled, solid Pyrex spheres of several millimeters diameter also showed an intense strain when examined between crossed Nicols. Such spheres gave an angle of about 80° with water. It has been suggested that tangential surface stresses exist upon rapidly cooled solid glass spheres (8). Removal of the strain by careful annealing caused the spheres to give zero solid-water-air contact angles. It is interesting to note that freshly blown hollow Pyrex bulbs gave zero solid-water-air contact angles; these bulbs appeared unstrained when examined in polarized light.

To substantiate the results with stressed specimens, the drop-on-plate method was employed. Compression of a Pyrex glass plate caused the solid-water-air contact angle to increase from zero to about 10°. Release of the compressive force gave a surface which showed a zero contact angle with water. When brass plates were subjected either to compressive or to extensive stress, the solid-water-air contact angle could be increased from a value of 45° to a value of about 60°.

Carefully annealed glass surfaces, giving zero solid-water-air contact angles, when allowed to stand in air showed an increase of contact angle with time of standing (6). Such changes were generally of the order of 15° to 20° for glass, but even greater effects were obtained with advancing angles on metals. Sorption of gases or vapors (5) from the air may have been responsible for these changes.

EFFECT OF HEAT TREATMENT ON SILICA

The effect of heat treatment on solids seemed, from the preliminary tests, to be readily duplicable in the absence of strain. The major portion of the remainder of this investigation has been concerned, therefore, with such effects under diverse, though exactly defined, conditions.

A summary of results obtained with silica against α-bromonaphthalene and against acetylene tetrabromide is given in table 1.

The results illustrate clearly that the previous treatment of the solid is an important factor in determining the size of the contact angle. A fresh silica surface, that is, one that had been prepared by carefully drawing out a large, clear, fused silica rod, showed a moderate hysteresis effect, or difference between the advancing and receding contact angles with α-bromonaphthalene and acetylene tetrabromide. Silica that had been cleaned with hot chromic acid, washed with water, steamed, and dried at 100°C. showed approximately the same effects.

A silica rod that had been heated to 400°C. gave an advancing angle of practically the same value as the receding angle. This change was not permanent, however, for if the silica that had been heated at 400°C. was allowed to stand for a few hours in dry air the contact angle returned to a value as great as or greater than the original value for the freshly drawn rod. Contact angles could be readily duplicated to ±4°. The general results obtained were in good agreement with those presented by Bartell and Wooley (1) for similar systems, but obtained by a different method of measurement.

TABLE 1

Advancing and receding contact angles for the systems α-bromonaphthalene-silica-air and acetylene tetrabromide-silica-air

PRETREATMENT	HEAT TREATMENT TEMPERATURE	TIME OF HEATING	α-BROMONAPHTHALENE		ACETYLENE TETRABROMIDE	
			θ_a*	θ_r†	θ_a	θ_r
	°C.	*hours*				
Newly drawn surface			12°	5°	19°	14°
Steamed	100	1	13°	6°	21°	16°
Steamed	400	1	6°	5°	15°	14°
Steamed	400	3	0°	0°	15°	14°
Steamed	400	3‡	15°	6°	22°	15°

* θ_a = advancing contact angle.

† θ_r = receding contact angle.

‡ Then stood in dry air at 25°C. for 12 hours.

EFFECT OF HEAT TREATMENT ON METALS

Gold and platinum were chosen for the study of contact angles on metals. Because of their resistance to corrosion it was believed that surfaces of greater constancy in properties could be obtained with these metals than with less noble metals. When these metals had been heated, both the advancing and receding solid-water-air contact angles were found to have decreased. In order to evaluate if possible the effect of heating upon the behavior of the metal surface, a method of pretreatment of the surface was sought by means of which one might obtain a surface in an easily reproducible condition. The criterion of constancy of surface condition was the solid-water-air contact angle formed on the metal surface.

The surfaces of the metal rods were carefully polished with the edge of a finely ground glass plate, washed briefly in acid, washed thoroughly with water, steamed, and then heated in an oven at 100°C. for one hour. It was found that the surfaces so prepared exhibited with water, within comparatively narrow limits, ±4°, the advancing and receding angles of contact shown in table 2.

Heating to higher temperatures caused a decrease in both the advancing and receding angles. A fairly wide variation of values was found with some of the systems, which indicated that it was not easy to reproduce, exactly, surface conditions of the solid. The free surface energies of the solids appeared to change rapidly when exposed to air at room temperature, as was noted by taking contact angle readings at intervals of even a few minutes (6). Metal surfaces differed from silica surfaces in that there was no apparent tendency for receding angles to increase upon exposure of the surface to air for a period of time. It was evident that in a study of metal surfaces great care must be taken to follow given methods of pretreatment so as to prepare standard surfaces for use as surfaces of reference.

TABLE 2

Contact angles of the water–gold and water–platinum systems

TREATMENT	CONTACT ANGLES	
	Gold	Platinum
1. Metal polished, steamed, heated at 100°C. for 1 hour		
Water advancing	70°	63°
Water receding	40°	28°
2. Metal polished, steamed, heated at 600°C. in air for 1 hour		
Water advancing	13°	0°
Water receding	0°	0°
3. Metal polished, steamed, heated at 600°C. in hydrogen for 1 hour		
Water advancing	20°–30°	35°–41°
Water receding	0°	0°
4. Metal polished, steamed, heated at 600°C. in air for 2 hours		
Water advancing	0°	0°
Water receding	0°	0°
5. Metal polished, steamed, heated at 600°C. in air for 2 hours, then 24 hours in air at 25°C.		
Water advancing	65°	
Water receding	0°	0°
6. Metal polished, steamed, heated at 600°C. in air for 1 hour, then 24 hours in air at 25°C.		
Water advancing	55°	51°
Water receding	0°	0°

Measurements of interfacial contact angles formed on metals by the interface water–organic liquid were also made. The values obtained varied within fairly wide limits, depending upon the precise pretreatment of the solid, just as did the values for the solid–water–air angles. Data obtained will not be presented in this paper, inasmuch as results have since been obtained for similar systems, but with metal rods that were pretreated in a manner which has been found to give more exact and reproducible results. These results will be presented in an early paper.

SUMMARY

1. A method has been developed for the measurement of contact and interfacial contact angles against either transparent or opaque solids which can be formed into rods. This method is called the vertical-rod method. The method appears to be accurate and can be used to follow adhesion tension changes, and hence gives information concerning free surface energy changes which occur on the surface of solids. The solids studied in this investigation were Pyrex, silica, gold, and platinum.

2. It has been shown that the precise method of pretreatment of a solid surface is important in a study of its surface properties.

3. The presence of strains in glass appears to account for the large water-air contact angles observed on strained glass surfaces. Removal of the strain by careful annealing decreases the contact angle of water on such surfaces to zero.

4. Aging of glass and metal surfaces increases the magnitude of the solid-liquid-air contact angle formed upon them.

5. Heat treatment of solids can greatly alter the magnitude of the contact angle.

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ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. II

Effect of Heat Treatment of Metals in Air

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It was shown in a previous paper (2) that the vertical-rod method can be used for the measurement of solid–liquid–air and solid–liquid–liquid contact angles and that it is particularly suitable for obtaining information concerning changes in free surface energy of metals and of other solids which can be obtained in the form of rods. In the present investigation the effect of heat treatment in air on gold, platinum, and steel was studied by means of the vertical-rod method. The liquids used were water, benzene, α-bromonaphthalene, and acetylene tetrabromide, purified according to methods presented in earlier papers from this laboratory.

PREPARATION OF A STANDARD SURFACE

In order to measure the change in the angle of contact formed by a liquid on a metal after heat treatment of the metal, it was necessary that the initial surface condition of the metal be definite and reproducible. A method of pretreatment of gold and platinum was found which gave a standard surface whose solid–water–air contact angle could be reproduced to within ±4°. The gold or platinum rod was first carefully and completely scraped with the edge of a carborundum crystal, was next polished with the edge of a roughly ground glass plate, and was then polished with a finely ground glass plate until the surface, as observed under a microscope, was practically free of microscopic striations. The rod was handled at all times with clean tin foil. After polishing, it was washed briefly in concentrated hydrochloric acid, then thoroughly with distilled water. It was then steamed for one hour and finally heated at 100°C. in an electric oven in air for one hour. The standard surface gold–water–air contact angle was 68° ± 4°. The standard surface platinum–water–air contact angle was 63° ± 4°. Only rods giving values within these limits were used for subsequent heat treatment.

Steel, owing to its greater susceptibility to oxidation, did not give a "standard" surface after the same pretreatment as that given to gold and platinum. Various attempts to obtain a standard steel surface were made, but no satisfactory method of treating steel in air was found. Measurements on heat-treated steel were made, but since no satisfactory reference value was found, data on steel will not be given in this paper.

The thorough polishing given the metals in the pretreatment tends to make the surface entirely amorphous (4). This polishing removes the effects of previous heat treatments so far as the surface is concerned, for, though evidence obtained from the literature (5, 6), as well as from our own experiments, indicates that heat treatment may produce certain specific internal effects as well as surface effects, the surface appears to be affected by internal conditions only if the rod is not sufficiently polished or if it is allowed to stand too long a time before being used after polishing.

TABLE 1

Equilibrium advancing contact angles and adhesion tension values for water on heat-treated gold and platinum

HEAT TREATED FOR 1 HOUR AT	ADVANCING CONTACT ANGLES AND ADHESION TENSION VALUES					
	Gold			Platinum		
	θ_{12}	Cos θ_{12}	A_{12}	θ_{12}	Cos θ_{12}	A_{12}
°C.						
100	68°	0.3746	26.97	63°	0.4540	32.69
200	57°	0.5446	39.21	49°	0.6561	47.24
300	45°	0.7071	50.91	36°	0.8090	58.25
400	36°	0.8090	58.25	25°	0.9063	65.25
500	25°	0.9063	65.25	13°	0.9744	70.16
600	13°	0.9744	70.16	0°		

TABLE 2

Alteration with time of standing in air of equilibrium advancing contact angles and adhesion tension values for water on heat-treated gold

HOURS IN AIR	GOLD PREVIOUSLY HEAT-TREATED AT 100°C. FOR 1 HOUR			GOLD PREVIOUSLY HEAT-TREATED AT 400°C. FOR 1 HOUR			GOLD PREVIOUSLY HEAT-TREATED AT 600°C. FOR 1 HOUR		
	θ_{12}	Cos θ_{12}	A_{12}	θ_{12}	Cos θ_{12}	A_{12}	θ_{12}	Cos θ_{12}	A_{12}
½	68°	0.375	26.97	36°	0.809	58.25	13°	0.974	70.06
1	69°	0.358	25.81	39°	0.777	55.95	22°	0.927	66.76
5	70°	0.342	24.62	48°	0.669	48.18	38°	0.788	56.74
10	68°	0.375	26.97	50°	0.643	46.28	47°	0.682	49.10
24	71°	0.326	23.44	51°	0.629	45.31	53°	0.602	43.33
120	70°	0.342	24.62	57°	0.545	39.21	55°	0.574	41.30

CONTACT ANGLE MEASUREMENTS ON HEAT-TREATED GOLD AND PLATINUM IN AIR

The metal rods were first treated so as to obtain the standard surface. They were then heated for one hour at a definite temperature, the temperatures for the different rods ranging in 100°C. steps from 100° to 600°C. ± 5°. The contact angle was measured not later than fifteen minutes after the rod had cooled to room temperature, this length of time being necessary to set up the rod system and to obtain proper focusing of microscope and camera. Measurements were carried out at a temperature of 25°C. ± 2°. The contact angle was photographed and its image was measured directly on the plate or was projected on a screen and measured (2). Table 1 gives the water-air advancing contact angles obtained with heat-treated gold and platinum, and the adhesion tension values, A_{13}, calculated from the cosines of these angles. It will be noted that the angle of contact decreases with progressively higher temperature of heat treatment.

TABLE 3

Interfacial contact angles, metal–water–organic liquid, for heat-treated gold and platinum

HEATED AT °C. FOR 1 HOUR	BENZENE			α-BROMONAPTHALENE			ACETYLENE TETRABROMIDE		
	θ_{n3}	Cos θ_{n3}	A_{1n}	θ_{n3}	Cos θ_{n3}	A_{1n}	θ_{n3}	Cos θ_{n3}	A_{1n}
				Gold					
300	141°	−0.7771	77.88	146°	−0.8290	85.40	138°	−0.7431	79.37
400	113°	−0.3907	71.81	111°	−0.3584	73.16	115°	−0.4226	74.44
500	89°	+0.0175	64.65	86°	+0.0698	62.35	88°	+0.0349	62.88
600	78°	+0.2079	62.95	74°	+0.2756	58.69	83°	+0.1219	65.49
				Platinum					
300	123°	−0.5446	77.15	123°	−0.5446	80.91	128°	−0.6157	81.83
400	85°	+0.0872	62.22	83°	+0.1219	60.28	86°	+0.0698	62.58
500	72°	+0.3090	59.44	77°	+0.2250	60.80	75°	+0.2588	60.25
600	61°	+0.4848	(55.18)*	63°	+0.4540	(53.11)*	65°	+0.4226	(55.81)*

* All the A_{1n} values except those marked ( )* were calculated from the equation $A_{13} - A_{1n} = S_{n3} \cos \theta_{n3}$ (see reference 3) using the data from tables 1 and 3. The three A_{1n} values marked ( )* were calculated from the empirical equation $A_{1n} = (12.8 - S_{n3}) \cos \theta_{n3} + 65.2$ (see reference 1).

When the heat-treated metals stood in air, the contact angle assumed a larger value (2, 7). The rate and magnitude of this change for gold are shown in table 2. Similar data were obtained with platinum. It will be noted that the initial change was very rapid. Such age-change phenomena were probably due to sorption.

WATER–ORGANIC LIQUID INTERFACIAL CONTACT ANGLE MEASUREMENTS ON GOLD AND PLATINUM

Gold and platinum rods were treated to obtain the standard surface, and the interfacial contact angle, metal–water–organic liquid, was measured.

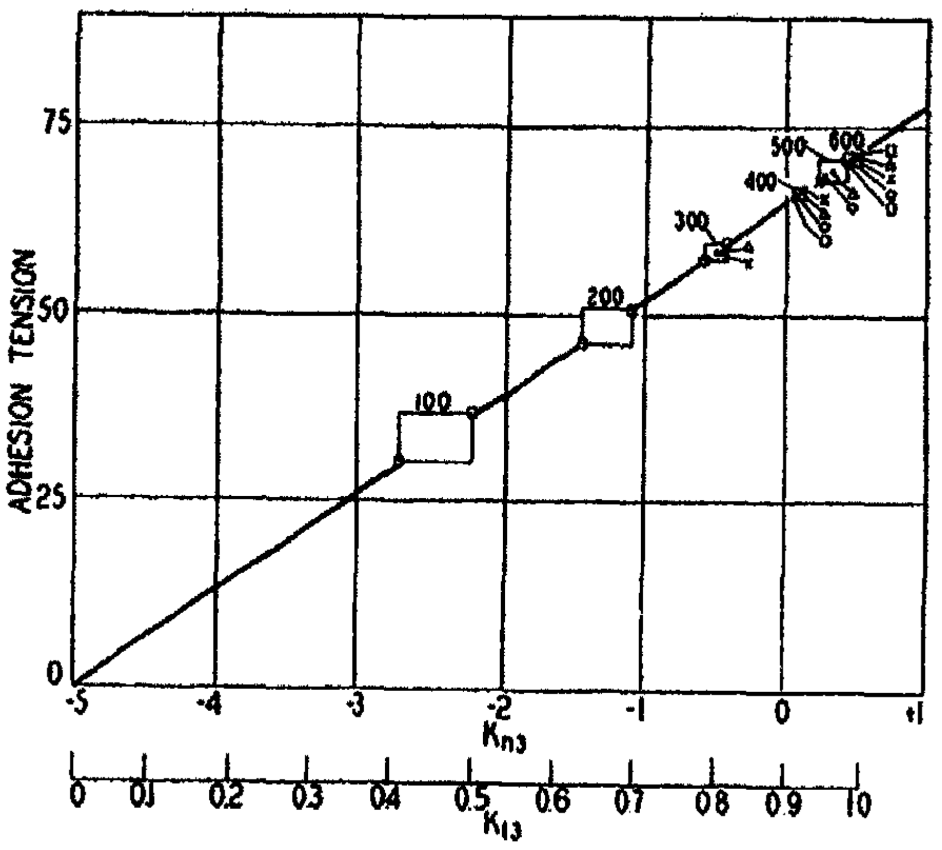

FIG. 1. Change in adhesion tension with heat treatment. Platinum one-quarter of an hour in air. □, platinum-water-air; △, platinum-benzene-water; ○, platinum-acetylene tetrabromide-water; ×, platinum-α-bromonaphthalene-water.

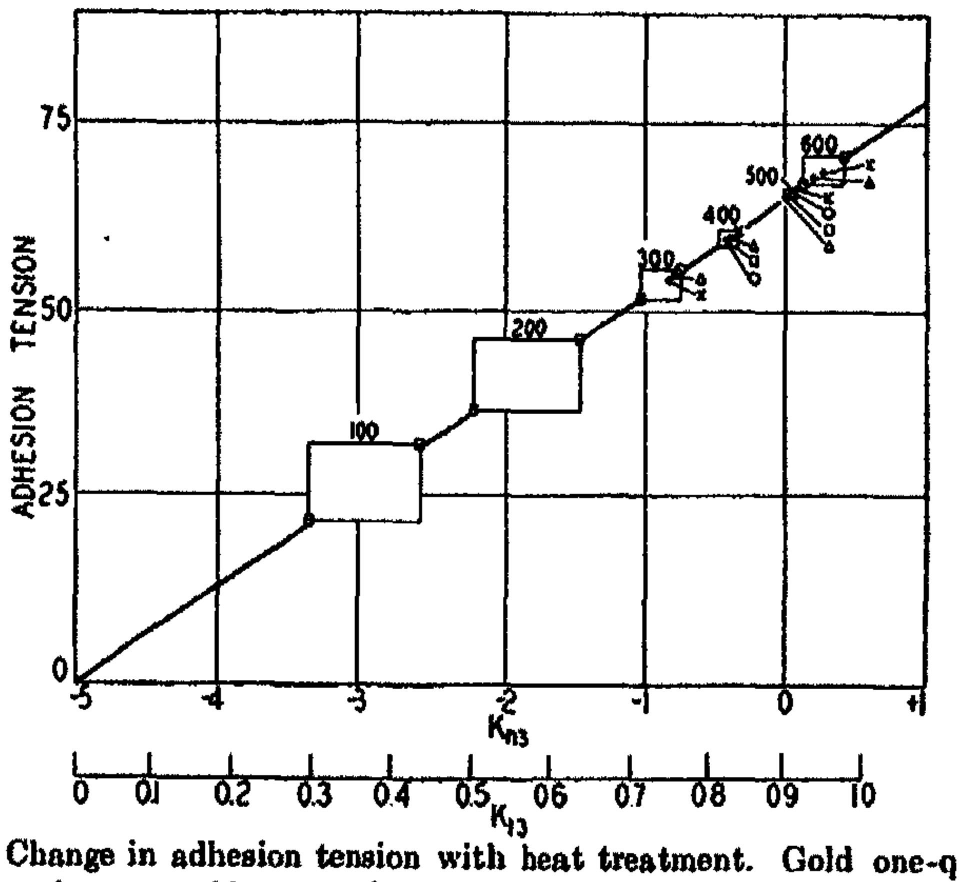

FIG. 2. Change in adhesion tension with heat treatment. Gold one-quarter of an hour in air. □, gold-water-air; △, gold-benzene-water; ○, gold-acetylene tetrabromide-water; ×, gold-α-bromonaphthalene-water.

The results are presented in table 3. All angles were measured through the water phase. As in the case of the metal–water–air angles, the metal–water–organic liquid angles decreased with increasingly higher temperature of heat treatment. For the three systems of liquids investigated, the interfacial contact angles were approximately the same against a given solid surface, the deviation in most cases being well within the limits prescribed for the standard surface (i.e., ± 4° for the metal–water–air contact angle).

Since the interfacial angles formed on these metals by the three organic liquids were all practically the same, the empirical equations developed by Bartell and Bartell (1), relating the cosine of the interfacial angle ($\cos \theta_{n3}$)[1] to adhesion tension, may apply to these metals. That they do apply can readily be shown.

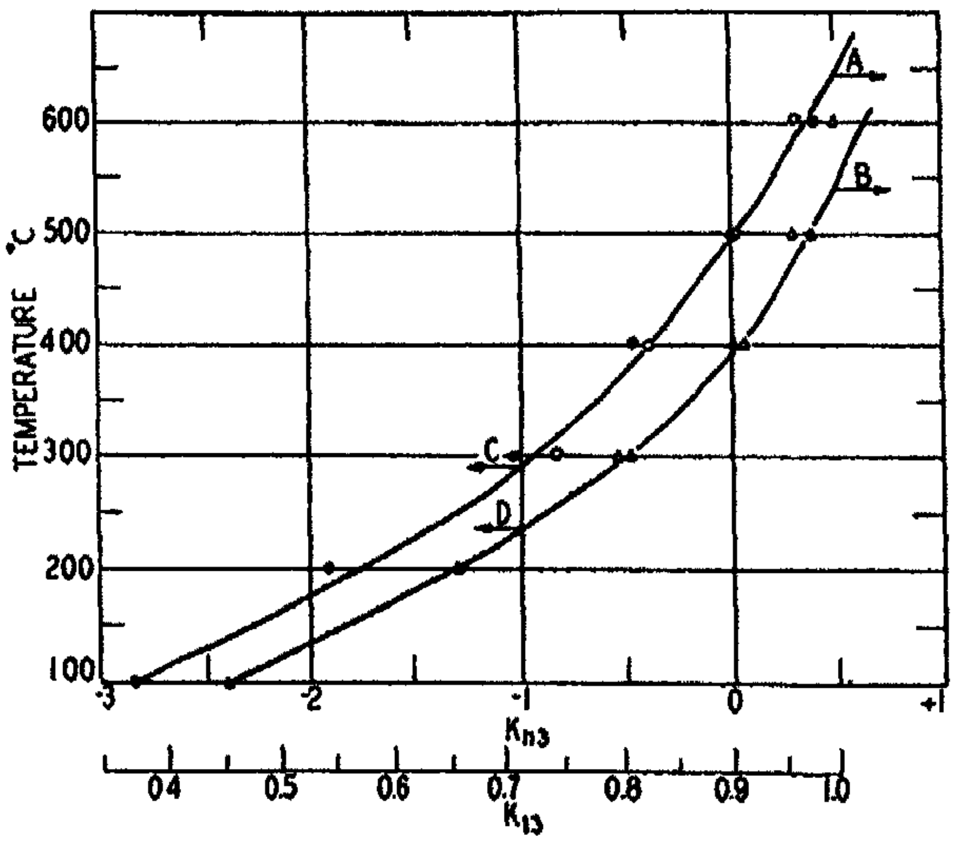

FIG. 3. Change of cosine of contact angle K_{n3} and K_{13} with heat treatment. ●, gold–water–air; ▲, platinum–water–air; ○, organic liquid–water–gold; △, organic liquid–water–platinum.

If adhesion tension values, calculated from the observed advancing water–air contact angles on metals after various heat treatments, are plotted against K_{13}, and if the corresponding K_{n3} values for the given heat-

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[1] The symbols used in this paper are the same as those used in recent papers from this laboratory, i.e., S represents surface tension, interfacial tension, or free surface energy, A represents adhesion tension, θ the contact angle, and K is the same as the cosine of θ within the limits of +1 and −1, but may take on values greater than +1 and less than −1. The subscripts 1, n, and 3 refer to the solid, any organic liquid, and water, respectively.

treated metals are plotted as a second abscissa scale, the graphs shown in figures 1 and 2 are obtained. The straight line drawn through these points is the so-called "water-line" (1) whose equation is:

$$A_{13} = 12.8K_{n3} + 65.2$$

The area enclosed in the rectangles represents the limits of experimental error for the given temperatures of pretreatment.

If temperature of heat treatment is plotted against K_{13} and against K_{n3}, smooth curves, as shown in figure 3, are obtained. From inspection of these curves it can be seen that gold and platinum, heat-treated at the temperatures corresponding to the ordinates of points A and B, respectively, should exhibit zero advancing water–air contact angles. Gold and platinum, heat-treated at temperatures corresponding to the ordinates of points C and D, respectively, should exhibit water–organic liquid interfacial contact angles equal to 180°. This was found experimentally to be correct.

SUMMARY

Rods of gold and platinum were given a special pretreatment so as to have standard surfaces for reference. Such a standard surface could not be produced on rods of steel treated in air. Standard surface rods of gold and platinum were subjected to heat treatment in air at given temperatures ranging between 100° and 600°C., and changes, due to heat treatment, in contact and interfacial contact angles were measured by the vertical-rod method.

With low-temperature treatment the metals were fairly strongly organophilic, while with higher temperature treatments they were less strongly organophilic and could even be caused to become hydrophilic in nature. The changes were probably due to oxidation and recrystallization. The surface properties were found to alter with time of standing after heat treatment.

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ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. III

Effect of Heat Treatment of Metals in a Vacuum and in Several Gases

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Recent communications from this laboratory (2, 3) have shown that large changes in surface properties of metals, caused by heat treatment of the metals in air, can be measured by measurement of the metal–water–air and metal–water–organic liquid contact angles. A method of pretreatment of metals to obtain a standard reference surface has been described (3). This method included polishing and mild heat treatment, both operations being carried out in air.

The present investigation had as its major aim the evaluation of the specific effects of the gas phase during heat treatment of metals. For this investigation a somewhat different method of preparation of standard metal surface was used, since metals polished in air undergo wear oxidation (5, 8) as well as grain or crystal fragmentation (6). Even noble metals such as gold are known to undergo wear oxidation (5) and to be capable of existing in several distinct oxidation patterns (7). For the present investigation standard metal surfaces were prepared by thorough polishing of the metals in an atmosphere of nitrogen and subsequent mild heat treatment in a vacuum. Differences of surface due to different degrees of crystal fragmentation were eliminated by the thorough polishing (4); and the use of a nitrogen atmosphere during polishing and of a vacuum (evacuated from a nitrogen atmosphere) during heat treatment, removed almost entirely the possibility of wear oxidation or heat oxidation.

The experiments on heat treatment of standardized metal surfaces fell naturally into two groups: (*a*) heat treatment of metals in a vacuum and (*b*) heat treatment of metals in different gases. In the experiments in a vacuum, gold, platinum, copper, and 18-8 stainless steel were used. In the experiments in gases, silver, aluminum, tungsten, and brass were used in addition to the metals listed above. The gases used were nitrogen, hydrogen, and oxygen. The nitrogen was purified by passing tank nitrogen successively through copper–ammonium carbonate solution, molten phosphorus, a reduced-copper furnace, and suitable drying towers. Oxygen and hydrogen were carefully dried before being used. The liquids used for contact angle measurements were water, benzene, α-bromonaphthalene, and acetylene tetrabromide, all carefully purified.

PRODUCTION OF STANDARD METAL SURFACES AND MANIPULATION OF THE VACUUM APPARATUS FOR SOLID–LIQUID–GAS CONTACT ANGLE MEASUREMENTS

For production of a standard metal surface, the metal rod was drastically polished in air, being handled with clean tin foil at all times. First, it was thoroughly scraped with the edge of a carborundum crystal, then it was polished with the flattened finely ground end of a quartz rod. The metal rod was then placed in the holder, V, figure 1, of the polishing apparatus and nitrogen was allowed to flow through this apparatus for at least one hour. After this the rod was polished in a nitrogen atmosphere in the same way as it had been polished in air, by means of the carborundum crystal, D, and the quartz rod, E. When a surface had been obtained which was practically free of microscopic striations, as shown by examination through the magnifying window, U, of the apparatus, the rod was released from its holder into the lower glass compartment, L, shown in figure 1, side view. In this compartment it was transferred in an atmosphere of nitrogen to the main vacuum apparatus, figure 2.

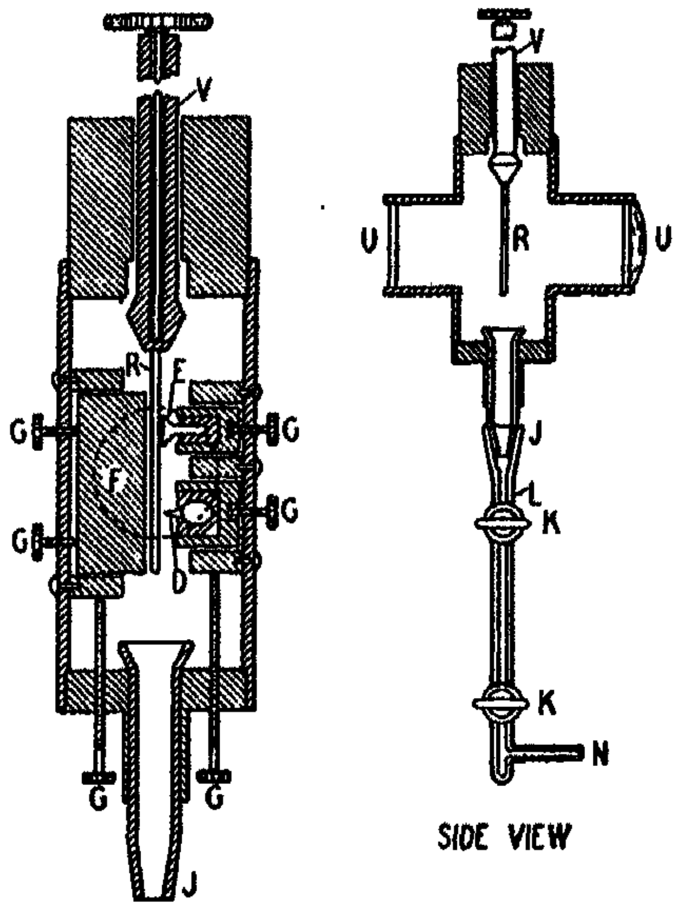

FIG. 1. Polishing apparatus

The vacuum apparatus had previously been swept out with pure nitrogen for at least one hour by means of a nitrogen line connected at B. With the gas flowing through the apparatus, the heating unit (carrying W, the heating coil) was placed in position. The apparatus was flushed out with nitrogen for another hour after the rod and heating unit were in place. The gas line was then disconnected; stopcock (mercury-seal type) S was closed, and a mercury-seal cap placed over the lower opening, B. The entire unit was then evacuated to a pressure of 10^{-5} mm. of mercury. The electric current was turned on in the heating coil, and the flow of electricity was regulated to a predetermined value. The amount of electricity required depended upon the temperature of the heat treatment and upon the radiation loss of the apparatus at that temperature. It had to be predetermined for each temperature of heat treatment. The temperature of the metal rods was measured with a calibrated iron-constantan thermocouple, T, in conjunction with a potentiometer and galvanometer. For the pretreatment to give a standard reference surface, this temperature was 100°C.

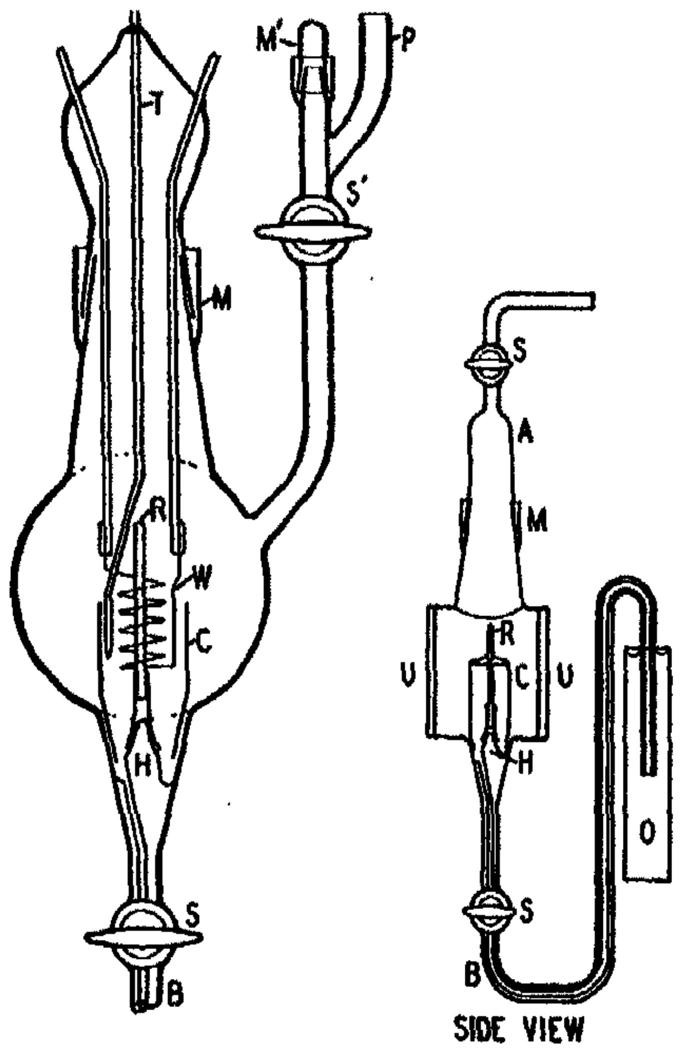

Fig. 2. Main vacuum apparatus

The time–temperature curve for the approach from 25°C. to the desired temperature of treatment was plotted so that the exact amount of heat energy communicated to the metal could be duplicated in subsequent measurements. When the temperature had attained the constant value of

100°C. (or whatever temperature was being used), the system was allowed to remain thus for exactly one hour, after which the current was turned off and the entire apparatus allowed to cool, the vacuum being carefully replaced with pure nitrogen. The time rate of cooling from a given temperature was made the same for each rod.

A blank run was made before each measurement at the temperature to be used in the measurement proper. This run was made in the hope of eliminating gases dissolved in the glass of the apparatus, which might be given off at the higher temperatures. In this way, it would seem that any gases given off from the glass up to and at the given temperature would be eliminated and pure nitrogen resorbed in their place. In the subsequent measurement at the same temperature, less, or practically no, foreign gases should be evolved from the glass. Nitrogen was kept flowing through the cooled apparatus until it was ready for the measurement proper.

A liquid-air trap was used between the apparatus and the vacuum pump. The vacuum pump was a mercury-vapor pump backed by a high-vacuum oil pump, used in conjunction with a McLeod gauge. All joints and stopcocks were of the mercury-seal type.

After a rod had been polished and heat treated at 100°C. to bring its surface to the standard reference condition, its surface condition was determined by measurement of the metal–water–nitrogen contact angle. This measurement was carried out in the following manner:

When the rod had cooled to 25°C., the heating unit was removed, with nitrogen flowing through the apparatus, and the unit A (figure 2, side view) attached in its place. The nitrogen line was disconnected, and the siphon attached in its place by means of the ground-glass joint. Water was then siphoned into the glass cup or cell, C, in the apparatus. The advancing contact angle was thus formed. Several measurements could be made on the same rod by raising the siphon reservoir and causing the liquid to advance slightly before each measurement. Lowering the siphon reservoir gave the receding angle. Each angle was either photographed or projected directly onto a special screen for measurement, as described in a previous communication (2). These angles could be readily duplicated to ±2°. A minimum of three check runs was made on each system investigated. The tabulated results represent the averages of all runs for a given system.

MANIPULATION OF VACUUM APPARATUS FOR THE MEASUREMENT OF SOLID–LIQUID–LIQUID CONTACT ANGLES

For the measurement of solid–liquid–liquid interfacial contact angles, various devices, depending upon the relative glass-wetting characteristics and densities of the two liquids, had to be used in conjunction with the apparatus shown in figure 2. The diagrammatic sketches of such mechanical devices have appeared in a previous paper (2). Except for the use of these additional devices the manipulation of the apparatus was the same as for the measurement of solid–liquid–gas contact angles.

TABLE 1

Alteration of magnitude of contact angles of several metals upon heat treatment of the metals in vacuum

HEATED 1 HOUR IN A VACUUM AT °C.	METAL-H_2O-N_2			METAL-H_2O-C_6H_6			METAL-H_2O-$AcBr_4$			METAL-H_2O-α-BrN		
	θ_{13}	K_{13}	A_{13}	θ_{n3}	K_{n3}	A_{1n}	θ_{n3}	K_{n3}	A'_{1n}	θ_{n3}	K_{n3}	A_{1n}
						Gold						
100	72°	0.309	22.3	180°		(139.3)	180°		(149.0)	180°		(163.5)
200	35°	0.819	59.0	120°	−0.500	76.3	120°	−0 500	78.1	120°	−0.500	79.8
						Platinum						
100	65°	0.423	30.4	180°		(125.1)	180°		(133.5)	180°		(145.5)
200	32°	0.848	61.1	108°	−0.309	71.8	109°	−0.326	73.5	109°	−0.326	74.6
						Copper						
100	60°	0.500	36.0	180°		(115.5)	180°		(122.8)	180°		(132.0)
150	40°	0.766	55.2	139°	−0.755	81.3	140°	−0.766	84.5	140°	−0.766	88.8
200	28°	0.883	63.6	96°	−0.105	67.2	96°	−0.105	67.6	96°	−0.105	67.9
250	20°	0.940	67.7	80°	0.191	61.0	80°	0.191	60.4	80°	0.191	59.7
						18-8 stainless steel						
100	41°	0.755	54.3	144°	−0.809	82.4	146°	−0.829	86.1	144°	−0.809	88.0
150	10°	0.990	70.9	64°	0.438	55.7	64°	0.438	54.1	64°	0.438	52.7
200	0°		(75.3)	40°	0.766	48.6	38°	0.788	45.1	38°	0.788	42.6
250	0°		(76.2)	32°	0.848	46.8	30°	0.866	43.7	31°	0.857	40.9

* The symbols used in this paper are the same as those used in recent papers from this laboratory, i.e., *S* represents surface tension, interfacial tension, or free surface energy, *A* represents adhesion tension, *θ* the contact angle, and *K* is the same as the cosine of *θ* within the limits of +1 and −1, but may take on values greater than +1 and less than −1. The subscripts 1, *n*, and 3 refer to the solid, any organic liquid, and water, respectively. $AcBr_4$ = acetylene tetrabromide; α-BrN = α-bromonaphthalene. Values in parentheses were extrapolated from diagram.

ALTERATION OF MAGNITUDE OF CONTACT ANGLES OF METALS ON HEAT TREATMENT OF THE METALS IN A VACUUM

The results of the investigation of contact angle changes on heat treatment of metals in a vacuum are given in table 1. All the angles given in table 1 are "equilibrium" advancing angles. The metal-water-nitrogen angle for a given metal heat-treated in a vacuum decreased in a regular manner with increasing temperature of heat treatment. For a given temperature of heat treatment the magnitude of this angle for the different metals varied in the order of their apparent reactivity. This might seem to indicate oxide film formation, due to the presence of traces of oxygen during the heating process, since progressive oxide film formation would give increasingly hydrophilic surfaces and decreasing contact angles with water. No temper colors, i.e., no visible indications of an oxide film, were noted, however, on any of the metals, even when they were treated for long periods of time at over 400°C. in the vacuum apparatus. It seems more probable, therefore, that heat oxidation had been eliminated in the vacuum apparatus, and that the decrease in the contact angle was caused by changes in the crystal structure of the metal during the heat treatment. Sorption of nitrogen by the metals probably also took place.

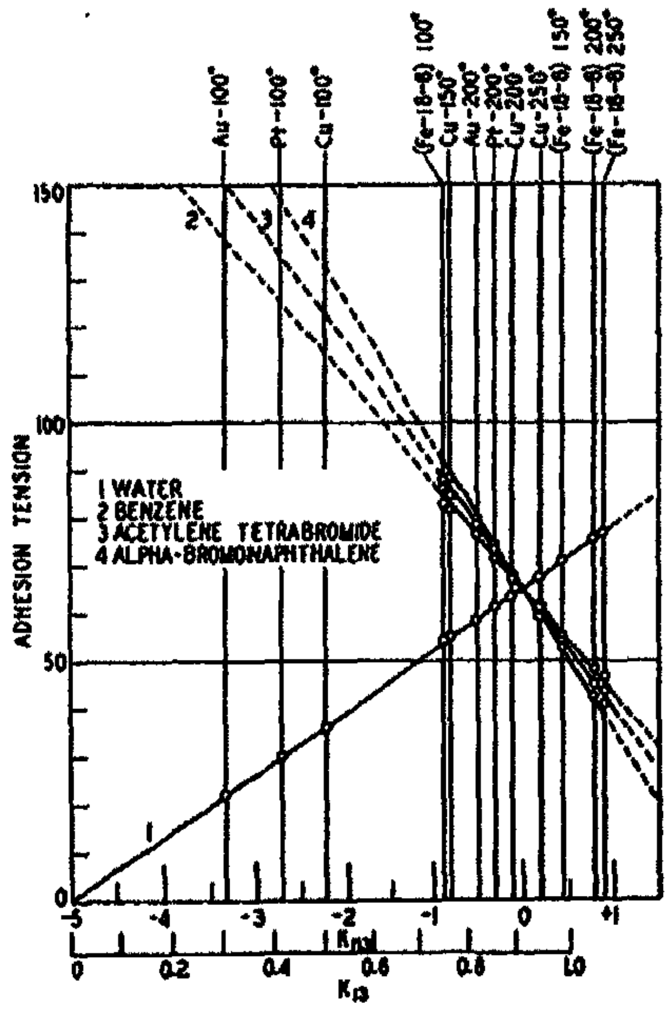

Fig. 3. K_{n3} versus adhesion tension

For the three different liquid-liquid systems tested, the interfacial contact angles on a given metal, heat-treated at a given temperature in a vacuum, were all the same within the limits of experimental error. The empirical equations of Bartell and Bartell (1) may then apply to these metals heat-treated in a vacuum. When the data obtained are plotted on a K_{n3} versus adhesion tension graph, as shown in figure 3, the points lie in straight lines whose equations are the equations cited above.

The progressive alteration of the contact angles of metals heat-treated in a vacuum is in accordance with results previously obtained for heat treatment of metals in air (3), and lends assurance to the previous conclusion that crystallization phenomena are in part responsible for such changes.

METHOD OF HEAT TREATMENT OF METALS IN DIFFERENT GASES

Standard surface rods were polished in the given gas in the apparatus shown in figure 1, transferred in an atmosphere of that gas to an especially designed induction furnace, and heated for one hour at 200°C. in the same gas at atmospheric pressure. The furnace was so designed that the rod could be loaded into it from the transferring unit, L, of the polishing apparatus, without coming into contact with air. The rod was freely suspended in the interior of the furnace without more than 2 mm. contact with any solid, i.e., the glass of the furnace interior. The current of gas entered from the rear to facilitate loading without introduction of foreign gases. After heating, the rods were removed by a special holder into a cooling compartment through which the given gas was flowing, and after rapid cooling to 25°C., transferred to the main apparatus, figure 2, which had previously been flushed out with the same gas. The measurements of contact angles were made in an atmosphere of this gas at atmospheric pressure. With surfaces treated in this manner, the contact angle could be checked in the majority of cases to $\pm 4°$.

ALTERATION OF MAGNITUDE OF CONTACT ANGLES OF METALS HEAT-TREATED IN DIFFERENT GASES

Some of the results obtained with metals heated in nitrogen and in hydrogen are given in table 2. For these metal–water–nitrogen and metal–water–hydrogen systems the angles formed showed no tendency to change over relatively long periods of time and were, apparently, equilibrium angles.

Table 3 gives the initial metal–organic liquid–nitrogen and the metal–organic liquid–hydrogen advancing contact angles for metals heated in nitrogen and in hydrogen, respectively. These initial angles are contact angles obtained immediately after immersion of the cooled metal rod into the organic liquid. They are finite, reproducible, advancing contact angles, but they decrease to zero angles with time. Somewhat analogous effects were obtained with rods which had been heated in oxygen.

Heating the metal rods in hydrogen or nitrogen apparently caused such a profound change in the surface structure (and, hence, in the free surface energy) that chemical reaction took place between the metal and the halogenated organic liquids used in this investigation. When such

TABLE 2

Contact angles of water on several metals and alloys heat-treated in various gases at 200°C. for one hour

METAL	METALS HEATED IN NITROGEN			METALS HEATED IN HYDROGEN		
	Metal-water-nitrogen angles			Metal-water-hydrogen angles		
	θ_{12}	K_{12}	A_{12}	θ_{12}	K_{12}	A_{12}
Gold	80°	0.174	12.5	56°	0.559	40.3
Platinum	58°	0.530	38.2	42°	0.743	53.3
Silver	69°	0.358	25.8	48°	0.669	48.2
Copper	90°	0.000	0.0	66°	0.407	29.3
Steel (18-8)	78°	0.208	15.0	60°	0.500	36.0
Aluminum	74°	0.276	19.8	70°	0.342	24.6
Tungsten	40°	0.766	55.2	68°	0.375	27.0
Brass	110°	−0.342	−24.6	43°	0.731	52.7

TABLE 3

Initial contact angles of organic liquids on several metals and alloys heat-treated in various gases at 200°C. for one hour

METAL	HEATED IN NITROGEN ATMOSPHERE						HEATED IN HYDROGEN ATMOSPHERE		
	Metal-acetylene tetrabromide-nitrogen			Metal-α-bromonaphthalene-nitrogen			Metal-acetylene tetrabromide-hydrogen		
	θ_{1n}	K_{1n}	A_{1n}	θ_{1n}	K_{1n}	A_{1n}	θ_{1n}	K_{1n}	A_{1n}
Gold	30°	0.866	42.4	8°	0.990	44.6	0°		
Platinum	0°			0°			0°		
Silver	12°	0.978	47.9	0°			0°		
Copper	34°	0.829	40.6	12°	0.978	43.0	0°		
Steel (18-8)	26°	0.899	44.0	0°			0°		
Aluminum	22°	0.927	45.4	0°			25°	0.906	44.5
Tungsten	0°			0°			20°	0.940	46.2
Brass	45°	0.707	34.6	16°	0.961	42.3	0°		

TABLE 4

Comparison of contact angles of water on gold and on platinum heat-treated one hour at 200°C. in a vacuum and in several gases

HEATED IN	GOLD			PLATINUM		
	θ_{12}	K_{12}	A_{12}	θ_{12}	K_{12}	A_{12}
Vacuum	35°	0.819	59.0	32°	0.848	61.1
Hydrogen	56°	0.559	40.3	42°	0.743	53.3
Air	57°	0.5446	39.21	49°	0.6561	47.24
Nitrogen	80°	0.174	12.5	58°	0.559	38.2

heat-treated rods were immersed in α-bromonaphthalene or in acetylene tetrabromide which had previously been saturated with water, metallic bromides were formed with those metals which exhibited finite initial contact angles. Metallic bromides were not formed with metals whose initial contact angle was zero.

Though one is not justified in calculating adhesion tension for a system which is not in equilibrium, adhesion tension values calculated from the initial advancing metal–organic liquid contact angles given in table 3 are some linear function of the adhesion tension of the corresponding metal–water–air contact angles (table 2). It is impossible, at present, to assign a precise meaning to such relations.

In table 4 the effects of heating gold and platinum in a vacuum and in several gases are compared through comparison of the metal–water–gas contact angles and the corresponding adhesion tensions. Gold and platinum are made progressively less hydrophilic by heat treatment in a vacuum, in hydrogen, in air, and in nitrogen, in the order given. For those solids to which the Bartell-Bartell (1) equations apply, a decrease in hydrophilic properties indicates a corresponding increase in organophilic properties. That these heat-treated metals have been made progressively organophilic is indicated by the fact that the least hydrophilic of them, the gold heated in nitrogen, actually reacted with α-bromonaphthalene and with acetylene tetrabromide.

SUMMARY

1. Rods of gold, platinum, copper, 18-8 stainless steel, silver, aluminum, tungsten, and brass were pretreated so as to have standard reference surfaces.

2. Heat treatment of the metals in a vacuum caused them to become more hydrophilic with increasing temperature of heat treatment.

3. The metals became progressively less hydrophilic when heat treated in a vacuum, in hydrogen, in air, and in nitrogen, in the order stated.

4. All the metals except platinum and tungsten, when heat treated in nitrogen, readily reacted chemically with acetylene tetrabromide; gold, copper, and brass, similarly heat treated, reacted with α-bromonaphthalene. Aluminum and tungsten, heat treated in hydrogen, reacted with acetylene tetrabromide.

5. The wetting characteristics of the different metals differ greatly, and the wetting characteristics of surfaces of the same metal differ greatly, depending upon the precise pretreatment of the metal.

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THE SOLUBILITY RELATIONSHIPS IN MIXTURES OF BRASSIDIC ACID WITH ERUCIC ACID, METHYL BRASSIDATE, AND ETHYL BRASSIDATE[1]

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INTRODUCTION

Some years ago, Timmermans and Viseur (19) made a thorough study of various binary mixtures of geometrical isomers and found that, in conformity with Bruni's rule, the *trans*-compounds showed a decidedly greater tendency than the *cis*-compounds to form mixed crystals with the corresponding saturated compounds. They therefore, along with Bruni, attributed to the saturated compounds a configuration similar to that of the *trans*-forms.

Shortly thereafter, Skau and Saxton (17) investigated mixtures of the two β-chlorocrotonic acids and found that the ideal solution law applied very closely.

No work of precision has, however, been done on mixtures of *cis–trans* isomers of high molecular weight, such as erucic and brassidic acids and their esters. Mascarelli and Sanna (12), it is true, have found that erucic and brassidic acids form a simple eutectic system, but, owing to the lack of purity of their preparations, their results need to be confirmed before they can be used for testing the applicability of the ideal solution law.

There is another problem upon which an accurate study of such mixtures may throw light, as will appear from the following considerations: Smith (18) finds that ethyl palmitate and ethyl stearate form mixed crystals, as do also hexadecane and octadecane, while hexadecyl iodide and octadecyl iodide form a system containing a compound with a non-congruent melting point. According to Bhatt, Watson, and Patel (2), such compounds are formed also in the following systems: caproic–stearic, lauric–myristic, lauric–stearic, stearic–behenic, and palmitic–stearic acids and in the system methyl palmitate–methyl stearate; but the pairs lauric acid–lignoceric acid, methyl laurate–methyl myristate, and methyl stearate–methyl behenate give simple eutectic diagrams.

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[1] This article is part of a thesis submitted by A. M. Maiden to the Faculty of Science of the University of Liverpool in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

On the other hand, Müller and Shearer (14) have proved by means of x-rays that the saturated fatty acids crystallize in double molecules, while Francis, Piper, and Malkin (4) have shown that compound formation occurs in equimolecular mixtures of such acids differing from each other by one, two, or three carbon atoms, the mixtures melting like a pure compound. Malkin (10) has established further that the methyl esters of the saturated fatty acids crystallize in double molecules, but are also characterized by a metastable form which crystallizes in single molecules. The ethyl esters were found to crystallize always in single molecules.

Thus it would appear that mixtures of substances of high molecular weight, which do not differ too much in carbon content and which crystallize in double molecules, yield phase-rule diagrams showing the presence of a compound with a non-congruent melting point. The exceptions to this rule, as exemplified by the systems methyl stearate–methyl behenate and methyl laurate–methyl myristate, may be apparent rather than real, for the results of Bhatt and coworkers (2) were obtained by cooling methods, which are liable in many cases to give erroneous data, as will be indicated in the course of the discussion of the results reported in this paper.

Since Müller and Shearer have shown that both erucic and brassidic acid crystallize also in double molecules, it is of interest to see whether a careful examination of their mixture will, from the point of view of the phase rule, show the presence of a molecular compound. The difference in their configuration would indeed not be expected to interfere with the considerations given above, as compound formation between these molecules appears to be a matter of the terminal groups only of the carbon chain.

An investigation of the systems of the type acid–ester might also prove interesting in view of the difference found by Malkin (10) in the states of aggregation of the acids and methyl esters as against that of the corresponding ethyl esters. Two such systems will be examined in the present paper.

APPARATUS

Figure 1 shows a cross section of the apparatus, which recalls in many respects that of Andrews, Kohmann, and Johnstone (1) and that of Skau and Saxton (17), except that it was so designed that the specimens might be kept *in vacuo* during each experiment, in view of their unsaturation and consequent liability to rapid oxidation.

The specimens (weighing 1.5 g.) were contained in small test tubes (internal diameter 1 cm.) connected with an exhausting tube by means of a short length of stout rubber tubing; this was surrounded by a split brass sleeve, tightened by a "Jubilee" circular clip. The melt was stirred by means of a miniature glass ring stirrer, attached by means of a stout platinum wire to a soft iron armature working inside a solenoid spool made of brass.

Temperatures were measured to within 0.1°C. by means of a two-junction, copper-eureka thermoelement, calibrated at every 10° from 20°C. to 90°C. against a standard thermometer. The E.M.F. was measured on a Cambridge thermoelectric potentiometer used in conjunction with a 400-ohm Cambridge "Ayrton-Mather" galvanometer. Fractions of 100 μ volts were obtained by the deflection method, whilst during all readings the potentiometer was frequently balanced against a standard cell. This electrical measuring system, which allowed readings to be taken to within 5 μ volts (corresponding to 0.05°C.), was entirely and adequately shielded against leaks from high potential circuits by supporting it throughout on metal, all the metal supports being electrically connected.

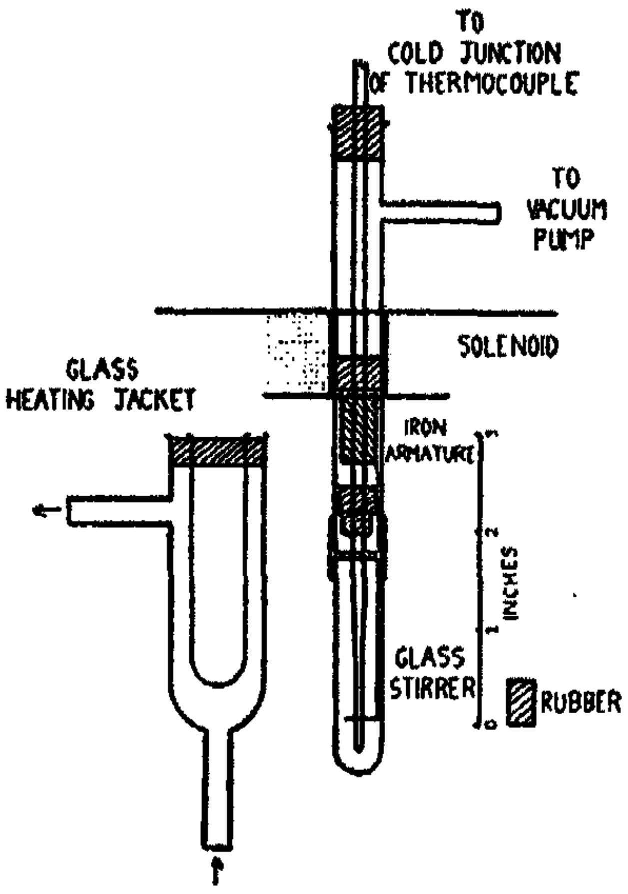

FIG. 1. The apparatus

For the determination of cooling curves the specimen was surrounded by a double-walled metal jacket, through which water at any convenient temperature was circulated from a thermostat.

For the determination of the melting point, the metal jacket was replaced by a double-walled glass jacket (see figure 1). In this manner the specimen was observed through only a thin layer of water and yet, as the thermostat contained 30 liters of water, very fine control over the rate of heating could be obtained.

TECHNIQUE

Mixtures of definite composition were made up by direct weighing into the specimen tubes, the total weight of the mixture being always 1.5 g.

The contents of the tubes were then just melted and well mixed, the tube placed on the apparatus, and the specimen allowed to set *in vacuo*. The mixture was now remelted and once more allowed to set *in vacuo*, so as to avoid completely the dissolution of gases as impurities.[3]

The type of system being dealt with was determined by taking cooling curves of the various mixtures prepared, the E.M.F. of the thermoelement being noted at regular time intervals. It was found that the convergence temperature for this apparatus was considerably below the temperature of the jacket, so that the method of correction of Andrews, Kohmann, and Johnstone (1) for the supercooling was inapplicable. As the mixtures showed in many cases considerable supercooling, this method could not in any case have been used with any satisfaction; the freezing points of the systems were therefore determined by observing the temperature at which the last crystal in the melt disappeared (cf. Johnstone and Jones (7), Smith (18), and Skau (16)). This temperature could be easily determined by means of the glass heating apparatus described. The specimen was heated rapidly until only a small portion remained solid, the glass jacket was then raised so as to surround the melt, and water at a temperature slightly below the expected melting point was circulated from the thermostat. The temperature of this water was now slowly raised, and when the details of the thermoelement wires could be seen clearly, the E.M.F. of the element was noted as the melting point. It was found that the last crystals disintegrating under the action of the stirrer gave a cloudy suspension. Very efficient agitation of the melt during such a determination is obviously necessary.

The results thus obtained are considered to be within 0.1°C. of the true freezing point. Repeat determinations always agreed to 0.05°C.

Eutectic temperatures were fixed by taking heating curves of mixtures which possessed very nearly the eutectic composition (as seen from the melting point–composition diagram). The procedure followed was similar to that for cooling curves, water slightly above the expected eutectic temperature being circulated through the brass jacket.

CONTROL OF PURITY FOR THE SUBSTANCES USED

The preparation and purification of the substances required for this research have already been described elsewhere (9).

The melting points and setting points of these substances were found

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[3] Such gases cause the molten specimen to froth if it is allowed to set under reduced pressure after exposure to the atmosphere. The fact that such substances, when in the molten state, are capable of dissolving appreciable quantities of gas from the atmosphere does not seem to have received very much notice in the past, although it must play an important rôle in the rate of oxidation of the substance (see, however, reference 6).

to be within 0.1°C., except in the case of ethyl brassidate, where the difference was 0.2°C., probably as a result of the complication due to extensive creeping. This coincidence of melting points and setting points is probably the most sensitive criterion of purity for long-chain compounds, particularly for the saturated ones, where there is no other available.[3]

In the case of unsaturated substances, the control of the purification should always be supplemented by the precise determination of the iodine values (8).

The results of such control of purity for the substances examined are shown in table 1.

RESULTS

System erucic acid–brassidic acid (see table 2 and figure 2)

Erucic and brassidic acids were found to have only one form in the region investigated. Mixtures containing up to 81 per cent erucic acid gave the normal cooling curve of a simple eutectic system, while for mixtures richer in erucic acid, the cooling curves were of a different type. Coincident with

TABLE 1

Purity of the substances examined

SUBSTANCE	IODINE VALUE		SETTING POINT	MELTING POINT
	Observed	Theoretical		
			°C.	°C.
Brassidic acid	74.7	75.0	59.8	59.75
Erucic acid	74.0	75.0	33.25	33.35
Methyl brassidate	71.2	72.1	30.0	30.1
Ethyl brassidate	68.7	69.3	24.8	25.0

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[3] The determination of the setting point alone does not always provide a sufficiently unambiguous guarantee of purity. For instance, after purifying a specimen of brassidic acid by removal of several per cent of impurities, the setting point increased only by 0.1°C., but the iodine number went up from 74.2 to 74.7. In another case further purification was accompanied by a rise of iodine number from 73.6 to 74.2 for the same small increase in setting point of 0.1°C. However, the melting point appears to be, at least in some cases, more sensitive than the setting point to the presence of impurities; e.g., while two specimens of methyl brassidate had the same iodine number and the same setting point, one of them melted as high as 32.35°C., against 30.1°C. for the other specimen.

The melting point may thus be used with advantage as a further control of purification, either with or without the simultaneous determination of the setting point. This will especially be the case when the compound examined is very nearly pure, and when the eutectic in the system compound–impurity lies very near 100 per cent pure compound.

this change, the phenomenon of a double melting point appeared. For example, by allowing a mixture containing 83.5 per cent of erucic acid to cool for some time after freezing had set in, one observed a melting point of 39.1°C., whilst if the melting point was taken immediately after freezing occurred, 30.7°C. was obtained. (Both results were repeatable.)

An increase of the erucic acid content to 87.0 per cent caused the cooling curve to become double-humped if determined with the specimen unseeded; for a specimen which was not completely melted, a cooling curve similar to that corresponding to 83.5 per cent of erucic acid was obtained.

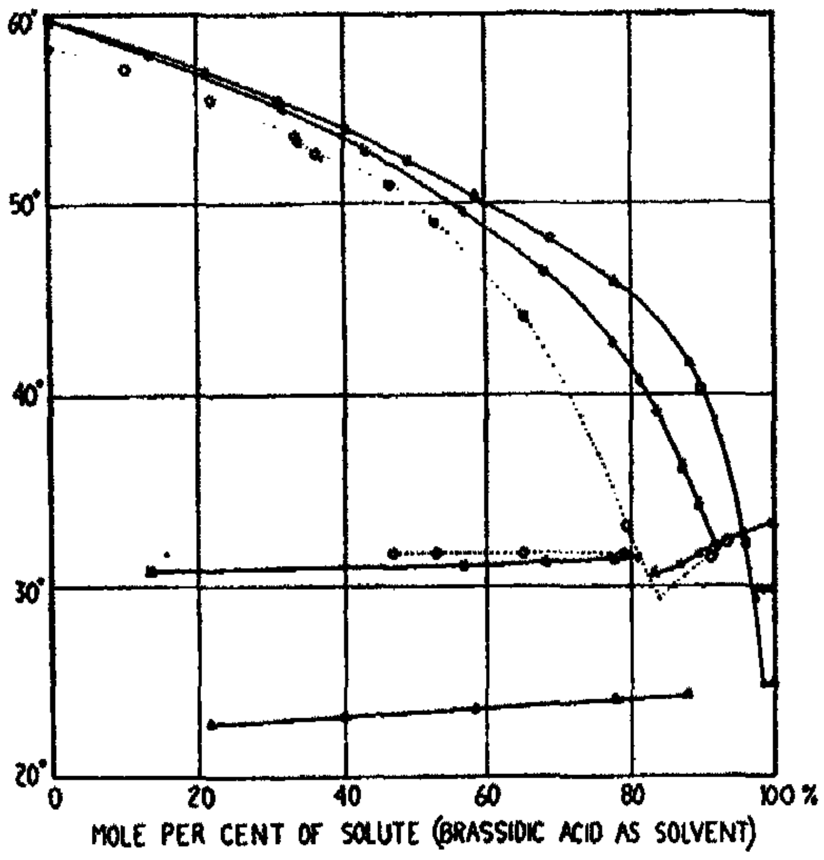

Fig. 2. Cooling curves. ×, the system brassidic acid–erucic acid (⊙ for the results of Mascarelli and Sanna); □, the system brassidic acid–methyl brassidate; △, the system brassidic acid–ethyl brassidate.

In this case, the specimen had a melting point of 31.2°C. if cooled until a few crystals appeared and then remelted; but if cooled until completely solid and then remelted, it was necessary to heat to 36.2°C. before the last crystal disappeared. Thus the change which occurred spontaneously with the 83.5 per cent mixture required nuclei to be present for it to occur with the 87.0 per cent specimen. As the higher melting point undoubtedly lies on the brassidic acid solubility curve, it would seem that the second hump corresponds to the crystallization of brassidic acid and the first to the crystallization of erucic acid.

Supercooling increases as the percentage of erucic acid in the mixture increases, and with 83.5 per cent of erucic acid the crystallization of the latter evidently occurs before that of the brassidic acid. In this case, therefore, the metastable erucic acid solubility curve can be followed up over a large range.

It is this particular phenomenon which renders it imperative to determine the melting points of these mixtures rather than their freezing points by the normal method, if the correct phase-rule diagram is to be constructed. It also caused Mascarelli and Sanna (12) to think that the eutectic mixture was about 80 per cent erucic acid, these workers not cooling to completion any mixture showing this phenomenon.

The eutectic temperature determined from the heating curves of the specimens containing 92 per cent and 89.6 per cent of erucic acid was 31.8–31.9°C., whilst the composition of the eutectic mixture determined from the melting point–composition diagram was 90.5 per cent erucic acid.

TABLE 2

The system brassidic acid–erucic acid

COMPOSITION IN MOLE PER CENT OF ERUCIC ACID	$\log_{10} N$	SOLID PHASE	MELTING POINT		$10^6/T$
			°C.	°K.	
0	0	Brassidic acid	59.80	332.8	3005
13.8	−0.064	Brassidic acid	57.85	330.8	3023
31.5	−0.164	Brassidic acid	55.10	328.1	3048
42.8	−0.243	Brassidic acid	52.80	325.8	3069
57.0	−0.366	Brassidic acid	49.65	322.7	3099
67.8	−0.492	Brassidic acid	46.45	319.5	3130
77.5	−0.648	Brassidic acid	42.75	315.8	3167
81.0	−0.721	Brassidic acid	40.70	313.7	3187
83.5	−0.782	Brassidic acid	39.10	312.1	3204
83.5	−0.078	Erucic acid	30.70	303.7	3294
87.0	−0.886	Brassidic acid	36.15	309.2	3234
87.0	−0.060	Erucic acid	31.15	304.2	3287
89.6	−0.983	Brassidic acid	34.20	307.2	3255
89.6	−0.048	Erucic acid	31.60	304.6	3283
91.2	−0.040	Erucic acid	31.95	305.0	3279
92.0	−0.036	Erucic acid	32.10	305.1	3278
95.1	−0.022	Erucic acid	32.60	305.7	3272
100	0	Erucic acid	33.25	306.3	3265

Mixtures containing more than 90.5 per cent of erucic acid have a melting point independent of the history of the specimen, as here it is normal for the erucic acid to crystallize out first.

The cooling curves of these mixtures show primary crystallization of erucic acid, but no eutectic halt, the crystallization of brassidic acid being unduly delayed. The heating curves, however, are those normally shown by mixtures with compositions near that of the eutectic.

The melting point–composition diagram, as determined for the present work, contrasts with that obtained by Mascarelli and Sanna (12) as shown in figure 2 (dotted curve). The displacement (towards the left) of the right-hand side of their diagram, caused by supercooling, is very evident.

The system ethyl brassidate–brassidic acid (see table 3 and figure 2)

The cooling curves of mixtures of brassidic acid with 22.0, 50.4, 59.1, 77.9, and 88.4 per cent of ethyl brassidate are those of a simple eutectic system. Those of mixtures containing 96.3 per cent and 98.4 per cent of ethyl brassidate are similar to that of the mixture of the previous system containing 83.5 per cent of erucic acid, but have no slight halt corresponding to a low melting point.

This type of curve is due to great supercooling, which causes the mixtures to behave as though they were richer in solute than they actually are, mixtures weaker than the eutectic mixture behaving like a eutectic mixture and setting at one temperature.

TABLE 3

The system brassidic acid–ethyl brassidate

COMPOSITION IN MOLE PER CENT OF ESTER	$\log_{10} N$	SOLID PHASE	MELTING POINT		$10^6/T$
			°C.	°K.	
0	0	Brassidic acid	59.80	332.8	3005
22.0	−0.108	Brassidic acid	57.00	330.0	3030
40.4	−0.225	Brassidic acid	54.15	327.2	3056
59.1	−0.389	Brassidic acid	50.65	323.7	3089
77.9	−0.657	Brassidic acid	46.00	319.0	3135
88.4	−0.934	Brassidic acid	41.80	314.8	3177
96.3	−1.434	Brassidic acid	32.50	305.5	3274
97.4	−1.589	Brassidic acid	29.45	302.5	3306
98.4	−1.803	Brassidic acid	24.90	297.9	3357
100		Ethyl brassidate	25.05		

All these mixtures have a single melting point.

The melting point–composition diagram for the mixture of ethyl brassidate and brassidic acid is notable for its asymmetry, this being sufficient to render the exact determination of the eutectic a difficult matter. The mixture containing 98.4 per cent of ethyl brassidate was assumed to have the eutectic composition.

Ethyl brassidate creeps to a remarkable extent when setting, and only starts to freeze after considerable supercooling. The cooling curve of the pure material always rises very slightly instead of remaining level during setting. For this reason the melting point instead of the setting point was used in the construction of the melting point–composition diagram.

No evidence of a second crystalline form of the ester was found.

Near the eutectic point, the brassidic acid solubility curve is so steep that the separation in a solid state of a very small amount of brassidic acid greatly influences the melting point of the mixture, it thus being very difficult to determine the exact melting points in this region. It is also clear that a cooling curve investigation in this region must be absolutely useless.

The system methyl brassidate-brassidic acid (see table 4 and figure 2)

The cooling curves of mixtures of brassidic acid with 30.9, 49.3, 68.9, and 89.4 per cent of methyl brassidate are those of a simple eutectic system; those of mixtures containing 96.2 and 97.5 per cent of methyl brassidate are similar to those of mixtures containing 96.3 and 98.4 per cent of ethyl brassidate.

Again the exact position of the eutectic point is difficult to ascertain. The melting point–composition diagram indicates that it is between 97.5 and 98.4 per cent methyl brassidate, a heating curve of the 89.4 per cent mixture gives 29.85°C. as the temperature, while the two solubility curves cut at 29.8°C. and 97.7 per cent.

TABLE 4

The system brassidic acid–methyl brassidate

COMPOSITION IN MOLE PER CENT OF ESTER	$\log_{10} N$	SOLID PHASE	MELTING POINT		$10^6/T$
			°C.	°K.	
0	0	Brassidic acid	59.80	332.8	3005
30.9	−0.161	Brassidic acid	55.65	328.7	3042
49.3	−0.295	Brassidic acid	52.65	325.7	3070
68.9	−0.508	Brassidic acid	48.50	321.5	3110
89.4	−0.975	Brassidic acid	40.40	313.4	3191
96.2	−1.420	Brassidic acid	32.60	305.6	3273
97.5	−1.606	Brassidic acid	30.10	303.1	3299
98.4		Ester	30.05		
100		Ester	30.10		

Pure methyl brassidate supercools considerably before setting, but it does not creep. Its cooling curve remains level during setting, and does not rise as in the case of ethyl brassidate.

No second form of methyl brassidate was found.

DISCUSSION

(A) The brassidic acid solubility curves in the systems methyl brassidate–brassidic acid and ethyl brassidate–brassidic acid are so remarkably similar that the two melting point–composition diagrams can be superimposed for the whole of the range (from 0 to 97 per cent) of concentrations (figure 2). One is thus led to the conclusion that methyl and ethyl brassidates have, when dissolved in brassidic acid, the same state of aggregation (cf. Malkin (10)).

This solubility curve of brassidic acid with respect to either ester lies only very slightly above that for the system brassidic acid–erucic acid, which tends to indicate that erucic acid, when in solution in brassidic acid, is in a state of aggregation identical with or at least very similar to that of the alkyl brassidates.

In none of the diagrams investigated is there any trace of compound formation. This, from the evidence given in the introduction, supports the assumption that all these substances exist in solution in the simplest possible molecules.

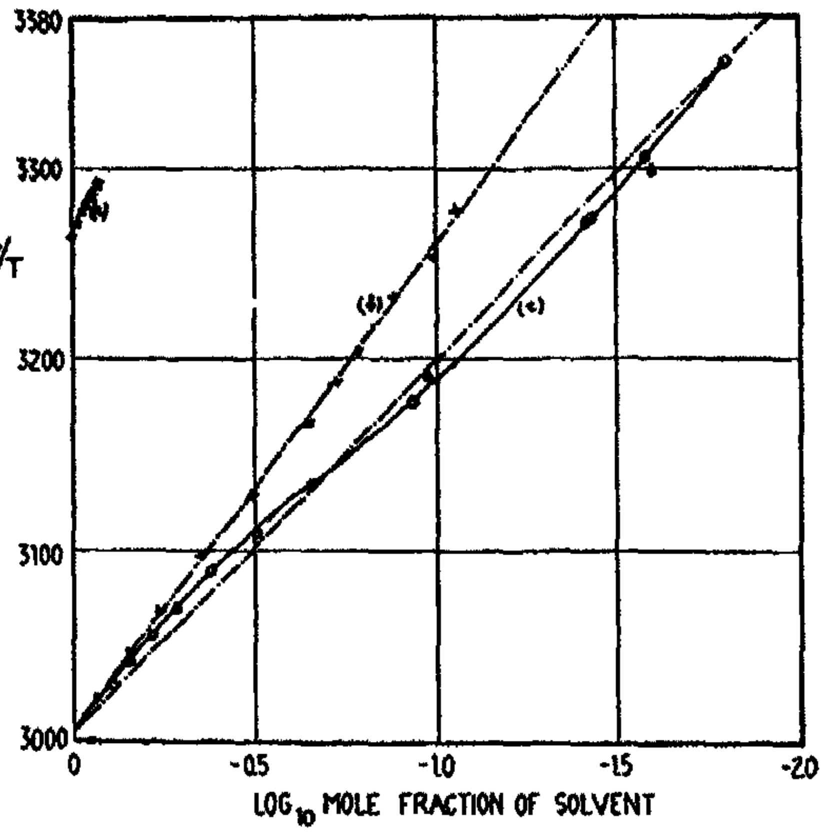

FIG. 3. Solubility curves. Curve a, brassidic acid in erucic acid; curve b, erucic acid in brassidic acid; curve c: ⊙, ethyl brassidate in brassidic acid; △, methyl brassidate in brassidic acid.

(B) It has been stated by various authors (see, e.g., Johnstone (7)) that, provided the constituents of binary mixtures of certain types of isomers are not too much alike, the plot of log N (where N is the mole fraction of the solute) against $1/T$ (where T is the absolute freezing point of the mixture) is a straight line. If, however, the constituents are very similar, mixed crystals are formed.

In order to form an opinion as to whether the pairs of substances investigated here form, or do not form, ideal solutions, the results have been plotted in the form $\log_{10}N$ against $10^6/T$ (figure 3).

For the system brassidic acid–erucic acid points from the erucic acid solubility curve lie on a straight line (figure 3, curve a), while the points from the brassidic acid solubility curve (figure 3, curve b) lie on a straight line up to 83.5 per cent erucic acid, after which the solubility of brassidic acid increases more rapidly than the ideal solution law would indicate.

The fact, however, that a straight line is obtained for such a large proportion of the diagram when the results are computed in the manner described indicates that erucic and brassidic acids have the same molecular complexity in solution in each other and behave to a large extent as ideal solutes; in particular it is evident that there is no change in their state of aggregation with change in concentration.

Only the points for the brassidic acid solubility curve can be obtained from the ester diagrams. These, when plotted, lie on one S-shaped curve (figure 3, curve c). According to Mortimer (13) this type of curve is obtained in systems in which one component is polar and the other is nonpolar, and where there is a great difference in the internal pressures. Unfortunately there are no data from which the internal pressures of these esters may be calculated. When the internal pressures of the acids themselves are calculated from the data of Semeria and Ribotti-Limone (15), values in the neighborhood of 400 atmospheres at 90°C. are found for both acids.

These authors determined the parachors of these two acids, and obtained values dependent upon temperature, a fact which would tend to show the presence of some association in these pure liquids. The results here reported show that no such association occurs.

Waentig and Pescheck (20) have inferred from freezing-point measurements that lauric and palmitic acids exist, to some extent, as double molecules when dissolved in carbon tetrachloride.

Our results for the ester systems show the danger of basing conclusions upon freezing-point depressions alone (see, for example, Bruni and Gorni (3)). The freezing-point depressions for the esters dissolved in brassidic acid are smaller than the ideal solution law would indicate. This might have been interpreted as evidence of solid solution formation; the determination of the cooling curves of the system showed, however, that this did not occur.

Thus while the true freezing point cannot be obtained with these systems from cooling-curve determinations, such measurements must be carried out for fixing the type of system being investigated.

The heat of fusion of brassidic acid, calculated from the slope of the $\log_{10} N_{\text{brassidic}}$ versus $10^6/T$ curve for the system brassidic acid–erucic acid is 18.0 kg-cal. per mole, while that of erucic acid, calculated similarly from the $\log_{10} N_{\text{erucic}}$ versus $10^6/T$ curve, is 12.3 kg-cal. per mole. Mascarelli (11), by similar means (using the normal freezing-point method and formula), found 17.8 and 12.1 kg-cal. per mole, respectively. As these methods do not permit of any great accuracy, the divergence between these results is within the experimental error.

These values, when compared with that determined calorimetrically by Garner and King (5) for behenic acid, namely 18.6 kg-cal. per mole, add further support to Bruni's contention that the structures of brassidic and behenic acids must be very similar.

On the other hand, Müller and Shearer have shown (14) that the long spacings of erucic and behenic acids are practically the same, while that of brassidic acid is much greater. From this it might have been expected that the heats of crystallization of erucic and behenic acids would have been closer to each other than those of the latter and of brassidic acid, instead of what has been found from the phase-rule diagrams. This remark shows that there must be, as has often been emphasized for other compounds, a very close relation between the heat of crystallization and the melting point, and that the length of the crystal cell plays only a secondary rôle in determining the magnitude of the heat of crystallization.

SUMMARY

1. An apparatus for the accurate determination of phase-rule diagrams for mixtures of long-chain compounds has been described. It has been found that melting points rather than cooling curves must be determined with these systems.

2. The systems brassidic acid–erucic acid, brassidic acid–methyl brassidate, and brassidic acid–ethyl brassidate have been investigated. All are simple eutectic systems. The brassidic acid solubility curves in the ester systems are superimposable.

3. The ideal solution law holds in the case of brassidic acid and erucic acid, but not for the ester systems; these latter give an S-shaped curve for the $\log_{10} N$ versus $1/T$ plot, the solubility of brassidic acid in this system being always less than the ideal solubility.

4. Evidence has been obtained that all these compounds exist in the simplest possible molecules in the liquid state.

5. No evidence for the existence of a second crystalline form of any of these compounds could be obtained.

6. The solubility of gases from the atmosphere in these compounds has been emphasized.

In conclusion the authors wish to thank Prof. E. C. C. Baly, F.R.S., for facilities granted, and the Imperial Chemical Industries, Ltd., whose United Alkali Scholarship was held by one of them (A. M. M.).

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ADDITION COMPOUNDS OF PHOSPHOROUS ACID WITH CERTAIN ORGANIC COMPOUNDS[1]

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In a previous communication (5) it has been shown that orthophosphoric acid forms addition compounds with several types of organic compounds; furthermore, Kendall's (2) rule of acidity held in all systems examined. It was the purpose of the present investigation to make a comparison of phosphorous and phosphoric acids with regard to their ability to form addition compounds with organic substances and to test further the validity of Kendall's rule of acidity.

In the study of these addition compounds, two methods have been employed. The most direct method is the determination of freezing-point curves in two-component systems. This method has certain advantages in that the compound is isolated, and furthermore the composition may be determined from the phase diagram. The second method of study is described by Knox and Richards (6). This method is based on the fact that strong acids added to solutions of weak acids decrease the solubility of the latter because of common-ion effect. In certain cases, however, decrease in solubility takes place to a certain point only, after which an increase in solubility occurs. This increase in solubility is attributed to compound formation.

EXPERIMENTAL

Phosphorous acid was obtained from Eimer and Amend and purified by recrystallization. The recrystallized acid melted at 74.4°C. (corrected), which is higher than previously reported. Most of the organic compounds used in this investigation were prepared by the Eastman Kodak Co., and in only a few cases was any special purification necessary.

The method of experimentation in determining freezing points has previously been given (5).

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[1] The material of this paper was presented by Herbert L. Redfield in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at The State College of Washington.

The solubilities of several organic acids and phenol were determined in solutions of progressively greater concentrations of phosphorous acid. About 20 cc. of the solution of phosphorous acid was placed in a large test tube, together with an excess of the solute. The tube and contents were heated to 50° to 60°C. for a short time to near saturation. The tube was then placed in a thermostat at 25°C., and the contents stirred several times daily for a period of ten days to two weeks. This was found to be a sufficient length of time for attainment of equilibrium. Portions of the samples were then pipetted off and analyzed.

METHODS OF ANALYSIS

Although several methods of analysis have been employed by other investigators, the method by which the solvent acid is determined gravimetrically and the solute acid by difference from total acidity, proved satisfactory. It was found that phosphorous acid could be oxidized quantitatively with concentrated nitric acid to which a small amount of hydrochloric acid was added, after which the phosphorus was determined as magnesium pyrophosphate. Total acidity was determined by titration with standard sodium hydroxide, using phenolphthalein as indicator. The end point is reasonably sharp.

For analysis of the phenol–phosphorous acid mixture, the phenol was precipitated as tribromophenol and weighed as such. The procedure was as follows: A suitable aliquot containing from 0.08 to 0.2 g. of phenol was diluted to 25 cc. and bromine water added slowly with rapid stirring. The phosphorous acid was oxidized slowly with the excess bromine. Any tribromophenol bromide formed is changed to tribromophenol by the phosphorous acid. The former bromine compound is yellow, while the latter is white. The precipitate was transferred to a Gooch crucible, washed, and dried over phosphorus pentoxide to constant weight. This method gave results which were uniformly 2.6 per cent low; however, by carefully standardizing the procedure and applying the above correction, very satisfactory results were obtained. The phosphorous acid was determined gravimetrically.

The oxalic acid was determined directly by titration with potassium permanganate after calcium oxalate had been precipitated in a buffered acetic acid solution.

EXPERIMENTAL RESULTS

The results of the freezing-point determinations are given in table 1 and of the solubility determinations in table 2.

The compounds used were considered representative for studies of binary systems to test further the rule of acidity. Curves are shown in figure 1. No evidence of compound formation was found in any of the

TABLE 1

Freezing-point data

MOLE PER CENT H_3PO_4	FREEZING POINT
Acetic acid	
	°C.
100	73.2
92	68.3
85.9	64.0
79.8	60.0
73.7	55.2
68.5	51.0
63.7	47.4
58.4	42.7
53.8	38.7
47.4	33.4
42.8	28.4
36.9	23.2
31.2	17.7
27.4	13.5
26.0	13.5
25.6	13.2
24.8	11.0
20.0	10.0
14.3	11.7
7.8	13.6
0.0	16.4
Trichloroacetic acid	
100	73.6
92.4	69.7
85.0	67.8
80.2	66.4
75.7	65.2
70.0	64.1
66.4	63.3
61.5	61.9
56.3	60.7
53.7	60.3
50.8	59.7
48.6	58.9
43.3	57.3
38.3	55.2
33.3	53.6
26.9	50.9
22.0	49.0
18.0	50.0
14.2	51.0
8.9	52.7
0.0	57.2
Pyruvic acid	
100	72.8
85.3	63.8
81.0	60.7
75.8	57.6
70.2	54.4
65.6	51.7
60.4	48.2
Pyruvic acid—*Cont'd*	
	°C.
56.2	45.7
51.8	42.8
51.3	43.2
48.2	40.6
43.9	38.1
39.1	34.4
33.4	31.3
30.1	29.3
24.8	24. (±0.5)
20.4	19. (±1.0)
12.7	7. (±2.0)
Phenol	
100	73.6
93.0	70.0
87.8	68.0
83.5	66.7
78.1	65.0
72.8	64.1
68.4	63.0
66.8	62.7
63.5	62.0
59.8	61.1
55.6	60.3
44.6	57.5
40.7	56.7
36.9	56.2
33.4	55.4
30.4	54.2
26.9	53.8
22.4	51.1
17.9	48.9
13.5	45.9 (36.2)
7.9	37.6
0.0	40.6
Acetophenone	
100	73.1
94.0	70.0
82.8	63.8
78.0	60.1
72.2	55.3
67.4	51.0
61.7	45.0
56.9	40.3
51.9	35.2
47.2	30.2
42.8	26.3
41.2	24.9
37.8	19.3
34.6	17.5
31.7	16.1
28.6	16.3
Acetophenone—*Cont'd*	
	°C.
24.7	16.7
20.5	17.1
16.5	17.7
11.2	18.3
5.7	19.0
0.0	19.7
Piperonal	
100	73.0
91.5	68.4
87.2	66.2
81.4	63.2
77.2	60.0
73.1	56.6
69.4	53.2
64.5	49.2
58.1	42.2
54.1	38.6
53.0	37.3
51.8	36.2
46.2	32.8
40.8	32.9
37.0	30.7
34.3	31.1
29.0	32.0
23.9	32.6
18.4	33.2
13.9	33.8
8.8	34.2
0.0	35.1
Coumarin	
100	74.5
90.4	69.4
82.4	63.6
77.1	59.0
72.4	53.3
68.6	47.5
66.6	44.5
62.3	39.3
58.8	40.4
54.8	43.7
50.8	48.8
49.8	50.5
45.9	54.6
41.6	57.8
37.7	60.1
32.8	62.1
30.1	63.1
25.0	64.2
20.1	65.3
14.0	66.4
8.1	67.3
0.0	68.7

TABLE 2

Solubility data: normalities of solvent and solute when varying concentrations of solvent are saturated with the solute

SAMPLE NO.	OXALIC ACID		CITRIC ACID		SUCCINIC ACID		PHENOL	
	$C_2H_2O_4$	H_3PO_3	$C_6H_8O_7$	H_3PO_3	$C_4H_6O_4$	H_3PO_3	C_6H_5OH	H_3PO_3
	N	*N*	*N*	*N*	*N*	*N*	*N*	*N*
1	2.407		12.61		1.347		0.896	
2	1.71	8.48	11.42	6.18	0.90	9.79	0.808	9.59
3	1.51	12.78	9.13	11.64	0.69	16.61	0.881	16.02
4	1.38	15.11	8.07	15.21	0.71	18.60	0.918	17.99
5	1.21	18.38	6.15	21.02	0.75	25.55	1.060	22.95
6	1.13	20.21	5.12	25.61	1.34	34.20	1.214	26.65
7	1.00	23.39	3.70	30.77	1.51	35.97		
8	0.77	30.77	2.66	37.38				
9	0.71	36.66	2.22	41.42				
10	0.81	42.02						
11	0.84	44.73						

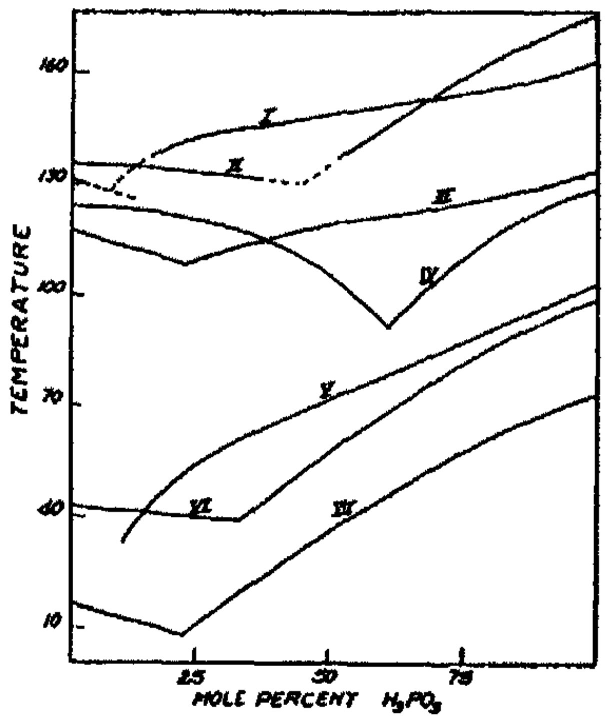

FIG. 1. Freezing points of binary systems of phosphorous acid and certain organic compounds. Curve I, phenol and phosphorous acid; subtract 90 from temperature scale. Curve II, piperonal and phosphorous acid; subtract 100 from temperature scale. Curve III, trichloroacetic acid and phosphorous acid; subtract 60 from temperature scale. Curve IV, coumarin and phosphorous acid; subtract 55 from temperature scale. Curve V, pyruvic acid and phosphorous acid; subtract 30 from temperature scale. Curve VI, acetophenone and phosphorous acid; subtract 25 from temperature scale. Curve VII, acetic acid and phosphorous acid.

above systems. Although some difficulty was encountered in determining freezing points in some of the systems, particularly in the region of the eutectic, still they are sufficiently accurate to leave little doubt as to the non-existence of a compound.

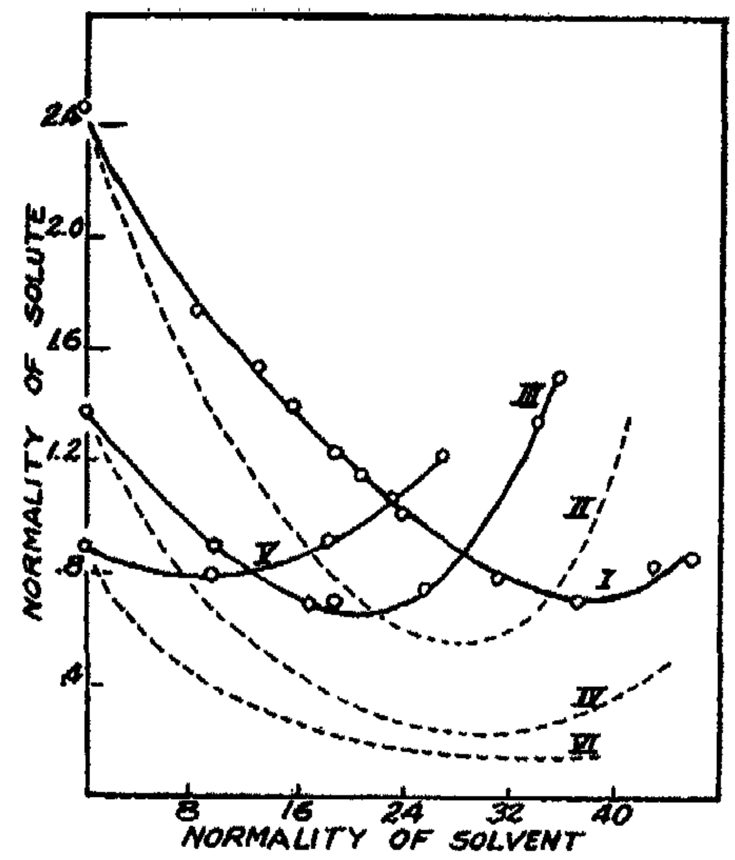

FIG. 2. Solubility curves of binary systems. Curve I, oxalic acid in phosphorous acid. Curve II, oxalic acid in phosphoric acid. Curve III, succinic acid in phosphorous acid. Curve IV, succinic acid in phosphoric acid. Curve V, phenol in phosphorous acid. Curve VI, phenol in phosphoric acid. Curves II, IV, and VI are taken from data of Kepfer and Walton (4).

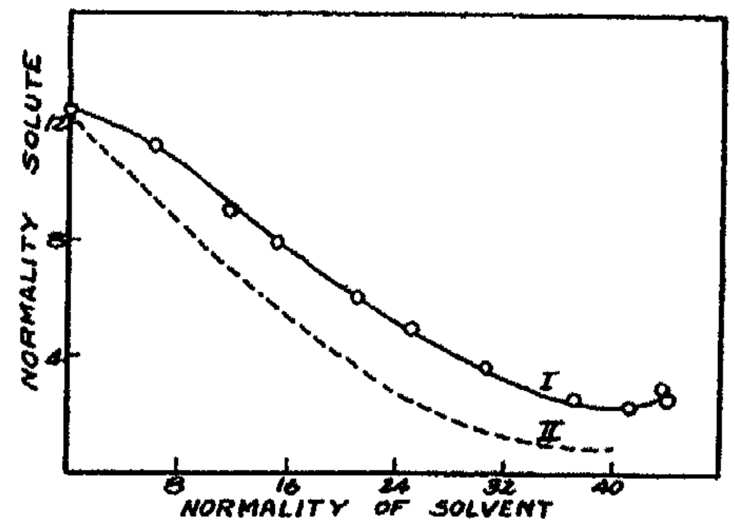

FIG. 3. Solubility curves of binary systems. Curve I, citric acid in phosphorous acid. Curve II, citric acid in phosphoric acid (taken from data of Kepfer and Walton (4)).

Curves for the various systems are shown in figures 2 and 3. For the purpose of comparison, the curves for phosphoric acid taken from data of

Kepfer and Walton (4) are shown. In all cases there appears to be definite evidence of the formation of addition compounds.

DISCUSSION

From the results of this investigation it appears that phosphorous acid forms addition compounds only in solution. Also Kendall's rule of acidity is borne out well in the solubility study, but in this case is not successful in predicting compound formation in freezing-point studies of phosphorous acid with a second component.

On the basis of Kendall's rule, phosphorous acid would be expected to form addition compounds, as it is of the same approximate strength as phosphoric acid, which yielded several compounds in a similar study of freezing-point curves. As a matter of fact, since phosphorous acid is slightly stronger, the tendency for compound formation should be slightly greater with certain organic compounds. However, Kendall's rule at best is a qualitative one and the results obtained here indicate that factors other than acidic strength, such as structure and nature of compounds involved, must play a not inconsiderate rôle in compound formation. Too, it is questionable that acid dissociation constants which have been determined in water solution should be carried over to a solvent other than water. However, Kendall's rule is well borne out in the solubility study, in which curves very similar to the ones formed in a similar solubility study with phosphoric acid are found. For purposes of comparison the curves obtained in the study with phosphoric acid are included in figures 2 and 3. The primary dissociation constants of the acids concerned in this study follow:

Acid	*K*
Oxalic acid (8)	3.8×10^{-2}
Citric acid (10)	8.0×10^{-4}
Succinic acid (9)	6.7×10^{-5}
Phenol (3)	1.08×10^{-10}
Phosphorous acid (7)	1.6 to 6.2×10^{-2}
Phosphoric acid (1)	1.1×10^{-2}

Compounds were indicated in every case. Assuming sharpness of break as indicative of relative tendency toward compound formation, phenol and succinic acid show the greatest tendency to form addition compounds with phosphorous acid, while citric and oxalic acids show a lesser tendency. This is to be expected in view of Kendall's rule, since the difference in acidic strengths between phosphorous acid and oxalic and citric acids is less than the difference between phosphorous acid and succinic acid and phenol.

When a comparison of phosphorous and phosphoric acids is made, generally speaking, phosphorous acid shows a slightly greater tendency to form addition compounds than phosphoric acid. Again this is in agreement with Kendall's rule.

It is to be noted that although phenol exhibits an unusually strong tendency toward compound formation in solution, no evidence whatever is obtained in a freezing-point study. This directly bears out the statement that phosphorous acid appears to form these addition compounds only in solution.

SUMMARY

1. The freezing-point diagrams of several binary systems in which phosphorous acid acts as one component have been determined. No compound formation was indicated.
2. The solubilities of phenol, oxalic acid, succinic acid, and citric acid have been determined in solutions of phosphorous acid of varying concentration.
3. Kendall's rule of acidity holds well in solution, but in the case of phosphorous acid fails in freezing-point equilibria.
4. A comparison of solubility curves of phosphorous and phosphoric acids has been made.
5. The melting point of phosphorous acid was recorded as 74.4°C. (corrected).

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A FURTHER STUDY OF THE EFFECT OF SUGAR ALCOHOLS AND THEIR ANHYDRIDES ON THE DISSOCIATION OF BORIC ACID

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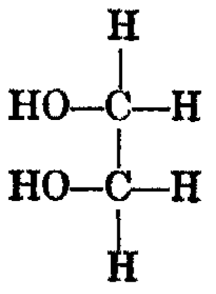
INTRODUCTION

Studies on the influence of mannitol and dulcitol and certain of their anhydrides on the dissociation of boric acid were reported in a previous communication (7). In general, the increased dissociation of boric acid produced by sugar alcohols was exhibited to a lesser degree or not at all by their anhydrides. Another series of these substances has been made available for study, and further investigations as to the effect of these compounds on the dissociation of boric acid have been instituted.

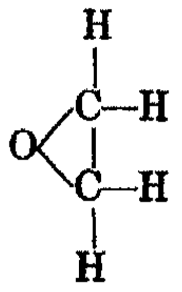
MATERIALS

The inositol, erythritol, pentaerythritol, and adonitol employed were Pfanstiehl's C.P. products and met the specifications of their catalogue. Ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, and trimethylene glycol were supplied by the Eastman Kodak Co. The dihydroxyacetone employed was Oxantin, prepared formerly by Merck and Co. The epihydrin alcohol was prepared from epibromhydrin (1). The *l*-epihydrin alcohol, distilling at 70°C. at 10 mm. pressure, was employed. The polygalitol was extracted from *polygala amara* (9). The compound melted at 138°C. (uncorrected). The erythritan was prepared from erythritol by dehydration with sulfuric acid (2, 6). Analysis gave the following composition: carbon, 45.21 per cent; hydrogen, 7.56 per cent. The calculated values are: carbon, 46.15 per cent; hydrogen, 7.69 per cent.

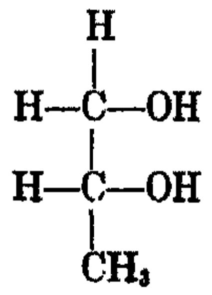
The following formulas indicate the structural relationship existing among these compounds.



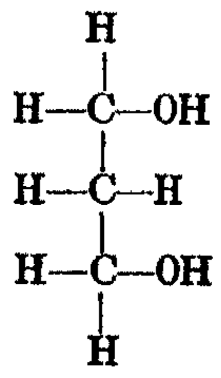
Ethylene glycol



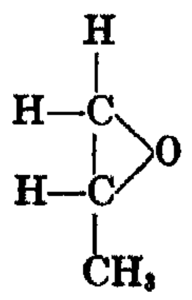
Ethylene oxide



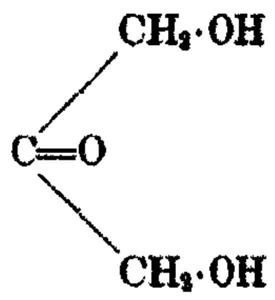
Propylene glycol



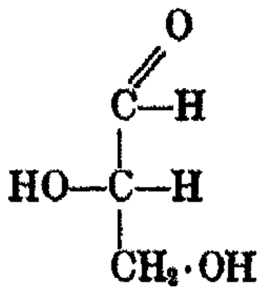
Trimethylene glycol



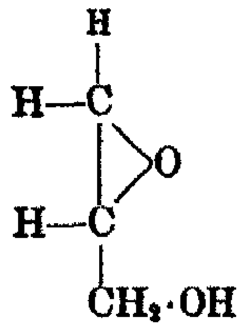
Propylene oxide



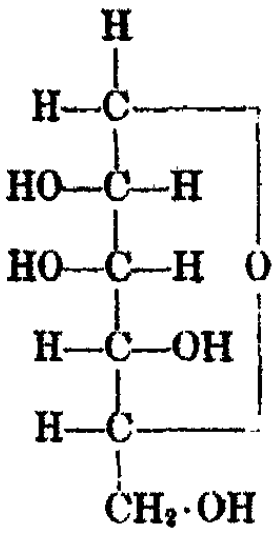
Dihydroxy-
acetone



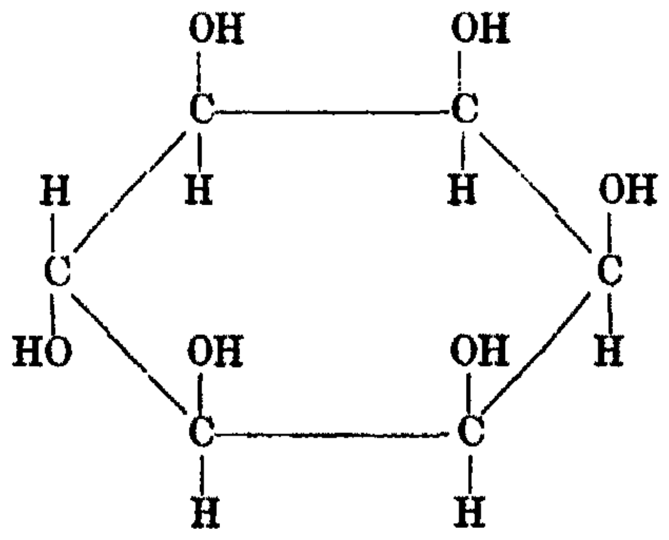
l-Glyceric
aldehyde



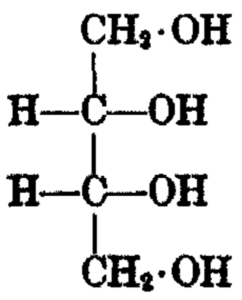
l-Epihydrin
alcohol



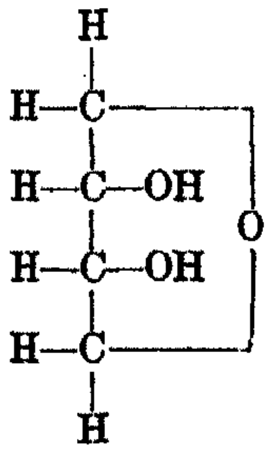
Polygalitol



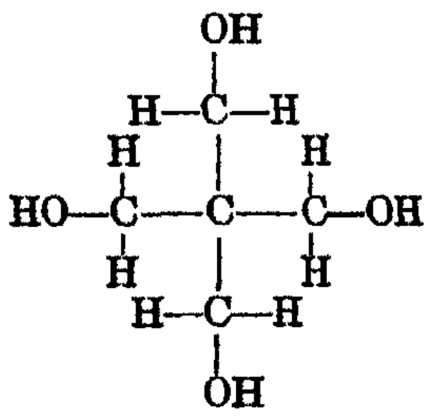
i-Inositol



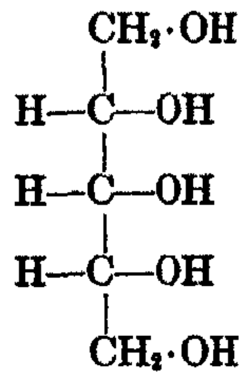
i-Erythritol



Erythritan



Pentaerythritol



i-Adonitol

METHODS

The solutions of the various compounds studied contained 4 g. of compound in 100 cc. of 0.1 molar boric acid. To 10-cc. portions was added 0.1 normal sodium hydroxide in quantities varying from 1 cc. to 12 cc. Immediately after the addition of the alkali the pH of the solution was determined electrometrically at 25°±0.5°C., using the Wilson-type electrode (11). The results are set forth in figure 1.

DISCUSSION

An examination of the graph shows that the substances studied divide themselves readily into three classes. Class 1 contains those compounds which do not affect the dissociation of boric acid. In this class, ethylene glycol, ethylene oxide, both propylene glycols, *l*-epihydrin alcohol, and propylene oxide occur. As glycerol affects the dissociation of boric acid, a summary of the results on these compounds would indicate that at least three hydroxyl groups on adjacent carbon atoms are necessary for a potentiation of the dissociation of boric acid, as neither propylene glycol nor trimethylene glycol influences it. Polygalitol, the 1,5 anhydride of mannitol, likewise does not affect the dissociation, yet mannitan, which is the 1,4 anhydride of mannitol, produced an intermediate effect be-

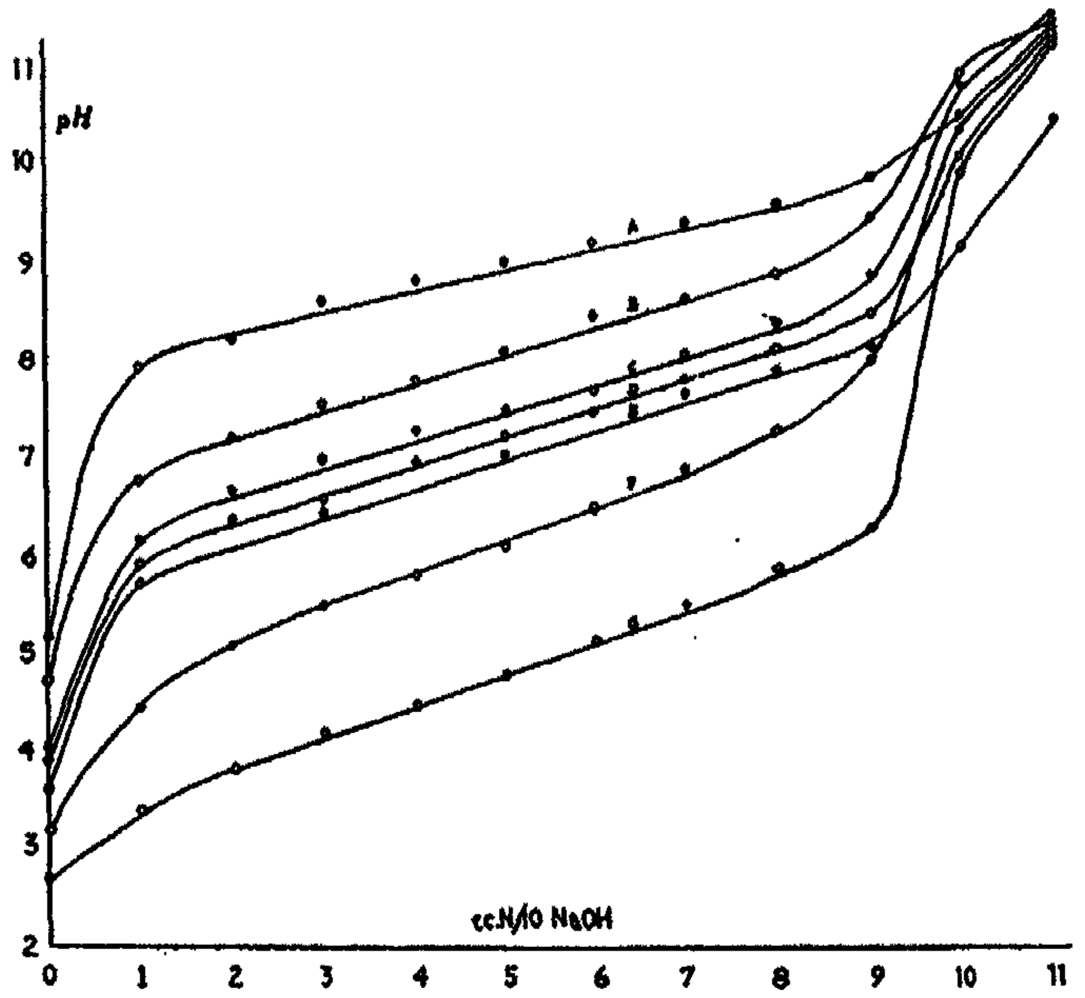


FIG. 1. The effect of sugar alcohols on the dissociation of boric acid. Curve A, *M*/10 boric acid; curve B, *M*/10 boric acid + 4 per cent glycerol; curve C, *M*/10 boric acid + 4 per cent erythritol; curve *D*, *M*/10 boric acid + 4 per cent adonitol; curve E, *M*/10 boric acid + 4 per cent dihydroxyacetone; curve F, *M*/10 boric acid + 4 per cent mannitol; curve G, *M*/10 boric acid + 4 per cent erythritan.

Class 1 substances corresponding to curve A: ethylene glycol, ethylene oxide, propylene glycol, trimethylene glycol, propylene oxide, *l*-epihydrin alcohol, polygalitol, and *i*-inositol. Class 2 substances corresponding approximately to curves C, D, and E: erythritol, pentaerythritol, adonitol, glyceric aldehyde, and dihydroxyacetone. Class 3: erythritan.

tween mannitol and polygalitol. Thus, by extending the oxide ring to include the hydroxyl group on the fourth carbon atom, the effect on boric acid is lost. Inositol, which is essentially cyclic mannitol—namely, with two hydroxyl groups in the ring—likewise falls into class 1.

The second class includes those substances which affect boric acid with approximately the same dissociation potentiation as does mannitol. This class includes erythritol, pentaerythritol, adonitol, glyceric aldehyde, and dihydroxyacetone. The first three compounds require no special comment. By virtue of their respective structures they fall into the general classification of substances studied by Böeseken (4) and recommended for study by van Liempt (10), i.e., those compounds having hydroxyl groups on the same side of adjacent carbon atoms. Dihydroxyacetone definitely differs from this class of substances, yet it strikingly potentiates the dissociation of boric acid with an effect equal to that of its isomer, glyceric aldehyde. Of special interest is the fact that the aldose and the ketose possess greater potentiation power than does the sugar alcohol, glycerol. Owing to the fact that crystalline dihydroxyacetone occurs in a dimeric form, the substance was subsequently resolved to its monomeric form by melting (3) and a second titration curve was prepared with the solution of the melted compound. The dimeric and monomeric curves were practically identical. The greater potentiation of the dissociation of boric acid exhibited by the aldose and ketose than that produced by glycerol seems to indicate that an aldehyde or a ketone group present in the molecule augments the potentiation by the hydroxyl groups. Mellon and Norris (8) have shown that the ketohexose fructose is more effective in potentiating the dissociation of boric acid than the isomeric aldohexose, glucose. In the trioses, dihydroxyacetone and glyceric aldehyde, the aldehyde and the ketone groups have equal value.

The third class contains only erythritan. Erythritan, 1,4-anhydroerythritol, with but two hydroxyl groups in the molecule and these enclosed in an oxide ring, is unique among the substances studied in this investigation. In addition it seems to be foremost among the compounds potentiating the dissociation of boric acid recorded in the literature. In a 4 per cent solution, its downward displacement of the titration curve of boric acid is greater than that of its mother substance, erythritol, with two more hydroxyl groups in the molecule, and also greater than that of the isomeric hexahydroxy sugar alcohols, mannitol, dulcitol, and sorbitol. In our previous studies (7) with the anhydrides of mannitol and dulcitol and in this work with 1,5-anhydromannitol, the removal of a molecule of water from the sugar alcohol with the formation of the oxide ring diminished greatly or obliterated its action on the dissociation constant of boric acid. In this regard erythritan is a striking exception. The results of Böeseken and his students indicate that in the sugar alcohols the increase in potentiation of the dissociation of boric acid varies with the number of hydroxyl groups in the molecule. Erythritan reverses this concept. This observation was considered so unusual that the compound was prepared by another method, namely, by the dehydration of erythritol by heating in a sealed tube (2). The compound after three distillations exhibited a pH of 6.6 in 1 per cent aqueous solution and affected the dissociation of boric acid to the same degree as did the substance prepared from erythritol by the action of concentrated sulfuric acid. The structure of the anhydride was established by Grimaux and Cloez (5) by demonstrating its relationship to furfuran.

CONCLUSIONS

1. The effect of a number of sugar alcohols, related compounds, and anhydrides of sugar alcohols upon the dissociation of boric acid has been studied.

2. In general, the anhydrides of the sugar alcohols potentiate the dissociation of boric acid to a lesser degree than do the sugar alcohols themselves. Erythritan is dissimilar in this respect, exerting an effect greater than either erythritol or mannitol.

3. Propylene glycol has no effect on the dissociation of boric acid. The introduction of a ketone or aldehyde group into the molecule with the formation of dihydroxyacetone and glyceric aldehyde, respectively, potentiates the dissociation of boric acid to a greater degree than does glycerol with three hydroxyl groups in the molecule.

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NEW BOOKS

Kolloidik. Eine Einführung in die Probleme der modernen Kolloidwissenschaft. By A. v. Buzágh. 323 pp. Leipzig: Th. Steinkopff, 1936. Price: unbound, 15 RM; bound, 16.50 RM.

The portmanteau word "Kolloidik" means colloid chemistry and colloid physics; in the language of a century ago, the natural philosophy of colloids. The author is evidently of a philosophical turn of mind, for the whole treatment of the subject is subordinated to his classification of matter according to degree of subdivision primarily and to morphology secondarily. The systematics may become a little tedious to English readers; experimental facts are mentioned strictly in their proper place according to the system of the book. Too often, facts are touched upon only incidentally in the development of the system of classification, and sometimes selection is rather oddly made; thus as functions of dispersity, under the heading "physical," are included transparency, hardness, photoelectric properties (of thin metallic films, which are apparently considered good instances of the effect of thickness on an otherwise homogeneous state of matter, an opinion which the reviewer certainly does not share), and catalysis; as "physicochemical" are mentioned some cases where the ordinary laws of solution or of electrolysis appear, at first sight, not to be obeyed by colloidal systems; and under "chemical," Smekal's theory of the mosaic structure of crystals. Later on in the book the author comes to rather closer grips with the results of experimental research; among many other things dealt with are the results of x-ray investigations into the structure of natural compounds of high molecular weight, liquid crystals, surface films, electrical double layers, the use of electron beams for studying surfaces, sedimentation volumes, theories of adsorption, peptization, swelling, coagulation, etc. But the treatment is rarely sufficiently profound or exact to give the reader a well-balanced idea of the essentials of the phenomena and of their explanation; and literature references are not sufficiently numerous or up-to-date to guide one who wants to master the original literature quickly. It may be that the author has been seriously handicapped by his desire to treat everything logically and systematically from the standpoint of dimensions and manner of aggregation. These are not the fundamental properties of matter; they are sometimes very important and dominate the phenomena, but often they are overshadowed by specific chemical properties, which indeed control them. A natural philosophy of that vast miscellany of phenomena loosely classified as colloids must not forget this; nor indeed is it generally profitable to treat experimental research as a mere handmaid to a subjective scheme of things. The book is tolerably well conceived, but it lacks thoroughness, and shows little originality.

N. K. Adam.

Reports on Progress in Physics. Published by the Physical Society. Volume II. 25 x 17 cm.; iv + 371 pages. London: The Physical Society, 1936. Price to non-Fellows: 21 s. net.

The second volume of this new venture resembles the first in being printed on excellent paper, with a dignified format and good binding, and in containing a set of reviews written by experts on the theoretical and applied sides, which provides material of the highest interest to physical chemists. The sections are (neglecting subsections): general physics (Brownian movement, surface tension, viscosity), quantum theory (including theory of valency), atomic physics, geophysical prospecting, radio-exploration of upper atmospheric ionization, sound, heat, electrical and magnetic measurements, the charge on the electron, electron tubes, x-rays (including structures of substances), spectroscopy, and optics. It will be seen that the volume resolutely avoids a narrow view of the subject and overemphasis of certain very new fields. The latter receive proper attention and their due space, but it is rather necessary to emphasize that this report does represent progress in physics rather than in a mere branch of physics, and its value to physical chemists is correspondingly enhanced. The volume is one which every physical chemist should read.

J. R. Partington.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium, Teil A, Lieferung 4. 26 x 17 cm.; pp. x + 535–682. Berlin: Verlag Chemie, 1936. Price: 18 RM.

This part of the volume on aluminum deals with the alloys of aluminum with S, Se, Te, Po, B, C, Si (pp. 536–627), P, As, Sb, Bi, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ra. The physical properties are given, with tables and curves, and the chemical properties discussed include corrosion. Literature references come to January, 1936. The volume is of particular interest from the chemical engineering point of view and the treatment is thoroughly sound.

J. R. Partington.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 55: Uran und Isotope mit einem Anhang über Transurane. 26 x 17 cm.; pp. xviii + 279. Berlin: Verlag Chemie, 1936. Price: 34.50 RM.

The volume on uranium is complete in itself and includes the chemistry of uranium and its isotopes, with a brief account of very recent experiments on the artificial production of elements of atomic number greater than 92 ("Transurane"). There is also a rather brief account of the radioactivity of uranium in which only elements in the series of atomic number 92 are considered, the relation to the actinium series being left rather vague. There is a section on salts of uranium with organic acids. The highly systematized arrangement necessary in a work of this kind has its disadvantages, since there is, for example, no account of uranium X, and uranic acid and uranates are separated, the latter (with other compounds) being included under the various metals. The volume maintains the high standard of the series.

J. R. Partington.

Stereoscopic Drawings of Crystal Structures. Edited by M. von Laue and R. von Mises; drawings by E. Rehbock-Verständig; text by G. Menzer. Part 2. 18 x 17 cm.; 56 pp. Berlin: Julius Springer, 1936. Price: in portfolio, 18 RM.

This collection of twenty-four stereoscopic drawings of crystal structures forms a continuation of the series published some years ago by the same authors. In the first volume the structures chosen were those of very simple types; here rather more complicated ones are depicted, although they are still comparatively simple, consisting of those of some of the elements which crystallize in a less regular way than most, and of compounds of two or three elements.

Even for these relatively simple structures the advantages of the stereoscopic method of representation is very considerable. One has only to try first to make out the details of a structure from the drawing without the use of the stereoscope, and then afterwards to view it stereoscopically to be at once convinced of the immense gain in clarity obtained by so doing. It is a real difficulty in work on crystal structure that the results of an analysis are not easily made clear to the chemist or mineralogist whom they might interest. The ideal method, the study of three-dimensional models, is rarely available, but sets of stereoscopic models of this kind make a very good substitute for models, and one could wish that more of them existed.

Mrs. Rehbock-Verständig has drawn the figures for this volume with much skill, and with the help of the text, which was contributed by Dr. G. Menzer and has been translated into English by Mr. Greenwood, the English and German versions being in parallel columns, it is easy to get a very good idea of the plan according to which the structures here shown are built up. Although, if necessary, this information can be obtained from the *Strukturbericht* of Ewald and Hermann, it would undoubtedly have been a convenience to the reader if references to the sources from which the structures are taken had been given in the text.

R. W. James.

Eclipses of the Sun. By S. A. Mitchell. Fourth edition, revised and enlarged. New York City: Columbia University Press. Price: $5.00.

The present, and fourth, edition of this standard treatise on eclipses differs from the previous issues chiefly in the addition of an extra chapter dealing with the recent eclipses of 1932 and 1934. It is unfortunate, in this connection, that at least a few allusions to these eclipses were retained uncorrected from the previous edition. Thus, we find that in 1935 the author still predicts what *will* happen in 1932.

This last chapter contains an excellent summary of some of the conclusions derived from crucial observations made at the occasion of these two recent eclipses, and a description of Lyot's success in obtaining spectra of the corona without an eclipse.

The remainder of the book is still essentially the same as in previous editions, and contains a description of historical eclipses and of the gradual development of and the improvement in the prediction of eclipses; furthermore, some chapters dealing with the working of the spectroscope and giving an outline of our present ideas on the structure of the atom and the theories of ionization and relativity. The remainder of the book is devoted to a detailed description of virtually all well-observed eclipses of modern times from 1842 onward. The arrangement of the chapters suggests that the author had a dual purpose in writing this book, namely, to make it appeal to both professional astronomers and the public at large. The very large amount of personal narrative included was doubtless a concession to the latter, but the reviewer feels that its omission would have made the book more acceptable to the former.

Similarly, in connection with the early historical eclipses a good deal of Egyptian history has been included and a rather invidious comparison made between the astronomical accomplishments of the early Egyptians and the Babylonians, which, in this reviewer's opinion, might well have been left out. Such comparisons represent, at best, only a consensus of opinion rather than a statement of fact, and in the present instance appear to be based chiefly upon the authority of a single egyptologist—Breasted—in a field of such great diversity of opinion.

The reviewer cannot help expressing the wish that the author, one of the foremost observers of eclipses of our times, would condense into a separate monograph all the facts and theories of interest to the professional astronomer, but without any concession to popular appeal in the form of discussions which are, after all, not very relevant from the astronomer's point of view.

W. J. Luyten.

Abridged Scientific Publications from the Kodak Research Laboratories. Volume XVI. Rochester, New York: Eastman Kodak Co., 1935.

This volume contains abbreviated reprints of thirty-four papers which were published from the Kodak Research Laboratories during the years 1933 and 1934. Fifteen of the papers are devoted to subjects more or less closely related to practical photography; six, to the description of scientific apparatus; and the remainder, to a variety of purely scientific subjects. The original papers were published in seventeen different journals, ranging in type from the *Journal of the Society of Motion Picture Engineers* to the *Transactions of the Faraday Society*. The abridged reprints are not mere abstracts, but are sufficiently complete to satisfy the general reader.

ROBERT LIVINGSTON.

Physical Aspects of Organic Chemistry. By WILLIAM A. WATERS, with an introduction by T. Martin Lowry. 14 x 21.5 cm.; xv + 501 pp. New York: D. Van Nostrand Co. Price: $9.25.

This book deals almost wholly with reactions of organic compounds and only incidentally with problems of structure. Of the seventeen chapters which make up the book, six are concerned with general considerations of the following: chemical affinity, physical theories of molecular structure, valency, electrical dipoles, chemical reactivity, and general polarity. The remaining eleven deal with applications of these considerations to the reactions of organic chemistry.

From the standpoint of physical organic chemistry as a whole this work represents no advance over treatises previously available; but it is of considerable importance as a textbook of the work of the modern English theoretical organic chemists. The author has used their point of view in interpreting the reactions of organic chemistry on an electronic basis. He has rendered a valuable service in collecting and presenting together the most comprehensive, lucid, and convincing body of this sort of material at present available in book form. Typical subjects dealt with from this point of view include: unsaturation, free radicals and their non-ionic reactions, ionization and ionic reactions, acidity, hydrolysis and esterification, molecular rearrangement, aromatic compounds. The arguments in the text are supplemented by abundant literature references. Therefore this should prove an extremely valuable addition to the libraries of those interested in the background of this fast-growing field.

ALBERTO F. THOMPSON, JR.

The Theory of Emulsions and their Technical Treatment. By WILLIAM CLAYTON. Third edition. vii + 458 pp.; 91 illustrations. London: J. & A. Churchill, Ltd. Price: 25/—.

The third edition of Dr. Clayton's well-known book will be welcomed by all interested in emulsions. It contains very much new material and is twice the size of the second edition, which appeared in 1928. The general arrangement of the book remains much the same, but every section has been greatly enlarged. New chapters include "Emulsifying Agents" (previously a short appendix), "The Preparation of Emulsions—Technical Operations," and "Emulsions in Biological Investigations." References to the recent literature are most complete and up-to-date. Much of the information is not otherwise readily available, this applying in particular to the many facts drawn from the patent literature. Considerable space is given to the new industrial emulsifying agents such as the numerous sulfonated compounds now in use.

The reviewer feels that the theoretical treatment of the subject would have gained considerably in clearness if the method of presentation had been entirely rearranged, instead of the facts being presented in an order determined by earlier editions.

Dr. Clayton is to be congratulated on producing a volume which will be invaluable to all investigators in this wide field.

C. ROBINSON.

The Nature of Physical Theory. By P. W. BRIDGMAN. Princeton: Princeton University Press, 1936.

In this book the author attempts to analyze critically the basis of physical theory in terms of possible operations (i.e., experimental observations). This operational analysis is applied not only to the several branches of modern physics, but even to such fundamental things as mathematics, logic, and human thought and language. In spite of the rather abstruse character of the subject, the presentation is remarkably clear and the style is simple and vivid.

To many theoretical physicists this book may prove stimulating and perhaps at times provocative. To that larger group who are content to follow the general trend of modern physical theory and occasionally to utilize some of its definite results, it whould be illuminating and intensely interesting. The layman should find it helpful in attempting to orient himself in a world of theory which is rapidly changing and sometimes apparently kaleidoscopic. He may also find a few weapons with which he may protect himself from the intellectual arrogance of some of the camp followers of modern physics.

The authors closing words will serve, better than any detailed description, to give the temper of this work; "logic, mathematics, physical theory, are only our inventions for formulating in compact and manageable form what we already know, and like all inventions do not achieve complete success in accomplishing what they were designed to do, much less complete success in fields beyond the scope of the original design, and—our only justification for hoping to penetrate at all into the unknown with these inventions is our past experience that sometimes we have been fortunate enough to be able to push on a short distance by acquired momentum."

ROBERT LIVINGSTON.

Differential Equations in Applied Chemistry. By FRANK LAUREN HITCHCOCK and CLARK SHOVE ROBINSON. Second edition. 120 pp. New York: John Wiley and Sons, Inc., 1936. Price: $1.50.

The second edition of this excellent little book has been improved by the addition of numerous problems and by the substitution of a treatment of Picard's method of solution of differential equations for the chapter in the first edition which dealt with the graphical evaluation of integral expressions. The six chapters are entitled: Introduction, Processes of the First Order, Processes of the Second Order, Simultaneous Processes, Equations of Flow and the Numerical Solution of Differential Equations. In Chapter V the explanation of the use of Fourier's series has been made much more detailed. This book can be recommended highly to chemists and chemical engineers.

F. H. MACDOUGALL.

Fundamental Experiments in Chemistry. A Handbook for Teachers and Students. By E. D. GODDARD. 19 x 12 cm.; xii + 147 pp. London and Boston: Ginn and Co., Ltd., no date. Price: 3s. 6d. net.

Although this book is primarily intended for chemistry teachers in schools and admirably fulfils its purpose in this field, it is noteworthy for the very detailed instructions it gives for assembling and performing some of the fundamental experiments relating to the composition of gases (water, hydrogen chloride, ammonia, carbon dioxide, carbon monoxide, nitrous and nitric oxides, and ozone) usually shown in lecture demonstrations, so that it would be a very useful book to have in the preparation room of a college chemistry department. In many cases such experiments fail for want of attention to some minor point, and Mr. Goddard's book will usually disclose this point. The details of apparatus are given, and the book may be strongly recommended. Teaching hints will be found useful in schools.

J. R. Partington.

Kurzgeschichte der Chemie. By F. Ferchl and A. Süssenguth. 26 x 19 cm.; 230 pp.; 200 illustrations. Mittenwald (Bavaria): A. Nemayer, 1936. Price: unbound, 12 RM.; bound, 15 RM. (less 25 per cent).

This book is a noteworthy supplement to all existing histories of chemistry in that it is mostly illustrative material. There is a satisfactory amount of text, and this takes account of recent studies in the subject, some of which have considerably modified older ideas. The illustrations are reproductions from actual manuscripts, old books, etc., and are very attractively printed on art paper with explanatory legends. The reviewer found the book absorbingly interesting, and he is sure that his colleagues will like to share his pleasure. There are many portraits of famous chemists, some unusual and some (e.g., of Libavius) rarely seen, and some illustrations of old laboratory interiors. One of the authors is Director of the Chemical Section of the Deutsches Museum, Munich, and has had unusual facilities for collecting material.

J. R. Partington.

Tables of Physical and Chemical Constants and some Mathematical Functions. By G. W. C. Kaye and T. H. Laby. Eighth edition. 25 x 16 cm.; 162 pp. London: Longmans, Green and Co., 1936. Price: 14 s. net.

Kaye and Laby's is the best known short book of tables. The fact that it has reached eight editions since its first publication in 1911 is proof that it fills a need. It is one which the individual worker can afford and find space for in his laboratory, the larger volumes of tables finding a place in the library. The revision has been successfully extended to several parts, but there are still some old values which there is no point in retaining. Hartmann's values for the ratios of specific heats of gases (p. 61) are worthless and might have been replaced; the book by Partington and Shilling is now available for reference here. Only very old values for the dielectric constants of gases are given on p. 88; some of the historical data on p. 1 is incorrect; the English silver coin has long ceased to have the composition attributed to it on p. 22; and the melting point of chlorine dioxide on p. 120 appears to be copied from the Landolt-Börnstein *Tabellen* and, as it is really in Fahrenheit degrees, is incorrect as it stands. These are examples of what the editors and their helpers should not have missed in their eighth edition. In future editions—which should be thoroughly overhauled—it would be better to send each section to specialists for comment. It could then become a really valuable book. As it is, no worker can safely rely on any figure unless he has also looked up the recent literature.

J. R. Partington.

Recent Advances in Organic Chemistry. Volume II. By A. W. Stewart, with four new chapters by H. Graham. 22 x 14 cm.; xiv + 489 pp. London: Longmans, Green and Co., 1936. Price: 21 s.

This is in the main a re-issue of the 1931 edition, but the four chapters by Dr. Graham are new and deal with such interesting and important topics as the bile acids and sterols, the cardiac aglucones, hormones, and vitamins. These chapters give the reader an excellent idea of the subjects mentioned, and constitute a valuable addition to the book. They bring the subjects as nearly up-to-date as could reasonably be expected.

With regard to the rest of the volume, this is, as ever, stimulating. It must surely induce enthusiasm in at any rate a few of those who come relatively fresh to the subject. It is a pity that the author appears to favor the views of certain schools to the exclusion of those of others whose contributions are quite as outstanding. For example, in the chapter entitled "Some Applications of Electronics," one finds no mention of either Ingold or Sidgwick, and Robinson is named only once. This same chapter gives the reader the idea (p. 373) that our knowledge of activation within aromatic systems has not advanced appreciably in the last thirty years. The chapter called "Some Unsolved Problems" deals with some slight questions to the exclusion of others of much greater profundity: the Wagner–Meerwein theory is not mentioned in that section which refers to the problem of the pinacol–pinacolin and similar changes, and a stereochemically improbable formula for diacetylacetone is given credence.

In the chapter dealing with "The Diphenyl Problem," the reader must remember that the "Recent Advances" are those before 1931. This particular problem is presented in a straightforward manner, although more could have been achieved in the space actually taken.

E. E. TURNER.

Physical Chemistry. By FRANK H. MACDOUGALL. 15 x 22 cm.; ix + 721 pp.; 97 figs. New York: The Macmillan Co., 1936. Price: $4.00.

If one were to judge this book only by an examination of the table of contents and by a brief perusal of its pages, he might be led to believe that it is only the Macmillan Company's competing book in a field which seems already well-supplied with text books. With a more thorough examination of its contents and of the author's style of presentation, it becomes apparent that Professor MacDougall has accomplished something very worth while in the teaching of physical chemistry.

The arrangement of the material is quite orthodox except that a short chapter (Chapter II) appears early on energy and the first law of thermodynamics, as does his consideration of the structure of atoms (Chapters VI and VII). As the author says in his preface, "*it is generally recognized nowadays that an adequate introduction to the science of physical chemistry must offer the student the opportunity of becoming acquainted with the elements of thermodynamics and with the more important thermodynamic relations.*" This opportunity is given in this book in a most thorough and rigorous way. To one who has not offered such material in a course in elementary physical chemistry it may seem to present too much difficulty for the average student, yet the treatment is so detailed and straightforward that this difficulty has been reduced to its minimum.

The author makes a point of his treatment of electromotive forces and potential differences, and his treatment of this subject is again characterized by both rigor and clarity of thought and expression.

Beginning with Boltzmann's theorem and Poisson's equation he gives a derivation of the Debye equation for the activity coefficient of strong electrolytes. This the author admits is beyond the beginning student in physical chemistry, but he includes it in the hope that it may be useful in later reference. There is so much material in its seven hundred-odd pages that some omissions would in any event be made. On the whole the text seems to be an excellent one, and there is every reason to believe that it will be enthusiastically received.

T. R. HOGNESS.

Elementary Principles in Physical Chemistry. By T. J. Webb. 16 x 23 cm.; x + 344 pp.; 25 figs. New York: D. Appleton Century Co., 1936. Price: $4.00.

In the preface the author states that this book was written for junior and senior students who have had preliminary training in the descriptive phases of chemistry, in general physics, and in the calculus. It takes no more than a general perusal of the contents to realize that he has written for the superior student who is to specialize in some field of chemistry.

The book differs from most texts in this field in that it is somewhat more advanced. Some of the theorems which are usually mentioned in an already developed form are developed in considerable detail, such as the Debye-Hückel limiting law of strong electrolytes, which includes a development of Poisson's equation, the Schroedinger equation, reaction velocities from the configuration-potential energy standpoint of Eyring, the quantum theory of the rotator and oscillator, and many theorems in thermodynamics. Most students taking an elementary course in physical chemistry are not sufficiently prepared for some of these considerations.

"The content of the book revolves about the two fundamental problems of theoretical chemistry, viz., the state of equilibrium in a chemical reaction and the rate at which the state of equilibrium is attained." Consequently, very little consideration is given to the physical properties of the liquid and solid state. For example, there is no discussion of the subjects of surface tension and dielectric constants. The book is replete with formulae and derivations and contains a relatively small amount of factual and descriptive material.

This should be an excellent text for the more advanced student in physical chemistry. If the student's only contact with physical chemistry is to be in a course in which this book is used as a text, a good deal of supplementary work on the part of the instructor will be necessary. However, during some time in his training the student in physical chemistry should become acquainted with those subjects the treatment of which distinguishes this book from those which have already appeared.

T. R. Hogness.

AN ELECTRONIC ANALYSIS OF SOME SURFACES BY MEANS OF SLOW ELECTRONS[1]

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INTRODUCTION

Much of our knowledge of matter is that of its surface. It is fortunate that we have such information concerning surfaces, for many different types of physical and chemical phenomena are quite dependent upon the nature of the surface. For example, the absorption and emission of heat and light, thermionic emission, secondary electron and photoelectron emission, contact potentials, surface tension, rate of a chemical reaction, catalysis, adsorption, friction and so forth are dependent upon the condition of one or more surfaces. A surface may be thought of as consisting of atoms or molecules distributed at random, or in some orderly fashion. The interaction of waves with a regularly arranged network of matter produces reflected waves, which combine in such a way that, from their space intensity distribution recorded at a distance from the network, some dimensions of the network may be calculated. Electron waves are now a reality and have become a useful tool in studying atomic and molecular networks found at and near the surface.

Since the discovery of the wave characteristics of electron beams by Davisson and Germer (2) many workers have used electron waves to investigate films and surfaces of crystalline solids. Some organic liquids have been studied (1, 3).

Slow electron waves have the least penetrating power of any radiation which exhibits a wave nature, therefore they are quite sensitive to surface layers. Low velocity electrons probably never penetrate more than ten atom layers. The major part of the diffraction of the electron wave by metals occurs in the first two layers.[2] Slow electrons are quite suitable for the study of surfaces which consist of only a few molecular layers.

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[1] Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

[2] "A known number of atom layers of one metal were deposited on the surface of a single crystal of another metal by evaporation in high vacuum. Direct results on depth of penetration were obtained from measurements on electron diffraction as a function of the thickness of the surface layer. A silver film deposited on a copper crystal is amorphous. A layer one atom deep reduces the maxima of the beams from

THEORETICAL DISCUSSION

An electron beam incident on a surface makes an angle θ with the surface. In order to measure distances normal to the surface by means of diffracting electron waves, the condition that the angle of incidence equal the angle of reflection must be satisfied, and this may be met by having the collector receive only those electrons reflected at an angle equal to the angle of incidence. If the surface is composed of atoms lying in planes spaced at a distance d, measured normal to the surface, and the Bragg condition

$$\mathrm{n}\lambda = 2d \sin \theta \qquad (1)$$

is satisfied, electron waves reinforce each other and a maximum collector current results. Here λ is the wave length of the electron wave as given by the de Broglie relation

$$\lambda = h/mv \text{ centimeters} \qquad (2)$$

where h is Plank's constant, m is the mass of the electron, and v is the velocity of the electron. In turn, v is given by

$$v = (2Ve/m)^{1/2} \qquad (3)$$

where V is the accelerating potential in absolute E.S.U., and e is the charge on the electron in absolute E.S.U. Substitution of this in equation 2 gives

$$\lambda = \frac{12.214 \times 10^{-8} \text{ cm.}}{(P)^{1/2}} \qquad (4)$$

where P is the accelerating potential measured in practical volts. Substitution of equation 4 in equation 1 gives

$$P^{1/2} \sin \theta = 6.107 \times n/d \qquad (5)$$

which is the condition that is satisfied for maximum collector current. This relation assumes no inner potential.

For a given surface having zero inner potential the condition for maximum collector current is $P^{1/2} = \text{constant} \times n$. If two maxima are chosen with quite a few others existing between, ordering of the maximum may be readily accomplished. For

$$P_1^{1/2}/P_2^{1/2} = n_1/n_2$$

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the copper lattice by at least seventy per cent for energies up to 300 electron volts. A number of foreign silver atoms equal to a few hundredths of that contained in one atomic layer can be detected by this method. A silver film deposited on a gold crystal is crystalline. The surface atomic layer of silver contributes at least ninety per cent. This predominating effect of surface atomic layers for primary energies as high as 300 electron volts is not in accord with the theoretical predictions of v. Laue." (Farnsworth, H. E.: Phys. Rev. 47, 331A (1935).)

where P_1 is the voltage where maximum of the order n_1 occurs, and P_2 is the voltage for maximum n_2. Now $n_2 = n_1 + a$, where a is the number of maxima existing in going from n_1 to n_2. Substitution for n_2 and rearranging gives

$$n_1 = a\frac{P_1^{\frac{1}{2}}}{P_2^{\frac{1}{2}} - P_1^{\frac{1}{2}}} \tag{6}$$

from which the order n_1 may be found.

The more general cases of diffraction of electrons must take into account the so-called inner potential, ϕ. The velocity of the electron wave within the lattice will be different from the velocity of the electron wave just outside the lattice, if the inner potential is different from zero. The ratio of these velocities, or in other words the index of refraction, μ, is given by

$$\mu = \left(1 + \frac{\phi}{P}\right)^{\frac{1}{2}} \tag{7}$$

and the maxima should obey

$$P^{\frac{1}{2}} \sin \theta = 6.107\,\frac{n}{d}\left(1 - \frac{4d^2\phi}{150n^2}\right)^{\frac{1}{2}} \tag{8}$$

APPARATUS

An electron diffraction apparatus (figure 1) was constructed which has the following features: (1) The specimen holder remains in a fixed plane. (2) The specimen holder may be quickly removed, and replaced when changing specimens. (3) The collector and electron gun can be simultaneously rotated in such a way as to satisfy the condition that the angle of incidence equal the angle of reflection. (4) The filament of the electron gun may be renewed through a side tube. (5) The entire apparatus is constructed of brass to avoid contact potentials.

The electron beam is produced by means of an electron gun (G), and is collimated by means of three thin circular apertures (S_1, S_2, S_3) 0.55 mm. in diameter. The entire slit system is mounted upon arm A_1, and may be adjusted by the two screws (V) for alignment. The collar (W) holds the filament system in the correct position, and may be removed when spot-welding a renewal filament, which consists of three turns of 0.005-in. tungsten wire forming a spiral 1 mm. in diameter. It is spot-welded onto two 0.040-in. nickel wire leads. The axis of the spiral is coaxial with the slit system. The filament spiral is 1 mm. from the first aperture (S_1). The nickel leads are supported by means of a lavite insulator. A copper strip $\frac{5}{8}$ in. long, $\frac{1}{16}$ in. wide, and $\frac{1}{32}$ in. thick, bent in the middle to form a split connector, is silver-soldered to each end of the nickel wire leads, and these connectors are held by means of two lavite blocks, the upper one of which has a brass screw (L) attached to it which passes through the hexagonal nut held by means of a shoulder in the brass case. Pressure is applied on the copper contacts when the nut is turned in a counter-clockwise direction, so that the two brass tips may be clamped in the copper connectors. These brass tips are mounted in a lavite block, which is supported on the shield K, which has a bearing in the center of the shaft connected to the electron gun arm and carries two flexible copper conductors, which consist of seventy-two strands of 0.005-in. wire, insulated from the shield by means of glass beads. The upper conductors are silver-soldered to the brass tips. The shield has a small rack attached to it

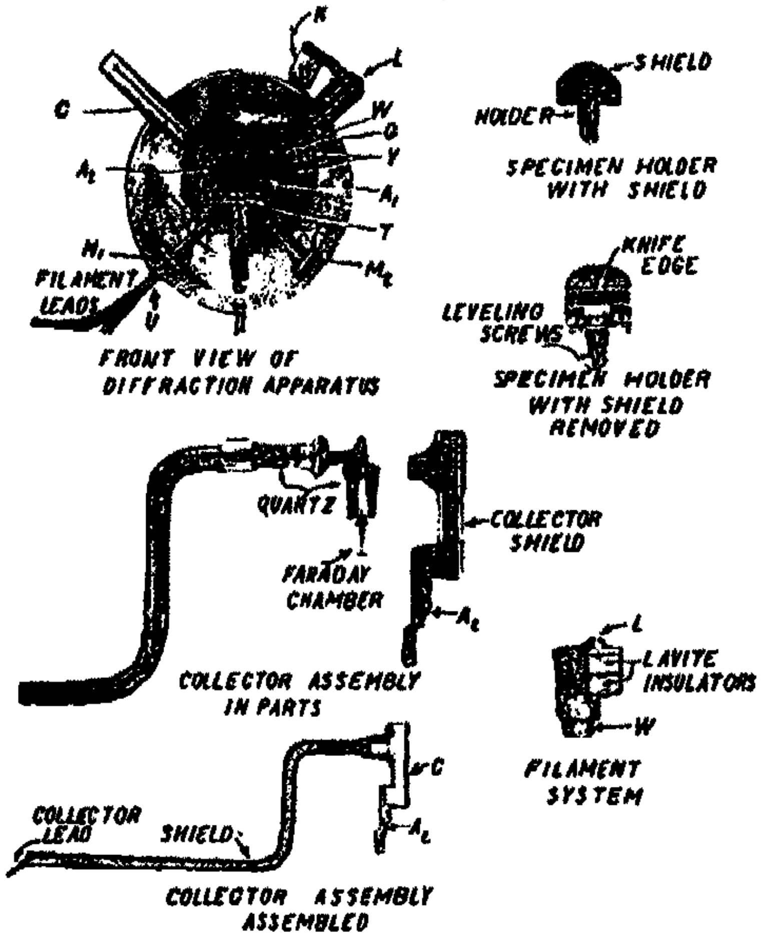

FIG. 1. Electron diffraction apparatus

which enables the brass tips to be slipped from between the copper connectors by means of a tool containing a small pinion gear, which centers on the brass nut. The filament assembly can be removed through a side tube when the brass tips are in this position. A small spring catch either holds the brass tips in between the connectors, or holds them away. The copper tubes (U) shield the filament leads up to the point at which they leave the glass enclosure. Shielding outside the enclosure is effected by means of a braided copper sheath.

The collector (C) consisted of a small Faraday chamber held in place by a quartz insulator behind the 0.55-mm. aperture, which is mounted on the arm (A_2). The lead to the collector is brought through a quartz tube (6 mm. outside diameter, 3 mm. inside diameter), and it is bent so that the electrometer lead leaves the quartz insulator coaxial with the mechanism used to rotate the collector and gun. A braided copper shield over the quartz serves for electrostatic shielding for the electrometer lead within the glass enclosure.

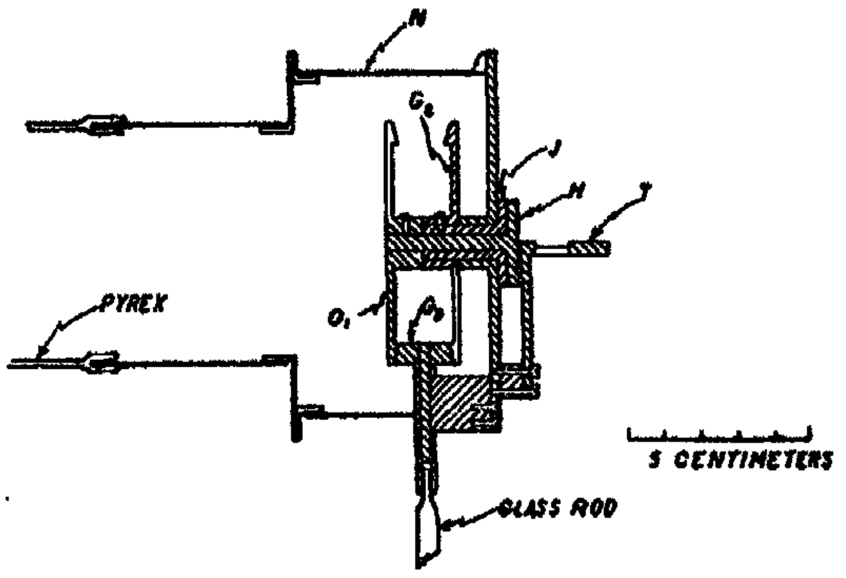

Fig. 2. Gearing mechanism

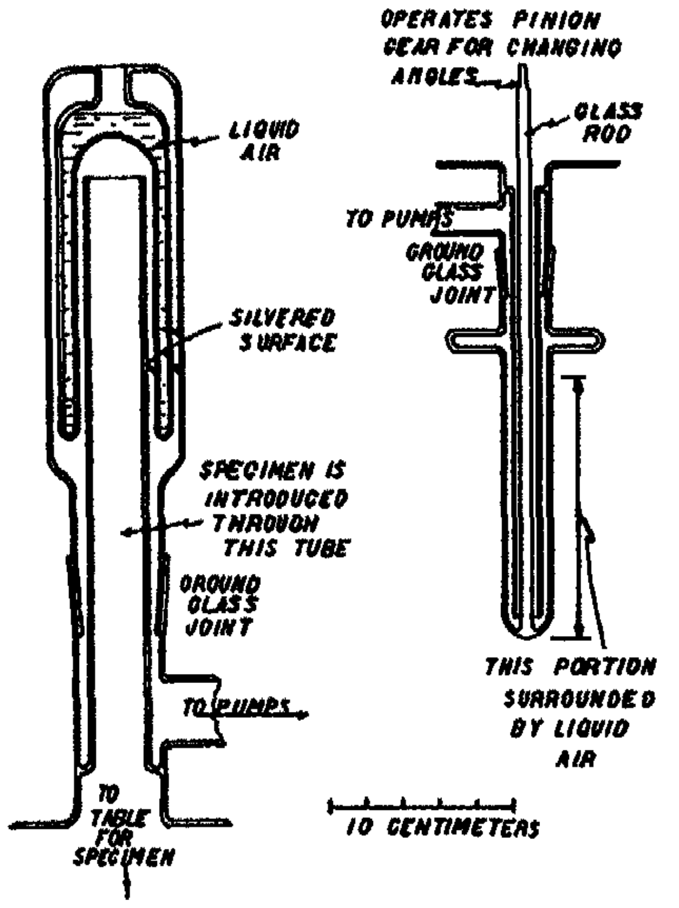

Fig. 3. Grease traps

The arm of the electron gun is fastened rigidly to the shaft H (figure 2), which is, in turn, fastened rigidly to the gear G. The collector arm is fastened rigidly to the shaft J, which is fastened to the gear G_2 by means of three set screws. Motion in opposite directions is imparted to the gears G_1, G_2 by the small gear G_3. The three set screws on the large gear (G_1) allow adjustment of the collector, so that the angle of incidence equals the angle of reflection. The angles are read from the scale engraved on the base plate by the two indexes (M_1, M_2) connected to the electron gun and collector, respectively. The base plate is mounted on the large copper tube N, which is mounted on a smaller copper tube (2½ in. in diameter) by a slotted flange. The other end of the smaller tube is sealed directly to the Pyrex glass.

The table T, mounted on the base plate, is adjustable for alignment. It has a milled channel to receive the specimen holder. The specimen is mounted on a circular table in the specimen holder. This table is held against three leveling screws by a tungsten spring.

A shield constructed of two semicircular pieces could be mounted upon the specimen holder to shield the electron beam from any electric field which might be created by charges accumulating on the glass wall of the enclosure approximately 76 mm. from the specimen. A 10° wedge placed between the two semicircular pieces with its knife edge 0.5 mm. from the specimen could be used to separate the incident electron beam from the diffracted beam.

It was necessary to use ground glass joints lubricated with stopcock grease on the control for changing the angle and on the tube through which the specimen is introduced into the apparatus. It is equally necessary to keep the stopcock grease from the surface of the specimen. Figure 3 illustrates the method used to prevent stopcock grease from entering the apparatus proper.

THE ELECTRICAL CIRCUIT (FIGURE 4)

The filament of the electron gun is heated by the battery (B_f, figure 4) and the filament heating is controlled by rheostat R_1, which gives a coarse adjustment, and by rheostat R_2, which gives a fine adjustment. The accelerating voltage is supplied from a 1000-volt lead storage battery (B_{A1}) in steps of 100 volts. Intermediate accelerating voltages are obtained by means of the potentiometer R_4 and the 50-volt auxiliary battery (B_{A2}). The accelerating voltage is measured by the potentiometer P and the volt-box R_3 through switches Q_2 and Q_3.

The collector current is measured with the Dershem electrometer (E). The electrometer leak (R_L) of 2.56×10^{11} ohms was not used in all of the experiments. The electrometer sensitivity control employed the following resistances: $R_5 = 80{,}000$ ohms; $R_6 = 2{,}000$ ohms; $R_7 = 80{,}000$ ohms; and R_8, which consisted of two variable resistances of 50,000 ohms and 1,000 ohms connected in series. The electrometer sensitivity was checked throughout an experiment by the potentiometer P, through the grounding key Q_1 and the switches Q_3 and Q_4.

In some of the experiments a constant retarding potential was applied to the collector by introducing a battery between points a and b. In later experiments apertures S_4 and S_6, 1 mm. in diameter, were added to the collector, and S_6 was enlarged to 1 mm. in diameter. The retarding potential was then applied between the aperture S_4 and S_5 and was equal to the accelerating potential minus the potential from battery B_R. If vacuum conditions were poor, positive ions would form around S_6, completely shielding it from the electron beam, and in order to stop electrons from entering the collector, it was necessary to make S_5 several volts (35 volts in some cases) more negative than the electron gun filament.

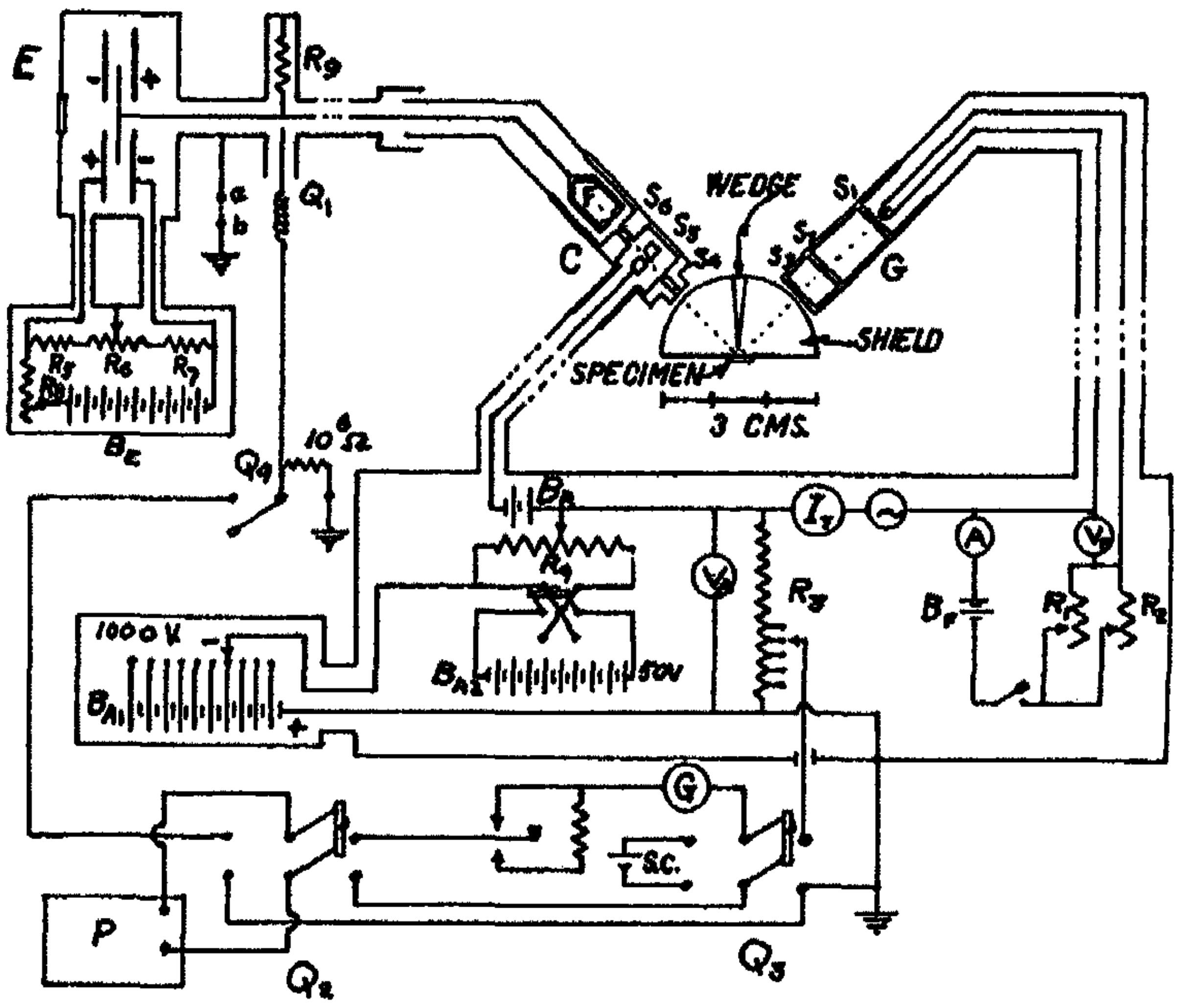

Fig. 4. Electrical circuit

All parts of the diffraction apparatus, with the exception of the electron gun filament, aperture S_5, and the Faraday chamber, were at ground potential.

MEASUREMENTS

Diffraction of electrons from oleic acid

Some of Kahlbaum's technical oleic acid, which had been further purified by evaporation in a vacuum at an extremely slow rate, was first investigated. The drift-rate method[3] was used to measure the collector current. The filament heating current was kept constant, and the thermionic emission was read for each accelerating voltage. The electron beam was interrupted between measurements.

Experiment with a fixed angle of 7°30′. The values of i_o/i_t (collector current/thermionic current) in arbitrary units are plotted as the ordinate, and values of $P_a^{\frac{1}{2}}$ (square root of accelerating voltage) in units of (practical volts)$^{\frac{1}{2}}$ are plotted as the abscissa in figure 5. Data for the curve follows a sequence in voltage from *A* to *B*, then *C* to *D*, and then *E* to *F*. The data form a smooth curve from *A* to *B*. Curves *CD* and *EF* are displaced, owing to the large jumps in voltage from *BC* and *D* to *E*. It is noted that the change in intensity (i_o/i_t) is greater for the jump *B* to *C* than for the jump *D* to *E*. Many workers[4] in electron diffraction have found reduction in intensity with continued bombardment with electrons, and have classified it as a "fatigue effect," possibly due to a growing surface charge. The effect above, however, is found when a large change in voltage is made, and might be classed as a fatigue effect in view of the fact that, if a period of half an hour is allowed to elapse, the erratic points return to normal values.

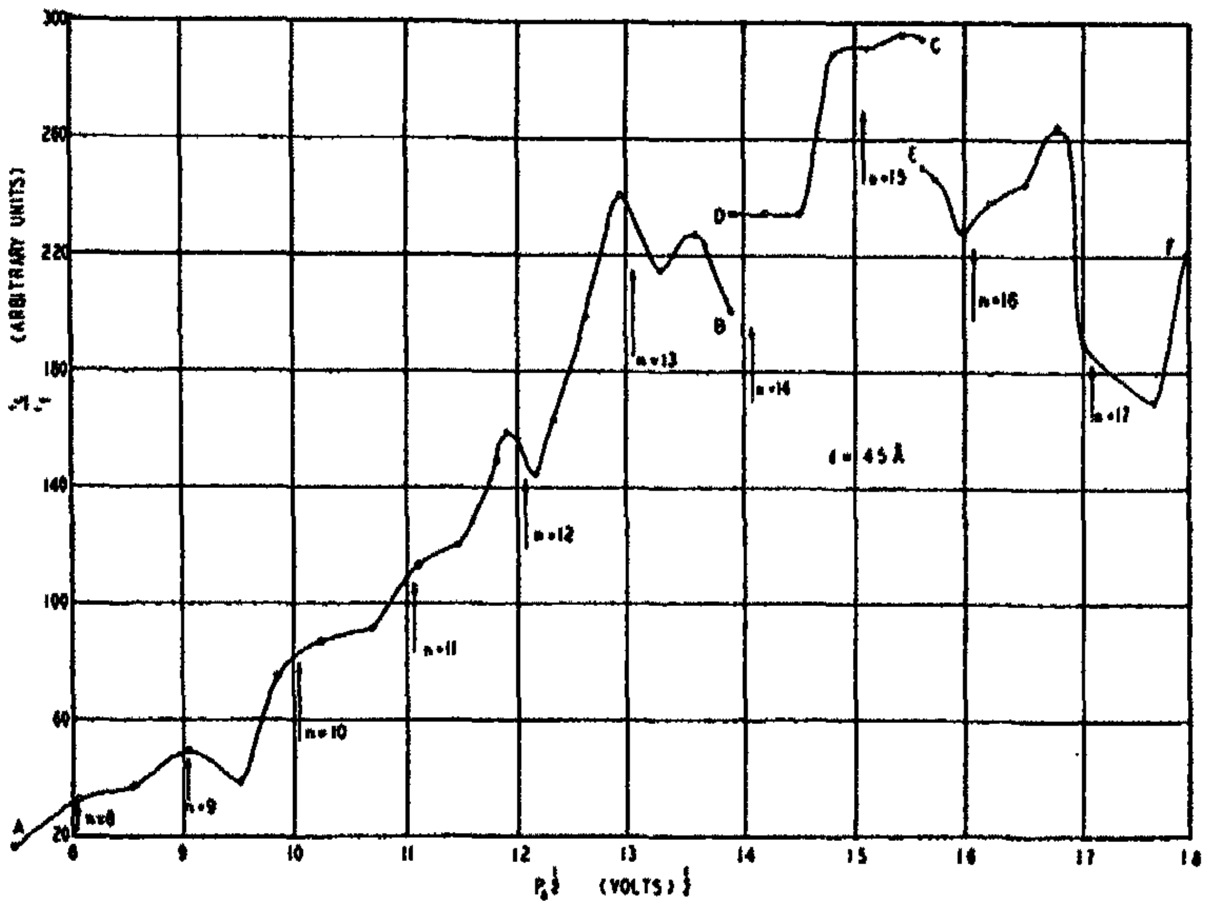

Fig. 5. Diffraction of electrons from oleic acid. $\theta = 7°30'$

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[3] The time required for drifting between two fixed points 20 mm. apart on the electrometer scale was measured. The current is inversely proportional to this time. The electrometer sensitivity was 500 mm. per volt.

[4] G. P. Thomson, Emslie, Rupp, Dames, and others.

In ordering the maxima it was assumed that the maxima in the curve from A to B belonged to the same spacing distance, and that the inner potential was zero. A maximum exists at $P^{\frac{1}{2}}_1 = 8.03$ volts$^{\frac{1}{2}}$, and another at $P^{\frac{1}{2}}_2 = 13.1$ volts$^{\frac{1}{2}}$. There are five maxima ($a = 5$) in going from n_1 to n_2. Substitution in equation 6 gives $n_1 =$ approximately 8, as n must be a whole number. Substitution of these orders in the Bragg equation gives

$$d = 44.9 \text{ A.U.}$$

Table 1 gives the various values of $P^{\frac{1}{2}}$ as calculated for $d = 44.9$ A.U. and the observed values of $P^{\frac{1}{2}}$.

The arrows in figure 5 indicate the positions of the calculated maxima. The calculated positions for the fourteenth and sixteenth orders are misfits.

TABLE 1

Calculated and observed values of $P^{\frac{1}{2}}$

ORDER	$P^{\frac{1}{2}}$ (CALCULATED)	$P^{\frac{1}{2}}$ (OBSERVED)
8	8.03	8.03 ± 0.05
9	9.04	9.05
10	10.04	10.05
11	11.05	11.05
12	12.05	11.95
13	13.06	12.95
14	14.07	13.6
15	15.08	Insufficient data
16	16.08	16.0 (minima)
17	17.09	16.8
18	18.09	Insufficient data

Experiments with a fixed angle of 30°. These data exhibit three rather broad maxima (figure 6). The best fit for these maxima corresponds to a spacing distance of 3.2 A.U. for the second, third, and fourth orders. This distance is considerably less than the 4.8 A.U. for oleic acid, which was found by Sogani (5) by diffraction of x-rays. However, Sogani's values are, for the most part, large. There are several minor peaks on the broad ones, which are outside of the experimental error. These might be assigned to the very large spacing found in the previous experiment. For a spacing of 45 A.U., $\Delta P^{\frac{1}{2}}$ should have a value of 0.271 volts$^{\frac{1}{2}}$. On examining the curve, several peaks are found which might belong to this spacing. However, for $P^{\frac{1}{2}}_a = 10$, the order is 43 and the intensity of these peaks is expected to be extremely weak.

The values on the curve were taken in the following order: from a to b; then the single point c; then d to e. Point c is far below the curve. The curve d to e was affected very little, if any, by the jump to point c, as only a single reading was taken there and it required a bombarding time of sixty-five seconds. This would seem to indicate that the charging up of the surface (if that is the case) requires a greater time than one minute.

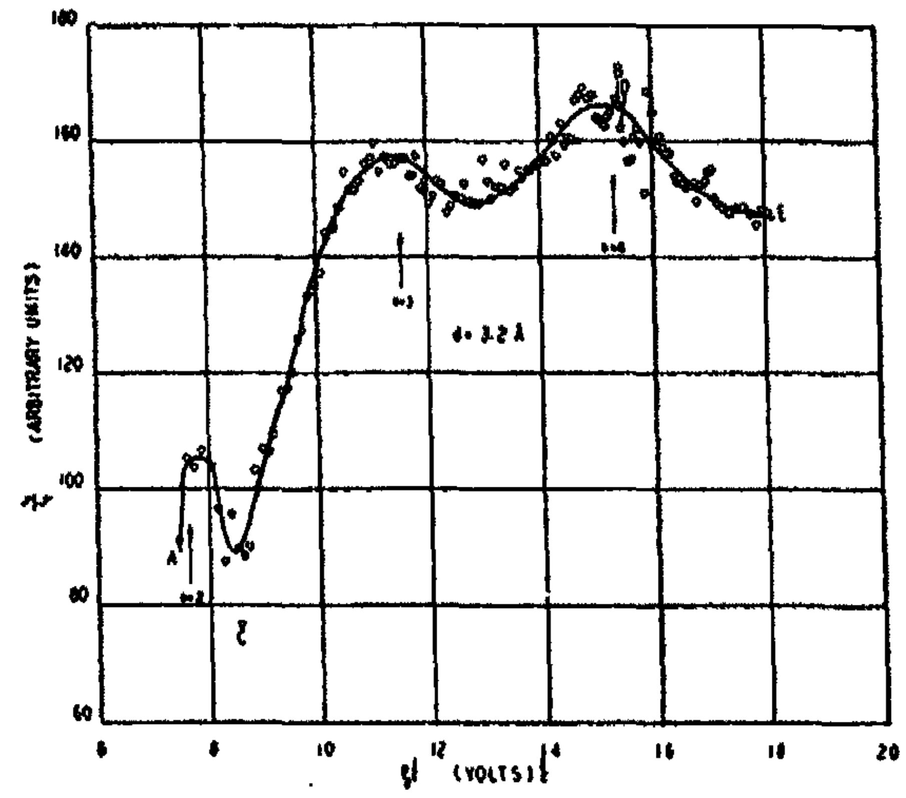

FIG. 6. Diffraction of electrons from oleic acid. $\theta = 30°$

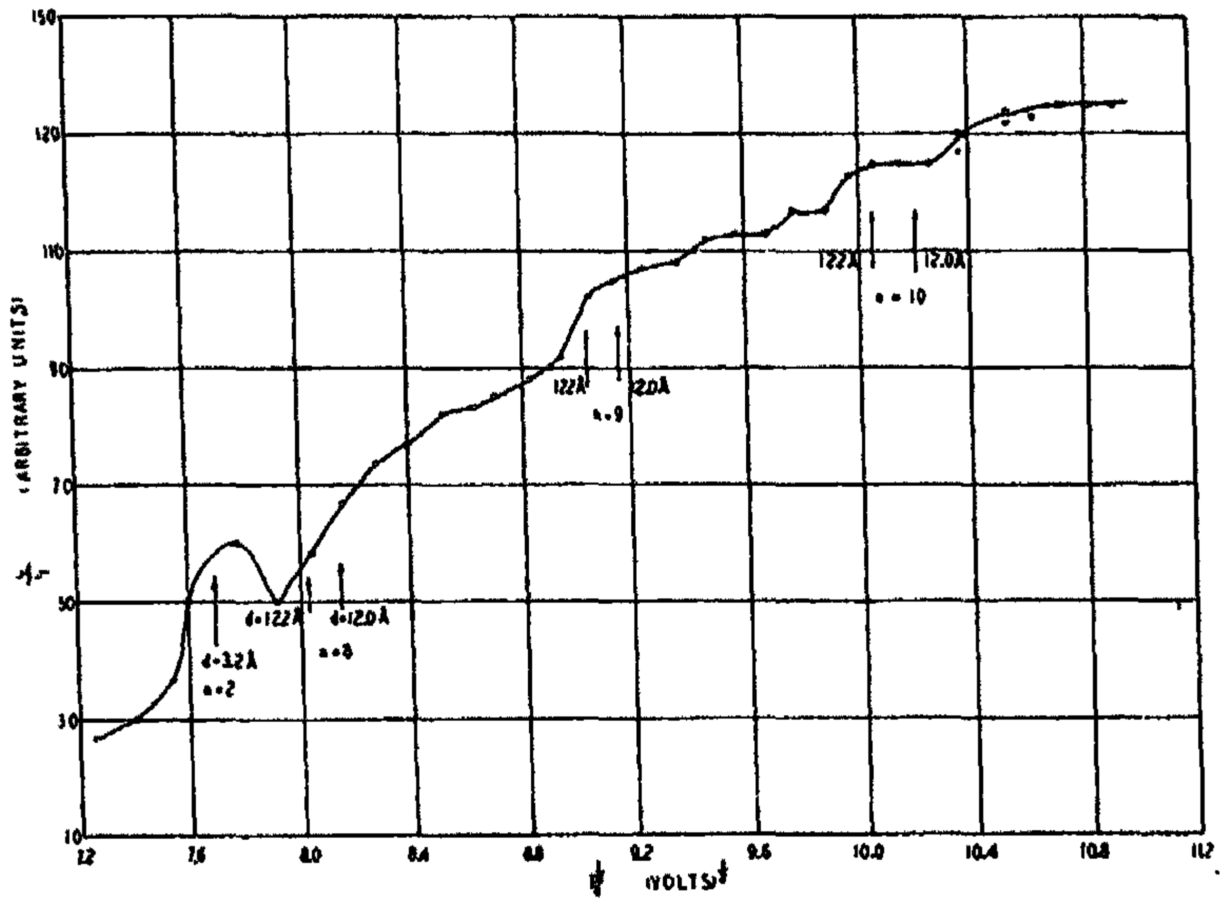

FIG. 7. Diffraction of electrons from repurified oleic acid. $\theta = 30°$

A portion of the sample of oleic acid used above was further purified by evaporation *in vacuo* at an even slower rate than previously. This process removed a very small percentage of solid acids. An experiment (figure 7) was made on this sample for the region from $P^{\frac{1}{2}} = 7$ volts$^{\frac{1}{2}}$ to $P^{\frac{1}{2}} = 11$ volts$^{\frac{1}{2}}$. The collector current was measured by taking the potential drop across a resistance of 2.56×10^{11} ohms by means of the electrometer. The thermionic current was kept at a fixed value by adjusting the filament current. A maximum, which corresponds to the second order for $d = 3.2$ A.U., is quite pronounced. This experiment, as well as all the others on oleic acid, failed to show good evidence for the distance of 12.0 A.U. as reported by Buhl and Rupp (1). The positions for the maxima corresponding to the eighth, ninth, and tenth orders for a spacing of 12 A.U. are indicated in figure 7.

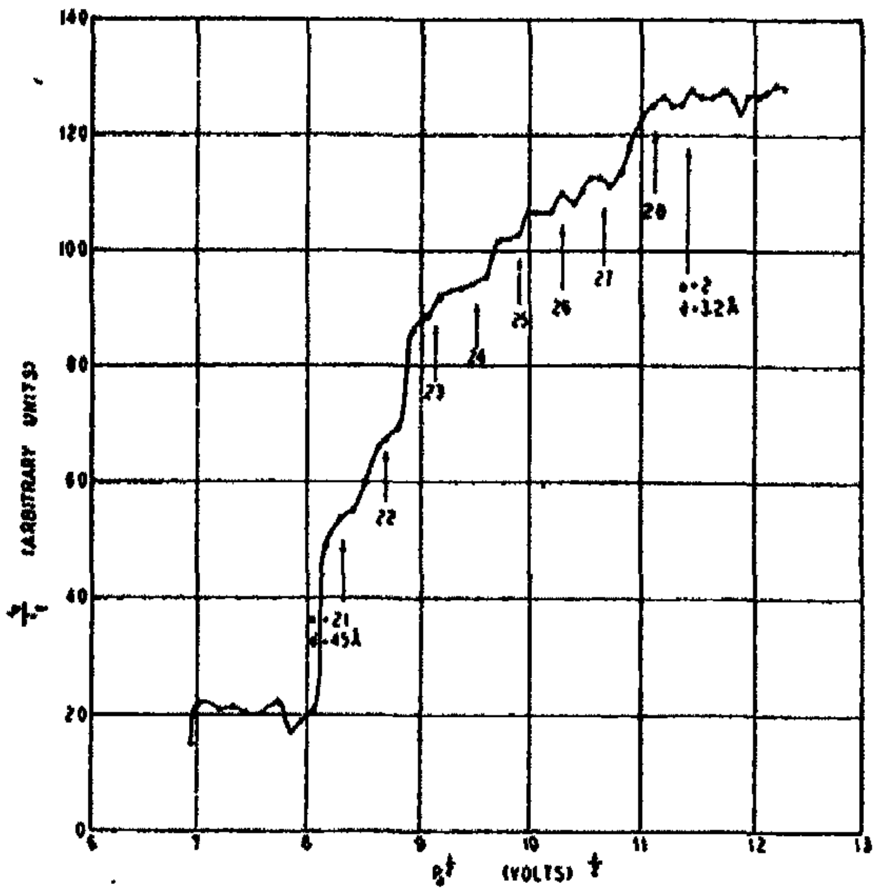

FIG. 8. Diffraction of electrons from oleic acid. $\theta = 20°$

Experiment with a fixed angle of 20° (oleic acid). The angle used in this experiment was such that the maxima for the 3.2 A.U. spacing were too broad ($P^{\frac{1}{2}}_a = 5.7$ volts$^{\frac{1}{2}}$), and the maxima for the 45 A.U. spacing were of high orders. The second order for a spacing of 3.2 A.U. and the twenty-first to the twenty-eighth order for a spacing of 45 A.U. are indicated by arrows on the graph for comparison (figure 8).

Diffraction of electrons from the (100) cleavage plane of a single crystal of sodium chloride

Large single crystals of sodium chloride were cleaved in order to obtain a fresh surface. The size of the crystal thus prepared was about 5 mm. x 5 mm. x 3 mm. The crystal was put on the holder and placed in the apparatus, and evacuation was begun at once. The diffracting surface was the (100) plane. The azimuthal orientation of the crystal was such that the (010) planes were parallel to the plane of the incident electron beam and the normal to the (100) plane at the point of incidence. In these experiments the filament heating current was kept constant. The collector current passed through a resistance of 2.56×10^{11} ohms and was measured with an electrometer, which registered the potential drop it created. The period of the electrometer under such conditions was approximately sixty seconds. The surface was bombarded with electrons for equal time intervals for each reading. The electrometer sensitivity was 500 divisions per volt. A retarding potential of 4.5 volts, applied to the collector, was used in the experiments with sodium chloride.

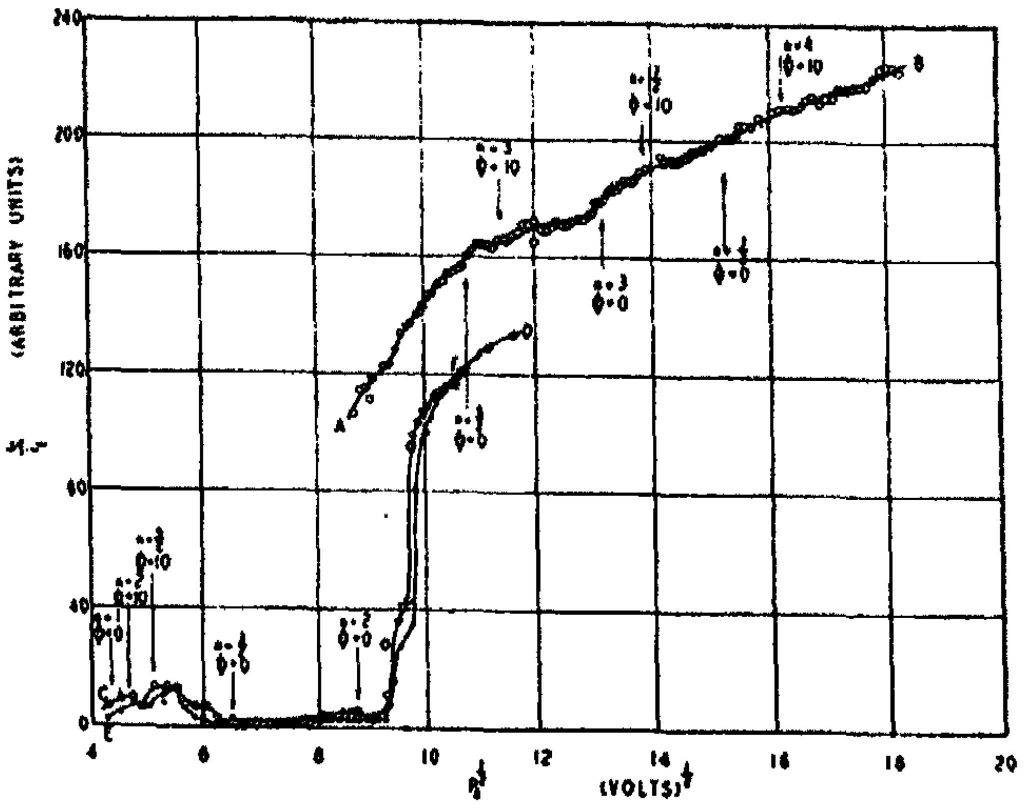

FIG. 9. Diffraction of electrons from the (100) cleavage plane of a single crystal of sodium chloride. $\theta = 30°$

Experiment 1, curve AB of figure 9 ($\theta = 30°$). Curve *AB* is a plot of the collector current against $P_a^{\frac{1}{2}}$. The surface of the sodium chloride crystal was bombarded with electrons for a period of sixty seconds at each voltage, and bombarding was discontinued for a period of ten to twenty seconds while the voltage was changed. Curve *AB* exhibits a broad maximum, which fits both the third order with an inner potential of 10 volts (4, 6), and the 5/2 order with an inner potential of zero. A second rather weak maximum corresponds to the 7/2 order with an inner potential of 10 volts, and the third order with an inner potential of zero. Four possible maxima ($n = 3, \phi = 0; n = 7/2, \phi = 10; n = 7/2, \phi = 0; n = 4,$

$\phi = 10$) would occur in the region from $P_a^{\frac{1}{2}} = 13$ volts$^{\frac{1}{2}}$ to $P_a^{\frac{1}{2}} = 16.2$ volts$^{\frac{1}{2}}$. This might explain why there are no well-defined maxima in this region.

Experiment 2, curve CD of figure 9 ($\theta = 30°$). The filament was allowed to burn for two hours before any data were taken. A well-defined maximum occurs corresponding to the second order for $n = 5/2$ and $\phi = 10$. This maximum exhibited a fluctuating intensity, though the average collector current was fairly constant. The encircled points on the curve are check points taken at the end of the experiment. The agreement is excellent.

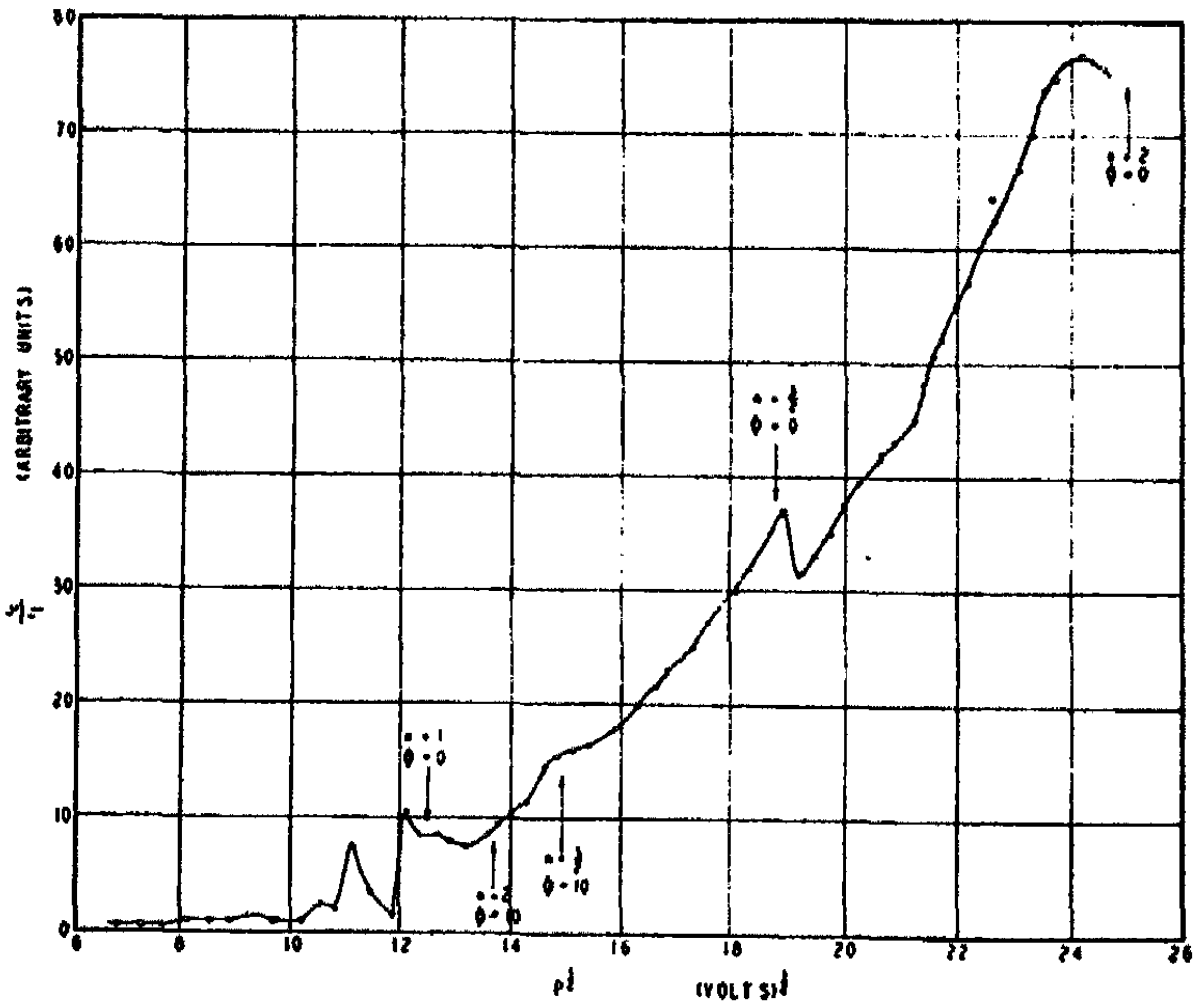

FIG. 10. Diffraction of electrons from the (100) cleavage plane of a single crystal of sodium chloride. $\theta = 10°$

Experiment 3, curve EF of figure 9 ($\theta = 30°$). The surface was bombarded for a period of ten seconds with 386-volt electrons. A period of fifty seconds was allowed to elapse before a reading which required sixty seconds to complete was taken. This curve shows fair agreement with curve *CD*. In addition to the maxima exhibited in curve *CD*, curve *EF* has two other rather weak peaks, which correspond to $n = 3/2$ and $\phi = 0$, and $n = 2$ and $\phi = 0$. Peaks corresponding to a lattice potential of zero are often weaker than the regular peaks for a great many substances.

The values $d = 2.81$ A.U., $\theta = 30°$, and $\phi = 10$ volts were substituted in equation 8, which yielded the condition for maxima

$$P^{\frac{1}{2}} = 4.34\ (n^2 - 2.106)^{\frac{1}{2}}$$

$P^{\frac{1}{2}}$ for the maxima, which correspond to $n = \frac{1}{2}$ and $n = 1$, has an imaginary value and the maxima should be absent.

Experiment 4, sodium chloride, figure 10 ($\theta = 10°$). A retarding potential equal to 6 volts less than the accelerating potential was applied between the apertures S_4 and S_5. Electrons which had lost 6 volts or more of their original energy did not enter the Faraday chamber. The curve exhibits four maxima, three of which agree best with $n = 1$, $n = 3/2$, and $n = 2$ for $\phi = 0$. The calculated and observed maxima are given in table 2.

The diffraction of electrons from the (100) cleavage plane of galena at 206°C.

A large single crystal of natural galena was cleaved into a smaller crystal (3 mm. x 3 mm. x 2 mm.). The (100) plane thus obtained appeared quite uniform to the eye by reflected light. Preliminary measurements on this crystal at room temperature failed to reveal any clearly defined peaks between 50 and 420 volts.[5] The furnaces used for degassing the apparatus were put in place and the entire apparatus was heated to 200°C. for seven days. At the end of that time the pressure in the apparatus was 7.0×10^{-6} mm. with the usual heating current passing through the filament. Nine maxima were found between 50 and 300 volts, with the angle of incidence equal to 75°. It was impossible to use retarding potential in this experiment, as the dielectric absorption current in the quartz insula-

TABLE 2

Calculated and observed values of $P^{\frac{1}{2}}$

n	$P^{\frac{1}{2}}$ (CALCULATED)	$P^{\frac{1}{2}}$ (OBSERVED)
		11.2
1	12.52	12.1
3/2	18.78	18.9
2	25.04	24.2

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[5] The previous experiments on sodium chloride gave maxima which were relatively weak in intensity. Laschkarew (Z. Physik **86**, 631 (1933)) and his coworkers found that a single crystal of graphite acted as an electron optical surface at room temperature. That is, the collector current exhibited no maxima or minima as the accelerating voltage was varied. However, upon heating the crystal for two hours at 200°C. and then making observations at that temperature, very intense maxima were found. They explained this as being due to the ability of the graphite to absorb gas at room temperature and inability to retain it at 200°C.

tion on the collector system required too long a time to reach equilibrium. The thermionic current was kept constant at 0.500 milliampere by adjusting the filament heating current with a variable carbon resistor. The electrometer leak was 2.56 × 10^{11} ohms, and the electrometer sensitivity was 250 divisions per volt.

TABLE 3

Experiments on galena with different cooling agents on the grease traps

DATE OF EXPERIMENT	CURVE IN FIGURE 9	COOLING AGENT ON GREASE TRAPS	COOLING AGENT ON OTHER TRAPS
August 7, 1935	AB	Crushed carbon dioxide in acetone	Liquid nitrogen
August 10, 1935	CD	None	Liquid nitrogen
August 11, 1935	EF	Liquid nitrogen	Liquid nitrogen

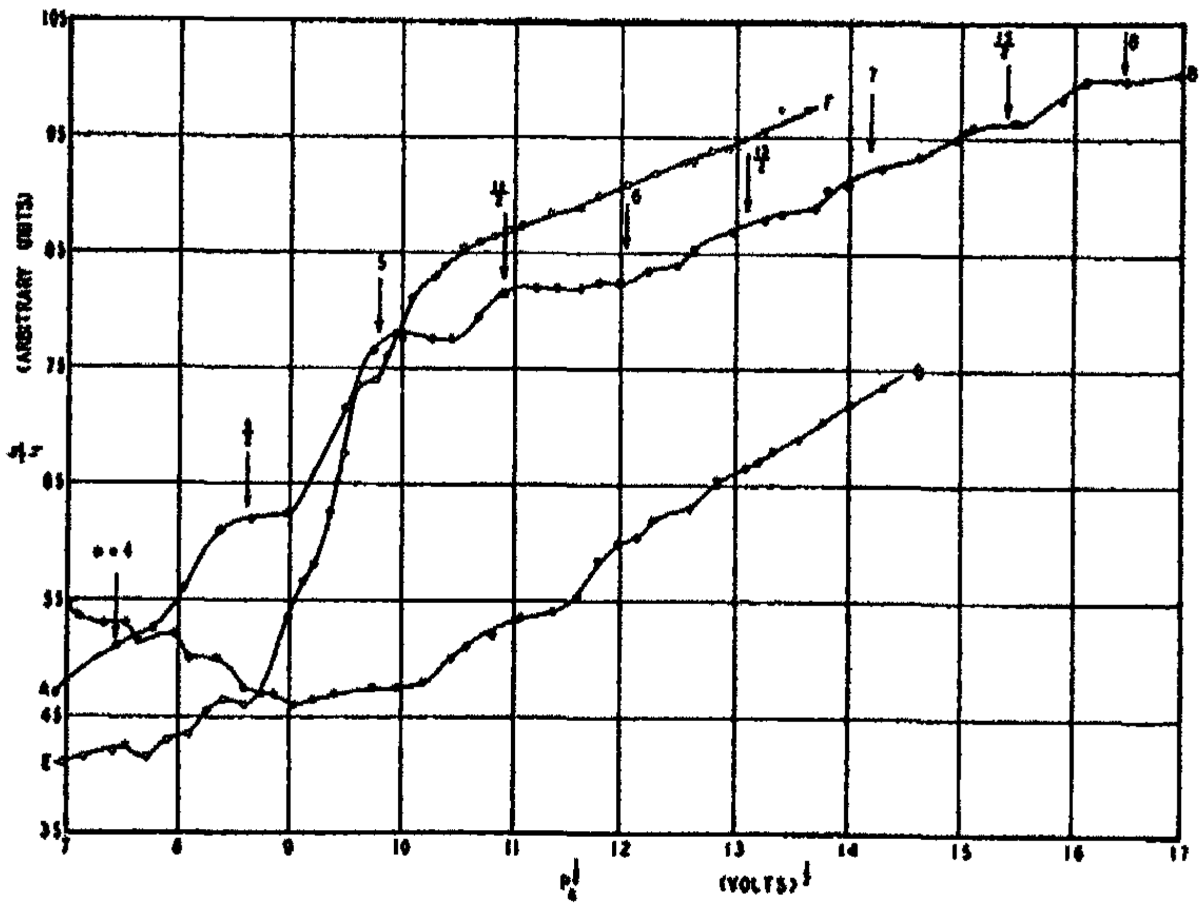

FIG. 11. Diffraction of electrons from the (100) cleavage plane of galena at 206°C. $\theta = 75°$; $\Phi = 16.9$ volts

All of the following experiments on galena were performed with the entire diffraction apparatus at approximately 206°C. The experiments differed only in the cooling agent used on the traps, as shown in table 3.

The values $d = 2.98$ A.U. and $\theta = 75°$, when substituted in equation 8, yield the condition for maxima that $0.222P = n^2 - 0.238\phi$. The values of P for each maximum on curve AB of figure 11 were plotted against various values of n^2, and the series of points which fell on a straight line parallel to the line $n^2 = 0.222P$ belonged to the correctly ordered maxima.

The difference between the experimental value of the voltage for a maximum and the value given by $P = n^2/0.222$ is the inner potential for that maximum. The average value of the inner potential for the best defined maxima (maxima with $n = 9/2, 5, 11/2, 13/2$, and 7) was 16.9 volts.

An experiment (curve *CD*) without any cooling agent in the grease traps completely changed the shape of the curve, and very weak maxima, if any, could be found. An experiment twenty-four hours later with liquid nitrogen in the grease traps yielded a still different curve without well-defined peaks. The collector current was greater, owing, more than likely, to the better vacuum conditions. It seems reasonable to suppose that during the second experiment the organic vapors present were decomposed by the electron beam at the surface of the galena, thus forming a semi-amorphous layer which remained on the surface for at least twenty-four hours. Consequently, liquid nitrogen on the grease traps failed to bring out any maxima. A dark brown spot was easily seen on the surface of the galena where the electron beam had struck it; this was probably decomposed organic matter. The "fatigue effect" in the case of the oleic acid might be explained on the basis that the electron beam tended to decompose the oleic acid where it struck the surface of the oleic acid and the decomposition product diffused away slowly.

Stearic acid

A minute amount of stearic acid was placed upon a polished platinum plate, the temperature of which was just above the melting point of stearic acid. A thin visible film of stearic acid formed over the surface of the platinum and was quite homogeneous when cold. No maxima and minima were found, and the visible film of stearic acid disappeared. In all probability the film had evaporated in the high vacuum, and something less than a monomolecular film was left.

SUMMARY

Slow speed electrons were used to study various surfaces by means of electron diffraction. The angle of incidence was kept fixed and equal to the angle of reflection, while the accelerating voltage of the incident electron beam was varied. The collector current–accelerating voltage curve showed three broad distinct maxima with a surface of bulk liquid oleic acid, which corresponded to a distance of 3.2 A.U. A long distance of 45 A.U. was also found for oleic acid when the incident beam made a small angle with the surface of the liquid. Oleic acid showed a pronounced "fatigue effect," probably due to a growing surface charge. The (100) cleavage plane of sodium chloride gave maxima corresponding to an inner potential of zero and one of approximately 10 volts. Two methods of measuring were found which apparently did not show a fatigue effect.

The (100) cleavage plane of galena gave no well-defined maxima at room temperature. At 206°C. several well-defined maxima were found which corresponded to an inner potential of about 16.9 volts. Half-order, as well as whole-order peaks were found. Bombardment of the surface with slow speed electrons, at 206°C. and in the presence of a trace of organic vapor, permanently destroyed the grating properties of the galena surface. Stearic acid films on a polished platinum surface vaporized in the high vacuum before an experiment could be performed.

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POLYMOLECULAR FILMS: MIXED FILMS WITH TWO OR MORE COMPONENTS. I

FATTY ACIDS AND NON-POLAR SUBSTANCES[1]

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I. INTRODUCTION

Monomolecular films of insoluble substances containing a polar group have been extensively examined by Harkins, Langmuir, Adam, Rideal, and other workers. Very little attention, however, has been paid to the more general case of polymolecular films composed of two or more substances. In 1925 Harkins and Morgan (6) examined the force–area characteristics of mixed films of stearic acid and phenanthrene, and showed that the stearic acid exists as a monomolecular film while the molecules of phenanthrene are mostly piled up over it, and the two together give a polymolecular film. de Haas (3) has recently examined films of mixtures of palmitic acid and paraffin, but the films exhibited quite anomalous characteristics

In view of the great value of a knowledge of the behavior of polymolecular films *as a fundamental approach to a generalized theory of surface* films, as well as the application of such knowledge to the practical problems of lubrication and cell-interface phenomena, cases in which polymolecular films exist beyond a doubt, the authors have undertaken an extensive investigation of these polymolecular films. Since the films studied both by Harkins and Morgan and by de Haas were solid films, it is quite likely that some of the phenomena exhibited by the films may have been due to this solidity, rather than to orientation effects alone. For this reason, in this investigation, liquid hydrocarbons were added to the polar substances to insure freedom for reorientation, if any, in the film.

This paper is to be considered as a rapid preliminary survey of the general characteristics of films of fatty acids to which were added, *before* spreading, various quantities of tetradecane or Nujol, non-polar hydrocarbon liquids of relatively low vapor pressure.

II. APPARATUS AND PREPARATION OF FILMS

The film balance, of the type designed by Adam (1) and modified by Harkins and Freud (2) and Harkins and Fischer (4), has recently been

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[1] Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11–13, 1936.

further modified and is described in detail elsewhere (7). The torsion head is shown in figure 1, and the film balance in figure 2. The recent improvements may be briefly summarized as follows: (1) A beam arrest, operating much as the balance beam arrest on an analytical balance, is mounted on the torsion head as shown and serves to prevent large movements of the torsion wire float assembly during a calibration or a determination of film pressure. This has resulted in precise calibrations and exact checks of "zero-point" readings. (2) The trough, 75 cm. long and 25.4 cm. wide, is supported by adjustable screws which in turn are mounted on amber posts for insulation purposes. The plate-glass sides of the box are covered with fine copper screens which are grounded, together with the chromium-plated framework. (3) The box containing the film balance is enclosed in a larger thermostatically controlled chamber, which may also be closed and grounded, enabling the experiments to be conducted under any desired gas and in total darkness, if necessary. (The work reported here was conducted at room temperature, prior to the construction of the thermoregulating devices.) (4) The surface is swept and the film compressed by means of barriers operated by rods extending to the outside of the box. The threaded lead-screw driving the compression barrier-holder is fitted on the exterior with a mechanical revolution counter, and areas are read in terms of revolutions of the lead-screw. Higher precision in area determinations is thus obtained. (5) The electrodes for contact-potential measurement are carried along the axis of the trough by a moving table which also serves as part of the top of the

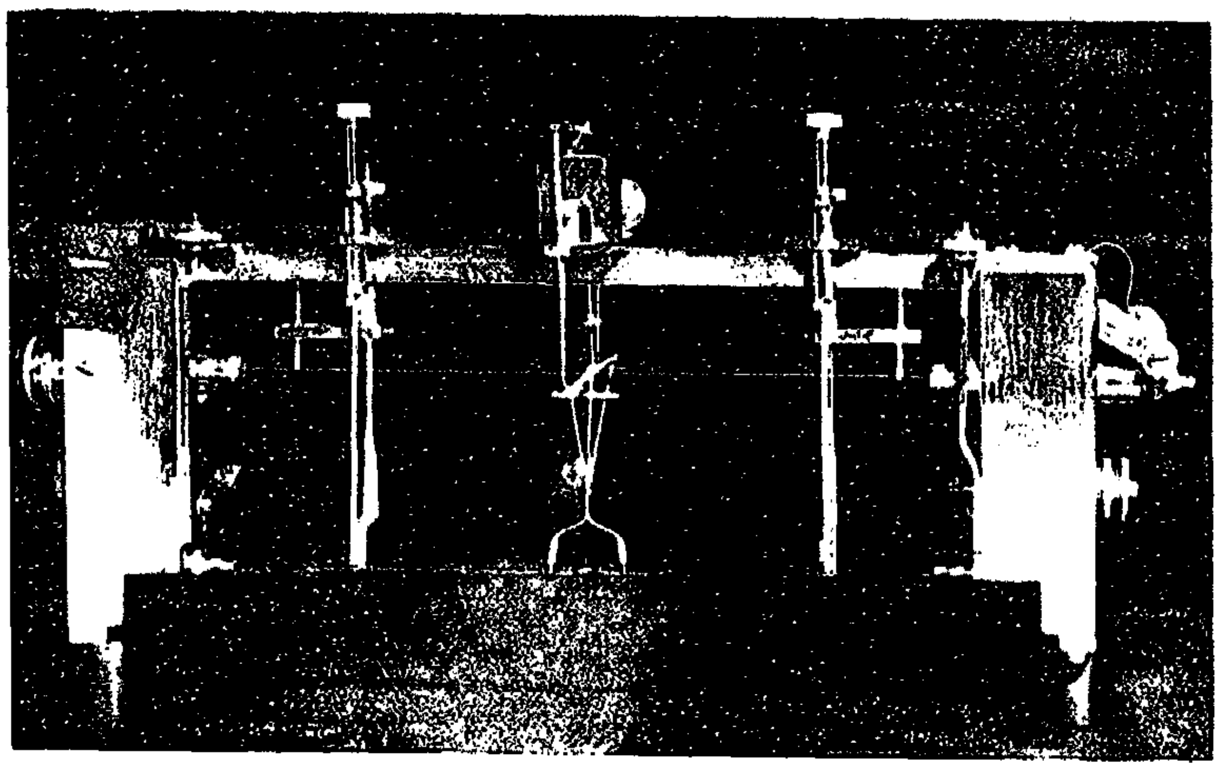

FIG. 1. The torsion head

inner box. This moving top slides in grooved bars across the top of the box and is also moved by a lead-screw. (Potential measurements reported in this paper were made on the apparatus of Harkins and Fischer, *as the potential circuit was under construction at the time of the experiments.*) This arrangement of the movable electrodes minimizes the number of moving parts over the trough, and in turn avoids to a great extent the danger of dirt falling upon the surface. (6) The divided drum attached to the torsion wire was mounted on the outside of the box, enabling all readings to be made on the exterior of the apparatus.

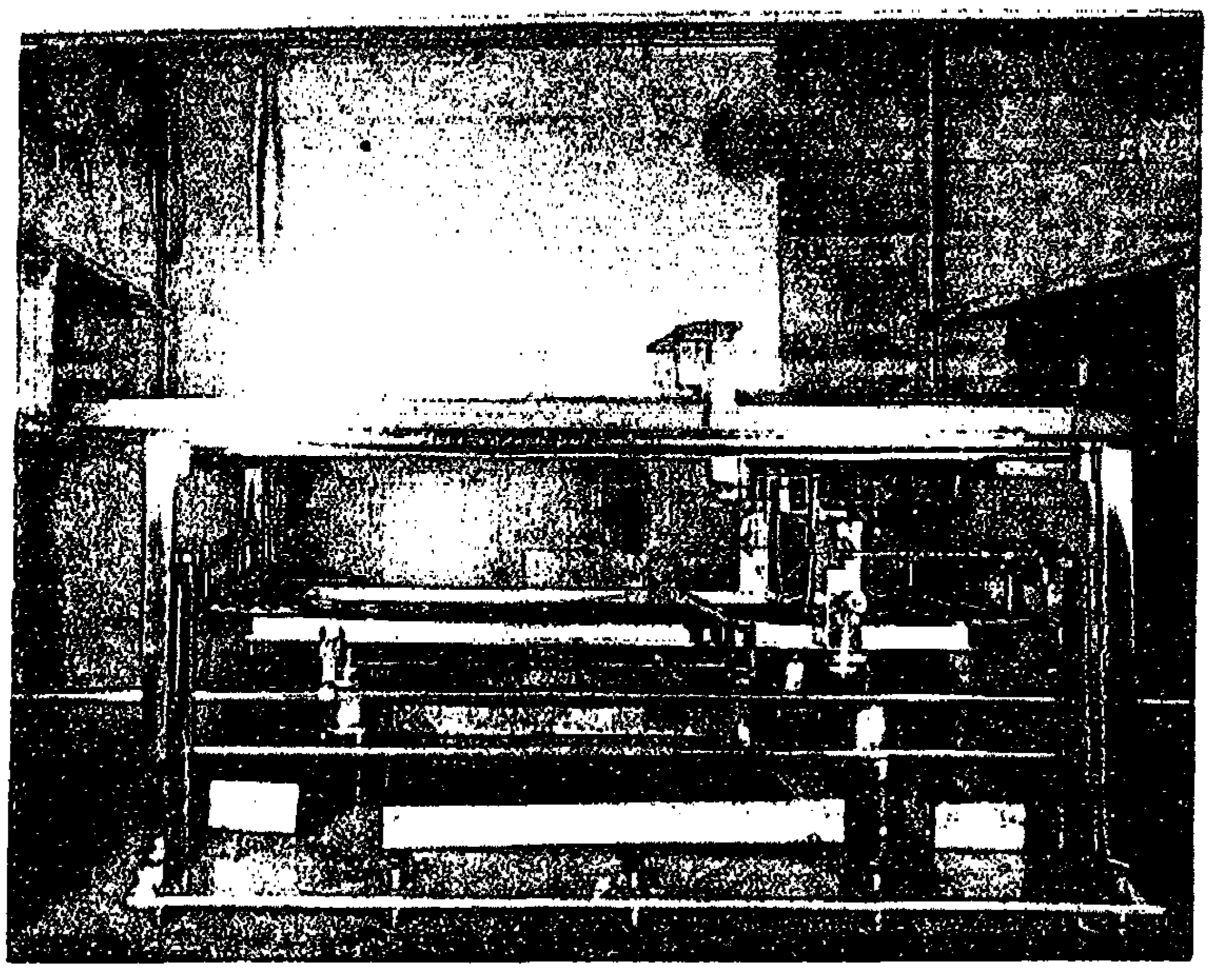

FIG. 2. The film balance

The fatty acids and the hydrocarbons were spread from ligroin as solvent. The ligroin was treated with activated silica gel followed by a distillation in an all-glass apparatus. The hydrocarbons, tetradecane and Nujol, were treated with fuller's earth and then centrifuged. Blank tests made on these purified materials failed to show any traces of spreading substances. The saturated fatty acids were generously loaned for this work by Professor E. Emmet Reid of the Johns Hopkins University. They were prepared by Miss Jane Dick Meyer and are of the very highest purity. The oleic acid was prepared by Dr. Robert J. Moon in this laboratory, by evaporation in a high vacuum. It was exceptionally pure and free from saturated acids.

The solutions for spreading were made by dissolving from 30 to 50 mg. of fatty acid in about 32 g. of ligroin. A special weight pipet designed by Harkins and Freud was used in dropping the material on the surface. The capillary tip was ground flat according to the directions of Harkins and Humphery (5) for the preparation of drop-weight tips. The drops formed slowly and broke off neatly, leaving a negligible quantity on the tip face. In this manner the evaporation error was entirely eliminated. A balance weighing to five decimals was used, since an error of 0.2 mg. in preparing the solutions or in weighing the pipet may result in as much as 1 per cent error. Assuming that all the errors are additive, we feel that the results reported herein are reproducible to less than 1 per cent.

In some cases the shift in the *F-A* curve produced by the added hydrocarbon is quite small. To eliminate the slight shift between curves caused by a weighing error between two solutions, the hydrocarbon was added directly to a weighed portion of the fatty acid solution, instead of attempting to prepare a new solution of the fatty acid.

III. FORCE-AREA RELATIONSHIPS OF FILMS OF FATTY ACIDS MIXED WITH TETRADECANE

The force-area curves of films of myristic, pentadecylic, stearic, and oleic acids mixed with various quantities of tetradecane or Nujol are shown in figures 3 to 9. All films were examined on 0.01 molar hydrochloric acid.

The lack of any appreciable effect of tetradecane on the force-area curves is quite striking. The effect of longer time intervals between points is shown in experiments 88 and 89 (figure 3). If readings are taken 2 minutes after a film is adjusted to a certain increment of pressure, during which time the areas are decreased sufficiently to maintain the film pressure constant, the curve of experiment 88 (figure 3) is obtained. If the film is held at each pressure level for 4 minutes, the curve of experiment 89 (figure 3) is obtained. These and other experiments point definitely to a need for the development of a standard rate of compression. This problem will be studied during the course of these investigations. For this preliminary survey an arbitrary interval of 4 minutes was adopted, except in those instances in which the "4-minute curve" was unchanged from the "2-minute curve."

The curves of figures 4 and 5 further illustrate the lack of effect of tetradecane on the force-area curves of myristic and pentadecylic acids. At this point in the work it was felt that an evaporation of the tetradecane was taking place. To prevent some of this evaporation, small quantities of dotriacontane[2] were added to the fatty acid-tetradecane mixtures

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[2] The dotriacontane was generously supplied by Dr. B. J. Mair of the National Bureau of Standards, U. S. Department of Commerce, Washington, D. C.

without appreciable effect. In the case of myristic acid (experiment 100, figure 5) the addition of dotriacontane displaced the *F–A* curve to larger areas, but the curve was parallel to that without dotriacontane. Examination of the film showed that it was solid, hence it was feared that some mechanical resistance due to the solidity might have produced the shift to larger areas. To restore the film to a liquid condition the tetradecane content of the solution was increased, when the curve of experiment 101 (figure 5) was obtained. The large amount of tetradecane has the effect

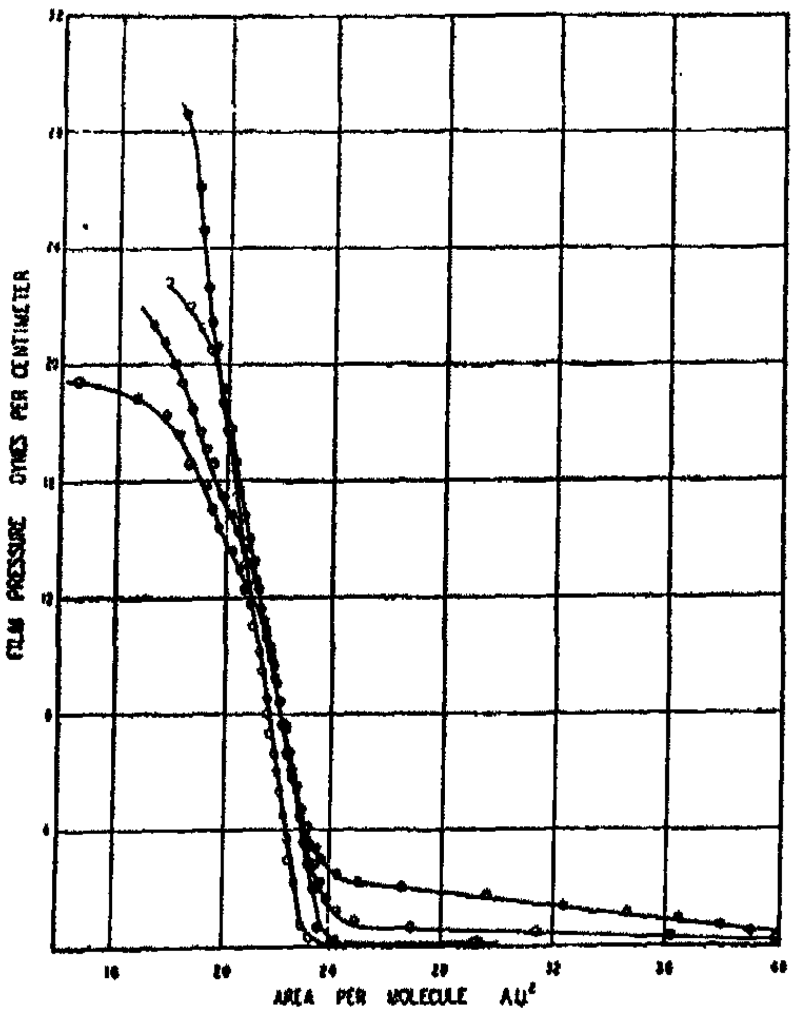

Fig. 3. Stearic acid–tetradecane mixtures

	EXPERIMENT NO.	MOLE RATIO		TEMPERATURE IN °C.	ΔT IN MINUTES
		Stearic acid	Tetradecane		
○	91	1	0	22.0	2
●	85	1	10	20.6	2
◓	88	1	50.5	22.0	2
◒	89	1	50.5	22.0	4

Areas per molecule have been calculated on the assumption that all the fatty acid is at the water surface. The experimental points are shown for a single experiment, although check determinations verify the position of the curve drawn. The concentrations with tetradecane are given in mole ratios; those with Nujol in composition by weight, for lack of data on the molecular weight of Nujol.

of increasing the areas greatly at low pressures, but as the film is compressed, the curve approaches that of myristic acid and collapses at nearly the same pressure. It is worthy of note that upon slow compressions of this character (time intervals 4 minutes) the myristic acid films collapsed at pressures but slightly above the kink point in the curve. This is quite different from the second curved portion above the kink in the F–A curve obtained by Adam (1). The pressures at the kink point are approximately the same as those given by Adam, but the areas throughout are somewhat smaller. We have attributed this to the high purity of our materials, inasmuch as a small amount of short-chain impurity would influence the areas more than the collapse pressures.

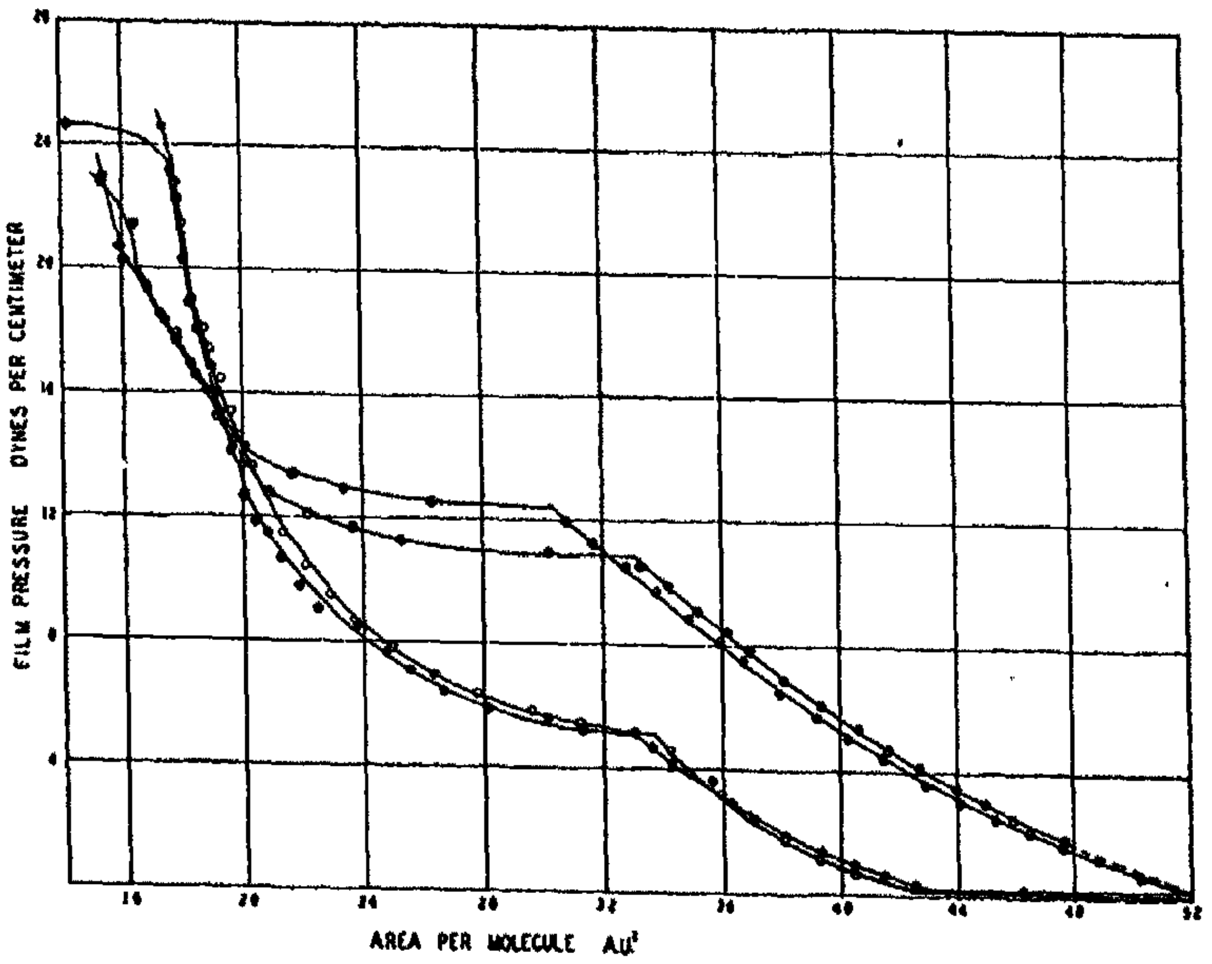

FIG. 4. Mixed films containing pentadecylic acid

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	116	Pentadecylic acid	22.1	4
●	97	1 mole pentadecylic acid and 16 moles tetradecane	22.8	4
◓	117	0.77 g. pentadecylic acid and 1.0 g. Nujol	22.1	4
◕	111	0.68 g. pentadecylic acid and 1.00 g. Nujol	24.4	4

In view of these results with tetradecane and dotriacontane it was felt that a more non-volatile liquid hydrocarbon would be preferable, as the error due to evaporation would be thereby lessened. The commercial hydrocarbon Nujol (Standard Oil Company of New Jersey) was selected for its purity, non-volatility, and low cost. In working with Nujol, it was possible to place large pans of the hydrocarbon below the film balance, in the interior of the box, through which a stream of nitrogen gas bubbled slowly, to saturate the air with Nujol vapor.

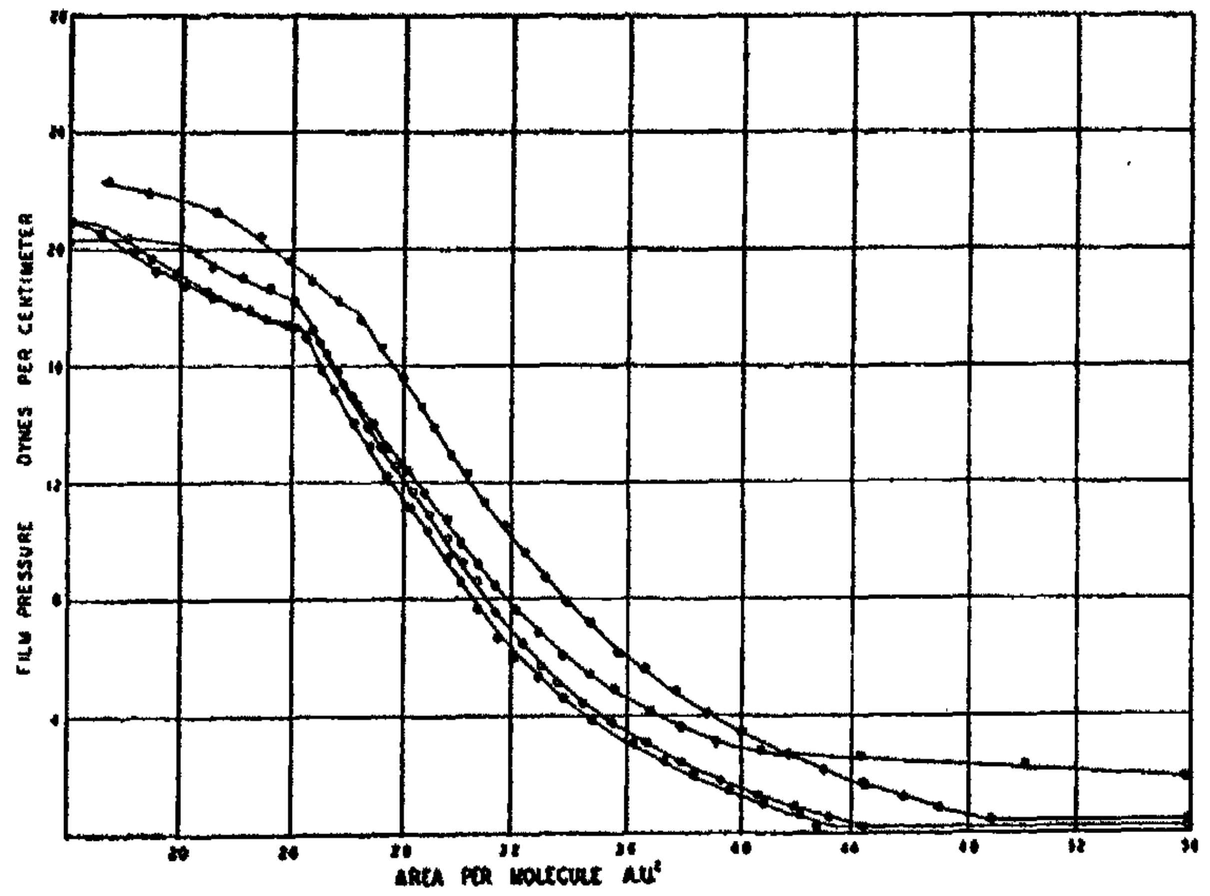

Fig. 5. Mixed films containing myristic acid

	EXPERIMENT NO.	COMPOSITION—MOLE RATIO			TEMPERATURE IN °C.	ΔT IN MINUTES
		Myristic acid	Tetradecane	Dotriacontane		
○	98	1	0	0	22.3	4
●	99	1	12.46	0	22.4	4
◓	100	1	12.46	1.10	22.6	4
◒	101	1	76.21	1.10	22.6	4

IV. FORCE-AREA RELATIONSHIPS OF FILMS OF FATTY ACIDS MIXED WITH NUJOL

Quite contrary to the case of tetradecane, the addition of Nujol to fatty acids produced great changes in the force-area curves of *expanded* films. In the case of stearic acid, a liquid condensed film, the addition of Nujol changed slightly the slope of the compression curve of stearic acid and facilitated collapse at a lower pressure (experiment 110, figure 6), but the areas at zero compression were the same as stearic acid alone, within experimental error. It is quite possible that larger amounts of Nujol would effect a change in the F–A curve, and this will be investigated.

In the case of myristic, pentadecylic, and oleic acids, the addition of Nujol produced marked effects on the F–A curve. Upon the addition of 1.67 g. of Nujol to 1.0 g. of myristic acid (experiment 106, figure 7), the character of the F–A curve is changed, giving larger areas at lower pressures, the curve approaching that of myristic acid alone at high pressures. No kink appears in the curve, and the area at zero compression is nearly 10 A. U.^{2} larger. The collapse point is the same as for myristic acid alone.

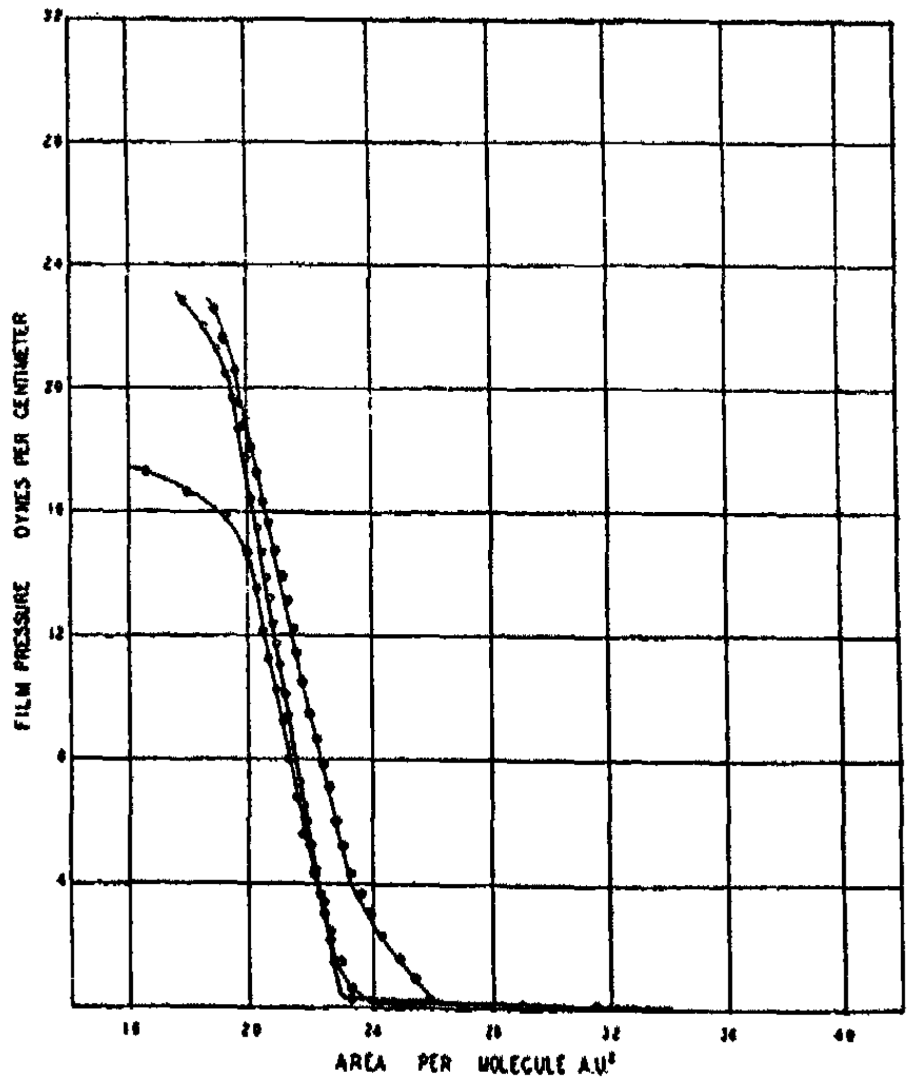

FIG. 6. Mixed films containing stearic acid

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	91	Stearic acid	22.0	2
●	93	1 mole stearic acid, 0.95 mole dotriacontane, and 0.95 mole tetradecane	21.7	2
◒	110	1 g. stearic acid and 1.61 g. Nujol	23.5	4

Upon the addition of Nujol to give 9.08 g. of Nujol per gram of myristic acid, the curve cuts across the myristic acid curve at 13 dynes, exhibits no kink, and continues without appreciable change in slope down to very small areas. The area at zero compression is again some 10 A.U.² larger. With a concentration of 49.8 g. of Nujol per gram of myristic acid, and in addition 31.5 g. of tetradecane, the film exhibits even less adhesion to the water surface. The area at zero compression is some 8 A.U.² more than that of myristic acid alone. No kink point in the curve was observed, and upon compression to very small areas small lenses were visible to the eye.

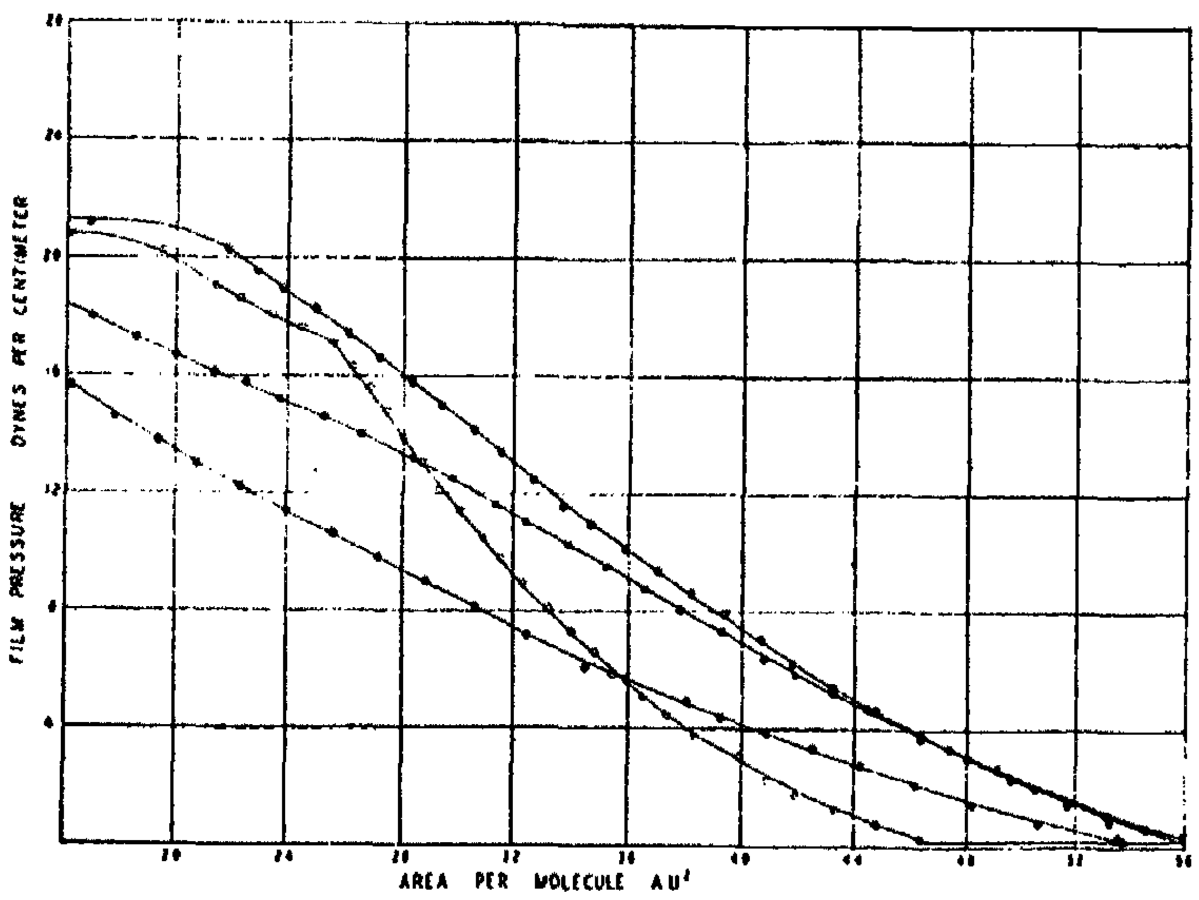

Fig. 7. Mixed films containing myristic acid and Nujol

	EXPERIMENT NO.	COMPOSITION IN GRAMS			TEMPERATURE IN °C.	ΔT IN MINUTES
		Myristic acid	Tetradecane	Nujol		
○	102	1	0	0	22.8	4
●	104	1	31.5	49.8	21.8	4
◓	105	1	0	9.08	22.4	4
◒	106	1	0	1.67	22.9	4

This was the only film on which lenses visible to the eye were noticed. It is quite possible that microscopic lenses may be present; the films are being reëxamined by optical methods to determine if the upper surface is heterogeneous. It is to be understood that these films exhibit slight contractions all along the curve, and that the "4-minute" points do not necessarily represent equilibrium areas at that particular pressure. Other time intervals may very well give rise to other curves, indicating again the great need for extended work on the character of a force-area curve as influenced by the rate of compression.

Experiments 111 and 117 (figure 4) illustrate a most interesting effect of the addition of Nujol to pentadecylic acid. The curves are very similar in shape to that given by pentadecylic acid alone; in fact, are quite parallel throughout the expanded range. The area at zero compression is some 9 A.U.^{2} larger when 1.0 g. of Nujol per 0.77 g. of pentadecylic acid is present. The kink occurs at nearly the same area, but some 6 dynes higher, at the same temperature. Beyond the kink a most interesting very flat portion appears which extends to a region around 21 A.U.^{2}, where the curve meets that of pentadecylic acid and again rises, but with less slope. The presence of the Nujol appears to facilitate collapse at a lower pressure. The flat portion of the curve suggested some sort of phase transition, and an examination of the contact potentials (4) of pentadecylic acid films with and without Nujol was undertaken to determine if any change

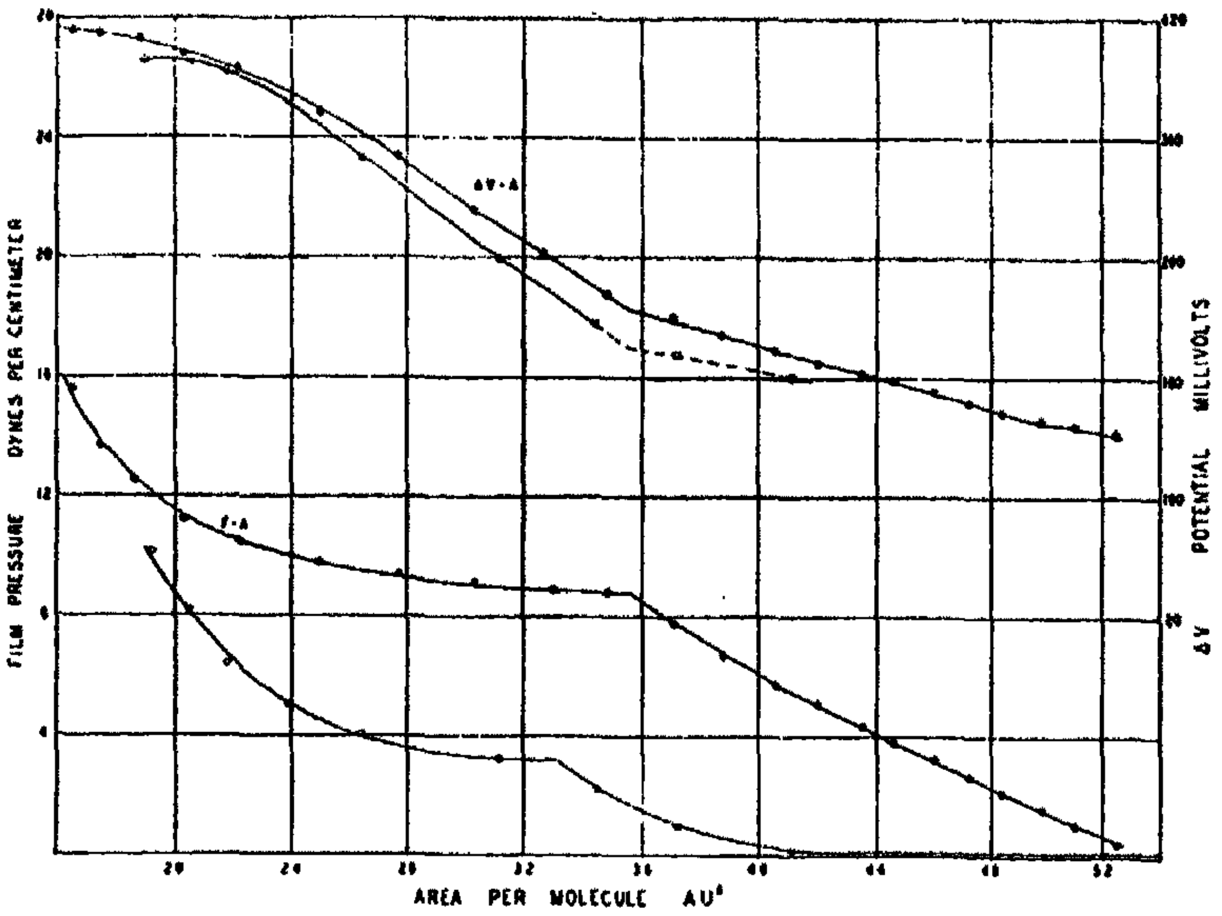

Fig. 8. Pentadecylic acid films

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	121	Pentadecylic acid	20.5	4
●	120	0.77 g. pentadecylic acid and 1.00 g. Nujol	20.5	4

occurred in the ΔV–A curves at this point. The results were most interesting, although they are to be considered as a very preliminary investigation of the contact potentials of the films (figure 8). The ΔV–A curve of the mixed film consists mainly of two straight lines which intersect at exactly the same area as the kink in the F–A curve. A very cursory examination of a pentadecylic acid film at the same temperature showed a similar break in the ΔV–A curve at the same point, although the kink in the F–A curve came at an area some 2 A.U.^{2} smaller. In view of the lack of sufficient data at this time, it appears hardly worth while to speculate on the nature of this interesting relationship.

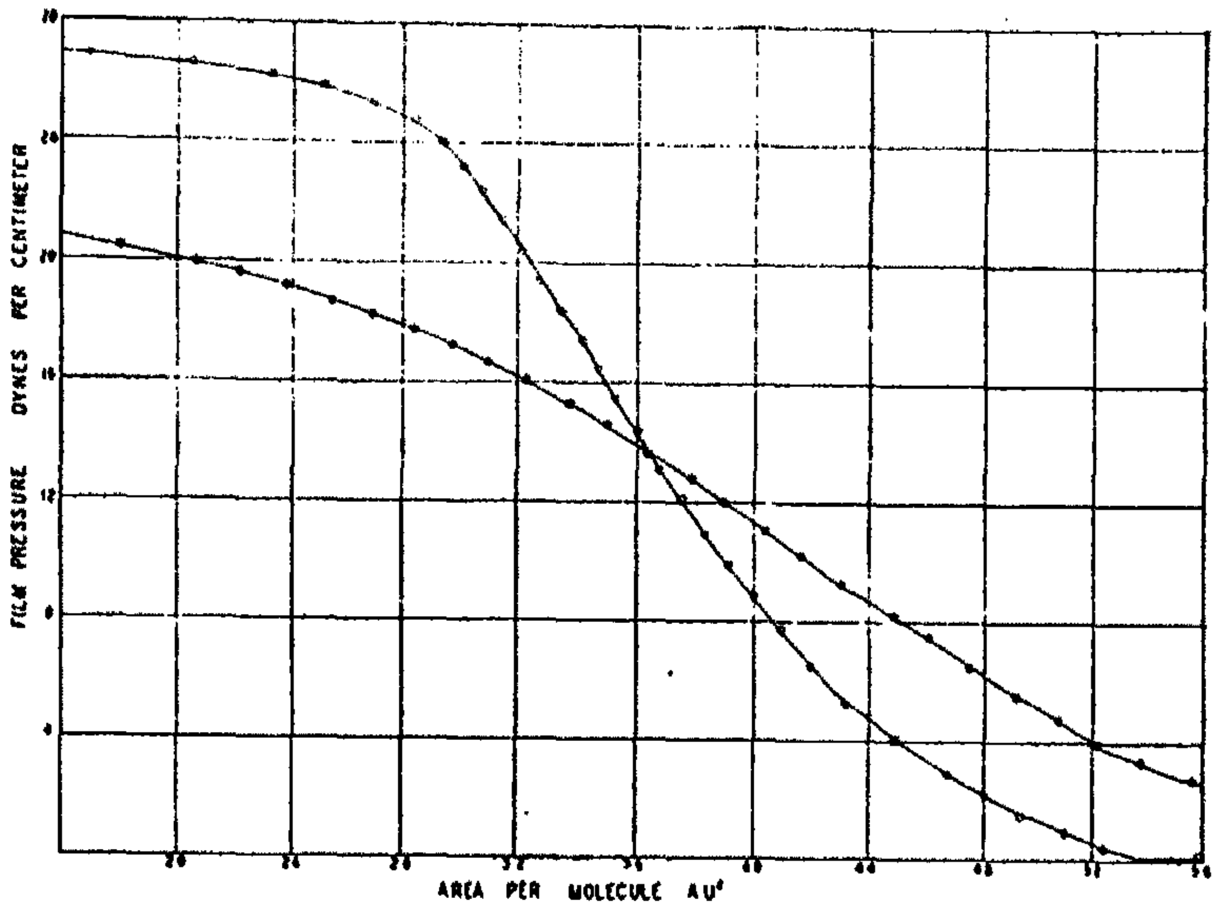

FIG. 9. Oleic acid films

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	107	Oleic acid	25.4	4
●	119	0.54 g. oleic acid and 1.00 g. Nujol	24.1	4

In the case of oleic acid (figure 9) the addition of Nujol caused a marked change in the film. The F–A curve crossed that of oleic acid at about 14 dynes, and extrapolated to an area at zero compression of about 70 A.U.^{2} as compared to 54 A.U.^{2} for the acid alone. Collapse set in much sooner when Nujol was present.

V. GENERAL DISCUSSION

The work reported here was done as a preliminary survey of the field. For this reason it is not possible to formulate any exact explanation of the effects observed. A few points, however, seem quite definite at this time. The marked difference between the effect of the addition of Nujol and that of tetradecane seems to indicate that almost all of the tetradecane evaporates from the surface, thus making it unsuited for an investigation of this character. The addition of solid hydrocarbons, such as dotriacontane or paraffin, on the other hand, may lead to anomalous results, hence it is advisable to select liquid hydrocarbons of a high degree of non-volatility.

The Nujol appears to affect most markedly the expanded portion of the F-A curve. It is reasonable to suppose that in this region some of the hydrocarbon gets down to the water surface, increasing the area per molecule of fatty acid. As pressure is applied, the hydrocarbon is probably squeezed up to the top of the film, where it may or may not exert a further influence upon the film, depending upon the quantity of hydrocarbon present. If sufficient hydrocarbon is present, a second phase may be formed, which the fatty acid molecules may enter with ease, and the collapse point of the film is correspondingly lower. If but a small amount of hydrocarbon is present, it is quite reasonable to suppose that it will have but a slight influence on the collapse pressure. This analysis raises the question: When is the mixed film no longer to be considered as a film but as a second phase with polar material at the oil-water interface? Only further work can give a suitable answer to this question.

The lack of any effect of Nujol upon the lower region of the stearic acid curve is quite striking. It may be tentatively ascribed to the rather low concentration of Nujol present.

The absence of lenses visible to the eye on all but one of the films seems to indicate at least a temporary stability of a thick film of a hydrocarbon oil with polar material at the oil-water interface. Thick films of polar material alone have been shown to be very unstable, if sufficient area is present for a monomolecular film to be formed. There is, however, the distinct possibility that thick films such as those studied here may be quite stable. In any case, it seems evident that a further study of these polymolecular films promises results of the greatest interest, both theoretically and from the practical viewpoint.

The presence of the hydrocarbon may facilitate phase changes in the film, merely by its action as a diluent. The results obtained with pentadecylic acid seem to indicate such an effect. It is more than likely that many obscure points regarding orientation in a monomolecular film may be clarified by aiding reorientation with the addition of a diluent.

VI. SUMMARY

A preliminary survey of films composed of fatty acids and tetradecane or Nujol has been made. The films containing Nujol exhibit many interesting characteristics, justifying further examination of films with two or more components.

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THE APPLICATION OF THE HIGH-SPEED MOTION PICTURE CAMERA TO RESEARCH ON THE SURFACE TENSION OF LIQUIDS[1]

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The high-speed motion picture camera with a stroboscopic source of light, as developed in the past years at the Massachusetts Institute of Technology (H. E. E.), has permitted the demonstration of many phenomena which so far have escaped direct observation. To test the opinion expressed by one of us (E. A. H.) that this technique might materially assist in obtaining a better insight into the actual mechanism of various physicochemical or colloid-chemical problems, two methods commonly used for the determination of surface tension of liquids—the so-called drop-weight and ring methods—were selected in a first attempt to apply the high-speed motion picture camera technique to such studies.

The large number of methods available for the measurement of surface tension, divisible into static and dynamic ones, is a consequence of the fact pointed out by Freundlich (8), that surface tension essentially determines the shape of the liquid in rest or in motion. The static methods are the following: (1) the direct measurement of curvature of the liquid surface; (2) the method of flat drops and bubbles on surfaces; (3) the capillary-rise method; (4) the method of adhesion plates and rings; (5) the determination of drop weights or volume and gas-bubble pressure. The dynamic methods are as follows: (1) the method of oscillating jets; (2) the method of vibrating drops; (3) the measurement of ripple waves. Many other methods of minor importance have been proposed.

Worthington (27) in 1881 was one of the first workers to utilize the first-mentioned static method. He projected the form of hanging drops of water upon a screen. By suitable measurements of the radii of curvature and the volume of the drop he was able to calculate the surface tension, for which he obtained a value of 73 dynes per centimeter. Later in 1912 Ferguson (6) amplified this work by photographing the drop. He obtained a value of 73.4 dynes per centimeter at 11°C. The most complete work on the forms assumed by drops of liquids hanging from a plane surface

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[1] Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

and by drops resting on a plane surface which the liquid does not wet, has been carried out by Bashforth and Adams (2).

The capillary-rise method has the simplest mathematical derivation and therefore probably has given the most accurate results. The theory in its simplest form assumes only that the liquid wets the tube perfectly, i.e., has a contact angle of zero, an assumption which seems to be justified for water and most of the common organic liquids against glass. The experimental difficulties, however, are large, for it is by no means easy to obtain truly uniform tubes, and to keep them absolutely clean. It is furthermore difficult to measure the height accurately. The method, therefore, is not suitable for rapid or routine work. Modifications of this method have been used by Ferguson (7), Kiplinger (14), and Jaeger (13).

The method of adhesion plates and rings has been used with many variations. The force necessary to draw a horizontal plate, a vertical plate, or a horizontal bar from a liquid surface furnishes the basis for several methods. The two most commonly used instruments are the du Noüy tensiometer (5) and the torsion balance developed by Lenard, Dallwitz-Wegener, and Zachminn (16).

A rough approximation for the surface tension by the du Noüy method can be made as follows: the force necessary to break the ring away from the surface is equal to the surface tension of the liquid multiplied by twice the length of the loop, since two films of water are broken away, one on each side of the ring, or, in another form,

$$\gamma = \frac{P}{4\pi r}$$

where P is the breaking force on the ring in dynes and r is the radius of the ring in centimeters. This is at best only an approximation. For this equation to hold, the two surfaces on each side of the wire must be vertical at the point of breaking, the ring must be truly horizontal, and the column of liquid held up directly under the wire must be negligible. The mean radii of the two surfaces would have to be the same as the mean radius of the loop. For large loops, several centimeters in diameter, made from wire of very small cross section, these conditions are approached quite closely. However, for small loops, such as used in the du Noüy instrument, none of these conditions is perfectly realized. The surfaces are probably never perpendicular, and a fair quantity of liquid is actually supported under the wire itself. Dorsey (4) has given an excellent discussion of this method and its faults.

Tichanowsky (26), Cantor (3), and Lenard (17) have developed better equations for this case, but they still may give results several per cent in error. Harkins, Young, and Cheng (11) have attempted a standardization of this method by comparing the values obtained in using rings of different sizes with numerous liquids whose surface tension was accurately known. Their equation is:

$$\gamma = \frac{P}{4\pi r} F$$

where F is a correction factor, which they discovered depended only on R, the radius of the ring, and r, the radius of the wire itself. They claim an accuracy of ± 1 per cent, and give tables of F for various values of R/r.

The du Noüy tensiometer is very rapid and easy to use, and the results are easily reproducible. It has proved of outstanding value in recording the change of surface tension in a liquid where adsorption is taking place in the surface (solutions of capillary-active substances).

The drop-weight method is also a very common method for the determination of surface tension. It consists in weighing drops falling from the end of a vertical tube. Although the mathematical theory has not been completely worked out, the method has been widely used because of its simplicity and rapidity.

The actual mechanism of fall is very complex, as will be demonstrated. Briefly, the drop grows larger and longer on the end of the dropping tip; then instability sets in, and a large part of the drop breaks off, leaving a narrow stem attached to the remainder of the drop. At the moment when the drop actually breaks off, it is nearly spherical. The narrow neck then breaks off from the main body of the liquid, and spontaneously constricts at one or more points, as revealed by the high-speed motion picture, followed by the formation of one or more droplets. A single secondary drop has been observed by early workers.

Guthrie (9) in 1863 observed the influence on the size of his drop of rate of fall, temperature, composition of the drop, and the sphere from which he caused all his drops to fall. He observed the formation of a secondary drop which "apparently" was projected up from the upper surface of the drop. Tate (25) in 1864 postulated that "other things being equal, the weight of a drop of liquid is proportional to the diameter of the tube from which it is formed," without himself actually going so far as to state that the weight of a drop falling from a tip is equal to the "circumference of the tip × surface tension," or $w = 2\pi r\gamma$, which today quite commonly is called Tate's law. It assumes that the entire drop falls off from the tip, while actually only about 60 per cent of it does. Worthington (27) also observed a secondary drop, and concluded quite correctly that "the secondary drop is due to the spontaneous segmentation of the cylindrical neck of liquid, which joins the upper and lower portion up to the last moment before complete separation takes place, and that it is the same phenomenon that was first observed by Plateau (22) in his experiments on mercury." Guye and Perrot (10) in a comprehensive experimental treatise studied the shapes of dynamic drops. It should be noted that part of this work was done with a motion picture camera taking sixteen pictures per second. They, too, observed the formation of a secondary drop. However, they were of the opinion that the second drop forms from the stem immediately when the first drop falls, and also that just prior to the falling off of the main drop there is a visible oscillation of the surface of the drop. Morgan (21) and his coworkers found "that under certain definite conditions the drop weights of liquids dropping from any one tip are proportional to their surface tensions at the same temperature." The mathematical theory involves, as Adam (1) points out, two points: the size of the drop at the point where instability sets in, and the fraction of the drop which falls. The mathematical theory has been incompletely worked out, but Lohnstein's (20) work is the most thorough. He predicted that the fraction which breaks off is a function of r/a, where r is the radius of the tip, and a is the square root of the capillary constant. Harkins (12) found, as Lohnstein predicted, that the weight of the drop which falls is proportional to r/a and also to another dimensionless ratio $r/V^{1/3}$, where V is the volume of the drop which falls. He verified this assumption for three different organic liquids and for water. Harkins and others have pointed out the necessity of using a very accurately formed tip,—one that is truly flat and circular and with truly sharp edges. A common form is the Traube stalagmometer, which was used in this work. According to Traube's method the number of drops of water falling in a given volume is counted, and then for an unknown liquid the number of drops is counted which fall from the same volume. The surface tensions are presumed to be given in this ratio:

$$\frac{\gamma_A}{\gamma_B} = \frac{N_B \rho_A}{N_A \rho_B}$$

where N is the number of drops and ρ is the density of the liquid. It is a rough approximation only.

Adam (1) has shown that the assumption that the correction factor depends only on r/a and $r/V^{1/3}$ is equivalent to assuming that the fraction of drops of similar shapes which breaks away is the same for all liquids. Adam further notes that if "the verification of this for four different liquid-air interfaces is thought an insufficient basis for measuring the surface tension of an unknown liquid, it may be possible to make a direct photographic test, whether the fraction breaking away is normal for that liquid. It seems unlikely that any error can arise except in case of liquids of high viscosity."

The method of vibrating jets has been developed by Rayleigh (23) and by Bohr (24). If a liquid is forced through an elliptical or triangular opening, it will tend to assume a spherical cross section and will thus vibrate about a spherical cross section as its form of equilibrium.

The other method which is of interest in this work is the measurement of oscillating drops. Rayleigh (23) developed by dimensional reasoning an equation for the time of infinitely small vibrations of an elliptical drop about its equilibrium shape, a sphere.

$$\gamma = \frac{3}{8}\pi P t^2$$

where P = weight of a drop in grams, t = oscillations per second, and γ = dynes per centimeter. For observing this phenomenon, Rayleigh used an oscillating spark which cast the shadow of the drops on an opaque screen, and by varying the length of the time between the drop fall and the spark flash, he was able to record the successive shapes of the drops. Neither Rayleigh nor Lenard (18) was able to observe the successive changes in shape of a single drop for the duration of its fall. The successive changes in shape observed by them correspond to a series of drops. They observed the successive shapes of different drops at progressive time intervals. Lenard continued this work, timing the fall of the drops so that a falling drop itself interrupted the current and caused the spark to illuminate the next falling drop. When photographic pictures were taken the shortest interval between two pictures was 0.01 second.

Kutter (15) measured drop oscillations by still another method. He found that the depth to which a drop falls under the surface of another liquid of equal density does not proportionately increase with the height of fall, but exhibits a periodic function of the falling time. The drops which strike the surface with their long axes parallel to the water do not sink to as great a depth as drops which strike the surface with their long axes vertical to the surface. Out of the falling time and the maximum depth reached by any one drop the period of oscillation was calculated. The surface tension was calculated by the Rayleigh formula. His experiments gave an average of 7378 mg. per millimeter at 18°C., which in the conventional units is 72.4 dynes per centimeter. His experiments showed that the oscillation is not uniform but that there is a decided difference between the stages maximum–minimum and minimum–maximum, which proves that the main oscillation is partly blurred by secondary oscillations. Lenard undoubtedly encountered his main difficulties here, since he was able to measure only one oscillation.

The experimental part of this research consisted of taking high-speed motion pictures of the drop-weight and ring methods of surface-tension measurements.

A series of pictures using distilled water at different times of drop formation, pictures of nitrobenzene, benzene, glycerol, and of solutions containing capillary-active substances, as for example triethanolamine oleate, were taken. Pictures of the ring method were taken using water, glycerol, and water containing small amounts of triethanolamine oleate. The series referring to the drop-weight method was run at a speed of 1200 exposures per second; those referring to the ring method at 600 exposures per second.

The electrical and photographic apparatus that was used in this investigation may be briefly described as follows: Since the exact moment at which a drop will break off is rather uncertain, it was necessary to operate the camera for as long a time interval as possible. This was accomplished by mounting a camera of the continuously-moving-film type on its side in order that a long, narrow picture could be taken. In this manner several exposures (four or five) could be taken on a single 35-mm. frame, thus materially increasing the duration of elapsed time covered by one film. In order to obtain a satisfactory slow-motion picture of the breaking-off process, the pictures were taken at the rate of 1200 per second, this frequency being secured from a commutator driven by a synchronous motor. The film strips bearing the important exposures were then rephotographed in consecutive order in the normal vertical position on a standard sized 35-mm. film. From this positive prints were transferred and edited on 16-mm. film.

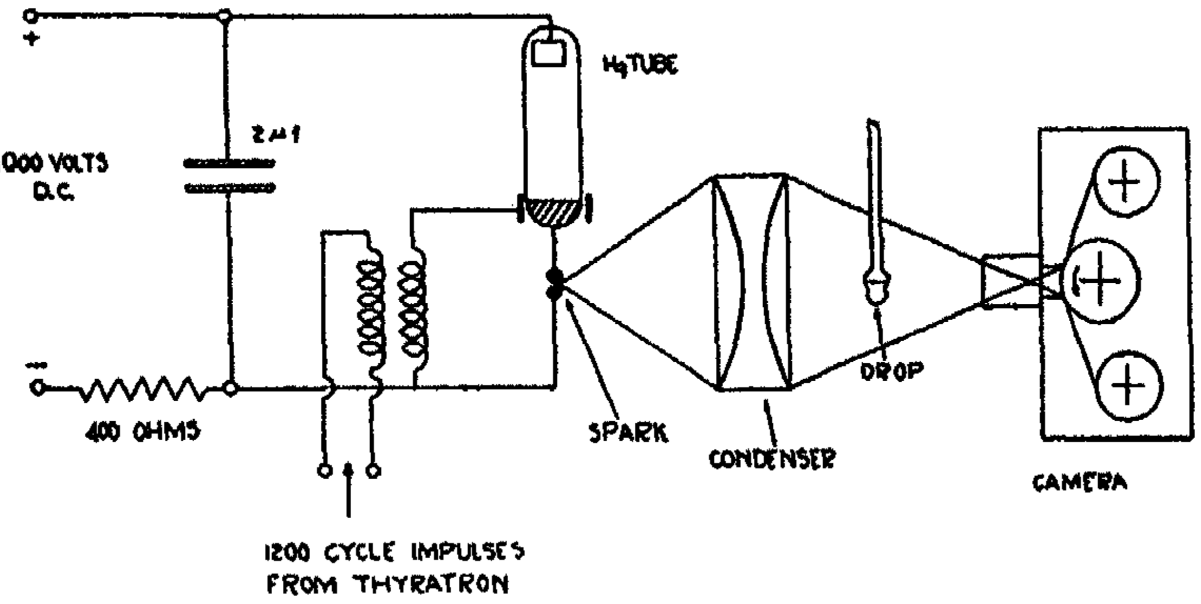

FIG. 1. Schematic diagram of high-speed camera set-up

The pictures of the drops are taken by transmitted light as silhouettes which give the outline of the liquid. A spark in air between brass electrodes spaced about one-eighth of an inch apart was used as a point source of stroboscopic light for exposing the photographs. The light was collected by a double-element condenser (10 in. diameter, 10 in. focal length) and directed into the lens of the camera. The object being photographed was located between the condenser and the lens.

Control of the starting of the spark was accomplished by using a pool-type, mercury-arc control tube[2] in series with the spark gap and the discharge condenser, as shown in figure 1. Between flashes the mercury tube is non-conducting and the 2-microfarad condenser is charged to about 1000 volts from the power supply through the 400-ohm resistor. An impulse of voltage (about 30,000 volts) on the external starting band of the mercury tube causes a spot to be formed on the cathode and allows the 2-microfarad condenser to discharge violently into the spark gap. The mercury tube, besides acting as a switch for turning on the circuit, acts as a rectifier and prevents oscillation of the current through the gap. The impulses of voltage were produced by a thyratron impulse amplifier such as is described in the previously mentioned article.

Special precautions were taken to insure the existence of a saturated atmosphere about the drops, particularly in the cases where the drops were suspended for any length of time, in order to avoid evaporation. The apparatus was firmly insulated against vibration. Needless to say, special precautions were taken to have all parts of the instruments scrupulously clean.

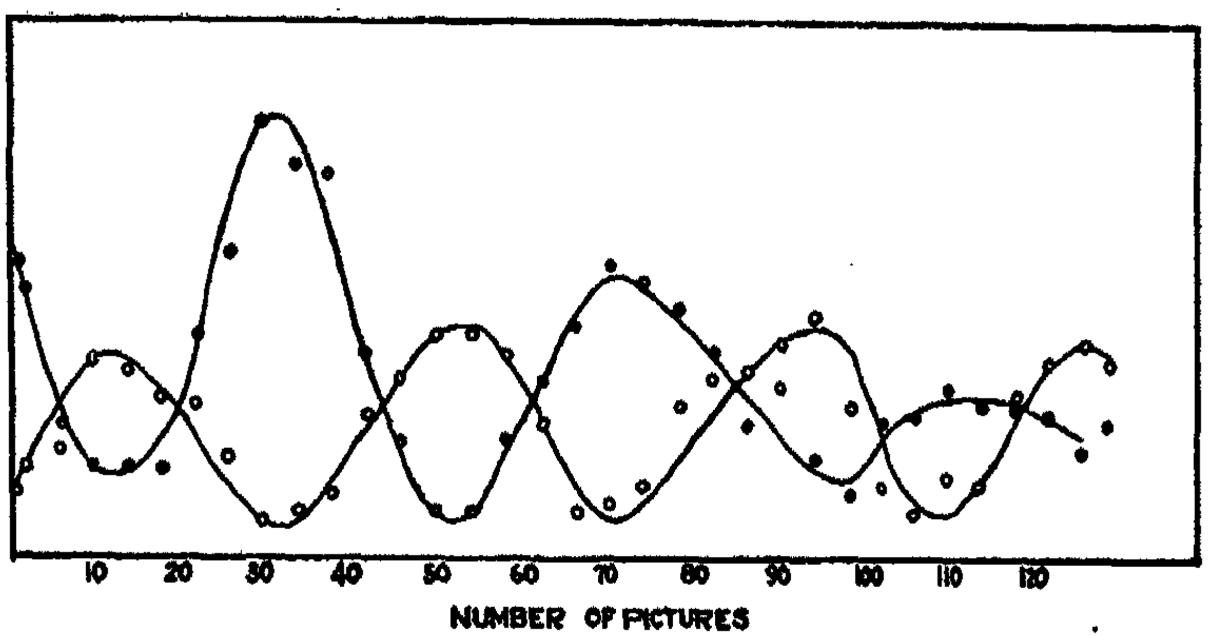

FIG. 2a. Oscillation of benzene drop. 960 pictures per second. Diameter of drop = 0.458 cm. ●, height; ○, width.

The mechanism of the formation of a drop falling off a tip can be described as follows: The drop grows longer and larger on the end of the tip. Instability sets in and a neck forms between the part of the drop remaining on the tip and the part that eventually falls off. This neck grows longer and narrower until the drop finally separates. At this point the drop is slightly ellipsoidal with the long axis vertical. The neck of liquid connecting the two parts of the drop narrows down to a point at the point of

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[2] Such as is described in Electrical Engineering, February, 1935, p. 149.

separation (figure 3). The main drop then separates and, owing to the slight tension caused by attachment to the stem, it flattens out somewhat immediately after separation takes place. The main oscillation is marred slightly by secondary oscillations set up at the same time, so that the drop assumes somewhat irregular shapes, though the main effect is a single oscillation about its form of equilibrium, a sphere. A graph showing the variation of the width and length of the drop as it falls is shown in figure 2. The effect of the secondary oscillations can be seen clearly.

The neck of remaining liquid segments at first into a series of nearly equal-sized nodes as shown in figure 4. In all cases observed, the stem of water coalesces rapidly into *one* drop. Sometimes, however, a third drop is projected bodily from the secondary drop with considerable force, in some instances even rising as high as the part of the drop remaining on the tip, as shown in figure 5. In the case of benzene, owing to the long stem formed, the node formation is exceptionally well pronounced, and the nodes finally break up into one to five drops which follow the main drop (figure 6). The nitrobenzene stem, which is somewhat shorter than the benzene stem, breaks up into three drops (figure 7). These drops fall together a short time after forming and then, contrary to what one might expect, spring apart and continue to fall as three separate drops. This phenomenon might be explained by assuming that electric charges are set up on the surfaces of each droplet which would cause the droplets to be repelled when coming in close contact. Reference should be made here to the work of Lenard (19) on the electric charges of falling drops of water.

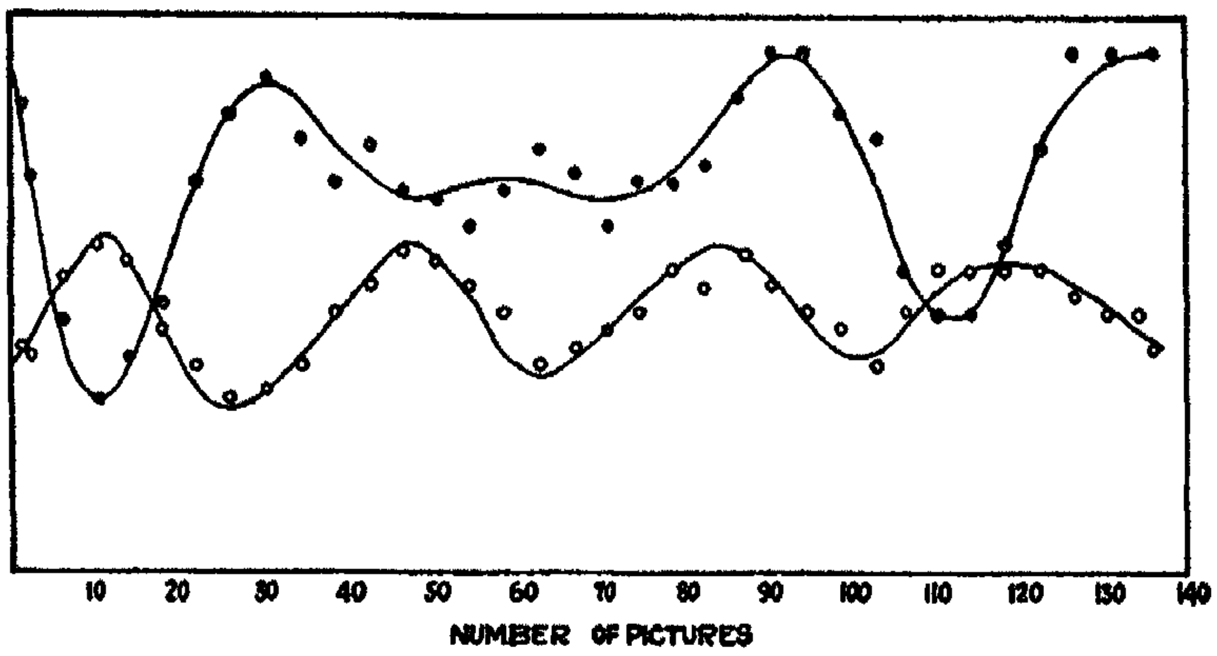
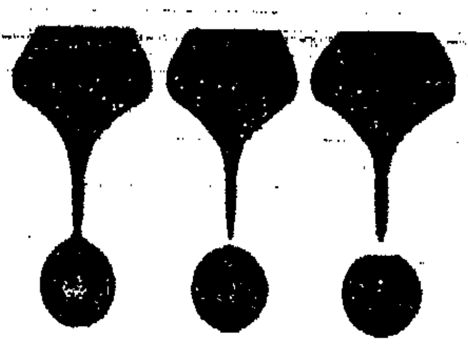


FIG. 2b. Oscillation of water drop, with surface-active substance added. 960 pictures per second. Diameter of drop = 0.476 cm. ●, height; ○, width.

A further suggestion of the presence of electric charges on the surface of the small drops (water) is observed from one of the motion pictures.



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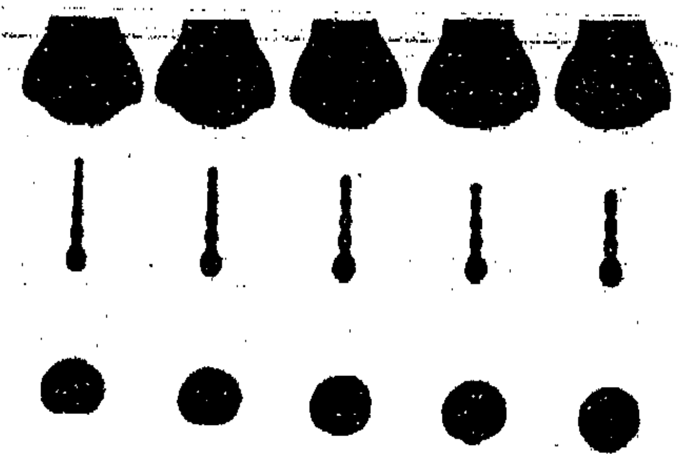

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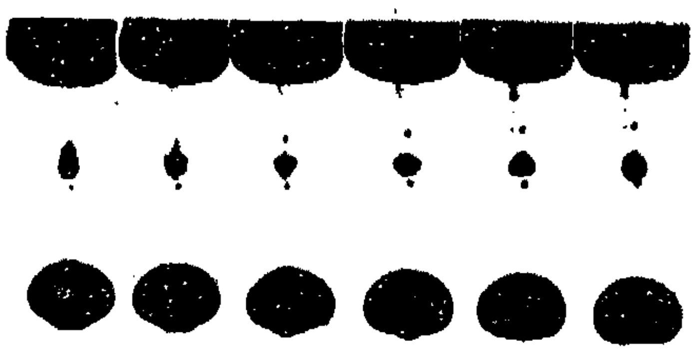

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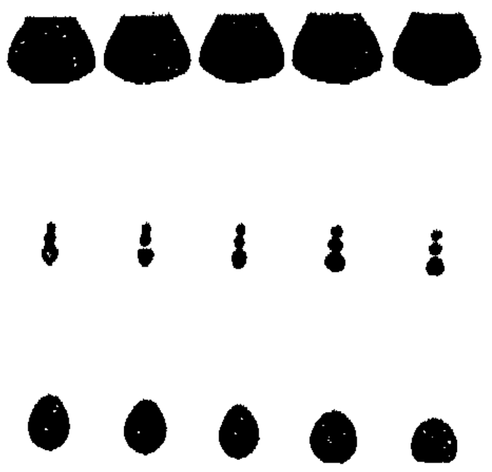

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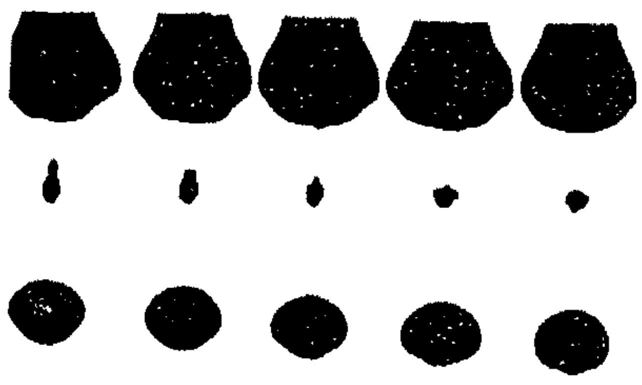

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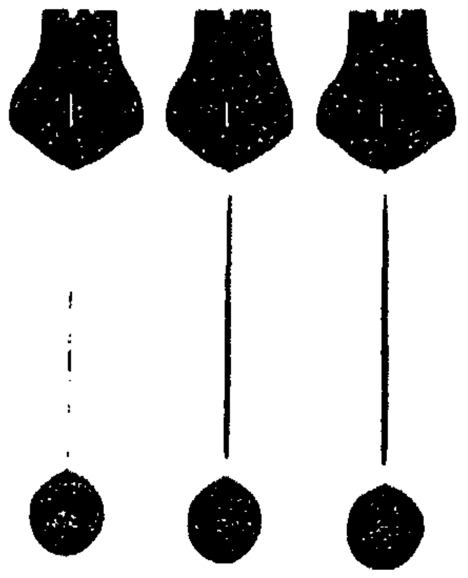

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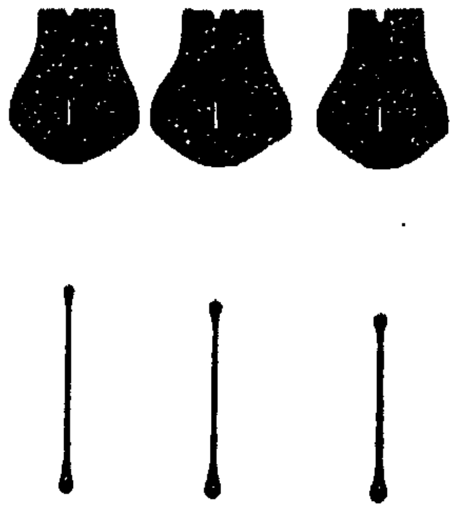

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FIG. 3. Water
FIG. 5. Water
FIG. 7. Nitrobenzene
FIG. 9. Glycerol

FIG. 4. Nitrobenzene
FIG. 6. Benzene
FIG. 8. Water
FIG. 10. Glycerol

The third drop, which is a very tiny one, is projected upward with such violence that it bumps into the residual drop remaining on the tip and very noticeably bounces back off the surface of the residual drop without joining it. This same effect may be noticed with secondary drops of benzene, for it can very easily be seen from the motion picture that the oscillation of the third and fourth droplets is greatly influenced by the presence of the other drops (figure 6). The third and fourth drops flatten out a great deal more than the others, and while one might expect that the drops would coalesce, they remain definitely apart for their entire period of fall.

In the case of water, the third drop is pinched off from the surface of the second drop at the moment when the column of liquid has coalesced into one drop. One can observe the small drop standing partly out of the surface, having never been quite absorbed by the larger one (figure 5). It is this tiny sphere which is projected upward with violence, probably owing to the surface tension forces operating on the large drop and causing oscillation. The tiny sphere before mentioned is not always projected up from the surface, but quite frequently joins the larger drop permanently (figure 8).

The secondary drop in most cases vibrates very violently and at first somewhat irregularly.

In the case of glycerol, which is a highly viscous liquid, the neck forms as above, but remains attached to the main drop for a much greater length of time, forming at the point of breaking a very fine thread, several times as long as the diameter of the drop (figure 9). Instead of segmenting as the other liquids do, the thread assumes a dumb-bell shape with the drops on each end growing larger and approaching each other very rapidly, until one drop is formed (figure 10). The drop at the lower end falls very slowly in comparison to the rate at which the one at the upper end approaches the lower one, owing to surface-tension forces acting with gravity on the upper end of the dumb-bell being formed and opposing gravity on the lower end.

From the results of drop calculations and measurements, the drops were arranged in order of the size of the main drop. While the correlation was not absolutely perfect, it can be generally said that the drops in all cases observed decrease in size with increase in the time of drop formation, being largest when the drop is formed fastest.

The stem length is the length of the cylindrical stem connecting the two parts of the original drop at the time when the stem separates from the residual part of the drop. This length is easily measured and correlation is perfect. Benzene, forming rapidly, has the longest stem length. Nitrobenzene comes next, followed by the rapidly falling water with the surface-active substance added. Pure water, which forms rapidly, is still shorter, and following it, the stem length decreases in general with increase in time of formation. The surface-active solutions show a marked progressive decrease in the stem length.

Of interest here is the fact that while the surface tension of the solutions of water containing capillary-active substances was considerably less than that of pure water, the stem lengths were the shortest observed, whereas in the case of pure liquids of low surface tension the stem lengths increased with decreasing surface tension.

Although considerably more experimental work will have to be done to be in a position to offer a satisfactory explanation for this discrepancy in the discovered correlation of stem lengths to surface tension, the following preliminary explanation might be considered. Whereas in a true liquid the molecular composition of the surface layer is the same as the interior of the liquid, in the case of liquids containing capillary-active substances there is a definite concentration and orientation of the molecules of said substance in the surface. This orientation undoubtedly has some bearing on the elastic properties of the surface layer, making it less elastic and offering a greater resistance to distortion. Therefore, it may be assumed that the stem breaks off more rapidly than is the case with true liquids, where free movement of the molecules should permit further elongation.

TABLE 1

LIQUID	TEMPERATURE	VISCOSITY η	SURFACE TENSION γ
	°C.	*centipoises*	*dynes per cm.*
Water	20	1.008	72.75
Glycerol	30	881.0	63.0 (20°C.)
Nitrobenzene	20	2.013	43.9
Benzene	20	0.647	28.88

We have calculated the volumes of the secondary drops and expressed them in per cents of the volumes of the large drops. For water, the volumes of the secondary drops average 3.12 per cent of the main-drop volumes. The volume of the secondary drop formed from the dumb-bell-shaped stem of glycerol is 5.92 per cent of the main-drop volume. The volume of the secondary drop of nitrobenzene is about 8.45 per cent of the main-drop volume, and the volume of the secondary drops of benzene averages 12.5 per cent of the main-drop volume.

Here again water containing capillary-active substances shows a discrepancy, since the rapidly forming drop gives a slightly higher volume percentage for the secondary drop than does pure water, the more slowly formed ones a smaller volume. This phenomenon stands in perfect accord, however, with the stem length discussed above.

The results of the four cases so far observed seem to demonstrate that the per cent drop volume of the secondary droplet of pure liquids increases with decreasing surface tension. It furthermore shows that the viscosity of the liquid under consideration seems to have no influence on this effect (see table 1).

CALCULATIONS OF SURFACE TENSION FROM SECONDARY-DROP OSCILLATIONS

This method permits, for the first time, the measurement of surface-tension values by observing the frequency of oscillation of one *single* drop during its *entire* fall. Furthermore, it permits the measurements of surface tension by observing the oscillation frequency of secondary droplets formed. The frequency of these latter observations is decidedly higher than the one with the primary drop. The results obtained with pure liquids gave satisfactory values.

The method furnishes, furthermore, a new tool for the determination of adsorption effects on very recently formed surfaces, which is of outstanding importance in connection with the study of solutions containing capillary-active substances. These observations seem to show that a considerable time is necessary to obtain equilibrium. At least in the majority of cases some adsorption has taken place on the drop surface immediately after forming—the drop oscillation having been measured less than one-tenth of a second after the surface had been freshly formed—but a considerable time has to elapse before perfect equilibrium is obtained.

The ring method

A series of high-speed motion pictures of the ring method were taken at a speed of 600 exposures per second, using distilled water, water to which a capillary-active substance had been added (triethanolamine oleate), and glycerol. The method as revealed by the motion picture camera can be described as follows.

The ring as it is raised pulls up with it a considerable volume of water. At the point of maximum tension the surface of the liquid on the inside of the ring is slightly concave, with the surface at the edge of the ring rather sharply bending up to the ring. In no case are the sides truly perpendicular, which theoretically would be necessary for the measurement of the true value of the surface tension (figure 11). As the ring is pulled further, the surface of the main body of the liquid starts to become more concave, showing an approximate hyperbolic curve; at the same time the surface between the ring drops down considerably as can be seen by the light reflection in figure 12. As the ring is raised further, a conical film of liquid forms below the ring holding up the remainder of the liquid above the surface. This inverted cone then tends to assume its equilibrium shape, a horizontal film, and in doing so imparts to the remainder of the liquid above the surface of the water a vertical force which causes this column of water actually to shoot above the level of the ring (figure 13). The force which causes the column of liquid to be forced up above the level of the ring is sufficient to project upwards several small droplets—in the case of water—which rise nearly to the height of the bar which raises the ring.

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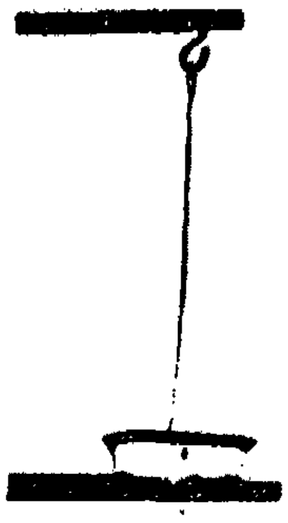

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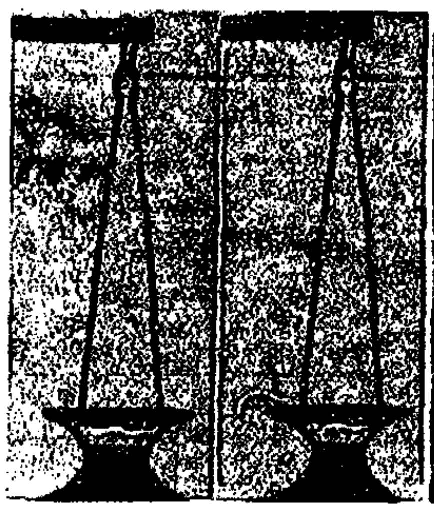

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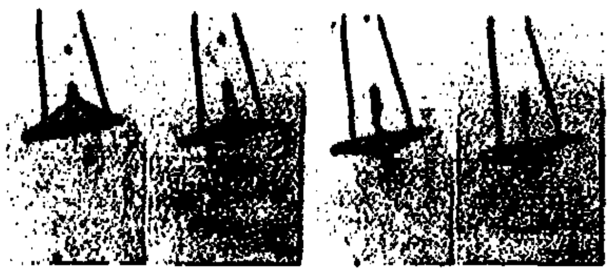

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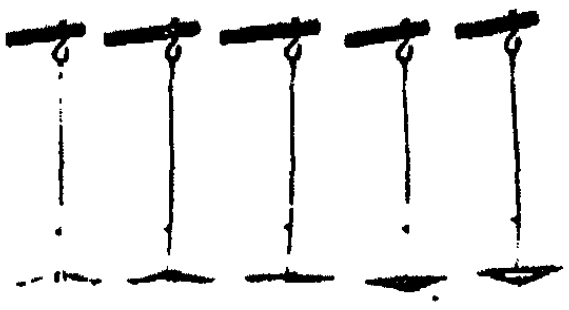

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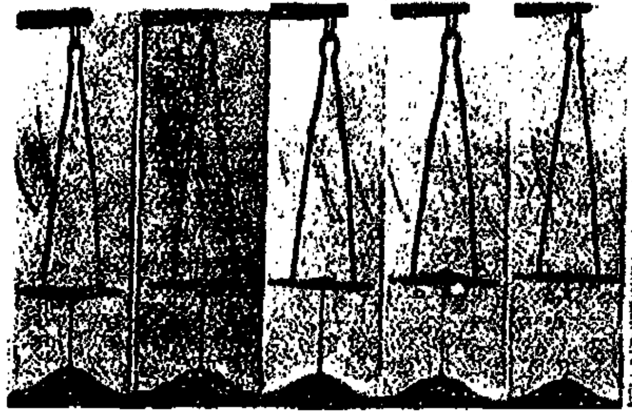

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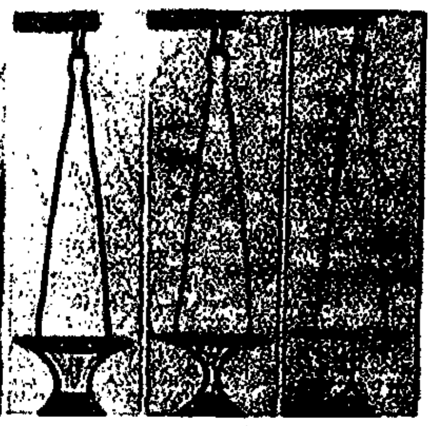

Fig. 11. Triethanolamine oleate
Fig. 12. Water
Fig. 13. Water
Fig. 14. Water
Fig. 15. Triethanolamine oleate
Fig. 16. Glycerol
Fig. 17. Glycerol

This column in the case of pure water and of water containing a surface-active substance then falls back and breaks away from the film of liquid left on the ring, finally collapsing into the main body of the liquid. The lamella of water remaining on the ring oscillates rapidly up and down until the bar to which the ring is attached comes to a stop. Then the film shoots up and forms a short column of liquid, which breaks up into several drops as shown in figure 14. This film oscillation can be better observed in figure 15, which shows water containing 0.01 per cent of triethanolamine oleate. For water 66.3 oscillations per second were observed, while the pictures taken with the above-mentioned solution showed 49 and 50 oscillations per second. The frequency was constant over the entire period which was observed.

If one assumes that the restoring force on the oscillating film is due solely to the magnitude of the surface tension on the film—a good assumption, if the film is very thin and if the viscosity is not great—and also assumes that the mass of the liquid forming the films is the same, then by simple proportion, the surface tension of the film can be calculated. Using the correct value for water of 72.8 dynes per centimeter, the surface tension of the surface-active film would be

$$\gamma = 72.8 \times \frac{50}{66.3} = 54.8$$

which has been ascertained to be the correct value for this liquid. So far as could be ascertained the oscillation of a thin film of liquid has never before been observed, nor used as a method of surface-tension determination.

Glycerol showed another interesting phenomenon. The initial stages of the breaking away were the same as with water, but a thin thread forms very rapidly, connecting the film left on the ring and the surface of the glycerol. As before, the film on the ring imparted a force on the thread of liquid which caused it to shoot up above the level of the ring (picture preceding the first picture on figure 16). The thread sprang back again, but instead of breaking, it again rose very slightly above the level of the ring. At this point it parted in several places along its length and formed several tiny drops which fell back into the main body of the liquid. Owing to the high viscosity there was no film oscillation to be observed on the ring (figure 16).

Another feature of interest is the regular streaks which appear on the conical film of glycerol below the ring before it forms the thread. This seems to show some peculiar orientation of the liquid film under tension.

One would normally not expect that homogeneous liquids would show orientation under any conditions. The orientation of gel structures under tension has long been observed, and the gels are assumed to have a more or less fixed structure which under tension aligns in a definite orientation. These pictures possibly indicate that in the case of viscous liquids there is some alignment which results in the appearance of a streaked surface of the film under tension. It is hoped that further observations of this sort will throw more light on the structure of liquids (figure 17).

SUMMARY

1. As a first attempt to apply the high-speed motion picture camera to the study of physicochemical or colloid-chemical problems, its application to the study of the mechanism of the drop-weight and ring methods in the measurement of surface tension is described.

2. The successive steps in the formation of drops, as revealed by this technique, are enumerated.

3. The formation of a stem following the main drop has been observed; the segmentation of the stem and the formation of one or more secondary drops is discussed.

4. In a pure non-viscous liquid, it has been shown that the size of the main drop decreases with increase in time of drop formation.

5. For pure non-viscous liquids, the length of the stem increases with decrease in surface tension of the liquid. The influence of viscous liquids on the stem is also referred to.

6. The size of the secondary drop, figured in per cent of the main drop, increases materially with liquids of decreasing surface tension.

7. For water containing capillary-active substances, the length of the stem is shorter than that of the pure water. An explanation for this discrepancy is offered.

8. The measurement of the oscillations of the secondary drops is described as a new means of studying adsorption effects in freshly formed surfaces.

9. The mechanism of the ring method for the determination of surface tension is described and demonstrated.

10. The oscillation of a thin film of liquid is demonstrated, and a possible new method for the determination of surface tension using extremely thin lamellae of liquid is indicated.

11. Interesting observations of the influence of viscosity in the mechanism of the ring method are described.

12. The stroboscopic analysis of the phenomena appearing in connection with surface-tension measurements by the drop-fall and the ring method show motions of such a high degree of complexity as to suggest that neither of these methods is ideal from the standpoint of accurately determining surface tension.

13. To obtain comparable data with solutions of capillary-active substances it seems indispensable to indicate the time of drop formation or rest period of the liquid surface when determining surface tension with the methods discussed.

We wish to express our great indebtedness to Dr. Vannevar Bush, Dean of Engineering, for the interest he has taken in this work and for the facilities he has placed at our disposal.

Our special thanks are due to the Research Associates of the Massachusetts Institute of Technology for a grant-in-aid which enabled us to carry out this project.

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UNIMOLECULAR FILMS OF NERVE PROTEINS[1]

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Since the modern developments in the theory of protein structure little work has been done on the characterization of the individual proteins of nerve and on the significance of the colloidal properties of these proteins in determining nerve structure and function. The mere classification of the various nerve proteins is still in considerable doubt and, with the possible exception of the so-called neurokeratin, the localization of these proteins in the nerve axon is altogether unknown. Recent experiments on living axons by means of polarized light have shown that the proteins of the axon sheath are organized in a manner quite different from those in the axis cylinder, and there is some evidence that there may be considerable difference in the molecular architecture of these various proteins. Obviously before the ultimate question of the rôle of these protein structures in nerve function can be answered, these preliminary points must be settled.

The present studies have been designed to aid in the characterization of certain of the nerve protein fractions now recognized. Comparison of the behavior of films of these proteins with films of various other proteins not only yields information of value for an interpretation of nerve structure, but furnishes additional facts for which the general theory of protein films must account.

MATERIALS AND METHODS

The nerve proteins were prepared from the leg and claw nerves of lobsters, according to the method described by Schmitt and Bear (9, 10). The finely cut nerve bits were successively extracted in neutral saline, borate buffer of pH 9 and 11, and in $N/100$ sodium hydroxide. In the fraction previously called neurostromin we now recognize three subdivisions: one coming out in $N/10$ sodium hydroxide and exhausted with successive changes of alkali, another obtained by relatively brief extraction with $N/2$ sodium hydroxide, and likewise diminishing in quantity in repeated extractions, and a third, removed by $N/2$ alkali only after twelve

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[1] Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

to eighteen hours of reaction. In $N/2$ sodium hydroxide the nerve shreds eventually swell and soften, so that violent shaking suffices to convert previously recognizable shreds into a strongly turbid solution. The main bulk of the nerve vanishes at this stage; strong centrifuging yields only a very small residue quite different from the original nerve fibers. The protein extracted in $N/10$ sodium hydroxide has a flocculation zone beginning at pH 5.5 with a maximum around pH 4.5, as determined turbidimetrically in acetate buffer. The first fraction coming out in $N/2$ sodium hydroxide is also precipitated at pH 4.5 by acetic acid. The fraction obtained after long standing in $N/2$ sodium hydroxide is not precipitated under the same conditions even with prolonged centrifuging. For the present film work only the fractions removed in $N/10$ sodium hydroxide and by brief extraction with $N/2$ sodium hydroxide were used, because of the instability of the fractions obtained with weaker alkalinity. Both preparations were purified by thrice repeated precipitation with acetic acid at pH 4.5. The precipitates were fairly readily redissolved in Sørensen borate buffer of pH 9, yielding stable, slightly opalescent solutions, especially if the precaution of washing out the acetate with a little borate is observed. The final preparation was analyzed for nitrogen by micro-Kjeldahl, the weight of protein being taken as 6.6 times the amount of nitrogen.

The egg albumin used for comparison was recrystallized four times according to the method of Sørensen as described by Morrow (8), and dialyzed in the cold until barium chloride gave no test for sulfate. The protein concentration was determined by drying to constant weight.

Force-area measurements were made with the Adam modification of the Langmuir trough. Surface potentials were measured by a modification of the vibrating condenser method of Yamins and Zisman (11). The film was applied by forcing the solution from a microburet, the capillary tip of which was held just inside the surface. By a rack and pinion stand the tip is pulled up slightly after touching the surface, to minimize the possibility of protein going into the bulk of the subsolution.

GENERAL CONDITIONS OF FILM SPREADING

Three considerations arising from the method of preparation of the nerve proteins may be of significance with regard to their spreading as monomolecular layers. The first is the possibility that nucleic acid from the nuclei abundant in nerve sheaths is dissolved in these extractions. Levene (7) obtained purine bases from the ammonium chloride extract of brain, as well as from a dilute alkali extract. However, Gorter, Ormondt, and Meijer (4) have shown that the addition of nucleic acid to protein solutions has no effect, at least upon area per milligram extrapolated to zero pressure.

The second consideration is the unknown partition of the lipoids between the different fractions. Although lobster peripheral nerve contains relatively less lipoid than does vertebrate medullated nerve, Schmitt, Bear, and Clark (10) obtained x-ray diffraction patterns characteristic of lipoids even in nerve protein fibers spun into and extensively extracted with alcohol. Apparently the union is very tenacious; just how the properties characteristic of large arrays of short amino acid residues are modified by hydrocarbon or sterol groups, themselves capable of forming films, remains to be determined.

The third consideration is the possibility of progressive hydrolysis and denaturation of the normal nerve proteins by the strong alkali solutions employed. It must be admitted that the extraction agents bring about permanent changes; for instance, the $N/10$ and first $N/2$ sodium hydroxide fractions after precipitation in acetic acid may be redissolved in weakly alkaline buffer solution of pH 9. However, the fact that at each of these stages the extractions go to completion rather than progressing steadily, seems to indicate that a definite portion of the large structure protein unit is being removed in each case, rather than that an indefinite and generalized attack on all the linkages is occurring.

Of interest in this connection is the fact that upon $N/300$ acetate buffer of pH 4.7 the $N/10$ sodium hydroxide extract forms elastic patches, whereas the $N/2$ extract gives fluid films. This property is observed by the movement of talc particles upon the surface under the influence of gentle puffs of air from a medicine dropper. The validity of interpreting this as indicating a difference in the particle size of the two protein fractions is rendered doubtful by the fact that on dilute hydrochloric acid of pH 2.5 the $N/10$ sodium hydroxide extract forms fluid films which become elastic at a pressure less than 1 dyne per centimeter. A difference in the constitution of the two fractions is more probably responsible for this difference in adhesion.

EXPERIMENTAL RESULTS

After the monomolecular layer of protein has been spread, either by its intrinsic spreading tendency or by the admixture of alcohol (3), it can be further studied by compression to smaller areas. Films not already elastic become so upon compression, and with increasing pressure become quite rigid.

The manner of compression has a marked influence on the type of curve obtained. At each step of compression to smaller areas the pressure rises quickly to a maximum, then decreases to a steady value higher than the previous equilibrium value. The magnitude of this pressure readjustment is shown in figure 1, which presents an experiment in which special care was taken to obtain complete equilibration. The small curves extending out to the side of each equilibration step having time as abscissae give the course of this adjustment. The irregularities imposed upon the equilibration curves at high pressures are probably due to the rigidity of the film and the difficulty of adjusting the torsion system to an exact balance. This experiment shows several other features: (1) The approximately linear portion of the equilibrium force–area curves which, extrapolated to zero pressure, is used as a quantitative measure of spreading area, following the convention of Gorter. (2) At low areas the increase of pressure with decrease in area is less rapid than in the linear portion of the curve. Similar effects have been observed also with casein and myosin. This region we shall refer to as the plateau. (3) Both initial and equilibrium pressure values undergo a final and rapid rise at very small areas. This apparently corresponds to the final close-packed condensed state of molecules with long hydrocarbon chains, such as fatty acids. Other experiments show rapid increases in the equilibrium pressure at lower areas

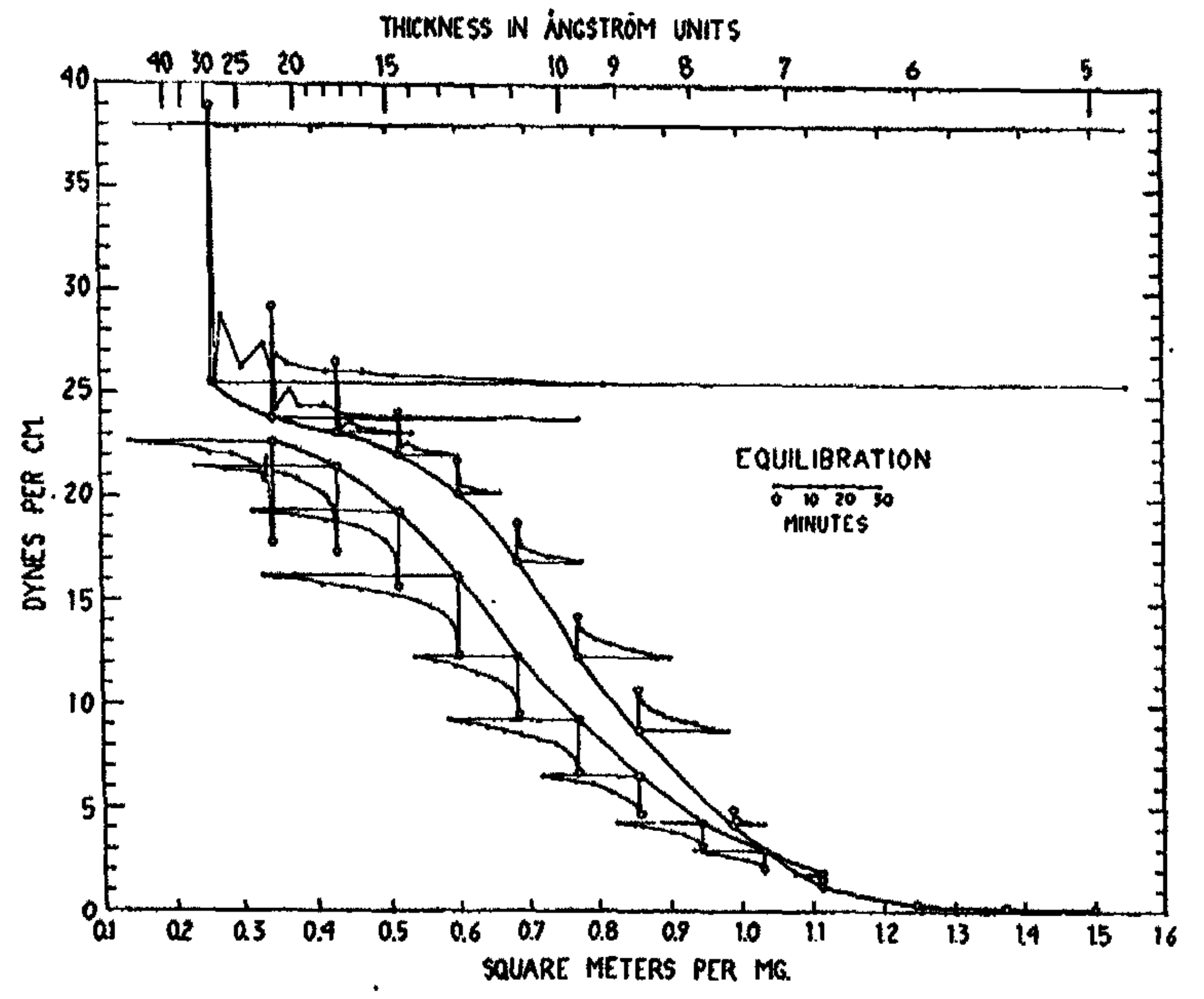

FIG. 1. Egg albumin on $N/300$ acetate buffer, pH 4.6. Unrestricted spreading at 1.5 m.^{2} per milligram. Ordinates, surface pressure; abscissae, for open circles, area per milligram of protein; for small points, time after obtaining initial pressure values. The open circles give initial and equilibrium pressure values at each area. The small points show the course in time of the corresponding equilibration. Thickness is calculated from the specific volume (0.75 cc. per gram) for dissolved protein.

than those of the plateau. (4) An equilibration takes place in the opposite sense on reëxpanding; this must be the reversal of the readjustments made in compressing the film. (5) The compression is reversible throughout the range of areas down to 0.25 m.^{2} per milligram, if equilibration is allowed. Further compression brings about a complete buckling of the film, properly comparable to the collapse of a fatty acid film, and irreversible, as noted by Devaux (2). We find, as did he, a tendency for the collapsed film to form fibers. These fibers when transferred to a slide and examined with polarized light showed birefringence positive with respect to the fiber axis. While the stretching necessary in the manipulation may have been responsible for a portion of the orientation, the fact is interesting as an indication that the protein in the film was in a state of partial degeneration or denaturation and capable, by interaction of side chains, of being integrated into a fibrous structure as postulated by Astbury, Dickinson, and Bailey (1).

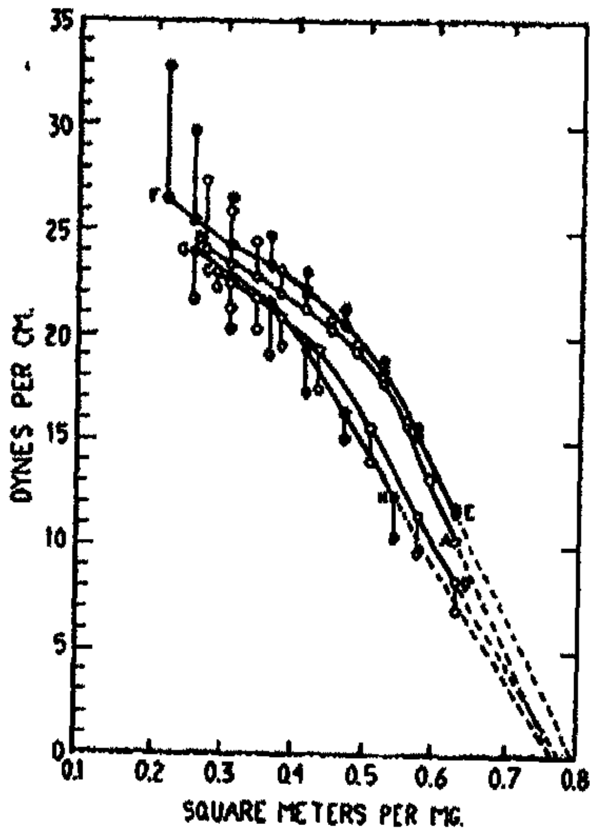

Fig. 2. Egg albumin on $N/300$ acetate buffer, pH 4.6. Restricted spreading at 0.63 m.^{2} per milligram. Coördinates as before. Initial and equilibrium pressure values shown at each area. *A* to *B*, compression; *B* to *C* to *D*, expansion; *D* to *E*, adjust water level; *E* to *F*, recompression; *F* to *G* to *H*, reëxpansion.

The initial points lie on a smooth curve only if the technique of compression, pressure adjustment, and further compression is maintained uniformly, whereas the equilibrium values are independent of further lapses of time, as figure 1 shows. In rapid compression an equilibration debt, as it were, is accumulated, which forces itself upon the attention of the observer only at relatively high pressures, if compression is rapid and uniform. The amount of equilibration in the first minute after obtaining the initial pressure is small at low pressure as the time curves show in figure 1. As the pressure increases, the fraction of the whole equilibration occurring within the first minute increases very greatly. This should not be confused with the more or less irreversible collapse of the protein film found after the condensed state is reached.

That the compression is reversible above an area of 0.25 m.^{2} per milligram is further shown by the experiment presented in figure 2, in which a film of egg albumin is compressed, expanded, recompressed, and reëxpanded. Only the initial and equilibrium points are shown at each step.

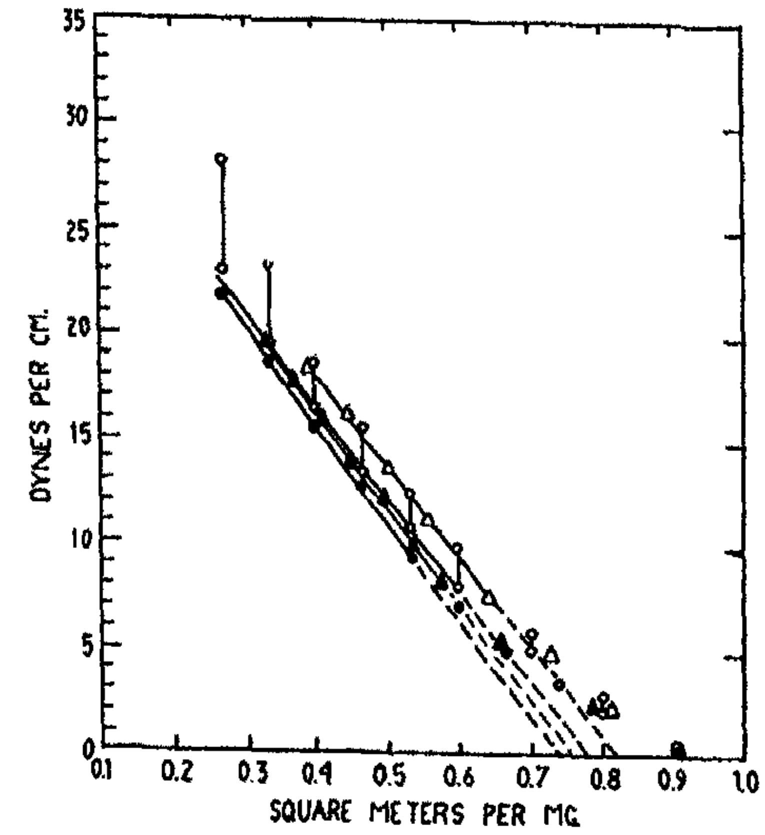

FIG. 3. Nerve protein extracted in $N/10$ sodium hydroxide. Spread on $N/300$ acetate buffer, pH 4.6, with aid of 4.25 per cent alcohol. Coördinates as before. Equilibrium points only, of four separate films, except open circles, which show both initial and equilibrium points.

Comparison of figures 1 and 2 shows that the areas at zero pressure extrapolated from the approximately linear portion of the equilibrium pressure curves are different in the two cases, although the buffer subsolutions were practically the same. This variation has been studied in other experiments and seems to be due to incomplete spreading of the protein when the surface available for its spreading is limited. It is not clear whether this is due to an incomplete uncoiling or degeneration, to use Astbury's term, of the protein from the dissolved (globular) state to its extended condition on the surface, or is caused by a partial passage of protein into the body of the subsolution in the trough. In such restricted spreading the pressure rises rapidly at first, then gradually approaches an equilibrium value. This spontaneous pressure rise is quite sensitive to the character of the subsolution and to the precise manner of application from the tip of the microburet.

Nerve proteins resemble egg albumin in showing equilibration, but the plateau effect between the linear portion and the final condensed packing is absent. In figure 3 are plotted the equilibrium points of four successive films of nerve protein extracted in *N*/10 sodium hydroxide, spread on *N*/300 acetate of pH 4.6 with the aid of 4.25 per cent alcohol. One set of initial points is included as well to show the similarity to other proteins. However, instead of showing a plateau, the curves at the lowest area seem to be passing over into the condensed packing. This is not so far-reaching a distinction between the proteins as might be thought, however, since casein, which shows the plateau markedly on some subsolutions, shows hardly any upon others. Moreover, definite indications of this plateau have been obtained for nerve proteins of the neurostromin group on other buffers. Fibrinogen films, although showing the plateau upon water, show little or none upon McIlvaine's phosphate–citrate buffer.

The general relations of the phase boundary potentials observed with these films are quite similar to those reported by Hughes and Rideal (6) and by ter Horst (5), using the polonium electrode method. At great areas the potentials fluctuate. With decrease of area, the time average of these potentials tends to rise and the range of fluctuation to decrease, until the potential becomes steady at the area at which the whole available surface is covered with film. In the case of elastic patch films this can be made plainly visible by dusting talc upon the surface previous to spreading. Depending on the resistance of the elastic patches, more or less pressure is required to deform them and thus to fill the available space. The steady potentials increase with decreasing area without showing any equilibration to correspond to the force changes within the sensitivity of our measurements (1 or 2 millivolts). At lower areas the potential levels out, becoming constant and independent both of area and pressure. This constant potential region extends into the final upturn of the force–area curves for condensed packing. Through the region of largest equilibration the potentials remain constant.

In spreading at restricted areas the potential changes cease long before the increase in pressure reaches equilibrium. This has been observed with fibrinogen on phosphate–citrate buffer of pH 7.4. Egg albumin on *N*/300 acetate, pH 4.65, shows a somewhat greater tendency for the potentials and pressure to change together, but even here the potential curve is changing less with time than the pressure curve. This probably indicates that in spreading at restricted areas there is an initial period in which the actual surface concentration of protein is changing, owing to translation of protein chains along the surface, but that the later and longer period of the changes is due to readjustments similar to the equilibration at each step in compression.

The experiments here presented extend to low pressures the range of the metastable state given by Hughes and Rideal (6) for gliadin films. The importance for the theory of film structure of the independence of potential and pressure in the plateau region has been emphasized by ter Horst (5). The facts shown in the present experiments, that potential depends only partially upon the area of the film (or surface concentration) and not at all upon equilibration of pressure, must be taken into consideration in any general theory of film structure.

SUMMARY

The method of preparation of certain nerve protein fractions and the general features of the unimolecular films formed by them on various subsolutions are described.

A phenomenon of pressure equilibration following change of area of these films has been observed. This equilibration is not associated with changes in phase boundary potentials and is distinct from irreversible collapse. The relation of this equilibration to film spreading at restricted areas is discussed.

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TRANSFERENCE NUMBERS OF COLLOIDAL "FERRIC HYDROXIDE"[1]

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INTRODUCTION

It was demonstrated by Laing (2), in her work with soap solutions, that colloidal electrolytes and ordinary electrolytes show the same type of electrokinetic behavior, and hence can be studied by comparable experimental methods. "Ferric hydroxide" sols are typical charged colloids differing only in degree from typical colloidal electrolytes. It is therefore to be expected that their transference numbers can be measured by the same methods that are used for simple electrolytes, namely, the analytical method of Hittorf and the method of moving boundaries.

The identity of these two methods for measuring transference numbers was pointed out by Miller (8) and by Lewis (3), and was experimentally verified by MacInnes and his coworkers (4, 5). Many colloid chemists, however, have not recognized that this identity must also hold true for colloids. It was therefore desired to demonstrate this truth by experimental measurements on a typical charged colloid such as a "ferric hydroxide" sol.

The requirements for reliable Hittorf determinations of colloids have been clearly stated by Laing (2). The requirements for moving-boundary measurements of ordinary electrolytes have been established by MacInnes and his coworkers (5), but have been applied to colloidal solutions only by Robinson and Moilliet (9) in their study of dye solutions.

The following are the most important conditions that should be observed in any moving-boundary determination: The slower ion, usually the indicator, should follow; only the receding boundary should be observed; the denser solution should be on the bottom; the concentrations of the two ions forming the boundary should be approximately in the ratio $C/T = C^1/T^1$, where C and C^1 represent concentrations and T and T^1 represent transference numbers; the concentration of the indicator should preferably be slightly less than that indicated by the equation; a tube of small bore should be used; one electrode compartment should be closed; the electrode

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in the closed compartment should be reversible; and volume changes on the closed side of the boundary should be known.

Colloidal "ferric hydroxide" is a good material with which to demonstrate the fact that accurate transference measurements can be made by both the Hittorf and the moving-boundary methods. Moderately concentrated sols can be prepared, and they exhibit a conductivity comparable to that of dilute solutions of ordinary electrolytes. It is therefore possible to find an ion of lower mobility that the colloid to serve as an indicator. The only uncertain factor is the presence of small amounts of hydrogen ion in all "ferric hydroxide" sols. It is, however, probable that there would be no appreciable disturbance of the boundary if the same concentration of hydrogen ion were present in the indicator as in the sol.

EXPERIMENTAL

Hittorf determinations

These experiments were carried out on "sol 13," the properties of which have been recorded in two previous communications (6, 7).

The method used for Hittorf determinations was similar to that described by Laing (2). Figure 1 shows the transference cell. It was of Pyrex glass, and had a capacity of about 100 cc. The usual silver coulometer was not sufficiently sensitive to determine the current passed through the cell. The current density was therefore measured by means of a galvanometer that had been calibrated as a milliammeter. The total current was determined by plotting current density against time and taking the area under the curve. Four B-batteries in series (200 volts) supplied the current. All portions of the circuit were insulated from the ground.

In these gravimetric Hittorf measurements the sol was placed so as to fill the middle portion (tubes 3 and 4) completely, and to extend half way up in tubes 2 and 5. Then with the cell in position, a known weight of 0.0001 N sodium nitrate solution was introduced from a separatory funnel with flaring, upturned tip, to serve as a guard solution. This prevents contact with the electrodes and also provides definite electrode reactions not interfering with the analysis employed. Before starting a run, the cell was allowed fifteen minutes to attain the temperature of the thermostat, 25° ± 0.02°C. During a run the current density was measured every 5 minutes, and the zero point of the galvanometer was checked frequently. Three middle portions, "AM," "M," and "CM," and both electrode portions were analyzed for iron and chlorine according to the methods described in a previous communication (7).

The transference numbers of ferric oxide and of chlorine were calculated relative to water. The final weight of water in each electrode compartment was determined by subtracting the weight of guard solution and the weight of ferric oxide found by analysis from the total weight of solution. The weights of ferric oxide and chlorine originally present were calculated from the composition of the sol.

The Hittorf migration results are given in table 1. The Hittorf number is defined as the number of chemical equivalents of the named constituent which pass from one electrode compartment to the other for each faraday (96,500 coulombs) of current passed through the solution. The middle portion remains unaltered in composition. For colloidal systems, as for electrolytes, the algebraic sum of the number of electrochemical equivalents or charges carried in the two directions must always add up to unity for each faraday of current passed. In the case of simple electrolytes carrying one charge per chemical equivalent, the same statement holds true for chemical equivalents. However, since a colloid may carry many chemical equivalents per electrical charge, the Hittorf numbers may be greater than unity, as in table 1. Here the migration numbers appear as 70.3 equivalents of iron and 2.50 of chlorine for each faraday, both moving towards the cathode. Thus, 2.50 more equivalents of un-ionized chlorine is carried in the positive colloidal particles towards the cathode than is simultaneously carried toward the anode by the corresponding free chloride ions.

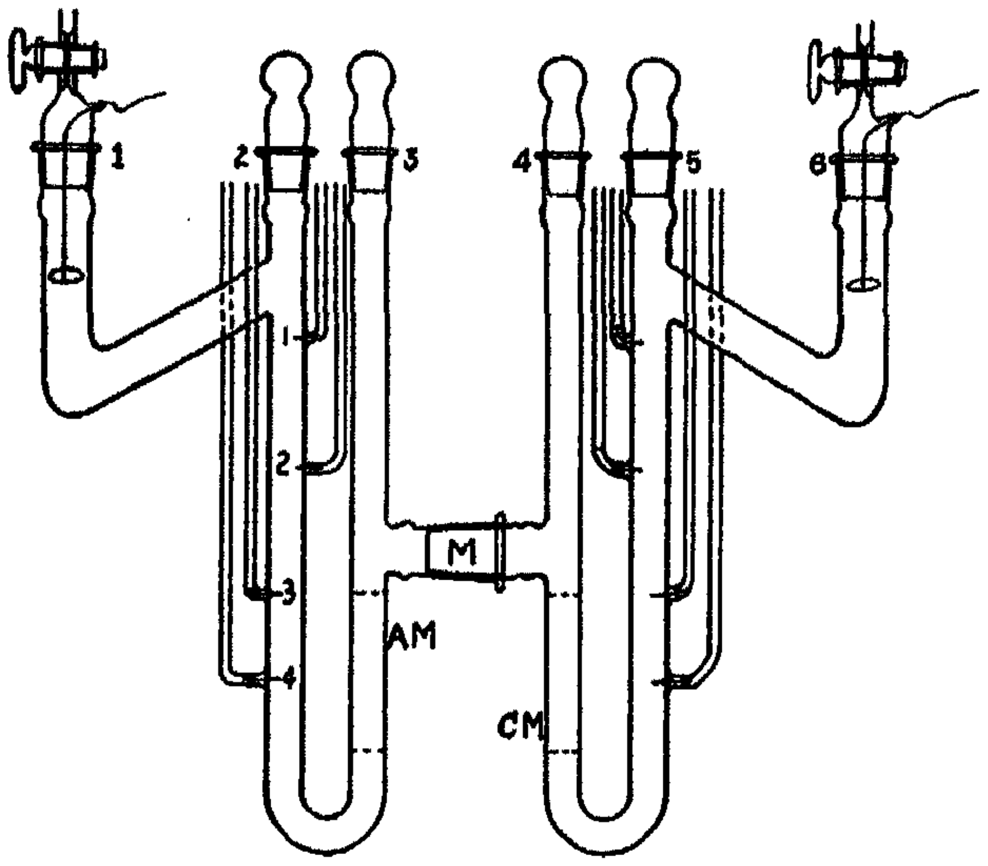

FIG. 1. Migration apparatus

Moving-boundary determinations

The migration velocity of colloidal "ferric hydroxide" was measured in the same cell that was used for Hittorf determinations. The guard solutions, now used as indicator solutions, were of lithium chloride, made to the same hydrogen-ion concentration as the sol with hydrochloric acid, and were equally conducting with the sol.

TABLE 1

Hittorf measurements of transference numbers expressed as chemical equivalents of iron and chlorine transported per faraday for "ferric hydroxide sol 13"

PORTION	TRANSFERENCE OF $Fe(OH)_3$		TRANSFERENCE OF Cl	
	Change in equivalents	Hittorf number	Change in equivalents	Hittorf number
Experiment 1: current passed, 4.66×10^{-5} faradays				
A	−0.00329	70.6	−0.000116	−2.51
AM	+0.00001		−0.000001	
M	+0.00002	69.6	+0.000003	−2.51
CM	+0.00004		+0.000002	
C	+0.00318		+0.000112	
Average		+70.1		−2.51
Experiment 2: current passed, 3.45×10^{-5} faradays				
A	−0.00245	71.0	−0.0000873	−2.56
AM	+0.00002		−0.0000000	
M	+0.00001	69.9	−0.0000007	−2.43
CM	+0.00002		+0.0000028	
C	+0.00238		+0.0000810	
Average		+70.5		−2.50

TABLE 2

Moving-boundary measurements expressed as transference numbers and as absolute velocities, showing identity with results of Hittorf method for "ferric hydroxide sol 13"

Indicator solution: 7.5×10^{-5} N hydrochloric acid + 5.5×10^{-3} N lithium chloride

TIME	MOVEMENT OF BOUNDARY	POTENTIAL GRADIENT	MOBILITY	HITTORF NUMBER
minutes		*volts/cm.*	*cm./sec./volt/cm.*	
119	5.04	1.57	4.45×10^{-4}	70.3
90	3.75	1.51	4.58×10^{-4}	72.4
From Hittorf number, table 1			4.45×10^{-4}	70.3

(C = 0.933 equiv. per liter on basis of analysis in Hittorf experiments.)

The potential gradient was determined by measuring the difference in potential between two of the platinum terminals shown in figure 1. The measurements were made by means of a Leeds and Northrup student potentiometer and a high-sensitivity, high-resistance galvanometer. The method was checked by using a dilute potassium chloride solution in the cell, the potential gradients observed between different terminals checking within less than 1 per cent.

The boundaries between sol and guard were formed in the manner that was described for Hittorf determinations. The cell was allowed fifteen minutes to attain the temperature of the thermostat. The boundaries were observed by means of a traveling microscope. Their position, when first formed, could be read to within 0.2 to 0.4 mm. After the current had been passed for about fifteen minutes, the anode boundaries were read to within 0.1 mm. Observations of potential gradient and of boundary position were made about every 5 minutes during each run.

The transference numbers of iron obtained by this method for "sol 13" are summarized in table 2 for two independent experiments, involving twenty-seven readings. They were calculated from the equation

$$T = \frac{UFC}{1000K}$$

where T is the Hittorf number, U is the absolute velocity in cm. per second per volt per centimeter, F is Faraday's constant (96,500 coulombs), C is the concentration in chemical equivalents per liter, and K is the specific conductivity.

DISCUSSION OF RESULTS

These results definitely prove the possibility of measuring the transference numbers of charged colloids as well as colloidal electrolytes by both the analytical and the moving-boundary methods. The values obtained by the two methods agree within the experimental error of the moving-boundary measurements as made in these experiments. More accurate results could be obtained by more rigid adherence to the principles listed in the introduction.

The chief source of inaccuracy was in the use of an apparatus with both electrode compartments open, making the application of exact volume corrections impossible without further study (3). However, since the total current passed was very small, about 5×10^{-5} faradays, volume changes due to electrode reactions were practically negligible. The only appreciable errors were due, first, to the slight hydrostatic readjustment of the liquid boundary caused by the transference or displacement of the "ferric hydroxide" in density, and, secondly, to the slight volume changes accompanying the transference. This might make the results low by about 2 per cent.

A third source of error was due to the use of an indicator solution that was more concentrated than the required value, 4.2×10^{-3}, calculated from

$C/T = C^1/T^1$. However, it has been found (1) that the range of adjustment is relatively great for solutions of this dilution, so that the error was probably very slight and would tend to cancel the error due to transference of "ferric hydroxide."

COLLECTED PROPERTIES

A summary of the chemical and physical properties of "ferric hydroxide sol 13," as presented in this and two previous communications (6, 7), is given in table 3. The second column gives properties of the actual sol, containing both colloid and small amounts of free hydrochloric acid. The third column represents an "ideal" sol containing only the positive colloidal particles and the corresponding chloride ions. These values are obtained by correcting the values in column two for the effect of the ultrafiltrate.

TABLE 3

*Summary of properties of "ferric hydroxide sol 13" at 25°C.**

	ACTUAL SOL	"IDEAL" SOL
Equivalents of Fe per 1000 g. H_2O	0.934	0.934
Equivalents of Cl per 1000 g. H_2O	0.0449	0.0430
C_{H^+}	6.3×10^{-6}	1×10^{-7}
Specific conductivity, in mhos	5.70×10^{-4}	5.40×10^{-4}
Hittorf number of Fe	70.3	74.2
Hittorf number of Cl (not Cl^- only)	−2.51	−2.65
Mobility of Fe in cm./sec./volt/cm.	4.52×10^{-4}	4.52×10^{-4}
Mobility of Cl^- in cm./sec./volt/cm.	7.91×10^{-4}	7.91×10^{-4}
Equivalent of Fe per faraday of free charge†	206	206
Concentration of free chloride ion†	0.0064	0.0045

* The diffusion coefficient of "sol 20" at 25°C. was found to be 0.613 as compared with 0.46 for sucrose by McBain, Dawson, and Barker (J. Am. Chem. Soc. 56, 1021 (1934)).

† Calculation as given below.

The number of chemical equivalents of iron per faraday of free charge, m_{Fe}, was calculated by means of the Laing equation (2),

$$T_{Fe} = \frac{m_{Fe} f_{Fe} c_{Fe}}{\mu}$$

where T_{Fe} is the Hittorf number, 74.2, f_{Fe} is the conductivity contributed by one chemical equivalent, c_{Fe} is the concentration in chemical equivalents per 1000 g. of solvent, 0.934, and μ is the conductivity of that amount of solution containing 1000 g. of solvent, approximately $1000 \times 5.40 \times 10^{-4} = 0.540$ mho.

All the above quantities are experimentally determined except m_{Fe} and f_{Fe}. The latter can be eliminated by means of the independent equation,

$\mu = c_{\mathrm{Fe}} f_{\mathrm{Fe}} + C_{\mathrm{Cl}^-} v$, where C_{Cl^-} is the concentration of free chloride ions and v their mobility. Solving for f_{Fe} and substituting $C_{\mathrm{Cl}^-} = c_{\mathrm{Fe}}/m_{\mathrm{Fe}}$ gives

$$f_{\mathrm{Fe}} = \frac{\mu m_{\mathrm{Fe}} - c_{\mathrm{Fe}} v}{m_{\mathrm{Fe}} c_{\mathrm{Fe}}}$$

Substituting this in the Laing equation,

$$m_{\mathrm{Fe}} = \frac{T_{\mathrm{Fe}} \mu + c_{\mathrm{Fe}} v}{\mu}$$

T_{Fe} is taken as the value for the "ideal" sol or 74.2, v is assumed to be the same as at infinite dilution or 76.3, and μ may be taken equal to $K \times 1000$ or 0.540. This gives $m_{\mathrm{Fe}} = 206$. The corresponding concentration of chloride ion due to dissociation is $0.934/206 = 0.0045\ N$. This free chloride ion, 0.0045 N Cl^-, is only 10.5 per cent of the total chloride, 0.0430 N, carried in the sol, the other 89.5 per cent being carried in the positive particle in undissociated unconducting form.

As compared with the equivalent conductivity of the free chloride ion, 76.3 mhos, the conductivity of one equivalent of positive charges carried on the positive particles is 43.6 mhos; hence that of the amount of charge carried by one chemical equivalent of iron is 206 times less, or 0.212 mho. A positive charge on the colloidal particle thus conducts 43.6/76.3, or 57 per cent as well as an ordinary chloride ion.

Finally the so-called zeta potentials, which, since they have never been measured directly are always calculated by multiplying the observed linear mobility by $4\pi\eta/D$ or 129,700, come out as +58.6 mv. for the positive colloidal particles and −102.6 mv. for the ordinary free chloride ions.

SUMMARY

The transference numbers of iron and chlorine in a "ferric hydroxide" sol were measured by the Hittorf and moving-boundary methods, which were found to give identical results within the limits of experimental error.[2]

The importance of making such measurements in accordance with methods established for use with simple electrolytes was pointed out.

The interesting and significant physicochemical properties of "sol 13," as reported in this and two previous communications, are summarized.

[2] *Footnote added in proof:* Roberts and Carruthers (J. Phys. Chem. **40**, 703 (1936)) have now shown that the moving boundary and the observation of a single particle give identical results. This is inevitable, if electrode changes do not reach through the middle portion, since all movement is referred to motionless solvent. On the whole, apart from slight density changes outside the middle portion, the solvent does not move in either a closed or an open U-tube.

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A DIFFUSION STUDY OF DYES[1]

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The interest in the relationship of the substantive dyeing of cotton to the colloidal state of dyes in solution has led to extended investigations of the particle radius and the state of aggregation of representative water-soluble colors by Robinson and Mills (29), Ruggli and coworkers (34, 35), Haller (8), Schäffer (36), Schramek and Götte (37), Brass and Eisner (1), Rose (31), Valkó (40), the authors (14, 15, 16), and others. Diffusion measurements offer one of the simplest experimental approaches to a study of the colloidal state of dyes in solution. However, progress in the field has been slow because experimental methods were not well adapted to a study of dyes under actual dyeing conditions and because a suitable theoretical background for applying the measurements was lacking. Recent theoretical and experimental work of Hartley and Robinson (10), Bruins (2), and McBain (17, 18, 19, 20) and his coworkers has led to a correlation of the rate of diffusion of a colloidal electrolyte with the magnitude of the charge on the particle and the distribution of ions in the surrounding medium. The microdiffusion method of Fürth and Ullmann (4, 5) and the porous-plate method of Northrop and Anson (25) have been successfully applied in studies of colloidal electrolytes by Robinson (27, 28), Nistler (24), Schramek and Götte (37), McBain (17, 18, 19, 20) and his coworkers, and Valkó (40). The authors (14, 15) have recently applied both methods in a study of the diffusion of four chemically pure dyes. The dyes were as follows: (I) *p*-sulfobenzeneazobenzeneazo-6-benzoylamino-1-naphthol-3-sulfonic acid (sodium salt) (Colour Index No. 278); (II) *p*-sulfobenzeneazobenzeneazo-6-benzoyl-*p*-aminobenzoylamino-1-naphthol-3-sulfonic acid (sodium salt); (III) *o*-tolidinebisazo-1-naphthylamine-4-sulfonic acid (sodium salt) (benzopurpurin 4B, Colour Index No. 448); (IV) *m*-tolidinebisazo-1-naphthylamine-4-sulfonic acid (sodium salt) ("meta" benzopurpurin 4B).

Dye I and dye II are of the same chemical type but possess widely different colloid-chemical properties. Dye I is characterized by its excel-

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lent level dyeing properties, poor fastness to washing, and poor exhaust from the dye bath on cotton. Dye II, in contrast, is more difficult to dye level and shows superior wash fastness as well as a high exhaust from the dye bath. The identifying difference in the formulas of dye I and dye II is the presence of a second benzoyl group in dye II. Dye III and dye IV are of another chemical type and differ between themselves only in the position of the methyl groups of the tolidine nucleus. The spatial change in the position of the methyl groups is associated with a great difference in the substantivity of the dyestuffs toward cotton.

The microdiffusion method used in this work was essentially the same as that of Fürth (4), and has been described by the authors (16). For most measurements, the microdiffusion cell was housed in an air thermostat whose temperature was held with a maximum variation of ± 0.5°C.

The porous-plate method was applied as described by McBain and Liu (20). Its adaptation to dyestuff measurements was described by the authors (14).

The dyes used in this work were prepared from purified intermediates by methods in current use for manufacturing azo colors. The dyes were freed of electrolytes by the method of Rose (32, 33). This method (14, 15) consists in converting the dyes to their arylguanidine salts (preferably di-*o*-tolylguanidine), which are insoluble in water. The dyes are washed free of inorganic electrolytes, are dissolved in alcohol, and are converted by metathesis with sodium hydroxide to the sodium salts. The precipitated sodium salts of the dyes are filtered and washed free of the arylguanidine with alcohol.

I. DIFFUSION AND AGGREGATION OF PURE DYES IN WATER

Herzog and Polotsky (12) showed that some purified dyes diffuse as electrolytes; Freundlich (3), Svedberg (38), and Tiselius (39) have pointed out the necessity of considering ionic forces in dealing with diffusion and sedimentation phenomena. Despite these facts the Stokes–Einstein equation

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \tag{1}$$

has been applied indiscriminately for the calculation of the particle radius of dyes in solution until the recent theoretical treatment of Hartley and Robinson (10), who showed that theoretically the minimum diffusion constants for a number of dyes would be approximately 5.1×10^{-6} cm.^{2} per second. Robinson (27) has demonstrated that representative purified dyes diffuse at an appreciably greater rate than the theoretical minimum (see table 1). Valkó (40) estimated that dyes which are the sodium salts of monobasic or dibasic acids may diffuse at rates as high as 7.2 to 8.2 ×

10^{-6} cm.^{2} per second. The data of Valkó on the diffusion of a number of representative pure dyes are of the same order. The authors obtained values of 8.8 to 9.0 × 10^{-6} cm.^{2} per second for the diffusion of dye I and a value of 7.7 × 10^{-6} cm.^{2} per second for the diffusion of dye II in water solution. These last values are about double those required for diffusion of the molecularly dissolved dye according to the Stokes–Einstein equation.

TABLE 1

Diffusion coefficients of pure dyes at 25°C.

DYE	MEASUREMENTS BY	CONCENTRATION RANGE	$D \times 10^{-6}$
		grams per liter	*cm.^{2} per second*
Orange II, C.I. 151	Valkó	1.0–15.6	6.68–7.99
Azogrenadine S, C.I. 54	Valkó	0.5–5.0	8.38–7.86
Bordeaux Extra, C.I. 385	Robinson	0.8–2.5	5.42–5.66
Congo rubin, C.I. 376	Robinson	5.0	5.51–5.59
Congo red, C.I. 370	Valkó	0.1–5.0	6.63–7.73
Congo red, C.I. 370	Robinson	5.0	5.68
Benzopurpurin 4B, C.I. 448	Valkó	0.2–5.0	6.12–7.48
Benzopurpurin 4B, C.I. 448	Robinson	5.0	6.57
"Meta" benzopurpurin	Robinson	5.0	5.43–5.91
Dye I, C.I. 278	Lenher and Smith	0.5–1.0	8.84–9.01
Dye II	Lenher and Smith	0.5	7.73

TABLE 2

Diffusion rate of dyes I and II into water and into dilute sodium chloride solutions at 25°C.

DYE	CONCENTRATION	DIFFUSING INTO NaCl SOLUTION	$D \times 10^{-6}$	CALCULATED PARTICLE WEIGHT
	grams per liter	*grams per liter*	*cm.^{2} per second*	
I	0.5		9.01	80
	0.5	0.087	3.84	1100
	1.0		8.84	90
	1.0	0.174	4.07	924
	1.0	0.500	3.10	2095
II	0.5		7.73	120
	0.45	0.074	4.21	770
	0.45	0.067	2.93	2280

The results for Congo red and benzopurpurin 4B in table 1 are considerably higher than a number of determinations reported by previous investigators (1, 5, 12, 24). The difference in the rate of diffusion is probably due to differences in the degree of purity of the dyestuffs, for both dyes are highly susceptible to aggregation in the presence of inorganic salts.

Hartley and Robinson (10) and Valkó (40) are agreed that, even after the effect of the charge on the ions is considered, it is not possible to determine the state of aggregation of a pure dye in water solution from diffusion measurements. Hartley and Robinson (10) explain the high rate of diffusion of the color ion in solution as due to its attraction for the highly mobile sodium ion, i.e., both ions must diffuse into water at the same rate. It appears that for a completely dissociated dye, electroneutrality of the color ion with respect to the sodium ion in the diffusion cell would be established by carrying out the diffusion of the dye into an electrolyte solution containing an equivalent concentration of the metal ion. The authors studied this effect by determining the rate of diffusion of the sodium salt of dye I and dye II into dilute sodium chloride solutions. The measurements were made in the Fürth microdiffusion cell at 25°C. The data are summarized in table 2.

In table 2 the particle radius is calculated from equation 1. It is assumed that the dye molecules or micelles are large in comparison with the solvent and that they are spherical. Herzog, Illig, and Kudar (11) showed that the error caused by assuming the particles to be spheres is relatively small except in cases involving extreme elongation. The authors (16) have shown that the ultramicrons of most dyes in sodium chloride solutions are practically spheres. The particle weight is calculated from equation 2 where the specific gravity (g) is 1.72 for dye I and 1.58 for dye II.

$$m = \frac{4}{3}\pi r^3 g N \tag{2}$$

The substitution in equation 1, and indirectly in equation 2, of the diffusion constants of dye I and dye II into water gives particle weights which are small fractions of the formula molecular weights, as is to be expected on theoretical grounds. The rate of diffusion of dye I into an equivalent concentration of sodium chloride gives particle weights of 900 to 1100 as compared with an ion weight of 629. The agreement is considered remarkably good, since the experimental error in the microdiffusion method is at least 5 per cent. An error of this magnitude might account for about half the difference between the calculated particle weight and the ion weight. In addition, the density of the dye particles in solution is not accurately known. The data indicate that the chloride ions from the salt solution diffusing in the opposite direction have very little effect on the rate of diffusion of the color ions. It appears that the negatively charged dye ion diffuses as a neutral particle in the presence of a uniform distribution of a common positive ion in the cell. The data of table 2 show that the rate of diffusion of dye I into a sodium chloride solution of three times the equivalent concentration is further retarded, as would be expected, since the diffusion occurs against a concentration gradient of sodium ions.

The value of D for the diffusion of dye II into an equivalent concentration of sodium chloride also corresponds to that expected for the molecular diffusion of a neutral particle. However, diffusion into a higher salt concentration is accompanied by boundary disturbances, while the diffusion rate into a slightly lower (10 per cent) concentration of sodium chloride is, contrary to expectations, about 30 per cent lower. It appears that the distribution of positive and negative ions in a solution of dye II does not correspond to that of a molecularly dissolved, completely ionized dyestuff. The differences in the behavior of dye I and dye II in these experiments indicate that dye I closely approaches the molecular state in solution, while dye II is aggregated into micelles.

The successful application of the above method to dye I and dye II suggests that it is possible to determine whether water-soluble dyes are in true solution by observing the rate of diffusion into an equivalent concentration of sodium chloride.

II. DIFFUSION AND AGGREGATION OF DYES IN SALT SOLUTIONS

The necessary conditions for determining diffusion constants that may be substituted in the Stokes-Einstein equation to estimate the particle radius of dyes in solutions containing inorganic electrolytes have been considered recently in a number of papers. Hartley and Robinson (10) and Valkó (40) are of the opinion that diffusion experiments with dyes must be carried out in the presence of a uniform concentration of a foreign electrolyte to permit application of the diffusion constants in the Stokes-Einstein equation for the determination of the particle radius. The authors (14, 15) were unable to apply this principle in a study of dye I and dye II because of boundary disturbances which occurred in the microdiffusion cell. The same trouble was experienced by Robinson (27) with dye IV, but only at relatively high (0.25 *N*) concentrations of sodium chloride. If a uniform concentration of the foreign electrolyte were required, it would be expected that the diffusion rate of the dye would increase when diffusion occurs into a sodium chloride solution of lower concentration than that present in the dye solution, and that a further increase would occur for diffusion of the dye from the salt solution into water. The authors (14) tested this theory by measuring the rate of diffusion of dye I and dye II from a solution containing 1.0 g. of sodium chloride per liter into water and into a solution containing 0.5 g. of sodium chloride per liter. The data are given in table 3.

Practically identical diffusion constants were obtained for the movement of the color ion from a sodium chloride solution into water, and for diffusion into a sodium chloride solution of half concentration. Robinson (27) obtained practically identical diffusion constants for the diffusion of dye IV from a 0.004 *N* (0.232 g. per liter) sodium chloride solution into water and into a 0.004 *N* sodium chloride solution. It is apparent, from these data, that the rate of diffusion of the ordinary water-soluble dyes from a salt solution whose concentration is 0.02 *N*, and possibly as low as 0.004 *N*, into water is the same as the rate of diffusion into salt solutions of the same or lower concentrations. It is apparent that the diffusion of sodium ions from these solutions is accompanied by movement of the highly mobile chloride ions in quantities that prevent the establishment of a potential gradient between the sodium and dye ions. The data show that the only requirement for independent diffusion of the dye ion, in a manner analogous to the diffusion of an electrically neutral particle, is the presence of several times the equivalent concentration of sodium chloride in the dye solution. The diffusion rate of the dye ion from a salt solution into either water or another salt solution represents the normal independent diffusion rate of the dye ion.

TABLE 3

Diffusion of dye I and dye II in the presence of electrolytes

DYE	SOLUTION		AGE OF SOLUTION	DIFFUSION INTO NaCl SOLUTION	$D \times 10^{-6}$
	Dye +	*NaCl*			
	grams per liter	*grams per liter*	*hours*	*grams per liter*	*cm.^{2} per second*
I	0.5	1.0	168		2.38
I	0.5	1.0	168	0.5	2.45
I	1.0	1.0	90		2.31
I	1.0	1.0	90	0.5	2.40
II	0.5	1.0	48		0.94
II	0.5	1.0	72	0.5	0.93
II	1.0	1.0	336		0.96
II	1.0	1.0	312	0.5	1.04

III. AGING PHENOMENA OF DYES IN SALT SOLUTIONS

The degree of aggregation of a dye in solution frequently varies with the age of the solution. Experiments with dye I (summarized in table 4) show that particle growth at room temperature occupies several days. The particle weight in a solution containing 1.0 g. of sodium chloride per liter increased by 30 per cent on aging from two days to a week, and was practically doubled on aging for a month. The maximum aggregation with dye II in a salt solution is reached within a few hours.

Solutions of dye I containing sodium chloride, on aging for several weeks, develop abnormal diffusion properties as compared with fresh solutions. In these experiments solutions containing from 0.5 to 1.0 g. of dye per liter and 1.0 g. of sodium chloride per liter were aged forty-eight to ninety hours at room temperature. The diffusion rates of the color ion into water and into sodium chloride at concentrations up to 0.5 g. per liter were practically the same. Similar dye solutions were prepared and aged for four weeks.

It was found on measuring the diffusion rate of the color ion into water and into sodium chloride solutions (0.125 to 0.5 g. per liter) that a measurable accelerated diffusion occurred into the salt solutions. The data are summarized in table 4.

In table 4 each figure given represents at least two individual diffusion experiments in each of which at least eight determinations were made during a period of twenty to thirty minutes.

The data in table 4 show that diffusion of the color ion from the aged dye solution into the salt solution became more highly accelerated the greater the sodium-ion concentration of the solution into which diffusion occurred. When more sodium chloride was added to the dye solution and the diffusion of the color ion was measured into water and into a salt solution, as indicated, no acceleration in the diffusion rate was observed, i.e., diffusion occurred in the normal manner.

TABLE 4

Diffusion properties of aged dye solutions

DYE	CONCENTRATION		AGE OF SOLUTION	T	DIFFUSION INTO NaCl	$D \times 10^{-6}$
	Dye +	NaCl				
	grams per liter	*grams per liter*		*°C.*	*grams per liter*	*cm.^{2} per second*
I	0.5	1.0	2 days	29		3.13
I	0.5	1.0	2 days	30	0.5	3.22
I	0.5	1.0	1 week	30		2.66
I	0.5	1.0	1 week	28	0.5	2.62
I	0.5	1.0	3.5 weeks	25		2.13
I	0.5	1.0	3.5 weeks	26	0.125	2.58
I	0.5	1.0	3.5 weeks	25	0.25	2.96
I	0.5	1.0	3.5 weeks	26	0.5	3.18
I*	0.5	2.0	3.5 weeks	26		2.17
I*	0.5	2.0	3.5 weeks	26	1.0	2.08
I	1.0	1.0	4 days	27		2.46
I	1.0	1.0	4 days	27	0.5	2.40
I	1.0	1.0	4 weeks	29		2.14
I	1.0	1.0	4 weeks	30	0.25	2.67
I	1.0	1.0	4 weeks	30	0.5	3.03

* This solution was dye I, 0.5 g. per liter, plus sodium chloride, 1.0 g. per liter, aged for 3.5 weeks. Then sodium chloride was added to make the salt concentration 2.0 g. per liter, and the measurements were made with this solution immediately.

The mechanism of the change in properties of the dye solution is not understood. It appears that the accelerated diffusion can be accounted for only on the basis of the presence of an ionic gradient between the dye and the salt, since the diffusion rate varies with the concentration of sodium ions in the solution into which diffusion occurs.

IV. DEPENDENCE OF DYE PARTICLE SIZE ON SALT CONCENTRATION AND TEMPERATURE

The effect of electrolyte concentration and of temperature on the degree of aggregation of dyes in solution is of great practical importance, since the size of the dye micelle is a controlling factor in dyeing processes.

The preceding résumé shows that the diffusion rate of dyes from solutions containing an inorganic electrolyte, as sodium chloride, into either water or any concentration of the electrolyte up to that present in the dye solution may be used to calculate the particle radius from equation 1. The history of the dye solution must be known to establish accurately the effect of electrolyte additions, since the state of aggregation may depend on the age of the solution. Extended aging may introduce complications due to acceleration of the diffusion rate into salt solutions.

TABLE 5

Effect of sodium chloride on colloidal state of dyes in solution at 25°C.

DYESTUFF	CONCENTRATION	CONCENTRATION OF NaCl	$D \times 10^{-6}$	$R \times 10^{-8}$	PARTICLE WEIGHT	AGGREGATION NO.
	grams per liter	*N*	*cm.² per second*	*cm.*		
Orange II, C.I. 151	0.05–0.1	0.02	5.10	4.77	413	1.2
	0.2	0.05–0.2	4.05	5.74	564	1.7
Azogrenadine S, C.I. 54	0.05–0.5	0.02–0.05	4.74	5.12	511	1.1
	1.0	0.1	3.82	6.35	976	2.1
Benzopurpurin 4B, C.I. 448	0.02–0.1	0.01–0.02	2.43	10.0	3810	5.6
	0.05–0.2	0.02	2.08	11.7	6100	9.0
Congo red, C.I. 370	0.05–0.1	0.02–0.05	1.85	13.1	8560	12.0
	0.5	0.1	1.50	16.2	16200	24.0
Chicago blue 6B, C.I. 518	0.02–0.2	0.02–0.05	2.55	9.55	3310	3.7
	0.2	0.1	2.08	11.7	6100	6.8
	0.2	0.2	1.62	15.0	12800	14.0
	0.2	0.5	1.39	17.5	20400	23.0

Valkó (40) studied the effect of varying salt concentrations on the rate of diffusion of two acid dyes and three substantive dyes by the porous-plate method. Part of the data are summarized in table 5.

The data show that the acid dyes are in molecular solution at salt concentrations up to 0.02 *N*, while the substantive dyes are aggregated into micelles. The acid dyes in solution are much less readily agglomerated by additions of sodium chloride than are the substantive dyes. However, in all cases there is an increase in the degree of aggregation of the dyes at sufficiently high concentrations of sodium chloride.

Brass and Eisner (1) reported on the basis of diffusion measurements that the particle size of pure dyes in solution is much smaller than the particle size of unpurified samples.

Schramek and Götte (37) studied the effect of various electrolytes on the degree of dispersion of two substantive dyes (C. I. 385, C. I. 390) in water solution by the Fürth (4) method. Their values for the rate of diffusion of the pure dyes in water are much lower than would be expected.

TABLE 6

Agglomeration of dyes by electrolytes at 25°C.

SOLUTION OF		+ NaCl	+ Na_2SO_4	$D \times 10^{-6}$	ESTIMATED RADIUS $R \times 10^{-8}$	PARTICLE WEIGHT (m)	AGGREGATION NO.
Dye	*grams per liter*	*N*	*N*	*cm.² per second*	*cm.*		
Dye I	0.5	0.027		2.08	11.7	6990	11
	0.5		0.027	3.19	7.6	1920	3
	0.5	0.107		1.52	16.0	17900	28
	0.5		0.107	2.50	9.7	3990	6
Dye II	0.5	0.027		0.71	33.7	153500	205
	0.5		0.027	1.32	18.4	25000	33
	0.5	0.107		0.72	34.2	160400	214
	0.5		0.107	1.60	15.2	14100	19
Dye III	1.0	0.01		2.69	9.0	2800	4
	1.0		0.01	4.52	5.4	605	0.9
	1.0	0.025		0.92	26.4	71000	105
	1.0		0.025	1.91	12.7	7900	12
	1.0	0.05		0.39	62.2	928000	1370
	1.0		0.05	0.75	32.3	130000	190
	1.0	0.01		2.99	8.1	2160	3.2
	1.0		0.01	4.45	5.5	675	1.0
	1.0	0.025		2.02	12.0	7020	10
	1.0	0.05		2.06	11.8	6675	10
	1.0		0.05	4.20	5.8	790	1.2
	1.0	0.1		1.64	14.8	13170	19
	1.0		0.1	3.49	7.0	1390	2.1

They found that additions of sodium chloride, sodium sulfate, sodium carbonate, and magnesium sulfate all act at low concentrations to disperse the dyes, and at higher concentrations as agglomerating agents. A dispersing action of small additions of sodium sulfate on pure dyes in solution was also reported by Ostwald (26).

The authors (14, 15) used the microdiffusion method to determine the rate of diffusion of dyes I, II, III, and IV in the presence of electrolytes at 25°C. The dye solutions were prepared at the boil and aged at 25°C.

for eighteen hours before the measurements were made. The diffusion rate was measured from the electrolyte solution into water. There was no indication that the concentration of inorganic electrolyte in the dye solution changed sufficiently during the short diffusion period of twenty to thirty minutes to cause a change in the colloidal state of the dye during measurements. The data are summarized in table 6.

The data in table 6 show that the four dyes are characteristically different in the extent to which they are agglomerated by electrolyte additions. Dye II and particularly dye III are highly sensitive to additions of sodium chloride and sodium sulfate. Dye I and dye IV are much less aggregated, especially in the presence of sodium sulfate. In general, sodium chloride exerts an appreciably stronger agglomerating action than does sodium sulfate with corresponding dyestuffs.

Robinson (27) showed, from measurements by the microdiffusion method, that benzopurpurin 4B (C. I. 448) and Congo red (C. I. 370) are considerably more highly aggregated by sodium chloride than either Bordeaux Extra (C. I. 385) or "meta" benzopurpurin. He found that the diffusion constants of Bordeaux Extra and "meta" benzopurpurin, obtained in the presence of increasing salt concentrations, fall to a constant minimum for both dyes. The minimum diffusion constant for Bordeaux Extra in salt solutions corresponds approximately to that for a molecular solution, and it is inferred that the dye is in the molecular state in water. The minimum diffusion constant for "meta" benzopurpurin in salt solutions shows that the dye is associated into micelles of more than ten molecules. Robinson (27) has interpreted the data as showing that the dye is also in the form of micelles of more than ten molecules in water solution. As Robinson (27) points out, this extrapolation gives a result which is in agreement with osmotic-pressure measurements, but is too high in comparison with the mobility measurements of Robinson and Moilliet (30). Such an extrapolation of the data appears hazardous, in view of the ease with which dyes are aggregated in dilute solutions of electrolytes. The data of table 6 show that diffusion constants for "meta" benzopurpurin (dye IV) in the presence of sodium sulfate are much higher than at equivalent concentrations of sodium chloride. It is shown that dye IV is in the molecular state in sodium sulfate solutions up to 0.05 *N*, and it is inferred that the dye is in true solution in the absence of electrolytes. These results correspond more nearly to the state of aggregation for "meta" benzopurpurin (1.2) deduced by Robinson and Moilliet (30) from mobility experiments. The data of table 6 also show that benzopurpurin 4B (dye III) is in the molecular state in 0.01 *N* sodium sulfate solution, and it is inferred that the dye is in true solution in water. Robinson and Moilliet (30) found from mobility experiments that the degree of aggregation of benzopurpurin 4B in solution is 1.5. It appears that the differences in the colloid-chemical properties of benzopurpurin 4B and its isomer arise from the great difference in the sensitivity of the two dyes to agglomeration by inorganic salts, rather than from a large difference in the state of the pure dyes in water solution.

The data of Valkó (40), Robinson (27), and the authors (14, 15) show that the only effect of the addition of sodium chloride and sodium sulfate to a number of representative dyes is to increase the particle size of the dyes in solution. As pointed out above, Schramek and Götte (37) found that low concentrations of electrolytes first disperse some dyes and that greater concentrations produce reagglomeration. The wide variation between the diffusion constants of the pure dyes of Robinson (27), Valkó (40), and the authors (14) compared with the diffusion constants for the dyes of Schramek and Götte (37) suggest that the widely different methods of purification give dyes of a different degree of purity. The conflicting results from diffusion measurements made in solutions containing low concentrations of electrolytes are probably due to a difference in the degree of purity of the dyes.

It has been commonly recognized that increased temperatures lead to increased dispersion of dyes in colloidal solution. The authors (14, 15) made a quantitative study of the effect of temperature on the degree of dispersion of dyes I, II, III, and IV in electrolyte solution by carrying out diffusion measurements with the porous-plate type of cell. In these experiments the diffusion of the dye was carried out from a salt solution into another salt solution of equal concentration. Quantitative observations of the increase in the dispersion of the dyes with increase in the temperature are summarized in table 7.

The particle weights were calculated by equation 2, using the following experimentally determined values of g: dye I, 1.72; dye II, 1.58; dye III, 1.52; dye IV, 1.60.

The data in table 7 show that while a general decrease in the degree of aggregation of dyes occurs with increasing temperatures, specific differences in behavior occur. Dyes I and IV are only slightly aggregated in 0.1 N sodium sulfate solutions; the average particle weights in 0.1 N sodium chloride solutions are less than 18,000. On raising the temperature to 94°C. the two dyes are dispersed to aggregates of average particle weight less than 3500. Dye III is precipitated in either 0.05 N sodium chloride or 0.05 N sodium sulfate solution at 25°C., and is partially precipitated in 0.075 N sodium chloride or 0.075 N sodium sulfate at 50°C. At 65°C. the dye is dispersed into aggregates of particle weight about 15,000 in 0.1 N sodium chloride, while at 95°C. the average particle weight is decreased below 2000. Dye II appears completely dissolved in a 0.1 N sodium chloride solution at 25°C. Diffusion measurements show that the dye is aggregated into micelles of a particle weight of at least 60,000. The micelles remain unchanged at temperatures up to 65°C. At 80°C. dispersion is well under way, and at 95°C. the average particle weight is reduced to less than 5000. Experiments with dyes III and IV show that sodium chloride is a stronger agglomerating agent than sodium sulfate at elevated temperatures as well as at room temperature.

TABLE 7

Effect of temperature on aggregation of dyes in presence of electrolytes

DYE	DYE CONCENTRATION	ELECTROLYTE	ELECTROLYTE CONCENTRATION	T	$D \times 10^{-6}$	$R \times 10^{-8}$	PARTICLE WEIGHT (m)	AGGREGATION NO.
	grams per liter		*N*	*°C.*	*cm.² per second*	*cm.*		
I	0.5	NaCl	0.107	25.0	1.52	16.0	17880	28
	1.0		0.107	50.1	3.10	13.7	11220	18
	1.0		0.107	65.8	5.61	10.2	4630	7.4
	1.0		0.107	80.0	7.10	9.3	3510	5.5
	1.0		0.107	95.5	10.05	9.0	3180	5.0
II	0.5	NaCl	0.107	25.1	0.96	25.3	64950	87
	1.0		0.107	50.1	1.75	24.6	59700	80
	1.0		0.107	65.5	2.26	25.2	64180	86
	1.0		0.107	80.6	3.86	18.8	26650	36
	1.0		0.107	95.4	7.80	11.3	5790	7.7
III	1.0	NaCl	0.01	50.5	5.25	8.2	2120	3.1
	1.0		0.025	50.5	4.3	10.0	3800	5.7
	1.0		0.05	50.5	3.35	12.9	8280	12
	1.0		0.075*	50.5	1.19*	36.3	184500	272
	1.0		0.05	65.2	5.32	10.6	4590	6.8
	1.0		0.10	65.2	3.5	16.2	16400	24
	1.0		0.10	94.2	10.92	8.1	2050	3.0
III	1.0	Na_2SO_4	0.05	50.5	4.09	10.6	4590	6.8
	1.0		0.075*	50.5	1.28*	33.8	148700	219
	1.0		0.05	65.2	5.76	9.8	3630	5.4
	1.0		0.10	65.2	4.83	11.7	6180	9.1
	1.0		0.10	94.2	11.62	7.6	1690	2.5
IV	1.0	NaCl	0.1	94.2	11.8	7.5	1710	2.5
	1.0	Na_2SO_4	0.1	94.2	12.88	6.9	1330	2.0

* Dye partially precipitated in cell.

The data presented show that with the possible exception of dye II, the representative acid and substantive dyes studied by a number of workers are close to the molecular state in solution in the absence of electrolytes. The addition of inorganic electrolytes agglomerates both types of colors; substantive dyes are much more strongly aggregated than are acid dyes at the same salt concentrations. Elevation of the temperature disperses the dye micelles. Data on technical dyestuffs (16) show that a number of strongly substantive dyes are aggregated to micelles of at least one hundred molecules in 0.1 *N* sodium chloride. The data of this paper indicate that the degree of aggregation of substantive dyes in 0.1 *N* sodium chloride at the boil is less than ten molecules per micelle, and that in most cases the dyes approach the molecular state under practical dyeing conditions.

V. RELATION OF PARTICLE SIZE TO SUBSTANTIVITY OF DYES

It is well established that electrolyte-free cellulose has very little affinity for chemically pure dyes. The addition of an inorganic electrolyte, as sodium chloride, is required to promote the adsorption of dyes on cotton and rayon. The relative importance of the salt on the electrokinetic as compared with the mechanical factors in the dyeing process has been a source of extended experimentation and speculation.

Schäffer (36) states that a particle diameter of 4.5 millicrons represents the limiting size above which dyeing does not occur on cotton. The authors (16) showed from a study of the properties of twelve technical substantive dyes that dyeing at 25°C. on cotton does not progress readily unless the radius of the dye particles is less than 18×10^{-8} cm. Further studies (14, 15) were made with purified dyes. Dye I and dye II offer an interesting comparison, since they are markedly different in their dyeing properties and colloidal characteristics. The average particle radius of dye I in a dye bath containing 6.25 g. of sodium chloride per liter is less than 18×10^{-8} cm. (the estimated maximum for dyeing) over the temperature range 25° to 95°C. Dye II in a similar dye bath remains aggregated to particles of average radius greater than 18×10^{-8} cm. at temperatures up to 65°C. and possibly to 80°C. The particle radius rapidly decreases above 80°C. In dyeing experiments carried out to equilibrium, dye I is adsorbed by cotton most heavily at 25°C.; the degree of adsorption of dye I at the boil is only 40 per cent as great. Dye II is adsorbed by cotton from the dye bath very much less at temperatures below 65°C. than at temperatures greater than 80°C. Approximately four times as much of dye II is adsorbed at the boil as at 25°C. Rapid adsorption of dye II occurs only at temperatures above 75° to 80°C., i.e., at temperatures sufficiently great to disperse the dye to aggregates smaller than the maximum size for dyeing. The data are interpreted as showing that the highly salt-sensitive dye II is much more substantive to cotton than dye I. Marked adsorption of dye II is not obtained unless the proper degree of dispersion in the dye bath is obtained to permit penetration of the dye particles into the intermicellar spaces of the cotton.

Dyeing experiments were carried out with dye III and dye IV in which comparisons were made of the degree of adsorption of the dye by cotton at the end of one hour. The dye baths contained varying concentrations of sodium chloride and sodium sulfate up to 0.2 *N*, while the temperatures were 25°, 50°, and 100°C. The data obtained show that the marked differences in the degree of aggregation of dye III and dye IV in salt solutions are reflected in the dyeing process. Adsorption of dye IV, whose average particle radius is always well below 18×10^{-8} cm., increases with increasing electrolyte concentrations and decreasing temperatures. In contrast, with dye III an optimum concentration of electrolyte exists above which the rate of adsorption is decreased at 25° to 50°C. This decrease, occurring at a 0.05 *N* salt concentration at 25°C. and a 0.075 *N* salt concentration at 50°C., corresponds with the attainment of an average particle radius in the dye bath greater than 18×10^{-8} cm.

Neale (6, 7, 9, 22, 23) and his coworkers have shown with a number of substantive colors that increasing concentrations of salt in the dye bath increase the absorption of dye, while increasing temperatures decrease the absorption of dye by cellulose at equilibrium. It is the point of view of the authors that these generalizations hold true only if the average particle size of the dye micelles in the dye bath permits penetration into the intermicellar spaces of the cotton. An average micellar radius greater than 18×10^{-8} cm. may act to retard the rate of dyeing without affecting the degree of adsorption at equilibrium, or it may inhibit dyeing to produce appreciably weaker dyeings. For example, a dye-bath of dye III containing 0.075 *N* sodium chloride at 50°C. is 95 per cent exhausted on cotton in one hour. At this concentration of salt the dye is partially precipitated from the bath and the average particle radius is 36×10^{-8} cm. This average particle radius for the dye in a bath which is partially flocculated indicates that a portion of the micelles is present as particles of radius less than 18×10^{-8} cm. It is inferred that as the micelles in the dyeing range are adsorbed, the larger micelles disperse to maintain the distribution of particles in the bath, and that the dyeing process is continued in this manner until the bath is exhausted. Morton (21) reached the same conclusion for other dyes from a different experimental basis. Dye II, in contrast to dye III, is not heavily adsorbed from the bath even after three weeks, unless the average particle radius is below the estimated maximum. Adsorption of substantive dyes by cotton from a bath containing micelles of an average particle radius greater than the maximum is either retarded or partially prevented, depending on the size distribution of the particles which go to make up the average radius and the rapidity with which this distribution is reëstablished when it is disturbed by the adsorption processes occurring during the dyeing of cellulose.

All recent evidence shows that excellent dyeing with substantive colors on cotton may be obtained from baths containing micelles of any average radius below the estimated maximum. The data do not support a mechanical theory of dyeing; micelles of the same average radius in the dye bath vary widely in their dyeing characteristics. Since practical experience has shown that temperatures near the boil are best for dyeing substantive dyes for cellulose, it is probable that the best levelness and penetration in practical dyeing processes is obtained when the particle size of the micelles is nearest the molecular state.

The evidence presented in this paper shows that the substantivity of the dye molecule for cotton is qualitatively related to its salt sensitivity. The degree of adsorption of substantive dyes at the boil increases, and the ease of reversibility of the dyeing process decreases with increasing salt sensitivity. It is probable that the same forces which lead to an agglomeration of molecules of substantive dyes into micelles are instrumental in causing adsorption of the dye by cellulose.

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CATALYSIS OF IONIC OXIDATION-REDUCTION REACTIONS BY DYES AND ITS PROBABLE MECHANISM[1]

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In order to make clear the significance of the main results to be reported briefly in this paper, and indicated in its title, some introductory explanation is called for.

The basic idea underlying nearly all of present-day theory of chemical kinetics is that only *activated* molecules react, and that the absorption of a critical increment of energy is the process of activation. From this point of view reaction velocity is thought to depend merely upon the proportion of the total molecules having a certain energy content or distribution; little or nothing is said about other properties the reacting molecules must possess. The rôle of catalysts, according to this view, is either to provide a different reaction path for which a lower activation-energy level suffices, or to furnish energy-rich molecules to supply the activation energy. Without venturing to estimate, in general, how successful the theoretical treatment based on these concepts is in predicting specific reaction velocity, it seems to the writer that there is reason to doubt whether the energy concept alone is adequate to account for the velocity of many reactions in solution. Additional concepts of a different sort appear to be necessary.

Because many, perhaps most, ionic reactions in solution are immeasurably rapid it has seemed to some logical to infer that ions in general are in an activated state and require for reaction little or no added energy of activation. In making this generalization it appears to have been overlooked that there are many cases where demonstrably ionic—and demonstrably "active"—substances, thermodynamically capable of substantially complete reaction, fail to react or react very slowly. And so far as I know no basis has been suggested for predicting whether a given ionic reaction will be immeasurably rapid or very slow. That there are cases of very slow reaction between demonstrably "active" ions—and also cases of very rapid reaction involving uncharged molecules—would seem to disprove the idea that the ionic state, without further qualification, represents a

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kinetically activated state. If this argument is valid, the question arises as to what other factors determine reaction velocity.

Some of the striking cases of slow ionic reactions are found among inorganic oxidation–reduction systems. Survey of a number of these (and comparison with rapid reactions of similar type in which one of the "slow" reactants participates with a different partner) led to the hypothesis that one important factor is the equality or inequality of valence change between oxidant and reductant. One of the most remarkable cases is the failure of reaction even on boiling of ceric sulfate and thallous sulfate, both components of reversible, ionic, electromotively active couples. When separated as half-cells of a battery or with a number of catalysts the reaction is fairly rapid and complete at room temperature (10). Another example: titanous chloride (a powerful reducing agent) and iodine in potassium iodide (a fairly strong oxidant) are toward many other substances very rapidly reacting reagents. Both are also electromotively active toward inert electrodes. It is therefore surprising to find that on mixing these two solutions (both in 1 *M* hydrochloric acid) reaction is quite slow, the half-period with 0.01 *N* concentrations being nearly an hour at room temperature. (A number of similar cases, some much more striking, have been examined.)

According to the equi-valence change principle a probable explanation of the slowness of reaction is that Ti^{3+} can give up one electron but not two, while I_3^- (or I_2) can accept two but not one. This explanation is supported by the fact that in this and other similar slow ionic oxidation reactions various substances have marked catalytic effect which are able to be reduced in two steps by the reductant and thereafter to yield two electrons to the oxidant, or *vice versa.*

Among the substances which exhibit marked catalytic effect on the Ti^{3+} and I^- reaction are various dyes, notably indigosulfonates, pyocyanine, and other phenazines, and to less extent rosindulin, flavins, indophenols, and anthraquinone- and naphthoquinone-sulfonates. Can it be shown that these dyes owe their catalytic effect in this reaction to an ability to accept or yield one as well as two electrons? If so, the hypothesis suggests itself that the same property may explain the marked catalytic effect of dyes in other reactions, notably in oxidations by molecular oxygen, including biological respiration. As a matter of fact it was this last problem, the "activation" or "transport" of O_2 in biological oxidations, which directed our interest to a study of the simpler ionic reactions.[2]

It was observed some years ago that while a number of inorganic ionic

[2] The points referred to were discussed in some detail in a paper before the Federation of American Societies for Experimental Biology at Cincinnati, April 12, 1933, and in later addresses before several local sections of the American Chemical Society, but have not so far been published.

oxidation reactions comply fairly well with the equi-valence change rule (that is, that reductants requiring the loss of one electron to pass to a known state of higher oxidation are rapidly oxidized by sufficiently powerful oxidants capable of accepting one electron, but generally not rapidly by oxidants requiring two or more electrons), the components of *organic* reversible oxidation-reduction systems appeared to be exceptions to this rule. In virtually all of the many cases of dyes which had been examined at that time, the oxidant and reductant differed by a *pair* of electrons, and the point was emphasized, notably by W. M. Clark, that the two electrons appeared to be gained or lost together, not separately. Yet the oxidized forms were found to be reduced about equally rapidly by, for example, titanous chloride (yielding one electron) and by stannous chloride (yielding two). Similarly the reduced forms are as rapidly oxidized by ferricyanide or ferric ions as by I_2 (or I_3^-), Hg^{++}, or Tl^{3+}, the last three being regarded as two-electron oxidants. This exceptional behavior of dyes was obviously a serious objection to the equi-valence change idea, and left unexplained the very remarkable catalytic action of the dyes in, for example, the reaction of Ti^{3+} and I_3^-, where the addition of a very small concentration of indigocarmine enormously accelerates the oxidation.

A possible way out of the difficulty was indicated by the discovery independently by Elema and by Michaelis of the two-step oxidation-reduction of the natural pigment pyocyanine, and identification of the intermediate between the fully oxidized and fully reduced forms as a unimolecular free radical, a semiquinone. The property thus established for this pigment (and soon thereafter also for rosindulin by Michaelis) of losing one electron in each of two separate steps (as well as two electrons in one step) is precisely the property needed to account for its reactions with both one- and two-electron oxidants and reductants and for compliance with our hypothesis as to the rôle of pyocyanine in catalysis. In the meantime the theory of the two-step reaction and semiquinone formation was formulated by Michaelis and by Elema (6). Could it be that the same property is possessed by the other organic reversible systems above named, even by those for which it has been looked for and not found? This has proved to be the case with a number of these systems, of such diverse structure that it now seems permissible to predict that the two-step oxidation-reduction with intermediate semiquinone formation may be a rather general property, in varying degrees, with many organic systems.

The first case we studied was that of the indigosulfonates. These had been systematically investigated in 1923 by Sullivan, Cohen, and Clark (11), who found no evidence for the existence of an intermediate form. That an intermediate does nevertheless exist seemed probable from the fact that on cautious or slow reduction of indigocarmine at about pH 12 a cherry-color appears between the blue and the yellow of the fully oxidized and fully reduced forms. A careful reinvestigation of the four indigosulfonates, in collaboration with Dr. P. W. Preisler and later with Dr. E. S. Hill and Mr. Robert Loeffel, gave data the interpretation of which, according to the principles of W. M. Clark and of Michaelis, proves the existence of well-characterized semiquinones. Only preliminary (5, 7, 9) reports have so far been published. In the meantime the catalytically active natural alloxazine pigments, the flavins, were shown by Stern, Kuhn, Hastings, and Stare to exhibit the two-step property on reduction in acid solutions. (The flavins were found to be catalytic in the Ti^{3+} and I_3^- reaction.)

We next turned to the anthraquinonesulfonates, which have the advantage of fair stability in highly alkaline solution, where Michaelis predicted that anionic semiquinones should appear. The anthraquinonesulfonates had been studied by Conant and coworkers (3), who observed abnormal slopes of potentiometric titration curves, which they interpreted as due to meriquinone formation. Dr. E. S. Hill and I (4) found with several of these quinones clear evidence that semiquinones are formed on reduction. On cautious reduction (or reoxidation) an intermediate reveals itself by a characteristic color, the intensity of which is independent of dilution; the slope of the potential-titration curves increases systematically with rise of pH, the E_0' values being independent of concentration. Very recently Hill and I have reëxamined also several hydroxynaphthaquinones, including phthiocol, a pure sample of which was kindly furnished by Professor R. J. Anderson. The latter substance had been studied by Ball (1), who concluded that there was no evidence for semiquinone formation or two-step oxidation. We find, however, what seems to be conclusive evidence with phthiocol of two-step oxidation–reduction at high pH, with semiquinone formation which reaches a maximum of about one-half of the total. The evidence is based on the criteria developed in Michaelis' theoretical analysis and mentioned above in connection with the anthraquinonesulfonates. Statement of the data and their interpretation will be presented in papers now in preparation.

Finally Michaelis (8) reports data showing that β-naphthaquinonesulfonate exhibits semiquinone formation. We had also observed the abnormal slopes of titration curves and the existence of a colored intermediate with this quinone.

It is significant for our argument that the naphthaquinones and anthraquinones, as well as indigo, pyocyanine, flavin, and rosindulin are all markedly catalytic in the Ti^{3+} and I_3^- reaction and also in the oxidation of glucose in sodium hydroxide solution by oxygen.

There are of course many dyes capable of reversible oxidation–reduction and having catalytic properties in oxidation reactions, for which the two-step process has not so far been demonstrated. Whether in these cases also the existence of semiquinones can be proved remains to be seen. But in view of the variety of types of structure in which semiquinones have already been found, it seems not unlikely that this property is rather general among reversible organic oxidation-reduction systems, and the writer is disposed, tentatively, to attribute the catalytic activity of such systems in oxidation reactions to the possibly widespread existence of this property. It should be noted in this connection that there are doubtless other ways in which organic systems may exert catalytic activity,—such as complex formation. Also that substances capable of semiquinone formation are not by any means all equally catalytic in any one reaction. The relative levels of the potentials—of the catalyst with respect to that of the primary reductant and of the primary oxidant—appear to be very important. This point obviously concerns the old unsolved problem of the possible relation between dynamics and kinetics (2).

In conclusion I desire to mention a point concerning the behavior and potential of molecular oxygen, and a suggestion as to the possible rôle of catalysts which promote aqueous oxidations by dissolved oxygen. The calculated potential usually cited for the oxygen electrode is 1.23 volts, a value which corresponds to a very intense oxidant, an intensity which if applied unchecked to biological systems should destroy them. The fact is somehow overlooked that this potential is for the reduction of O_2 to $2H_2O$, i.e., for the acceptance by O_2 of four electrons (and $4H^+$ ions). But if the reductant yields to O_2 only two electrons (and $2H^+$ ions are added) H_2O_2 is formed, and for this reaction the normal potential is only 0.68 volt, which at pH 7 is not very far above the intensity level of methemoglobin, an active natural oxidant. Since hydrogen peroxide is known to be formed in many autoöxidations by air or oxygen, it seems probable that oxygen in aqueous solutions (including biological respiration) acts at this lower intensity level. If, however, it could be shown that reversible catalysts exist which are capable of yielding simultaneously four electrons to O_2, (and subsequently accepting electrons in steps of one or two) the full oxidizing intensity of 1.23 volts might perhaps become available. By anchoring such a catalyst at a strategic point in the cell the large energy yield might conceivably be advantageously disposed of. Such a picture is pure speculation, but it provides a possible mechanistic reason for the known fact that the "oxygen-activating" type of respiratory catalyst is essential for the breathing of cells. I know of no other suggestion as to why this type of catalyst is essential.

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ADSORPTION ON IONIC LATTICES[1]

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Although there is an extensive literature on the subject of adsorption by ionic lattices, our knowledge of the subject is still very limited. The adsorbent properties of ionic precipitates are attributed to residual valence forces of the ions in the surface of the lattice. It should be realized that the residual valence forces of ions located on the edges are greater than the forces of those located on the plane surfaces, and the valence forces of ions located on corners are still greater than those of ions on the edges. Hence the adsorptive power of lattice ions located on corners is greater than that of ions on edges, and, in turn, the adsorptive power of ions on the edges is greater than that of ions on the plane surfaces. We will call the area occupied by ions *not* located on the plane surface, *active surface.* At present no method is available for the determination of the active surface. Knowing the microscopic dimensions of a particle, it is possible to calculate the fraction of the surface occupied by ions on the corners and the edges. However, the true active surface may be much greater than that calculated from the microscopic dimensions, since in the latter case it is tacitly assumed that the surfaces are plane. Actually, most of the surface, as a rule, is not perfectly flat, but rather irregular; it contains submicroscopic pits and humps. Especially when dealing with relatively fresh ionic precipitates, the active surface is much greater than that calculated from microscopic measurements. Upon aging, a perfection of the particles takes place, and finally the active surface will approach the value calculated from the microscopic dimensions.

In a study of the adsorbent properties of ionic precipitates it should be realized that quantitatively, as well as qualitatively, adsorption on the active surface may be different from that on the plane surface. There are many indications that colloidal suspensions owe their stability to potential-determining ions adsorbed on the active surface. Upon aging, the particles become more and more perfect, resulting in a decrease of the active surface and consequently in a decrease of the charge of the particles, and in a decrease of the stability of the sol.

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Various attempts have been made to derive rules which would permit certain predictions regarding the adsorbability of various ions. Originally it was thought (F. Paneth) that the adsorbability of an ion increases with decreasing solubility of the compound formed between the adsorbed ion and the lattice ion of opposite charge. The study of Beekley and Taylor (2) on the adsorption of silver salts on silver iodide showed that this relation between adsorbability and solubility holds very roughly only, and that numerous exceptions occur. Recently Kolthoff and MacNevin (13) investigated the adsorption of various barium salts on well-aged barium sulfate from a medium of 50 per cent ethanol. The following table shows the order of adsorbability and solubility. It was found that the adsorption isotherm follows the Freundlich expression:

TABLE 1

Solubility and adsorbability

Barium salts in 50 per cent ethanol on barium sulfate

BARIUM SALT	ORDER OF ADSORBABILITY EXPRESSED IN $a \times 10^4$*	RELATIVE SOLUBILITY IN 50 PER CENT ETHANOL	ORDER OF INCREASING SOLUBILITY
1. Bromate	1.80	1	1
2. Formate	0.91	81	3
3. Nitrate	0.69	33	2
4. Perchlorate	0.59	1610	7
5. Chloride	0.54	223	4
6. Bromide	0.37	848	5
7. Iodide	0.35	1477	6
8. Thiocyanate	0.26	1663	8

* a in the expression: $\frac{x}{m} = ac^{1/n}$ $(1/n = 0.38)$.

$$\frac{x}{m} = ac^{1/n}$$

$1/n$ being about 0.38 for the various barium salts, and the constant a, given in table 1, being a measure of the adsorbability.

Again it is seen that there is no close parallelism between adsorbability and solubility. Particularly the perchlorate is out of place; it is more strongly adsorbed than barium chloride, bromide, or iodide, although its solubility in 50 per cent ethanol is greater than that of the three halides. The adsorbabilities of the bromide and iodide are practically the same, although the solubility of the iodide is much greater than that of the bromide. Fajans and Erdey-Grúz (7) pointed out that in addition to solubility other factors, such as deformation, size of the adsorbed ions, and dissociability of the adsorption complex formed have to be taken into account. Moreover, the charge (valence) of the adsorbed ions and the deformability of the lattice ions will play a part. Considering the many factors that influence the adsorbability, it is quite plausible that the so-called Paneth–Fajans–Otto Hahn rule can be only of a highly approximate character. On theoretical grounds it might be expected that there should be a simple relation between the heat of solution of the adsorbed compound and its adsorbability; the latter should increase with decreasing heat of solution. Unfortunately, not enough data on the heats of solution in extremely dilute solutions are available in the literature to test the validity of the above rule.

In making systematic adsorption studies, it is of great importance to distinguish between various kinds of adsorption which may occur. This distinction has been overlooked frequently in the literature. This neglect is the cause of considerable confusion regarding the interpretation of experimental results, as will be shown below. In the following, five different kinds of adsorption will be discussed.

1. Adsorption of a salt having an ion in common with the lattice: adsorption of potential-determining ions

Ionic lattices have a pronounced tendency to adsorb lattice ions from a solution. As a matter of fact, the growth of an ionic crystal is a result of successive additions (adsorption) of lattice ions to (on) the surface of the growing particle.

According to Haber and Beutner (8, 19, 25) the thermodynamic potential E of an ionic precipitate, say of silver iodide is equal to:

$$E = C + \frac{RT}{F} \ln a_{\mathrm{Ag}^+} = C' - \frac{RT}{F} \ln a_{\mathrm{I}^-} \qquad (1)$$

in which C and C' are constants and Ag^+ and I^- the "potential-determining ions" (20). The adsorption of potential-determining ions is accompanied by the adsorption of an indifferent ion of opposite electrical charge, the total adsorption giving rise to the formation of the so-called double layer. With constant capacity of the double layer, the amount of I^- or Ag^+ (x) taken up by a given amount of silver iodide is proportional to E. Since E is a linear function of $\ln a_{\mathrm{Ag}^+}$ or $\ln a_{\mathrm{I}^-}$ it is found (1) that

$$\begin{aligned} x &= k_1 + k_2 \log C \\ \Delta x &= k\Delta \log C \end{aligned} \qquad (2)$$

in which x is the amount adsorbed and C the concentration (actually the activity) of the potential-determining ion.

It should be noted that according to equation 2, the amount of potential-determining ion adsorbed (x) is a simple logarithmic function of the activity of the ion in the solution, but that no provision is made for the effect of the indifferent ion which is adsorbed simultaneously. Still, we have seen before that the adsorption of a salt containing a lattice ion is also a function of the nature of the indifferent ion.

The validity of equation 2 has been shown to hold true for one case only, namely, for silver iodide. Lange and Berger (21) determined the adsorption of silver nitrate and potassium iodide on freshly precipitated silver iodide at various temperatures. They found that the adsorption of the potential-determining silver and iodide ions agreed with the expression $\Delta x = k\Delta \log C$. They also concluded that silver ions are more strongly adsorbed than iodide ions at the same equilibrium concentration in the solution. This conclusion was based on the erroneous assumption that neither adsorption of silver ions nor of iodide ions occurs at the potentiometric end point or equivalence potential where $c_{Ag^+} = c_{I^-}$. Verwey and Kruyt (28), working with well-aged electrodialyzed silver iodide sols, found that the adsorption of iodide ions follows the expression $\Delta x = k\Delta \log c$. By extrapolation to the point of zero adsorption, they concluded that the zero point charge or isoelectric point of aged silver iodide is found at a silver-ion concentration of 10^{-6} molar, hence in a solution in which the silver-ion concentration is about 10,000 times greater than the iodide-ion concentration. In a precision study carried out in this laboratory by Kolthoff and Lingane (12), it was found that the isoelectric point of fresh silver iodide is at pAg = 6.0 and that the adsorption of silver ions follows the expression $\Delta x = k\Delta \log c$. As a result of the asymmetric location of the isoelectric point the "equivalence potential" ($c_{Ag^+} = c_{I^-}$) does not coincide with the stoichiometric end point. As a matter of fact, it was found that upon mixing silver nitrate with potassium iodide at room temperature, the silver iodide at the equivalence potential contained 0.1 of a per cent of iodide in excess. Expressed in other words, on mixing equivalent amounts of silver and iodide the supernatant liquid contains a slight excess of silver and the precipitate a slight amount of adsorbed iodide. Only at the isoelectric point is the silver iodide free of adsorbed silver or iodide salt. Hence it is impossible to prepare pure, relatively fresh silver iodide in equilibrium with its saturated solution in water ($c_{Ag^+} = c_{I^-}$). The solid consists of pure silver iodide only when the silver-ion concentration in the supernatant liquid is equal to 10^{-6} molar. Upon washing such a precipitate with water an adsorption of iodide ions, supplied by solution of the solid silver iodide, will occur. Upon continued washing the counter ions adsorbed with the iodide ions will be hydrogen ions, supplied by the water.

The amounts of silver and iodide adsorbed by the fresh silver iodide in the above experiments were found to be extremely small, although the fresh silver iodide had an extremely large surface. Apparently the adsorption of silver and iodide ions takes place on the active surface only. If the silver iodide was prepared by slow precipitation at 95°C. the adsorption of silver and iodide ions was found to be reduced to almost negligible quantities, owing to rapid perfection of the particles with a resultant decrease of the active surface.

Although theoretically not expected, it was found by Kolthoff and MacNevin (13) that the adsorption of barium salts from 50 per cent ethanol on barium sulfate does not follow expression 2, but over a wide range of concentrations the relation $\Delta \log x = k\Delta \log C$. The barium sulfate used was a fine, well-aged product, the average dimension of the particles being 0.14 micron. From aqueous medium the adsorption of the barium salts was so small that it was hardly detectable. From a medium consisting of 50 per cent ethanol a marked adsorption occurred; apparently the energy of desolvation of the adsorbed ions is much less in this medium than in water. It may be mentioned that the possibility of the adsorption of un-ionized salt should not be overlooked. It is planned to make a more extensive study of the medium effect upon the adsorption. It was noted that the barium sulfate, upon shaking with solutions of various barium salts in 50 per cent ethanol, had a pronounced tendency to go into colloidal solution. Hence, one would expect to be dealing with adsorption of potential-determining ions (equation 2). On the other hand, the amounts of barium salts adsorbed were found to be much greater than would correspond to an adsorption on the active surface only. It may be that the adsorption on the active surface is governed by equation 2, whereas the adsorption on the plane surface is determined by the Freundlich adsorption isotherm

$$x = ac^{1/n} \text{ or } \Delta \log x = k\Delta \log C \qquad (3)$$

which expression was found to hold in this particular case. It may be mentioned that a marked adsorption of calcium bromate (in the form of $Ca(OH)(BrO_3)$ as a result of hydrolytic adsorption) and of potassium bromate was found from a medium of 50 per cent ethanol. In these cases we are dealing with a true salt adsorption in the absence of a potential-determining ion, and there is a possibility that in the above case the adsorption of the barium salts is mainly of the latter type.

In the determination of the adsorption of a salt containing a lattice ion, equivalent amounts of cations and anions are found to be removed from solution. Such an experimental result does not always allow the conclusion that equivalent amounts of potential-determining ions and indifferent ions of opposite charge are actually adsorbed. There is a possibility that an exchange, discussed in the following paragraph, occurs with subsequent precipitation of the excess of lattice ions in solution, with lattice ions of opposite charge sent into solution, as a result of exchange.

2. Exchange adsorption between lattice ions in the surface and foreign ions from the solution

When an ionic precipitate is in equilibrium with a solution, the speed with which ions leave the surface is equal to the speed with which the ions deposit from the solution on the surface. The equilibrium is kinetic rather than static. One might say that there is a statistical distribution of lattice ions between the surface and the solution. The determination of the specific surface of lead salts with thorium B as radioactive indicator (23, 15) is based upon this principle. Upon shaking a lead salt with a solution containing thorium B, the following relation holds when there is kinetic exchange equilibrium:

$$\frac{(\text{ThB surface})}{(\text{ThB solution})} = \frac{(\text{Pb surface})}{(\text{Pb solution})} \tag{4}$$

When the solution contains foreign ions which are strongly adsorbed by, and fit into, the lattice a similar exchange may be found between the lattice ions and the foreign ions. For example, upon shaking barium sulfate with lead chloride it was found (22) that lead ions but no chloride ions were removed from solution. Moreover, it was found that for each lead ion removed, a barium ion entered the solution. These experiments show conclusively that the "adsorption" of the lead ions involves an exchange reaction, represented by the equation

$$\underset{\text{Surface}}{BaSO_4} + \underset{\text{Solution}}{Pb^{++}} \longrightarrow \underset{\text{Surface}}{PbSO_4} + \underset{\text{Solution}}{Ba^{++}}$$

Part of the barium ions in the surface are replaced by lead ions. Quantitatively the adsorption is determined by neither equation 2 nor equation 3 (case I) but by an expression similar to equation 4:

$$\frac{(\text{Pb surface})}{(\text{Pb solution})} = K\,\frac{(\text{Ba surface})}{(\text{Ba solution})} \tag{5}$$

in which K represents the distribution coefficient of lead between solution and the surface of barium sulfate. The value of K has been determined by Kolthoff and MacNevin (14) by working with barium sulfate of known surface; it was found to decrease with increasing mole percentage of lead in the surface of lead sulfate. A similar exchange occurs in the following cases:

$$\mathrm{BaSO_4} + \mathrm{CrO_4^{--}} \longrightarrow \mathrm{BaCrO_4} + \mathrm{SO_4^{--}}$$

$$\underset{\text{Surface}}{\mathrm{AgCl}} + \underset{\text{Solution}}{\mathrm{Br^-}} \longrightarrow \underset{\text{Surface}}{\mathrm{AgBr}} + \underset{\text{Solution}}{\mathrm{Cl^-}}$$

In all these cases the foreign ion fits in the lattice of the adsorbent, and its size is of the same magnitude as that of the replaced ion.

It was found in this laboratory that an exchange of the above nature is not limited by the similarity in size of the exchanging ion and the exchanged lattice ion. As a matter of fact, it is even not necessary that both ions carry the same charge. Below are given some examples of exchange reactions that have been studied, thus showing the general occurrence of the phenomenon; in each case the literature reference follows the equation.

$$\mathrm{3PbSO_4} + \mathrm{2Ponc.^{--}} \rightarrow \mathrm{Pb_3(Ponc.)_2} + \mathrm{3SO_4^{--}} \qquad (16)$$
$$\mathrm{PbSO_4} + \text{wool violet}^{--} \rightarrow \text{Pb wool violet} + \mathrm{SO_4^{--}} \qquad (17)$$
$$\mathrm{CaOx} + \mathrm{SO_4^{--}} \rightarrow \mathrm{CaSO_4} + \mathrm{Ox^{--}} \qquad (18)$$
$$\mathrm{CaOx} + \mathrm{Ba^{++}} \rightarrow \mathrm{BaOx} + \mathrm{Ca^{++}} \qquad (18)$$
$$\mathrm{AgCl} + \text{eosin}^{-} \rightarrow \text{Ag eosin} + \mathrm{Cl^-} \qquad (10)$$
$$\mathrm{BaSO_4} + \mathrm{2IO_3^-} \rightarrow \mathrm{Ba(IO_3)_2} + \mathrm{SO_4^{--}} \qquad (22)$$
$$\mathrm{2AgCl} + \text{wool violet}^{--} \rightarrow \mathrm{Ag_2}\text{ wool violet} + \mathrm{2Cl^-} \qquad (29)$$

In none of these cases is an equivalent adsorption of cation and anion found, the exchanging ion being removed only, whereas an equivalent amount of exchanged lattice ion is sent into solution. It is possible to interpret the experimental results by a mechanism different from an exchange, although it should be stated that the other interpretations are not very plausible in the cases referred to. More work should be done in order to decide whether all the exchange reactions occurring can be interpreted by the same mechanism. Let us take as an example the adsorption of wool violet on lead sulfate (17). On shaking lead sulfate with the sodium salt of wool violet it was shown experimentally that the dye ion is removed from solution, no sodium ion being adsorbed, and that for each adsorbed wool violet ion a sulfate ion is sent into the solution. The experimental results were interpreted by an exchange mechanism. However, another possible explanation is that the wool violet is adsorbed as lead salt on the surface of lead sulfate, the lead ions being furnished by the saturated solution of lead sulfate. As a result of the disappearance of lead ions, the solution is no longer saturated with the solid, and more lead sulfate will go into solution until equilibrium is restored. The final result then is that equivalent amounts of lead and wool violet ions leave the solution and the latter, therefore, must contain sulfate ions in excess. Verwey (26) has proposed a mechanism different from exchange and from the adsorption of the lead salt of wool violet. According to his interpretation there is a possibility of the formation of a triple layer, the dye ions being truly adsorbed on the surface. Since the thermodynamic potential of the precipitate is hardly changed by the adsorption, some lead ions are adsorbed in the surface, but most of the lead ions are adsorbed as counter ions. If this interpretation is correct it should be possible to replace the lead ions adsorbed as counter ions by any other cation. Such experiments have not yet been made.

At this point we should add a few words to what has been said in the previous section (case I) on the mechanism of the adsorption of a salt having an ion in common with the lattice. If the ion of the salt foreign to the lattice gives a marked exchange with the lattice ion of the same electrical sign in the surface, we cannot conclude from the experimental results that an equivalent adsorption of lattice ion and foreign ion has occurred. It is true that equivalent amounts of lattice ion and foreign ion are removed from solution, but the foreign ion may disappear as a result of exchange and the lattice ion by precipitation in the form of the adsorbent itself. Let us consider as an example the adsorption of the lead salt of wool violet on lead sulfate. The primary reaction is the following exchange:

$$PbSO_4 + \text{wool violet}^{--} \rightarrow \text{Pb wool violet} + SO_4^{--}$$

The sulfate ions entering the solution as a result of exchange are precipitated as lead sulfate by the excess of lead ions in the solution

$$Pb^{++} + SO_4^{--} \rightarrow PbSO_4$$

From the analytical results one might conclude that the lead salt of wool violet is adsorbed; actually, however, the wool violet is removed by exchange and the lead ions by precipitation. In experiments carried out by Sandell (18) it was found that iodate ions give an exchange with oxalate ions on the surface of calcium oxalate, but no exchange occurred between iodide and oxalate ions. Even the adsorption of calcium iodide on calcium oxalate was found to be negligibly small, whereas the adsorption of calcium iodate was pronounced. Naturally an excess of calcium ions in the solution favors the exchange between iodate and oxalate ions in the surface of the lattice, as the concentration of the oxalate ions in the solution is decreased by the excess of calcium. Hence, it is quite possible that in this case again we are dealing with an exchange of iodate ions and a subsequent precipitation of calcium oxalate.

3. *Exchange between adsorbed "counter ions" and foreign ions in the solution*

It is well known that colloidal solutions owe their stability in the first place to a primary adsorption of lattice ions, an equivalent amount of foreign ions of opposite sign being adsorbed as counter ions in the mobile part of the diffuse double layer. Exchange between these counter ions and other ions of the same electrical sign in the solution is determined in the first place by the Schulze-Hardy rule, the exchange ability of an ion increasing strongly with its valence (charge) as shown by Verwey and Kruyt (28) in the case of silver iodide sols. Such an exchange also occurs after the flocculation of the particles, and should be distinguished from true adsorption. Exchange of counter ions does not result in an equivalent adsorption of foreign cation and anion from the solution, but in a removal of the exchanging ion, the latter being replaced by an equivalent amount of the counter ion originally present on the surface. Silver iodide, for example, even after a thorough washing process, contains adsorbed iodide ions and an equivalent amount of hydrogen ions as counter ions. If such a precipitate is shaken, say, with a dilute lead nitrate solution, no nitrate ions are adsorbed, but lead ions exchange with hydrogen ions:

$$\mathrm{AgII^-} \,\vdots\, \mathrm{H^+} + \tfrac{1}{2}\mathrm{Pb^{++}} \longrightarrow \mathrm{AgII^-} \,\vdots\, \tfrac{1}{2}\mathrm{Pb^{++}} + \mathrm{H^+}$$

The quantitative relation between amount adsorbed and concentration is quite different from those discussed in the previous paragraphs. For two equally charged ions, for example H^+ and K^+, Verwey (27) derived that exchange equilibrium[2] is determined by the expression:

$$\left(\frac{\mathrm{H^+}}{\mathrm{K^+}}\right)_{\text{surface}} = K\left(\frac{\mathrm{H^+}}{\mathrm{K^+}}\right)_{\text{solution}} \qquad (6)$$

Apparently activities instead of concentrations should be written in the above expression. However, as long as we are dealing with two ions of the same electrical charge, the concentration relation may be expected to hold within a wide range of ionic strengths. When the two ions differ in charge, the expression may be expected to become extremely complicated. With the aid of the Debye-Hückel expression, the activity coefficients of the two ions in the solution can be calculated approximately with a reasonable accuracy, but nothing is known of the activity coefficients in the double layer. It well may be expected that the activity coefficient of the ions in the double layer will be a function of the thickness of the latter. This thickness depends on the kind and particularly on the valence of the counter ions, thus making a theoretical solution of the problem still more complicated. Numerous studies on the quantitative relationships in exchange reactions on zeolites and soils have been described in the literature, but the significance of activities has not been considered. It should be added that even in the simple case represented by equation 6 it is doubtful whether the value of K may be considered to be constant, when

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[2] See, however, the statistical treatment by Jenny (J. Phys. Chem. 40, 501 (1936)), which is quite different.

the surface contains centra of varying activities. Especially when dealing with exchanging ions of different charge, *K* may be expected to be a function of the activity of the surface. Summarizing then, it may be stated that our knowledge of the quantitative relationships of the exchange of counter ions is still very limited and that more systematic work is desirable.

A distinction between exchange of counter ions and other types of adsorption becomes of primary importance in studies on the adsorption of radioactive ions, in which the amounts of adsorbates used are extremely small. In comparing the kinetics of the adsorption of different radioactive ions, one has to ascertain in the first place whether one is dealing with the same kind of adsorption. This has been overlooked by Imre (9), who compared the adsorption of actinium (a lanthanum homolog) and of thorium B (a lead isotope) on barium sulfate. In the former case he undoubtedly was dealing with an exchange of counter ions:

$$3(\mathrm{BaSO_4SO_4^{--}} \,\vdots\, \mathrm{2H^+}) + \mathrm{2Act^{+++}} \longrightarrow \mathrm{3(BaSO_4SO_4^{--})} \,\vdots\, \mathrm{2Act^{++++}} + \mathrm{6H^+}$$

in the latter case also with an exchange between thorium B and barium ions in the surface of barium sulfate.

$$\mathrm{BaSO_4} + \mathrm{ThB^{++}} \rightarrow \mathrm{ThBSO_4} + \mathrm{Ba^{++}}$$

For this reason the time-adsorption curves of these two ions are not comparable.

4. *Molecular adsorption of non-electrolytes and true adsorption of salts*

Pure precipitates with ionic lattices attract and adsorb water from the atmosphere; this adsorption of water increases with increasing surface development of the precipitate. The adsorbed water can be held very tenaciously. deBoer and Dippel (3) were unable to remove adsorbed water from calcium fluoride at room temperature in a high vacuum. Even upon heating, the adsorbed water was not given off; at 400°C. the water layer could be removed, not by desorption but as a result of a chemical reaction:

$$\mathrm{CaF_2} + \mathrm{H_2O} \rightarrow \mathrm{CaF(OH)} + \mathrm{HF}$$

Miss deBroeckère (5) found that water adsorbed on barium sulfate was not removed after heating to 250°C., but that at temperatures between 250° and 300°C. it was desorbed quantitatively. Moreover, she claims that the water may be adsorbed in a monomolecular layer. Qualitatively as well as quantitatively, results obtained in this laboratory differ from those of deBroeckère; a final discussion of the matter will be postponed until more conclusive information has been obtained. Not only water, but also other substances with a dipole character can be adsorbed in a molecular form. We found, for example, that water-free precipitates may adsorb considerable amounts of methanol. In the Harkins' method for the determination of the specific surface with higher fatty acids, use is made of the fact that on the saturated surface these acids form a monomolecular layer, the orientation of the adsorbed molecules and their diameter on the surface being known.

Considering the strong electrical field around the cations and anions in the surface of the lattice, it may be expected that not only dipoles may be adsorbed, but ions as well. Thus, on shaking of an ionic precipitate with a solution of a salt having no ion in common with the lattice, an equivalent adsorption of cations and anions may be anticipated. Actually it is claimed by deBroeckère (6, 24) that various chlorides, bromides, and iodides are adsorbed on the saturated surface of barium sulfate as a monomolecular layer, and that the relation between adsorption and concentration is quantitatively expressed by equation 3. From dilute aqueous chloride solutions there is mainly an adsorption of water molecules, the latter being gradually replaced by the metal chloride with increasing concentration of the latter in the solution. We (11) have not been able to duplicate deBroeckère's experiments, and a final discussion must be postponed until later.[3]

Recently it has been found in this laboratory (13) that the adsorption of salts depends greatly upon the nature of the solvent. For example, we found that the adsorption of potassium and calcium bromate on barium sulfate was negligibly small from dilute aqueous solutions, whereas a pronounced adsorption occurred from solutions of 50 per cent ethanol. The potassium bromate gave an equivalent adsorption of cations and anions, but in the case of calcium bromate, a hydrolytic adsorption as $Ca(OH)BrO_3$ occurred. We plan to study this medium effect in greater detail.

5. *Activated adsorption*

In the preceding section we have seen that non-electrolytes and very weak electrolytes may be molecularly adsorbed on the surface of ionic precipitates. If the adsorbate is a weak acid and the adsorbent a base (hydrous oxides) two different kinds of adsorption may occur:

a. Molecular adsorption. This type of adsorption, for example, occurs upon shaking a suspension of hydrous aluminum oxide with dilute solutions

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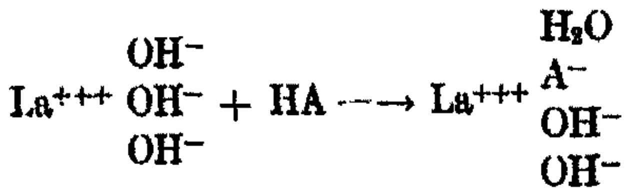
[3] Miss de Broeckère and the author will exchange samples of barium sulfate, in order to decide whether the discrepancy can be attributed to a great difference in specific surface of the products with which the work was performed.

of phenolphthalein or thymolphthalein, in which case the undissociated acid molecules are adsorbed.

b. Activated adsorption. If the adsorption energy is great enough to overcome the dissociation energy of the adsorbate, the latter will be adsorbed in the ionized form. This case occurs, for example, upon shaking a suspension of lanthanum hydroxide with thymolphthalein:



$$\mathrm{La}^{+++}\begin{array}{l}\mathrm{OH}^-\\ \mathrm{OH}^-\\ \mathrm{OH}^-\end{array} + \mathrm{HA} \longrightarrow \mathrm{La}^{+++}\begin{array}{l}\mathrm{H_2O}\\ \mathrm{A}^-\\ \mathrm{OH}^-\\ \mathrm{OH}^-\end{array}$$

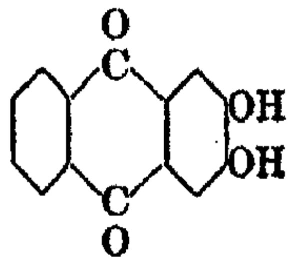
Lanthanum hydroxide is a strong, but only slightly soluble base, its saturated solution in water having a pH of about 9. At this pH thymolphthalein is still present in the colorless form. When a suspension of the base is shaken with the indicator the color turns to a beautiful blue. After settling, the supernatant liquid is colorless; but the precipitate, containing the adsorbed indicator in the ionized form, is strongly colored. This distinction between molecular and activated adsorption may permit us to draw definite conclusions regarding the basicity of the hydrous oxides in the solid state.

Dependent upon the experimental conditions, a substance may be adsorbed in the molecular or activated form. Reference is made to the beautiful investigations of deBoer (4) and coworkers on the adsorption of alizarin and other compounds from the gaseous phase on thin sublimed layers of calcium, barium, and strontium fluorides and barium chloride. At temperatures below 300°C. a molecular adsorption of alizarin on calcium fluoride occurs. The adsorbed dye has a red-brown color and can be extracted completely with amyl alcohol. When the temperature is increased to 400°C. the color of the adsorbed alizarin changes from a red-brown to a brick-red. The dye is now adsorbed in the activated state

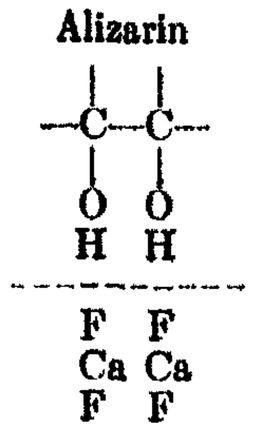
$$\mathrm{CaF_2} + \text{aliz.} \rightarrow \text{Ca aliz.} + 2\mathrm{HF}$$

and cannot be removed from the surface by extraction with amyl alcohol. Treatment with hydrochloric acid is necessary in order to decompose the adsorption compound. In this case of activated adsorption the fluoride ion in the calcium fluoride functions as the base similar to the hydroxyl ion in the lanthanum hydroxide.

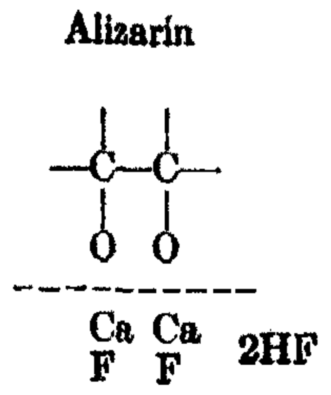
Schematically the two kinds of adsorption may be represented in the following way:



Alizarin



Molecular adsorption



Activated adsorption

In this case the type of adsorption is determined primarily by the dissociation energies of the adsorbed acid and of hydrofluoric acid. If the adsorbate is a relatively strong acid, its proton can be captured by the fluoride ion at low temperatures and an activated adsorption will be found. This case occurs with picric acid. If, on the other hand, the adsorbate is an extremely weak acid, such as *p*-nitrophenol, a molecular adsorption will result only, as the dissociation energy of the adsorbed acid is much greater than that of the hydrofluoric acid. The case of alizarin is intermediate between these two: at lower temperatures (300°C.) its dissociation energy is greater than that of hydrofluoric acid (we neglect polarization of the alizarinate or fluoride ion), at higher temperatures the reverse is true.

Comparable to this case is the adsorption of water on calcium fluoride. We have seen that at low temperatures the water is adsorbed in the molecular form, but that at 400°C. an activated adsorption occurs with the evolution of an equivalent of hydrogen fluoride.

SUMMARY

In systematic studies of the adsorbent properties of ionic precipitates distinction has to be made between different types of adsorption. These various types are discussed from a qualitative and quantitative viewpoint.

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THE GELATION OF BENTONITE SUSPENSIONS[1]

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It has been known for some years that certain sols, on standing, form gels which can be reliquefied by shaking. This phenomenon was first discovered by Schalek and Szegvary (13) in 1923 for ferric oxide sols to which a small amount of electrolyte, for example, sodium chloride, had been added. Since then many cases of this isothermal reversible sol–gel transformation, which Freundlich has termed "thixotropy," have been reported.

Bentonite, a clay-like material, probably of volcanic origin and found largely in Wyoming, exhibits thixotropy to a marked degree in aqueous suspensions. Suspensions of suitable concentration will set to a gel in a few seconds, although a number of other factors materially influence this setting time. Particle size undoubtedly plays a great part, since centrifuged suspensions will give dispersions showing thixotropy down to at least a concentration of 1 per cent, whereas ordinary bentonite suspensions require a concentration of over 4 per cent.[3] The hydrogen-ion concentration of the suspension, as might be expected, was also found by Freundlich, Schmidt, and Lindau (5) to be of great importance. Acid-washed bentonite or electrodialyzed bentonite suspensions do not show thixotropic behavior. In this paper the effects of temperature and concentration upon gelation are described. No attempt has been made to determine the influence of pH, the hydrogen-ion concentration being kept as constant as possible.

METHODS OF MEASUREMENT

The investigation of thixotropy is greatly hampered by the lack of an adequate method of measurement. The inverted-tube method first introduced by Schalek and Szegvary (14) has been most commonly used. The sol is introduced into a tube, which is stoppered or preferably sealed

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[1] Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11–13, 1936.

[2] Fellow of the Salters' Institute of Industrial Chemistry, London, England.

[3] Centrifuged dispersions will be termed "ultrabentonite" in the following in order to distinguish them from ordinary bentonite suspensions.

off. After vigorous shaking the tube is allowed to stand undisturbed in a vertical position for a known time and then inverted. If flow occurs down the wall of the tube, the sol is said to be still liquid. If no flow is apparent then the sol is said to have solidified. By trial and error a time interval can be found below which flow occurs and above which there is no flow. This is called the setting time; its reciprocal is taken as the rate of gelation.

TABLE 1

The effect of the amount of material upon the time of setting

Ultrabentonite, 2.09 per cent; pH, 7.84; T, 27.5°C.

TUBE DIAMETER	AMOUNT OF LIQUID	SETTING TIME
mm.	*cc.*	*seconds*
7.5	1	405
	1.5	395
	2.0	405
9.6	1.0	1485
	2.0	1485

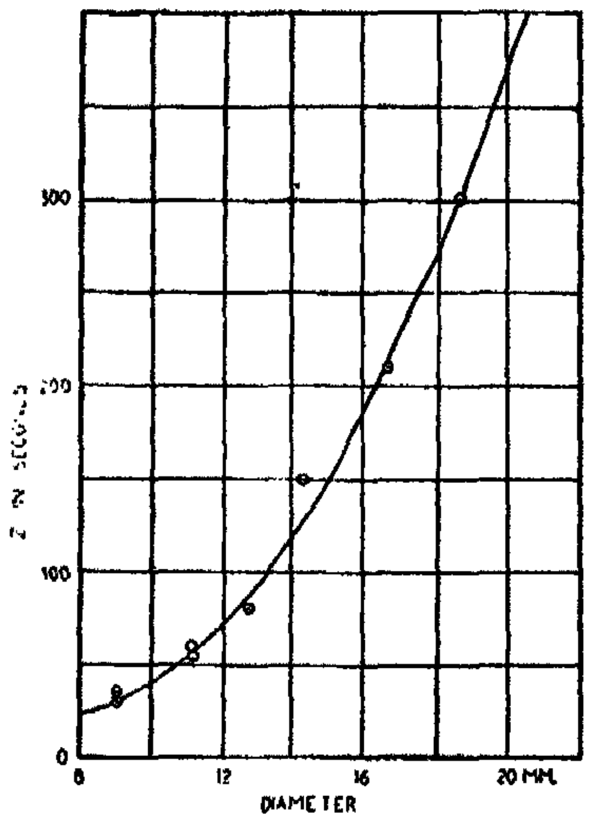

FIG. 1. Effect of diameter of tube upon time of setting of ultrabentonite at 27.5°C.

Theoretically, it is seen that this setting time must depend upon a number of factors,—the strength of the gel formed, its weight, the surface tension of the suspension, etc. Practically, it varies greatly with the diameter of the tube; also great care has to be taken in inverting the tube, since slight shaking may cause flow to occur when none would take place with gentle inversion. With care consistent results can be obtained, although these vary with the observer. One would desire a true history of the development of gel structure, i.e., of resistance to initiation of flow, but the inverted-tube method unfortunately only gives one point upon such a curve.[4]

In spite of the extensive use of the inverted-tube method, little appears to have been published upon the influence of amount of material enclosed in the tube, the diameter of the tube, etc. As is evident from table 1, within reasonable limits the former has no effect upon the setting time. On the other hand, the diameter of the tube has a very marked effect, as seen from figure 1. Approximately, at least, the relation between tube diameter and setting time for a given suspension and temperature is

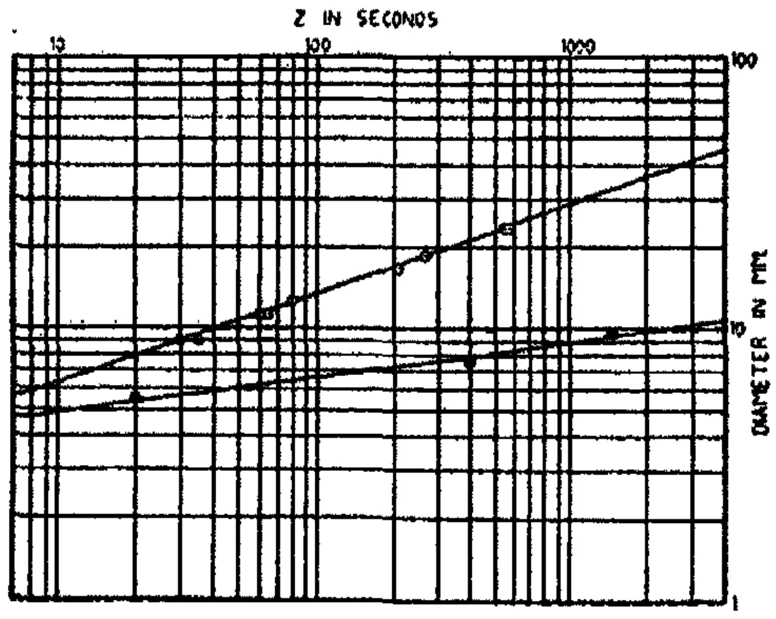

FIG. 2. Effect of diameter of tube upon setting time at 27.5°C. ⊙, 6.60 per cent bentonite; ⊗, 2.09 per cent ultrabentonite.

$$z = kD^n \qquad (1)$$

where z is the setting time, D the internal diameter of the tube, and k and n are constants. Figure 2 shows that the diameter of the tube has a greater influence upon ultrabentonite than upon the crude suspensions. Its influence also decreases with temperature.

The values of k and n unfortunately vary according to the suspension examined, so that no general correction factor can be given for changing tube diameter (table 2). Furthermore, as will be shown later, the temperature coefficient of the setting time of a given suspension is not independent of the tube in which it is measured.

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[4] As Freundlich and Rawitzer (4) have stated, "The setting time is characterized neither through a certain variation of tensile strength nor through an abrupt variation in the velocity of transition. In no respect does it represent a unique point on the solidification curve. For comparison of different sols the setting time is nevertheless very suitable."

These considerations led to the view that another method of measuring the rate of gelation of thixotropic suspensions would be desirable. Freundlich and Rawitzer (4) measured the tensile strength of a ferric oxide sol by means of a cup suspended by a torsion wire in the sol contained in an outer cylinder, which could be rotated. Pryce-Jones (12) adopted a similar but more elaborate device. Such methods, while useful in showing there is no abrupt transition between sol and gel, require elaborate apparatus and care in operation while still yielding only comparative results. A more natural property to investigate appears to be the viscosity of the sol. In fact, most studies of the gelation of emulsoidal solutions have been made by viscosity measurements. Gelation is a kinetic process, almost certainly consisting of the building-up of a structure, which inter-

TABLE 2

Values of k and n for different suspensions

TEMPERATURE	SUSPENSION	CONCENTRATION	*k*	*n*
°C.		*per cent*		
27.5	Bentonite	6.60	0.044	3.0
27.5	Ultrabentonite	2.09	0.000038	7.8
75.0	Ultrabentonite	2.09	1.8	2.1

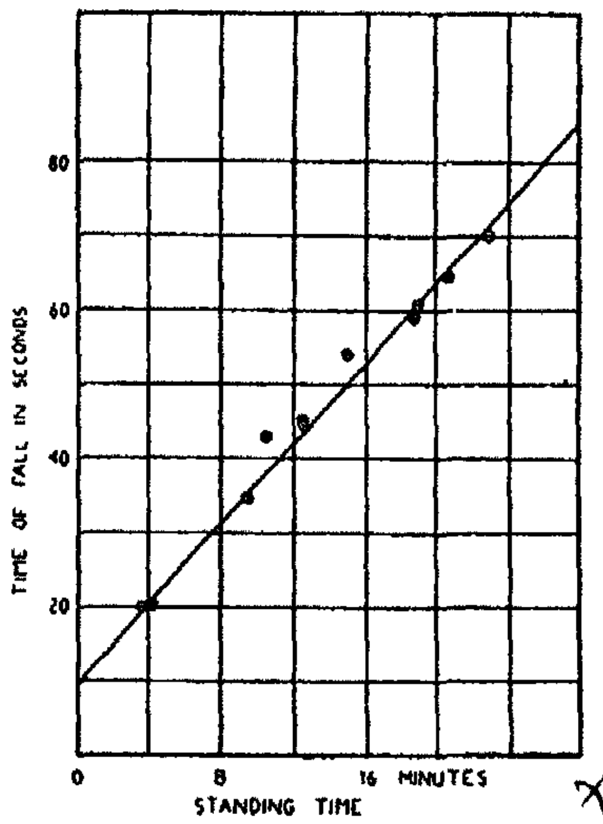

FIG. 3

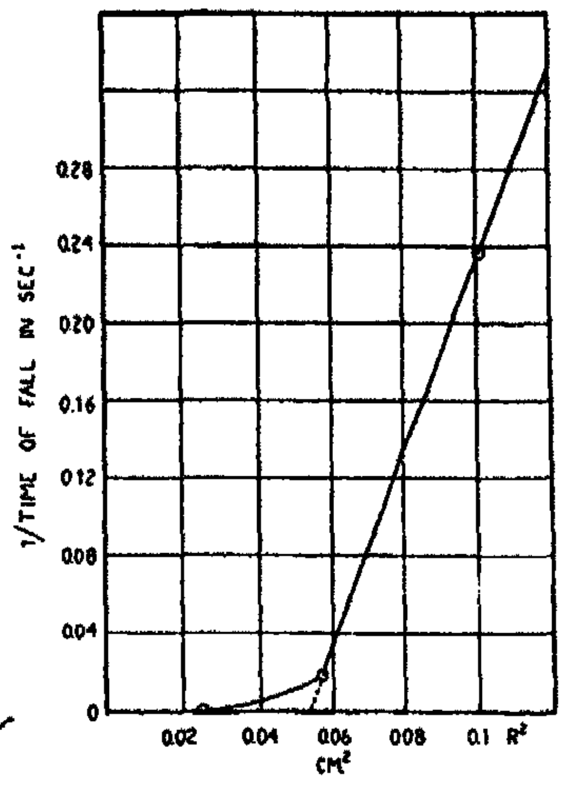

FIG. 4

FIG. 3. Effect of diameter of viscometer upon time of setting. ⊙, viscometer I, internal diameter 1.2 cm.; ⊗, viscometer II, internal diameter 1.5 cm.

FIG. 4. Ultrabentonite at 55°C. Standing time, two hours. Velocity of sphere plotted against the square of its radius.

feres with the flow of the liquid. Unfortunately most methods of measuring viscosity cause simultaneously the breakdown of this gel structure to an unknown degree. The falling-ball viscometer has, however, the advantage that the sphere continuously passes on to the undisturbed suspension, so that its travel is relatively free from the effects of structure breakdown. This led to a decision to use the falling-ball method in measuring the rate of gelation of bentonite suspensions.

The ordinary type of falling-ball viscometer was used (1). The tube had a width of about 12.5 mm., and a glass tap was fused to the lower end to facilitate the removal of the dropped balls. The distance between marks was 13.9 cm. The viscometer was placed in a thermostat, the temperature of which could be kept constant to ± 0.25°C. Glass balls about 5 mm. in diameter were first used, since Freundlich (2) has pointed out that the pH, and as a consequence the setting time, of ferric oxide sols is altered by contact with metal. Steel balls about $\frac{1}{16}$ in. in diameter were afterwards used, but no irregularities in behavior were observed. The sol was placed in the viscometer, allowed to come to the temperature of the bath, shaken well, and replaced. After the sol had stood for a known length of time the ball was dropped and the time of fall taken. In this way a curve such as that shown in figure 3 could be obtained.

No attempt was made to convert the times of fall into absolute viscosities, for several reasons. Ultrabentonite belongs to the class of substances showing plastic flow. That is, it possesses a definite yield point and its apparent viscosity is not independent of the shearing force. For a true liquid the curve connecting velocity and the square of the radius of the sphere would be a straight line passing through the origin. This is not the case for ultrabentonite (figure 4). Furthermore, Stokes' law, upon which any calculations would have to be based, is derived for the case of a homogeneous fluid and cannot hold for a gelating sol. Nevertheless, measurements using the same sphere and viscometer give comparative results for the rates of gelation over the whole curve, and not merely for one particular point.

Time of fall is linear in standing time, at least during the early stages of gelation and

$$y = ax + b \tag{2}$$

where y is the time of fall, x the time of standing, and a and b are constants. Granting that the degree of development of structure, i.e., gelation, is proportional to the increase in time of fall, it follows that the rate of gelation, as measured with a given ball, is independent of the time of standing. This surprising result shows a marked difference from the case of emulsoidal gel formation. Thus Mardles (10), for cellulose acetate gels in benzyl alcohol and other solvents, found by the falling-ball method that

$$\eta - \eta_0 = ae^{kt} \tag{3}$$

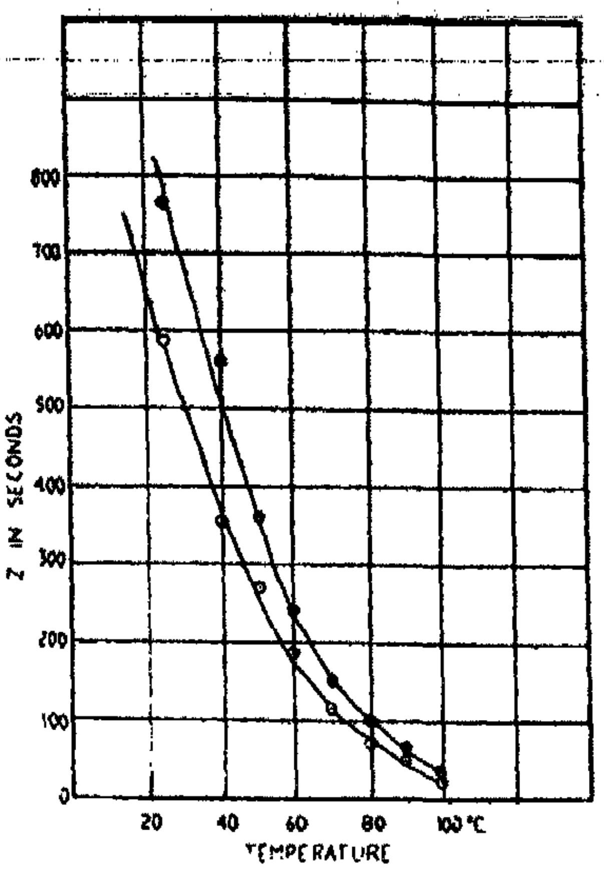

FIG. 5

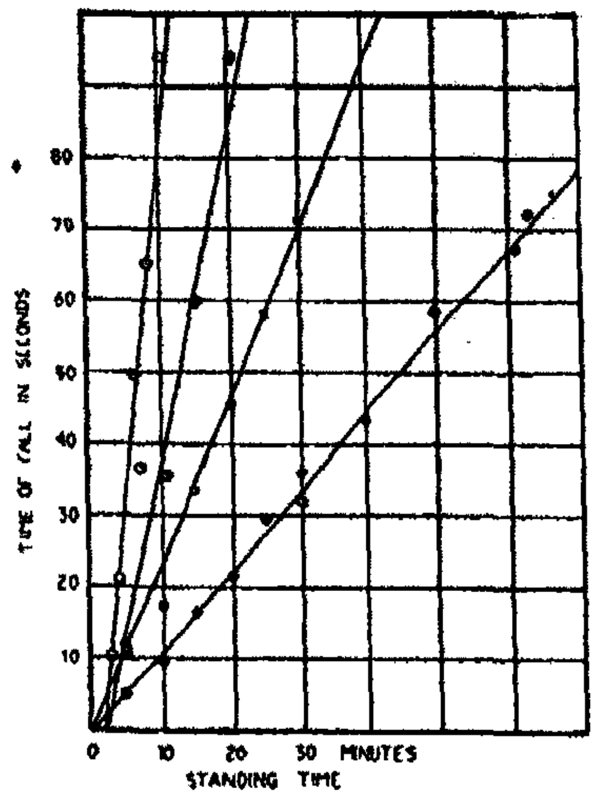

FIG. 6

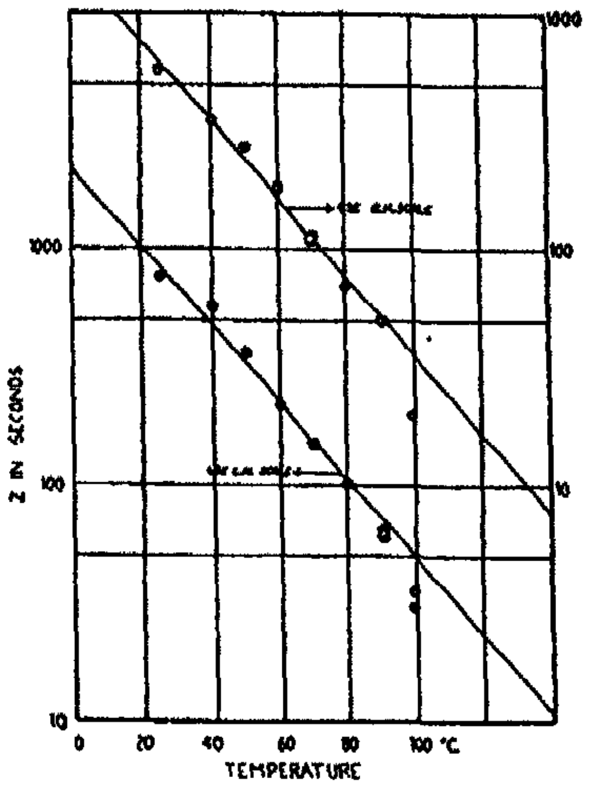

FIG. 7

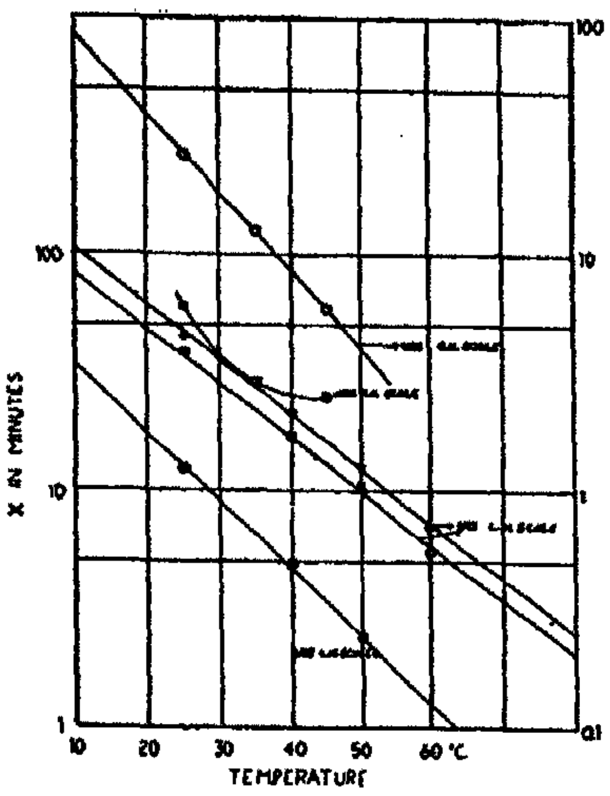

FIG. 8

FIG. 5. Effect of temperature on setting time. ⊗, 2.09 per cent ultrabentonite; ⊙, 2.19 per cent ultrabentonite.

FIG. 6. Effect of temperature upon setting time of 2.09 per cent ultrabentonite. ⊕, 25°C.; ⊡, 40°C.; ⊗, 50°C.; ⊙, 60°C.

FIG. 7. Effect of temperature upon setting time. ⊗, 2.09 per cent ultrabentonite; ⊙, 2.19 per cent ultrabentonite. Diameter of tube, 9.6 mm.

FIG. 8. Effect of temperature on standing time (x). Time of fall = 50 secs. ◇, 2.09 per cent ultrabentonite; ⊡, 2.19 per cent ultrabentonite; ⊗, 2.55 per cent ultrabentonite; ⊙, ultrabentonite and 15 per cent ethyl alcohol; ⊠, ultrabentonite and 0.5 per cent gelatin.

where η is the viscosity at time t, η_0 is the viscosity at zero time, and a and k are constants. These viscosities are proportional to his times of fall, since they were calculated directly from these, ignoring the objections mentioned above.

It will be noticed that the rate of gelation is also independent of the diameter of the viscometer tube.

TABLE 3

Values of A and B for two ultrabentonites differently prepared

CHARACTER OF SUSPENSION	CONCENTRATION	pH	*A*	*B*	*A'*	*B'*
	per cent					
Centrifuged twice	2.09	7.84	0.0165	3.34	0.021	1.98
Centrifuged once	2.19	8.40	0.0173	3.28	0.022	1.95

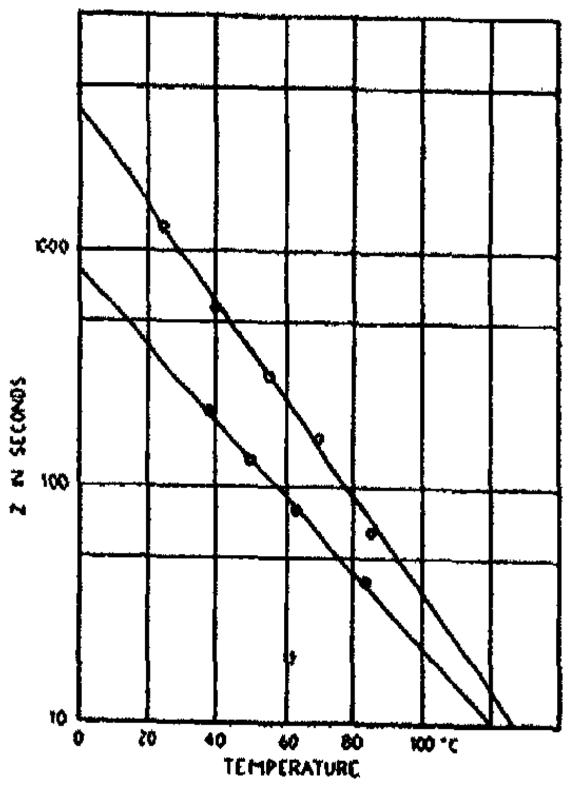

FIG. 9

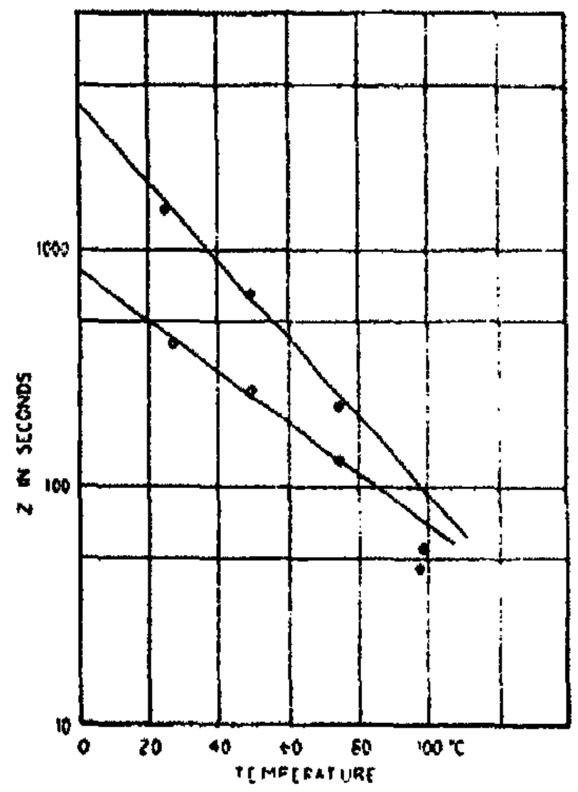

FIG. 10

FIG. 9. Effect of diameter of tube on the temperature coefficient. 2.55 per cent ultrabentonite. ⊗, diameter of tube 11.11 mm.; ⊙, diameter of tube 12.70 mm.

FIG. 10. Effect of diameter of tube on the temperature coefficient. 2.09 per cent ultrabentonite. ⊗, diameter of tube 9.5 mm.; ⊙, diameter of tube 7.5 mm.

THE EFFECT OF TEMPERATURE

The effect of temperature upon gelation was examined by both methods. Schalek and Szegvary (14) found for ferric oxide sols that if t is the temperature in °C. then

$$\log z = -At + B \tag{4}$$

where A and B are constants and z the setting time. Increase in temperature in bentonite suspensions likewise causes gelation to become much more rapid (figures 5 and 6), and for both methods the results can be expressed by equations of the form of equation 4. In the falling-ball method, if the standing times at various temperatures for a given time of fall are plotted against temperature on semilog paper, a straight line (figure 8) is again obtained or

$$\log x = -A't + B' \tag{5}$$

where x is the standing time and A' and B' are constants. Furthermore, it was found that two ultrabentonites, prepared by different methods and having slightly different compositions, gave the same values of A and B in the inverted-tube method, and also gave the same values of A' and B' in the falling-ball method, as shown by table 3.

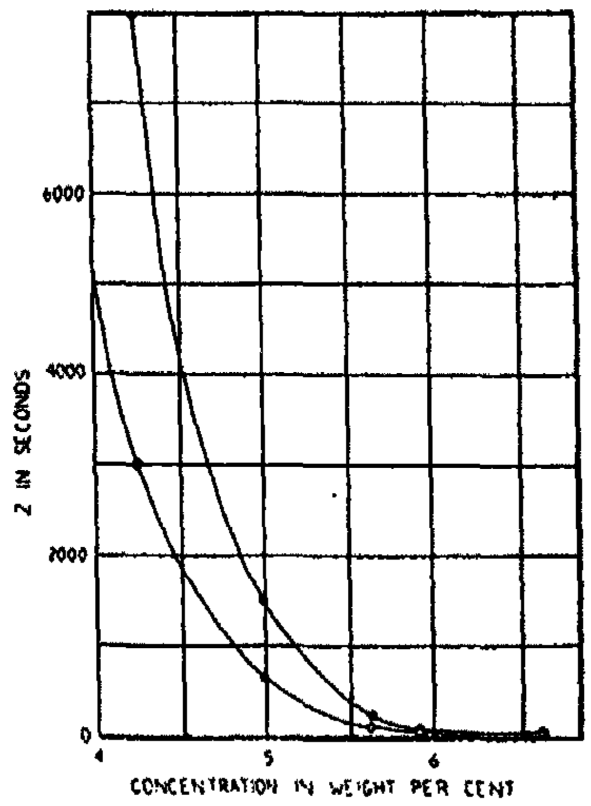

FIG. 11. Effect of concentration on time of setting in a 9-mm. tube. ⊗, 25°C.; ⊙, 55°C.

The constants A and B, however, are changed if tubes of different diameters are used for the same suspension, as shown by figures 9 and 10. This limits their value for comparative use, as, for suspensions of widely differing concentrations, measurements cannot be made in the same tube.

The effect of temperature upon the rate of gelation again presents a distinct difference from the behavior of emulsoid sols. Emulsoid sols, such as that of gelatin, do not gel under any conditions above a certain temperature, whereas bentonite suspensions apparently gel at any temperature. Furthermore, the rate of gelation of gelatin increases on lowering the temperature (8). In contradistinction to this, bentonite suspensions, as can be seen from figure 6, gel much more slowly at low temperatures.

THE EFFECT OF CONCENTRATION

Concentration has a very great influence upon the setting time of bentonite suspensions. The suspensions referred to in figure 11 were made up by diluting a strong suspension of bentonite and varied slightly in pH from 9.3 to 9.6, the weakest suspension having the highest pH. This change in pH was probably insufficient to affect the setting times materially.

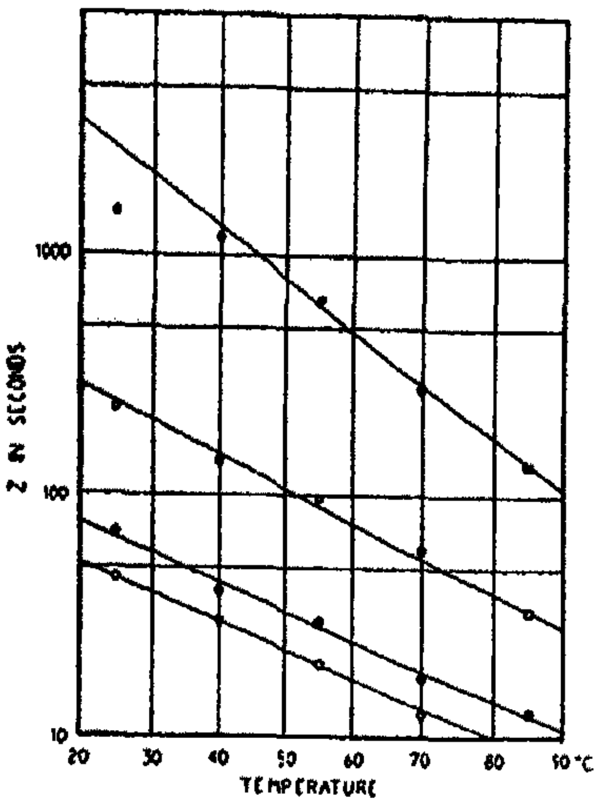

Fig. 12. *Effect of concentration on temperature coefficient. Diameter of tube 9 mm.* ⊠, 4.99 per cent bentonite; ⊡, 5.63 per cent bentonite; ⊗, 5.93 per cent bentonite; ⊙, 6.60 per cent bentonite.

Concentration does not affect the temperature coefficient A in equation 4 as greatly as does a change in tube diameter (figure 12).

DISCUSSION

It is seen that the inverted-tube method is capable of giving comparative results providing care in manipulation is exercised and the diameter of the tube in which the measurements are made is kept constant. The falling-ball method is preferable in that it gives the whole of the gelation-time curve and not simply one point. The results of the two methods appear to be in agreement.

The explanation of gelation and thixotropy, as shown by bentonite suspensions, is difficult. Hauser (6), observing the behavior of very dilute bentonite suspensions under the microscope, found the particles in Brownian motion. Addition of electrolyte caused translation to cease, and still greater quantities of electrolyte caused the cessation of rotary motion. Providing addition of electrolyte had not been too great these changes could be reversed by agitation. Addition of a hydrophilic sol, itself showing Brownian motion, e.g., gum mastic, resulted in cessation of the motion of the gum mastic particles when gelation occurred. There seems no doubt that some sort of structure is built up as the gel forms; the difficulty is to account for gelation at the extremely low concentrations at which it occurs (certainly less than 1 per cent in some cases). For bentonite, two alternative hypotheses have been suggested. The first might be termed the mechanical or "house-of-cards" theory, the clay particles being visualized as flat plates, so packed in three-dimensional, random orientation, edge touching edge in the gel, that movement is impossible and a solid house-of-cards structure is set up (9). The chief objection is that in order to obtain interference between the particles at the low concentrations at which gelation is observed, the particles must be plates, having a length and width much greater than their thickness, the ratio between these quantities being of the order of 100 to 1 or over, which seems extremely great. On the other hand, although direct microscopic evidence is lacking, this theory of the bentonite plates being of microscopic thickness and macroscopic length and width was first put forward by Wherry (15) on microscopic grounds. X-ray evidence has also shown that the bentonite clays are made up of silica and gibbsite ($Al_2(OH)_6$) layers, which are separated by water (11). The spacing due to this separation varies with the water content of the clay, and thus it appears that in a large excess of water, the layers may actually break away from each other and behave as plates of molecular thickness. Other properties of the bentonites, e.g., adsorptive power, are also in agreement with the thickness of the plates being of molecular or colloidal dimensions.

TABLE 4

Effect of a diluent on setting time

2.55 per cent ultrabentonite; 3 cc. used for each experiment

DILUENT ADDED	s (WATER ADDED)	s (C_2H_5OH ADDED)
cc.	*seconds*	*seconds*
0	165	165
0.125	420	210
0.25	720	370
0.50	1800	335
0.75		480

The only other theory to receive serious consideration has been the suggestion that the clay particles adsorb layers of water sufficiently thick to build up quasi-fluid particles occupying enough volume so that interference is sufficient to induce gelation. This hypothesis requires the formation of water hulls around the particles many molecules thick (which seems unlikely). Bentonite gels have also been shown to possess a tensile strength, which is hard to explain on the basis of particles with adsorbed water surfaces touching each other (9). As a general rule solvation decreases with temperature and one would, therefore, expect the water hulls, if such are formed, to decrease in thickness with increasing temperature, thus leading to a decrease and not an increase in rate of gelation. Further evidence against the water-hull hypothesis is also provided by experiments in which alcohol was added to a bentonite suspension (table 4). The setting time of the suspensions remained nearly constant, whereas addition of water in equal amounts by volume caused the setting times to become indefinitely great. Alcohol is usually considered to act as a dehydrating agent when added to aqueous colloids; thus, on the water-hull theory, one would expect it to be even more effective than water in increasing setting time. The viscosity of an alcohol–water mixture is greater than that of either pure component, hence Brownian motion would be retarded and an increase in this factor could not account for the more rapid gelation.

TABLE 5

Values of the temperature coefficient

	a_1/a_2
Temperature interval:	
40–50°C	2.02
40–50°C	1.52
40–50°C	2.22
Calculated value	1.24
Value from ordinary chemical reaction	2–3

On the other hand, the mechanical theory of gelation seems at first sight equally unable to account for the rapid increase in rate of gelation with temperature, unless further assumptions are made. Freundlich has attempted to draw a parallel between the coagulation of hydrophilic sols and the gelation of thixotropic sols. It is true that the rate of change increases with rise of temperature in each case, but the increases are of a different order of magnitude. According to the von Smoluchowski theory of coagulation the time of coagulation should be proportional to η/T, where η is the viscosity of the solvent and T the absolute temperature. This was experimentally confirmed by Freundlich and Basu (3) for the coagulation of a copper oxide sol by sodium sulfate. Some experimental values of the temperature coefficient, i.e., the ratio of the rates of change for temperatures 10°C. apart are compared in table 5 with the value which might be expected for aqueous bentonite suspensions. The constants *a* in equation 2 for the falling-ball method were used.

Evidently, the phenomenon of thixotropy in bentonite suspensions is not truly analogous to coagulation. On the mechanical theory the bentonite particles, even immediately after shaking, are in close juxtaposition, although the strength (and hence the apparent viscosity) of the gel is small. Each subsequent impact between particles builds up the strength as they become more firmly fixed in position, and thus the apparent viscosity increases. However, as the structure becomes stronger, collisions of ordinary impact energy have little or no effect, whereas collisions of abnormally great impact energy, of which there will always be some from the distribution theory, have a disproportionate effect in raising the strength. In a coagulation process the particles have a tendency to agglomerate, whereas in the thixotropic gelation of bentonite the particles have a tendency to keep apart and are only forced into contact by continual impacts. After a time, only impacts of exceptional energy are effective in causing increase in gel strength. Temperature causes an increase in these impacts of abnormal energy and hence a quite disproportionate increase in the gel strength. In other words, the gel strength is not proportional to the number of impacts, but depends much more upon their energy content. Hence the influence of temperature is explained by the

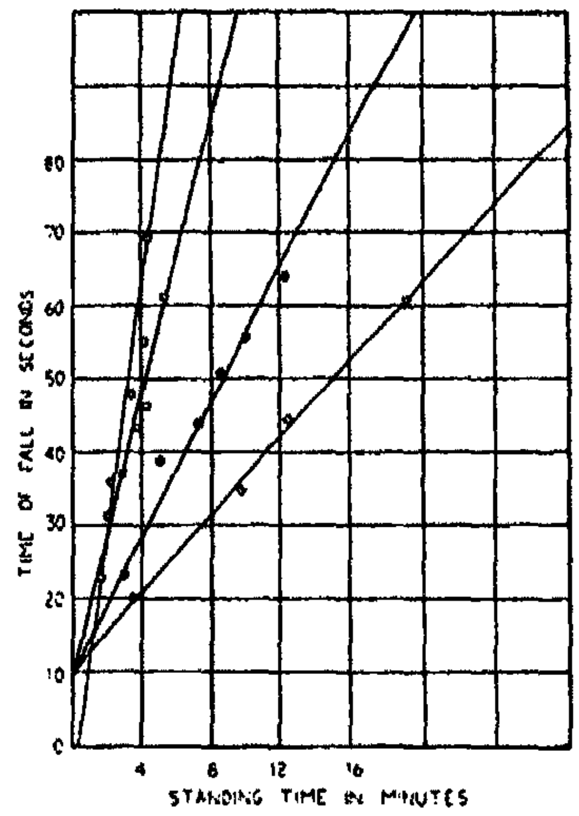

Fig. 13. Effect of addition of 0.5 per cent gelatin. ⊗, 25°C.; ⊡, 35°C.; ⊙, 45°C.; ◇, original sol at 25°C.

great increase in strength brought about by the greater number of high energy impacts.

The action of alcohol is difficult to explain; possibly it affects the ionization of the clay particles or the electrical forces acting between them. Gelatin likewise increases the rate of gelation, as can be seen from figure 13; possibly the adsorbed gelatin on the particles allows a structure to be built up more easily.

The mechanical theory of thixotropy also receives support from the fact that thixotropic sols, as far as has been at present investigated, show no change in their physical properties upon gelation. No work appears to have been done upon bentonite, but Heyman (7) has shown that if there is any volume change in an iron oxide sol upon gelation it is less than 0.0002 per cent. Other evidence, particularly the viscosity characteristics, has also been cited in a previous paper (9).

SUMMARY

Two methods have been developed for measuring the rate of gelation of bentonite suspensions. The first measures the time elapsed after the suspension has been shaken before a tube containing it can be inverted without flow. In the second the velocity of fall of a sphere through the suspension is measured at different times after shaking. Both give results qualitatively in agreement but the latter method is preferred, since it is independent of the diameter of the containing vessel and gives the entire gelation–time curve.

The results are found to be in conflict with the water-hull theory of gel structure and to be qualitatively in agreement with the mechanical theory, in which the gel is pictured as made up with bentonite plates of molecular thickness touching in completely random, three-dimensional orientation.

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THE ADSORPTION OF COMPLEX AMMONIO IONS BY SILICA GEL[1]

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The discovery that the complex ammonio ions of copper and nickel were strongly adsorbed by silica gel was previously reported by Smith and Reyerson (4). These authors used the adsorption of these complex ions to prepare silica gels containing finely divided metals on the surfaces of the gel by reducing these adsorbed ions at higher temperatures with hydrogen. It was found in the course of these studies that the adsorption forces were so strong that the silica gel containing the complex ammonio ions of copper could be shaken with distilled water for long periods of time, and yet the most sensitive chemical tests were unable to detect any traces of copper ion in the water, which remained colorless. Dr. M. G. Larian of this laboratory reported to the authors that 10 gallons of distilled water, to which ammonia had been added, contained sufficient traces of copper to induce a slight blue coloration in silica gel which was shaken with the water.

Ordinary electrodialysis failed to remove the adsorbed ions to any extent, but changes took place after a considerable time which indicated that a surface disintegration of the gel with its adsorbed ions had occurred. The granular character of the gel had disappeared, and a more gelatinous material remained in the dialysis cell. Electrodialysis has been used a great deal in this laboratory to purify silica gel, yet the hard granular character of the glassy gel has never been destroyed in the presence of salts except when these complex metal ammonio ions were adsorbed by the gel. It was felt that adsorption isotherms obtained under varying conditions might reveal something of the nature of this unusual ionic adsorption. The investigation here presented gives the preliminary results of the adsorption of silver ammonio complex ions by silica gel, together with a more complete investigation of the adsorption of the tetrammino cupric ion.

EXPERIMENTAL

The silica gel used in this study was the glassy porous variety prepared by the method of Patrick (3). It was washed free of salt and dried at

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[1] Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

about 100°C. It was then digested in nitric acid, washed, and finally electrodialyzed for a considerable length of time in an electrodialysis cell. After the resistance of the cell reached a constant high value the gel was removed, dried carefully, and placed in tightly stoppered bottles until used.

In the early part of the study, from 1 to 2 g. of gel was weighed out and added to solutions containing the complex ammonio ions of silver or copper. These solutions were prepared by adding ammonium hydroxide to known concentrations of copper or silver nitrate. Great difficulty was experienced in adding the ammonia solution to the varying strengths of the salt solutions so that the pH of the resulting solution was the same at the time the silica gel was added. Quantitative determinations of the amount of copper and silver present in the solutions before and after the addition of the silica gel made it possible to calculate the amount adsorbed. These early studies gave adsorption isotherms which fitted the Freundlich expression fairly well, but it was recognized that closer control of the pH of the solutions was necessary. It was also decided that other analytical methods would improve the results.

The glass electrode was adopted as the best electrode for determining the pH of the ammoniacal copper nitrate solutions, and it was found to work very well. The Coleman glass electrode was the type used, and it was standardized by the usual buffer solutions. This glass electrode made it possible to obtain electrometric titration curves for the addition of ammonia solutions of copper nitrate. These titration curves determined the pH range of the adsorption studies, as will be discussed later.

The removal of the adsorbed complex copper ions from the silica gel by treatment with 0.5 *N* sulfuric acid was found to be incomplete even after long standing. Experiments with the boiling electrolytic cell as developed by Exner (2) proved that quantitative removal of the copper from the silica gel was possible by this method. The boiling cell of Exner is a simple electrolytic cell consisting of a 300-cc. lipless beaker of the Berzelius type. The cathode consists of a platinum gauze cylinder and the anode consists of two platinum spirals, one inside the cathode and the other outside. A small flame under the beaker causes remarkably vigorous boiling or effervescence, which is undoubtedly aided by the evolution of oxygen at the anodes. Low voltage direct current was applied across the electrodes. During the heating of the cell to boiling a current of 1 ampere was allowed to flow, but this was increased to 6 amperes at 6 volts as soon as boiling had started.

In the present investigation the silica gel containing the adsorbed complex copper ions was removed from the solution in which the adsorption took place and transferred to the electrolytic cell, which contained a solution of 0.5 *N* sulfuric acid. The current was turned on and the removal of the copper from the gel was found to be complete after fifteen minutes of boiling. An additional hour of treatment showed no additional removal of copper and the gel appeared colorless. The results of a run carried out to determine the time needed for a quantitative experiment are as follows:

Weight of cleaned cathode at beginning of run	10.7587 g.
Weight after 15 minutes boiling	11.1012 g.
Weight after 1 hour additional boiling	11.1013 g.
Weight of copper removed from gel	0.3426 g.

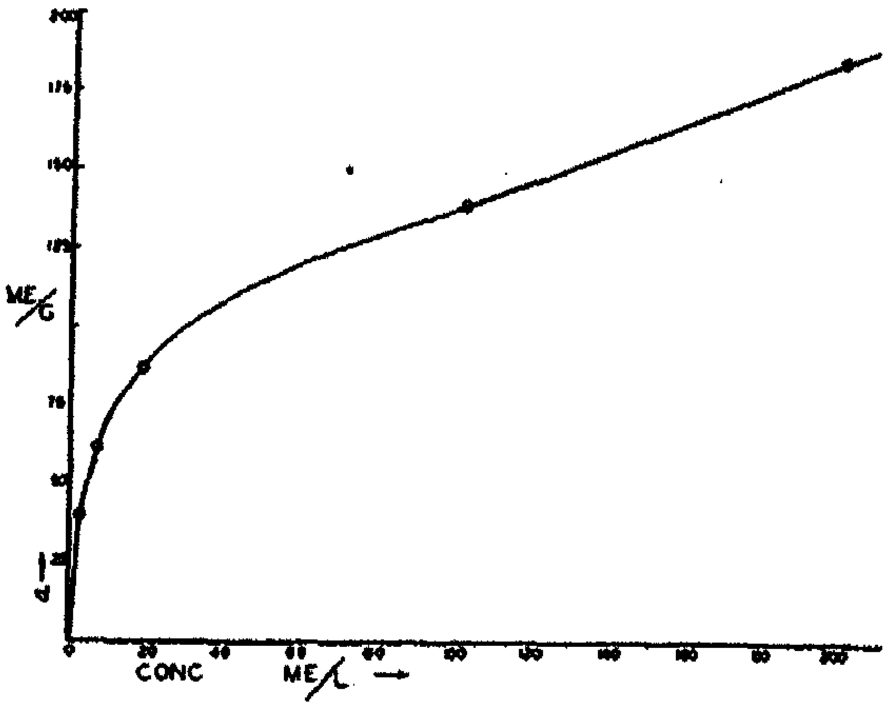

Fig. 1. Adsorption of silver on silica gel[3]

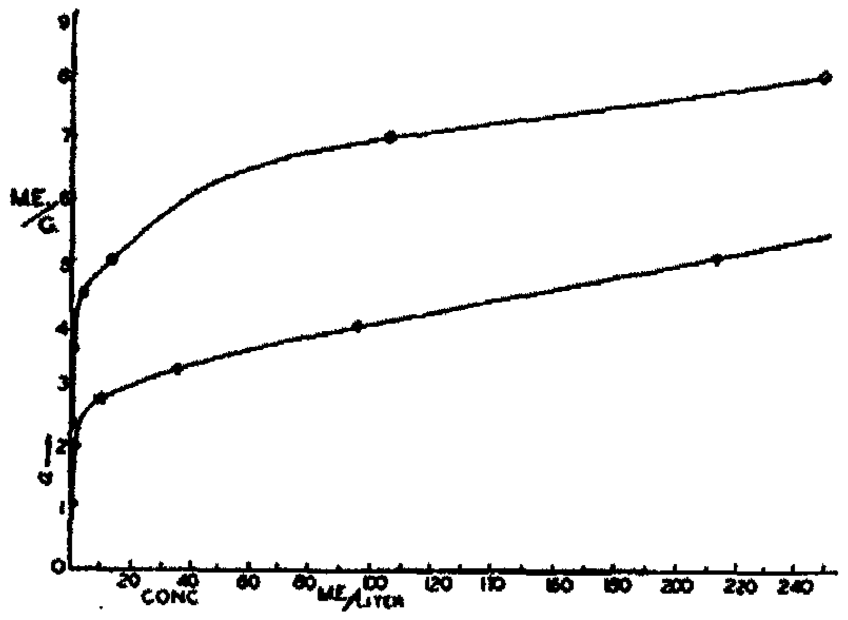

Fig. 2. Adsorption of copper on silica gel

The concentration of the copper complex ion remaining in the solution from which the silica gel had been removed was also determined by the same

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[3] The ordinates of figure 1 are expressed in (M.E./G.) × 10 instead of M.E./G. as shown in the figure.

electrolytic method. In some cases when the concentration of the copper ion originally present before adsorption was low, a precipitate remained undissolved during adsorption. When this was the case the solution was stirred rapidly, decanted from the gel, and filtered. The precipitate was dissolved in sulfuric acid, and the quantity of copper determined in the boiling cell. The total amount of copper obtained on the cathode of the boiling cell from the silica gel, the solution, and the precipitate, if any, checked the concentration of the original solution very well. The boiling cell of Exner is to be recommended as a rapid and accurate quantitative method for the determination of copper.

Using the above methods a series of adsorptions was run at five different pH values. Different concentrations of cupric nitrate solution were placed in a beaker in the presence of the glass electrode, and ammonia solution added until the electrode showed the proper pH. Sufficient time was taken to insure that equilibrium had been reached. The pH was checked occasionally during adsorption, and found to be the same within the limits of error of the glass electrode.

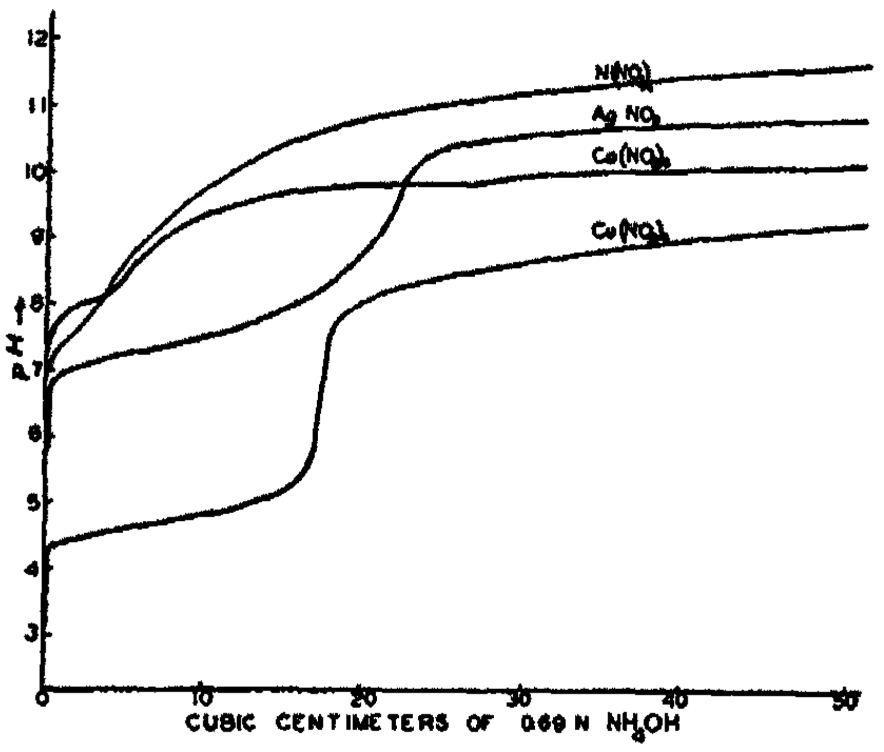

FIG. 3. Titration curves with glass electrode

RESULTS AND DISCUSSION

The preliminary results on silver and copper are given in figures 1 and 2. Here the abscissae are milliequivalents per liter of solution and the ordinates are milliequivalents of ion adsorbed per gram of silica gel. The pH values were held as nearly constant as possible. The pH for the upper curve in figure 2 and for silver in figure 1 was something over 10, while the pH for the lower curve in figure 2 was slightly over 7. These results indicated a strong early adsorption of these complex ions.

The potentiometric titration curves using the Coleman glass electrode are shown in figures 3 and 4. Figure 3 gives the titrations of solutions of the same normality of the salts indicated with ammonia solutions. The curves are considerably different for the different salts, and it is intended that further study be given to this point. Since it was decided to investigate the adsorption of the complex copper ions first, another set of titrations was run. Figure 4 gives the results of these titrations using the same solution of cupric nitrate in each case, with this difference, that 10 cc. of the solu-

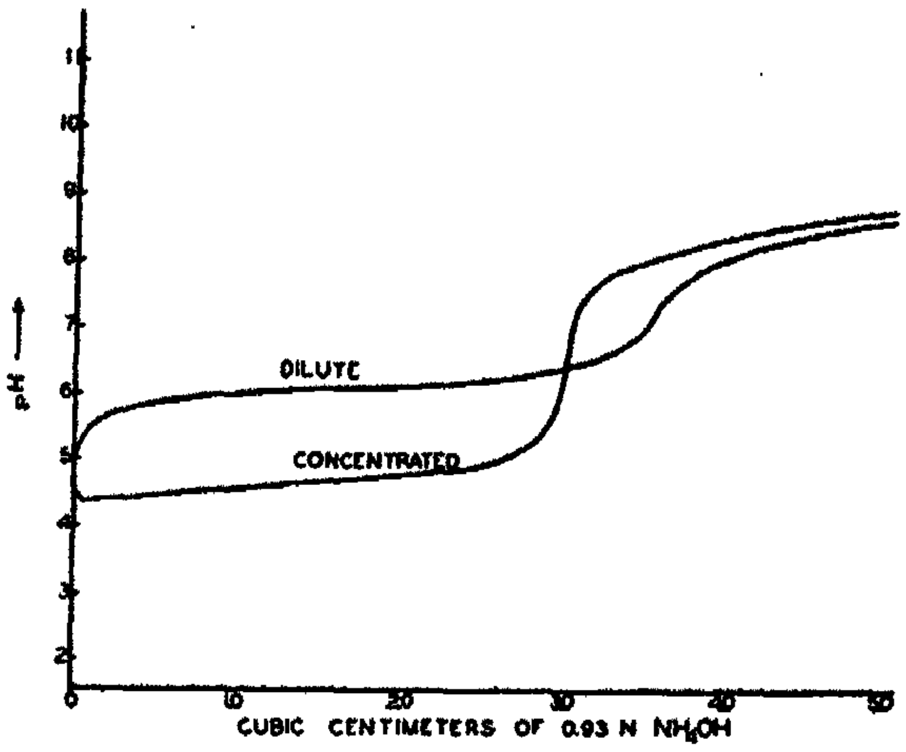

FIG. 4. Ammonia titration curves of cupric nitrate with glass electrode

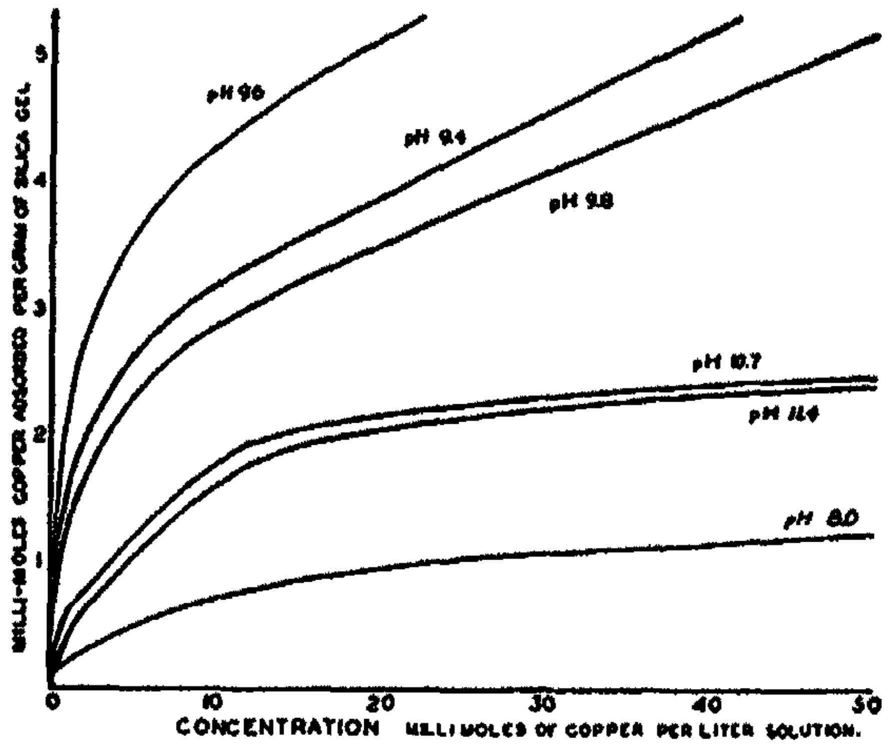

FIG. 5. Adsorption of copper on silica gel at pH values above 8

tion was titrated to give the curve marked "concentrated," while the same 10 cc. of solution was diluted to 300 cc. to give the curve marked "dilute." The differences are probably due to changes in activity and hydrolysis.

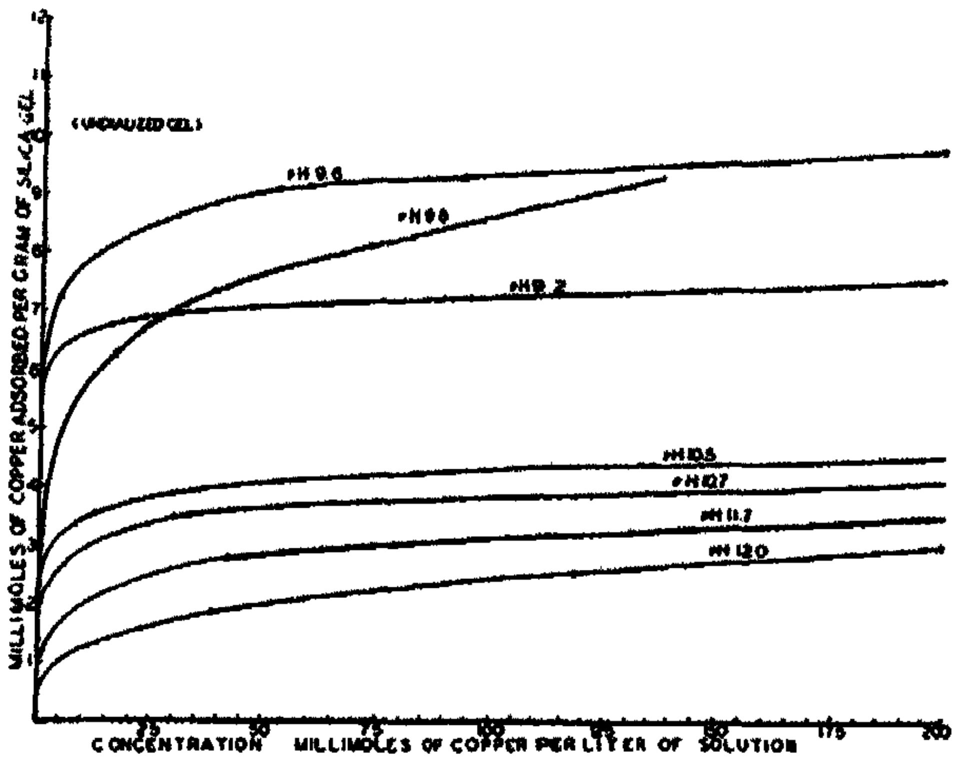

FIG. 6. Adsorption of copper on undialyzed silica gel

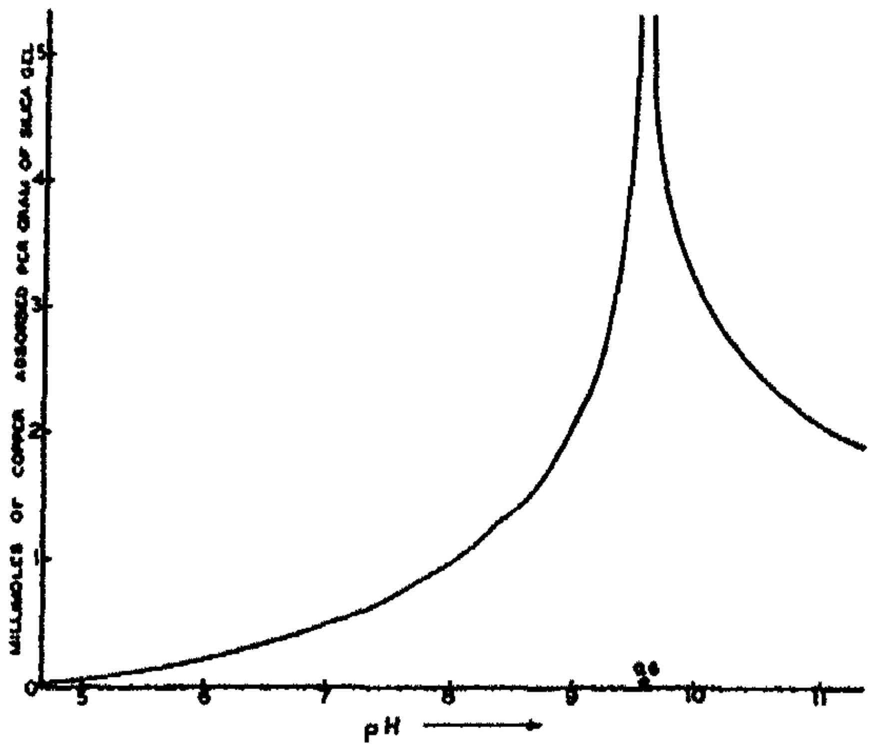

FIG. 7. Adsorption of copper on silica gel from ammoniacal solution

From these results it was evident that the best determination could be made at pH values above the break.

Accordingly, the adsorption measurements were made at pH values above 8. The results of five such adsorption determinations are presented in figure 5. Since the silica gel used in these experiments was electrodialyzed, it was decided to use some of the undialyzed gel from the same original source. This gel had been washed thoroughly free of electrolytes by distilled water. The adsorption isotherms for this undialyzed gel are given in figure 6. It is evident that electrodialysis has removed a part of the active surface of the gel as far as this type of adsorption is concerned. It is evident from these results that the pH of the solution plays a vital part in the adsorption of these complex ions. The adsorption reaches a maximum, as is shown in figure 7, at a pH of about 9.6. The character of the silica gel also plays an important part, for the adsorption is much greater on the undialyzed gel than it is on the dialyzed gel. It was felt at first that the silica gel tended to go into solution in solutions of higher pH. This might account for the lowered adsorption above a pH of 9.6. Accordingly a sample of silica gel was placed in a solution of copper ammonio nitrate solution at pH 9.6 and allowed to stand for ten weeks. At the end of this time less than 1 per cent of the silica gel had gone into solution. However, this small solubility of silica from the gel may account for the diminished adsorption, provided that the most active part of the surface dissolves.

TABLE 1

Results obtained in one of the adsorption determinations

EQUILIBRIUM CONCENTRATION OF Cu IN MICROEQUIVALENTS AT EQUILIBRIUM	pH	MILLIMOLES OF Cu ADSORBED PER GRAM OF SILICA GEL
0.37	10.70	0.614
3.12	10.71	0.914
11.75	10.70	1.930
27.72	10.75	2.292
42.23	10.74	2.430

An example of one of the adsorption determinations is given in table 1. The results here presented indicate that the adsorption is dependent not only on the concentration of the metal ion but also upon the pH of the solution and the character of the silica gel. The whole system is a complex one as has been shown recently by J. Bjerrum (1), who has determined the equilibrium constants for the addition of each successive NH_3 group to the copper. Additional work will be needed to clarify this complex problem further. The adsorption of the first complex copper ammonio ions is apparently strong and irreversible, leading one to suspect that a monomolecular layer of this ion is formed.

SUMMARY

The adsorption of complex ammonio ions has been measured under varying conditions of pH on both electrodialyzed and undialyzed silica gel.

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FACTORS INFLUENCING ADSORPTION AT SURFACES OF RED CELLS[1]

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We have recently shown (4) that the aggregation (as measured by sedimentation velocity) of red cells brought about by plasma globulins and by other proteins, as gelatin and casein, is not accompanied by an adsorption of these proteins at the cell surface. The proteins presumably act by depriving the red cells of adsorbed water, thus increasing their surface energy and tendency to aggregate. It was in fact shown that normal red cells do not adsorb non-specific proteins even in high concentrations; that the electrophoretic mobility of the cell, characteristic for each species, is determined by the composition of the cell membrane itself and is unchanged by washing away plasma proteins or even by thorough washing of hemolyzed cells in alkaline solution (6).

Bellis and Scott (2) report results which they interpret as indicating that considerable amounts of plasma protein are normally adsorbed on red cells. Dilution of the plasma with isotonic solutions removes some of this adsorbed protein, whereas dilution with hypertonic solutions causes a further adsorption of protein by the red cell. Their interpretation is directly opposed to the conclusions of Abramson (1) and ourselves that normal red cells do not adsorb plasma proteins.

The objects of the present paper are (1) to test the experimental evidence offered by Bellis and Scott for the adsorption of plasma proteins by normal red cells, (2) to investigate the conditions under which the surface of the red cells may become damaged, as evidenced by a decreased sedimentation velocity, and the result of such damage on the ability of the cells to adsorb proteins, and (3) to investigate the effect of lecithin on the charge and sedimentation velocity of normal cells.

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[1] Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11–13 (1936).

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EXPERIMENTAL

1. *Adsorption of plasma proteins by normal red cells*

According to the findings of Bellis and Scott the dilution of defibrinated beef blood with isotonic salt or sugar solution results in a higher concentration of protein in the supernatant fluid than is calculated from the known dilution of the plasma, allowing for changes in the volume of the cells as determined by hematocrit readings. The protein increase is proportional to the amount of dilution; with their greatest dilution (70 parts of isotonic salt to 30 of blood) it amounts to 1.3 g. per 100 cc. of serum. This means that the cells (approximately 60 cc.) contained in 100 cc. of serum give up to the surrounding medium 1.3 g. of presumably adsorbed protein, or 1 cc. of cells gives 0.022 g. of protein. A similar dilution of whole blood with hypertonic salt or sugar resulted, on the other hand, in a taking up of approximately 0.005 g. of protein per cubic centimeter of cells.

TABLE 1

Nitrogen in the supernatant fluid from packed cell mass

EXPERIMENT NO.	NaCl CONCENTRATION	NITROGEN IN SUPERNATANT FLUID	PROTEIN (N × 6.25) IN SUPERNATANT FLUID
	per cent	*mg. per cent*	*per cent*
1 (beef)	0.9	113	0.70
	8.1	90	0.56
2 (beef)	0.9	99	0.61
	8.1	102	0.63
3 (dog)	0.9	40	0.25

We have tested these conclusions in the following way. Instead of diluting the whole blood and depending upon hematocrit readings in the diluted media for true dilution values, we have added the salt solution directly to the packed cells. Fresh defibrinated beef blood was centrifuged for one and one-half hours at 3200 R.P.M. Unfortunately this was the highest speed obtainable with the available centrifuge when loaded with two 15-cc. tubes; undoubtedly better packing of the cells could be obtained with higher centrifugal speeds. The serum was drawn off and to one volume of packed cells was added one volume of isotonic (0.9 per cent) or hypertonic (8.1 per cent) sodium chloride solution. The cells were thoroughly mixed with the salt solution and allowed to stand for thirty minutes. The tubes were again centrifuged and the total nitrogen in the supernatant fluid determined by a micro-Kjeldahl method.[2] According to the calculations given above from the data of Bellis and Scott, assuming that no serum remained in the packed cell mass, the supernatant fluid in the case of the isotonic salt should contain at least 2.2 per cent protein, while the hypertonic washing fluid should contain no protein. Several such experiments on beef cells gave the results shown in table 1. Calculating all the nitrogen as protein the supernatant isotonic fluid contained less than one-third of the protein predicted on the basis of the results of Bellis and Scott. There is in fact even less protein in our supernatant fluid than the figures indicate, since 7 to 10 mg. of nitrogen per 100 cc. of supernatant fluid are in the urea from the cells. Since the hypertonic fluid contained *practically the same protein concentration, it is* evident that this protein must have been derived from serum remaining in the packed cell mass and not from protein adsorbed on the cells. If the original serum contained 8 per cent protein, this would mean that under the conditions of the experiment about 8 per cent of the packed cell volume consisted of serum, a not unreasonable figure considering the relatively low centrifugal speed at which the cells were packed. It seemed desirable to repeat the experiment on a type of blood in which the cells form large aggregates and would thus be expected to pack better at a given centrifugal speed. The results on dog cells are shown in table 1. Since appreciable hemolysis occurred in the hypertonic salt, only the isotonic was analyzed. If all the nitrogen is calculated as protein we obtain 0.25 per cent protein in the supernatant fluid, which means that in this case about 3 per cent of the packed cell mass consisted of serum.

2. *Effect of prolonged standing and of washing on the surfaces of the red cells*

It was emphasized in earlier publications (4, 6) that in order to obtain correct values for the sedimentation velocity of red cells, fresh cells (not more than three to four hours old) must be used. Allowing cells to stand for long periods or washing them with buffered isotonic sugar markedly decreased the sedimentation velocity. We have here made a more quantitative investigation of the conditions under which cells lose their capacity for rouleau formation. Dog cells, which were shown to have the highest sedimentation velocity and the highest electrophoretic mobility at pH 7.4, were used.

The sedimentation experiments of this section were carried out in a 1 per cent gelatin solution (Eastman's) made up in $M/50$ phosphate buffer (pH 7.4) plus 0.9 per cent sodium chloride. The pH of the buffer was not significantly changed by this concentration of gelatin. The cells were centrifuged for 15 minutes at 2000 R.P.M. and two volumes of the gelatin

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[2] We are indebted to Dr. W. B. Wendel for the nitrogen determinations.

solution were added to one volume of packed cells. The thoroughly mixed cell suspensions were sucked up into glass tubes of 3.5 mm. bore and 35 cm. long. The tubes bore short segments of rubber tubing on their lower ends, which, after filling, were closed with spring clips. The number of millimeters which the cells sank in a specified time was then measured. The sedimentation velocity is of course a direct measure of the degree of aggregation of the cells.

Electrophoretic determinations were carried out with a microscopic electrophoresis cell, using the technique previously described (7). The medium in which the cells were suspended was $M/50$ phosphate buffer (pH 7.4) plus 0.3 per cent sodium chloride plus 6 per cent sucrose. The proteins studied were dissolved in this medium. Sugar was substituted for part of the salt in order to cut down the current density. These determinations were made with the idea of detecting any adsorption of protein which might occur at the red cell surface. The electrophoretic mobility of the dog red cell is several times that of any of the proteins studied (as measured by the mobility of glass particles covered with these proteins). An adsorption of protein would therefore lower the red cell mobility; a complete coat would lower the mobility to that of the protein itself. Mobility determinations were made in diluted dog plasma, ordinary gelatin (Eastman) having an isoelectric point at pH 4.7, and a sample of gelatin obtained from the Heil Company which was found to have an isoelectric point at pH 7.4.

TABLE 2

Effect of standing on protein adsorption and sedimentation velocity of dog red cells

	MOBILITY IN MICRA PER SECOND PER VOLT PER CENTIMETER			SINKING IN 1 PER CENT NORMAL GELATIN IN 30 MINUTES
	Autogenous plasma diluted 1 to 200	0.01 per cent normal gelatin	0.01 per cent isoelectric gelatin	
				mm.
Fresh dog cells	1.52	1.53	1.55	113
After standing 1 day	1.52	1.54	1.54	59
After standing 2 days	1.46	1.51	1.50	30
After standing 4 days	1.45	1.48	1.48	13
Protein-coated glass particles	0.65	0.61	0	

As previously stated, allowing cells to stand in the ice box for long periods of time in their own serum or plasma decreases their sedimentation velocity. The decrease in sedimentation velocity for a given time of standing is, however, very irregular. Some samples of cells are cut down to a very small fraction of their original sedimentation velocity on twenty-four hours' standing. Other samples may require a week for the same change.

The change is not correlated with hemolysis; samples which show no hemolysis may show a very great decrease in sedimentation, and others which show considerable hemolysis on standing may have a normal sedimentation rate. In table 2 the sinking velocity in 1 per cent gelatin and mobility in various proteins of a sample of dog cells has been followed over a period of four days. The oxalated whole blood was allowed to stand in the ice box. Samples were removed each day and centrifuged, the packed cells being resuspended in the protein solutions. It is evident that a marked decrease in sedimentation velocity may take place before any measurable adsorption of protein has occurred.

Table 3 shows the effects of washing dog cells in isotonic salt and sugar.

TABLE 3

Effect of washing on protein adsorption and sedimentation velocity of dog red cells

CELLS	MOBILITY IN MICRA PER SECOND PER VOLT PER CENTIMETER				SINKING IN 1 PER CENT NORMAL GELATIN IN 30 MINUTES
	Buffer	0.01 per cent iso-electric gelatin	Autogenous plasma diluted 1 to 200	1 per cent normal gelatin	
					mm.
Fresh normal dog cells	1.55	1.56		1.44	90
After washing in 0.9 per cent NaCl	1.57	1.56			89
After standing 3 days in 0.9 per cent NaCl		1.56			21
After standing 3 days in serum		1.53			2
After washing in 10 per cent sucrose	1.58	1.38			0
After rapid washing in 10 per cent sucrose			1.54		3
After standing overnight in 10 per cent sucrose		1.55	1.56	1.22	2
After rapid washing in 5 per cent dextrose			1.56		1
After standing overnight in 5 per cent dextrose		1.54	1.58	1.25	2
Washed ghosts	1.54	0.99			

The data show that washing cells in 0.9 per cent sodium chloride solution has no immediate effect either on their sedimentation velocity or on their ability to adsorb gelatin. Also, cells allowed to stand in 0.9 per cent sodium chloride retain their ability to aggregate in gelatin solutions at least as long as cells which are allowed to stand in their own serum or plasma. Cells washed in isotonic sucrose, on the other hand, always show a great decrease in sedimentation velocity, which may or may not be accompanied by a measurable adsorption of protein from very dilute protein solutions. This has been found to be true also for the cells of other species (horse and human). Washing with isotonic dextrose gives similar results; as shown in table 3, cells may not adsorb protein after such washing but we have observed adsorption of gelatin, casein, and egg albumin from 0.01 per cent solution of these proteins at pH 7.4 by horse cells washed in isotonic dextrose. Hemolyzed cells washed free of hemoglobin (6) adsorbed protein still more readily.

It is to be noted, however, that irrespective of their treatment all dog cells, including the washed ghosts, have the same mobility in the absence of protein. That is, the change or damage to the cell surface which allows it to adsorb protein is not accompanied by any change in the electrophoretic properties of the cell in the absence of protein. Cells treated with isotonic sucrose or dextrose may not be altered sufficiently to adsorb measurable amounts of gelatin or plasma protein from dilute protein solution and will yet adsorb a measurable amount of gelatin from 1 per cent gelatin, the concentration in which the sedimentation velocities have been determined. This is shown by the findings in table 3 that cells after treatment with isotonic sucrose or dextrose adsorbed gelatin from 1 per cent solution (as evidenced by their lower mobility in 1 per cent gelatin than was that of fresh cells in 1 per cent gelatin), although they did not adsorb measurable amounts of protein from dilute gelatin or plasma.

Whether or not the adsorption of the protein by the red cells is the cause of the decreased ability to aggregate is not known; both phenomena may be separate manifestations of some unknown change in the physical state of the cell surface. It seems evident that the common practice of washing red cells with isotonic sugars prior to studies on their ability to adsorb specific antibodies is not without danger, since such washing may damage the cell surface in such a way that it is capable of adsorbing non-specific proteins. Washing with isotonic salt solution is to be preferred.

3. *Effect of lecithin on charge and on sedimentation velocity*

Kürten (3) and Theorell (5) report a decrease in sedimentation velocity of whole blood on the addition of lecithin. Both authors ascribe this stabilizing effect to a direct action on the cells; they assume an adsorption of lecithin at the cell surface with a resulting increase in charge.

We have investigated the effect of added lecithin on the sedimentation rate of dog red cells both in their own plasma and in 1 per cent gelatin. To our 1 per cent gelatin solution (made up as previously described in $M/50$ phosphate buffer plus 0.9 per cent sodium chloride) was added 0.05 per cent of egg lecithin (Pfanstiehl). The pH of the buffer was not significantly changed by this concentration of lecithin. Dog cells in the 1 per cent gelatin solution alone sank 113 mm. in 30 minutes; in the gelatin plus suspended lecithin they sank less than 1 mm. in the same time. Dog cells in their own plasma sank 51 mm. in 1 hour; in plasma plus 0.05 per cent of added lecithin they sank 8 mm. in 1 hour.

Electrophoresis determinations, however, demonstrate that the lecithin acts by a very different mechanism from that postulated by Kürten and by Theorell. The mobility of the dog red cell in the buffer-sucrose-sodium chloride medium is approximately 1.55 micra per second per volt per centimeter. When a dilute cell suspension and lecithin are mixed (in the absence of any dissolved protein) the cells become attached to the particles of lecithin and the mobility is intermediate between that of cells and that of lecithin. When more cells are added (the suspension is still much less dense than that used in sedimentation experiments) the mobility becomes that of the normal cells, the larger particles of lecithin being completely surrounded by "adsorbed" cells. In a 1 per cent gelatin solution made up in the same medium the mobility of the cells is 1.41 micra per second per volt per centimeter. This decrease in mobility in concentrated gelatin is due to increased viscosity in the double layer, not to adsorption of gelatin (6). The mobility of the lecithin particles in a 1 per cent gelatin solution becomes the same as that of the gelatin itself, approximately 0.5 micra per second per volt per centimeter; i.e., the lecithin is completely coated with gelatin. When the cells and lecithin are mixed in the presence of 1 per cent gelatin, the cells are seen to move at exactly the same rate as in the absence of lecithin, 1.40 micra per second per volt per centimeter. The lecithin particles, which can easily be distinguished from the cells, move at the same rate as gelatin, 0.5 micra per second per volt per centimeter. Obviously, the action of the lecithin in decreasing sedimentation velocity in the presence of protein is not due to an adsorption of lecithin and increased charge on the cells, but rather to a binding of the protein by the lecithin, resulting in a decrease in the effective concentration of protein. The fact that the same concentration of lecithin has a much greater effect on sedimentation velocity in 1 per cent gelatin than in plasma is presumably to be explained on the basis that a given concentration of lecithin binds a smaller fraction of the protein present in plasma than in 1 per cent gelatin.

SUMMARY

1. The conclusion of Bellis and Scott that beef red cells are normally coated with plasma proteins is not confirmed. Normal cells do not adsorb measurable quantities of gelatin or of plasma proteins.

2. Cells allowed to stand in the ice box in their own plasma or in 0.9 per cent sodium chloride gradually lose their ability to form rouleaux in gelatin solutions, as shown by a decreased sedimentation velocity. This change is accelerated by washing the cells in isotonic sugar and may be accompanied by a slow and incomplete adsorption of protein at the cell surface.

3. Small quantities of added lecithin inhibit the sedimentation of dog

cells in plasma or gelatin. This inhibition is due to an adsorption of protein by the lecithin, thus decreasing the effective protein concentration, not to a direct effect of the lecithin on the surface of the red cells.

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THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. VI

Cupric Ferrocyanide Sol[1]

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A mechanism to account for the coagulating action of electrolytes on hydrophobic sols has been proposed as a result of investigations on sols of the hydrous oxides of iron (9, 15), aluminum (11), chromium (10), of arsenic trisulfide (13), and of sulfur (14). For the sake of clarity the essential points of the proposed mechanism will be illustrated by a specific example: (a) The micelles of a ferric oxide sol are, in general, positively charged, owing to preferential adsorption of ferric and hydrogen ions from the intermicellar solution. These ions form the inner portion of a double layer, the outer portion of which is a Gouy diffuse layer, usually of chloride ions. (b) A part of the chloride ions in the diffuse outer layer are attracted (adsorbed) to the inner layer so strongly that they cannot be detected potentiometrically, whereas the remainder, because of their relatively higher kinetic energy, exert sufficient osmotic force against the electrical attraction of the inner layer that they are a part of the intermicellar solution, and so are measurable potentiometrically. (c) On adding to the sol an electrolyte such as potassium sulfate, the sulfate ions, being more strongly adsorbed than the chloride, take up a position closer to the inner layer of adsorbed hydrogen and ferric ions. This diminution in thickness of the double layer causes a decrease in the potential on the particles; when the potential is reduced sufficiently, coagulation results. (d) The adsorption of sulfate is accompanied by a displacement of adsorbed chloride from the innermost portion of the outer layer. (e) The difference between the chloride concentration before and after the addition of sulfate (in other words the displaced chloride) is not equivalent to the adsorbed sulfate, since a part of the sulfate which enters the layer corresponds to chloride in the intermicellar solution of the original sol. (f) The order of magnitude of the adsorption of similar ions of the same valence such as sulfate, oxalate, and chromate is the same; hence they possess a

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similar capacity to displace chloride and a similar coagulating power. (g) Ions such as ferricyanide, with three charges, are drawn closer to the inner layer than the divalent ones. Hence less of a trivalent ion needs to be adsorbed than of a divalent ion to reduce the potential on the particles to the same value. (h) The adsorption necessary to reduce the potential on the particles to the point of coagulation is less for trivalent ions than for divalent ions; and the displacement of chloride ions at the coagulation point is less with the former than with the latter. (i) Univalent ions, such as nitrate ion, are attracted toward the inner layer (adsorbed) much less strongly than multivalent ions; hence the potential on the particles is lowered much less for the same concentration of nitrate ion than for sulfate or ferricyanide ions. The displacement of chloride by nitrate is much less than for an equivalent amount of multivalent ions, since chloride is adsorbed somewhat more strongly than nitrate at the same concentration.

Although the adsorption mechanism proposed to account for the action of electrolytes on hydrophobic sols was suggested from observations of the advantages and limitations of the well-known Freundlich theory, the categorical statement of Verwey and Kruyt (6, 7) that "The Weiser theory does not differ essentially from that of Freundlich" is not justified. As a matter of fact, sixteen years ago the author (8) was the first to point out that one of the fundamental concepts of Freundlich's original theory was not supported by experiment, namely, that the adsorption of ions of varying valence is equivalent at the precipitation concentration of the ions. This has since been recognized by Freundlich (1) himself. The mechanism proposed above not only accounts for the variation from equivalent adsorption at the coagulation concentration of ions of varying valence, but also suggests why equivalent adsorption of ions of varying valence is unnecessary to effect precipitation at the varying precipitation concentrations. In the proposed mechanism, the reduction in the potential at the surface of the particles on adding electrolytes is attributed to a contraction of the double layer as a result of adsorption of the precipitating ions. Verwey and Kruyt accept Müller's (4) point of view and conclude that the lowering of the ζ-potential is "merely due to 'compression' of the diffuse outer layer and a subsequent increase of the capacity of this part of the double layer" (7). Since, in general, the thickness of the inner layer of the double layer is changed but little on the addition to sols of small amounts of electrolytes with high coagulating power, it follows that the decrease in thickness of the double layer, to which we have attributed the lowering of the ζ-potential, implies a compression of the outer layer. Hence it would appear that our point of view differs from that of Verwey and Kruyt chiefly in that the contraction of the double layer or compression of the outer layer is believed by us to result from adsorption of precipitating ions, whereas Verwey and Kruyt consider that adsorption is neither a necessary nor a sufficient cause of potential reduction at the surface of the particles. The conclusions of Verwey and Kruyt were based on the results of their important investigations with negative silver iodide sol (6, 7). With this sol it is claimed (a) that in some cases complete adsorption occurs at much lower concentrations than corresponds to the flocculation value, and (b) that in other cases flocculation occurs long before sufficient electrolyte is added to reach the maximum adsorption. An example of the first behavior is the adsorption of UO_2^{++} by a sol containing 75 g. of silver iodide per kilogram of sol. The precipitation value was 4 milliequivalents per kilogram of sol, but the maximum adsorption of 0.23 milliequivalent was reached when only 0.5 milliequivalent was added. In these adsorption studies Verwey and Kruyt determined the amount taken by analyzing the ultrafiltrates. Since ultrafiltration of a sol influences the adsorption equilibria, it is questionable whether the composition of the intermicellar solution should be deduced from an analysis of the ultrafiltrate. In this connection McBain and McClatchie (3) showed that the hydrogen-ion concentration of the ultrafiltrate from a ferric oxide sol varies many fold with the rate of ultrafiltration.

That flocculation may occur long before enough electrolyte is added to reach the maximum adsorption is illustrated by the flocculation of a silver iodide sol by adsorption of a very small amount of Ce^{+++} in the presence of a large excess of H^+. Thus an undialyzed sol containing 80 millimoles of silver iodide, 80 millimoles of nitric acid, and 8 millimoles of hydriodic acid per liter adsorbed little or no cerium at the coagulation value. In this case the combined adsorption of Ce^{+++} and H^+, chiefly the latter, accounts for the reduction of the ζ-potential to the coagulation point. Moreover, Verwey and Kruyt always observed a marked retrograde adsorption or falling-off of adsorption above the coagulation point, which they attributed to "a decrease in surface caused by a secondary change in the coagulum" (6). This factor may be, in part, responsible for the low adsorption of cerium under the above conditions.

The silver iodide sol is a comparatively simple system containing highly disperse silver iodide particles, which are negatively charged owing to preferential adsorption of iodide ions from the highly ionized hydriodic acid. Since this sol appears to behave differently in certain respects from the series of sols investigated in this laboratory, it seemed advisable to study the behavior of a sol of similar structure on the stepwise addition of electrolytes. The sol chosen was cupric ferrocyanide sol, which is negatively charged owing to preferential adsorption of ferrocyanide ions from the highly ionized hydroferrocyanic acid.

FORMATION OF CUPRIC FERROCYANIDE SOL

Preparation of $H_4Fe(CN)_6$. Pure cupric ferrocyanide is best prepared by the interaction of hydroferrocyanic acid and a cupric salt (5, 9). The gel, as ordinarily prepared from potassium ferrocyanide and a cupric salt, contains more or less of the potassium salt. Since it was essential in the present work to avoid the presence of cations other than hydrogen and copper, hydroferrocyanic acid was always employed in preparing the gel. The acid was prepared as follows: 100 g. of potassium ferrocyanide was dissolved in 500 cc. of water freshly boiled to remove dissolved oxygen. The solution was cooled to 10°C., and slightly more than an equivalent amount of concentrated hydrochloric acid was added. Any potassium chloride which precipitated was dissolved by adding a little water; then 125 cc. of cold ether was poured slowly into the bottle, which was shaken gently with a whirling motion in order to bring the ether slowly in contact with the solution. By this procedure a hydroferrocyanic acid-ether compound was precipitated as a coarse, crystalline mass which was transferred rapidly to a Büchner funnel and washed, first with a mixture of dilute hydrochloric acid and ether, and finally with pure ether. After the crystals were dry, they were transferred to a flask and dissolved in 250 cc. of absolute alcohol. The small amount of potassium chloride adsorbed by the crystals was insoluble in the alcohol and was filtered off. The solution was next mixed with absolute ether and the resulting crystals were transferred to a Büchner funnel and washed with absolute ether. The compound was then placed in a vacuum desiccator over sulfuric acid and evaporated with a water pump until most of the ether was removed, after which a high vacuum was maintained by the continuous operation of an oil pump for thirty-six hours. The resulting product was pure white and was quite stable in the absence of moisture.

Preparation of $Cu_2Fe(CN)_6$ *gel.* Sufficient hydroferrocyanic acid to make 2 g. of gel was dissolved in 200 cc. of water in an 800-cc. beaker and an equivalent amount of pure cupric acetate in 200 cc. of water was placed in a separatory funnel. The copper solution was allowed to run slowly into the hydroferrocyanic acid solution, which was stirred vigorously with a motor-driven stirrer. Since the gel was found to peptize most easily if an excess of copper was avoided, the precipitation was brought to completion carefully in the following way: after approximately 95 per cent of the necessary copper solution was added, the mixture was transferred to two 250-cc. Pyrex bottles and centrifuged in a No. 1 International Equipment Company centrifuge at 3000 R.P.M. for 5 minutes. Since most of the cupric ferrocyanide remained in the sol state in the presence of the excess hydroferrocyanic acid, copper solution was added to the bottles in 2-, 1-, and 0.5-cc. portions with intermediate centrifuging until the gel was thrown down and, finally, dropwise until the supernatant solution was clear or only slightly turbid. After the gel was well matted down by centrifuging, the supernatant liquid was poured off and the gel was washed in the following way: approximately 100 cc. of water was added to each of the bottles, which were shaken vigorously to break up the gel thoroughly. The bottles were then filled with water; after shaking they were centrifuged as before. Again a considerable portion of the gel was peptized to the sol state, and copper solution was added dropwise with intermediate centrifuging until the supernatant solution was almost clear. This was poured off and the washing was repeated two more times by the same procedure. In this way a 1-g. portion of cupric ferrocyanide was washed three times with 250-cc. portions of water, thereby removing the reaction product, acetic acid, almost completely.

Peptization of $Cu_2Fe(CN)_6$ *gel.* The 2 g. of washed gel was suspended in approximately 100 cc. of water, and sufficient hydroferrocyanic acid was added to make a solution between 0.001 and 0.002 *N*. After shaking at intervals for an hour or two, the mixture was allowed to stand. The resulting sol was quite clear and deep red in color. The small amount of unpeptized solid was removed by centrifuging, and the sol was ready for the titration and adsorption studies. Since hydroferrocyanic acid is instable in contact with water, undergoing an internal oxidation–reduction reaction with the formation of Prussian blue and hydrocyanic acid, it might be expected that the sol would be quite unstable; but this is not the case. Although free hydroferrocyanic acid is quite unstable, the adsorbed acid is stable. Sols prepared by the above method have stood for weeks without appreciable sedimentation. Of course, any unadsorbed hydroferrocyanic acid in the intermicellar solution will decompose gradually, but in the sols prepared as above described, only a little excess hydroferrocyanic acid was present. In any event, sols which had stood three or four days underwent no change in hydrogen-ion concentration during the course of the experiments.

TITRATION AND ADSORPTION EXPERIMENTS

The stepwise addition of electrolytes to sols and the measurement of the accompanying change in concentration of "counter ions" is termed titration.

The method of procedure employed in the present investigation was similar to that described in former papers in this series: 20 cc. of sol was placed in the outer compartment of an all-glass mixing apparatus and a definite volume of electrolyte diluted to 5 cc. in the inner compartment. The electrolyte and water were measured with calibrated 2-cc. Mohr pipets graduated in 0.01 cc. After thorough shaking, the mixture was transferred to 50-cc. Pyrex flasks and allowed to stand four hours. The hydrogen-ion concentration was determined by means of the glass electrode, using a Youden apparatus with a glass-bulb electrode prepared with Corning 015 glass.

The adsorption of barium and strontium ions, at or above the precipitation concentration for the sol, was determined as follows: 50- or 60-cc. portions of sol were precipitated in Pyrex bottles under the same conditions as described above, and after standing four hours, the mixture was centrifuged and 50-cc. samples of the supernatant liquid were taken for analysis. The barium and strontium were determined as sulfate following standard methods of procedure.

TABLE 1

Titration of sol I

0.02 *N* $BaCl_2$ ADDED TO 20 CC. OF SOL. TOTAL VOLUME, 25 CC.	$[H^+] \times 10^3$ IN SOLUTION	$[H^+] \times 10^3$ DISPLACED	$[Ba^{++}]$ ADDED	$[Ba^{++}] \times 10^3$ ADSORBED
0.0	1.29	0.0	0.0	
0.5	1.50	0.21	0.4	
1.0	1.68	0.39	0.8	
1.5	2.03	0.74	1.2	
2.0	2.10	0.81	1.6	
2.5	2.19	0.90	2.0	
3.0	2.19	0.90	2.4	2.22
4.0	2.19	0.90	3.2	
5.0	2.19	0.90	4.0	2.84

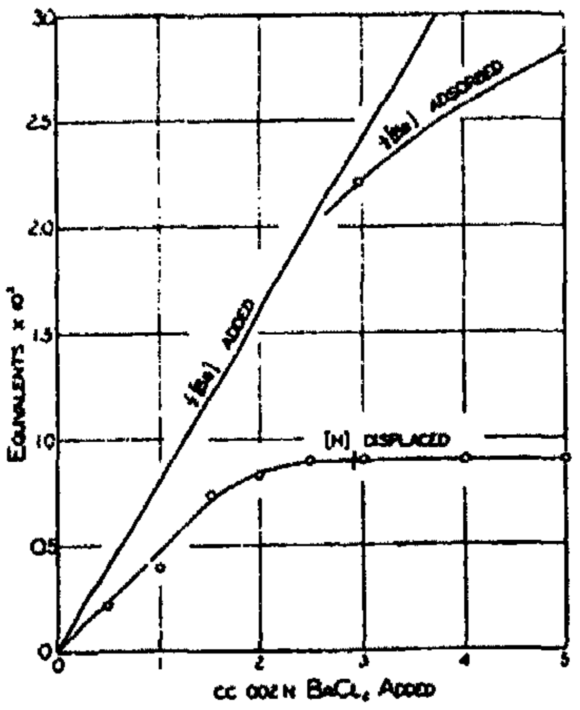

FIG. 1. Curves for adsorption of Ba^{++} and displacement of H^+ in the titration of cupric ferrocyanide sol I with barium chloride.

Experiments with sol I. The experiments were limited to salts of the alkalis and alkaline earths, since the ferrocyanides of the other metals are insoluble. After preliminary work had demonstrated the applicability of the experimental technique to the case at hand, observations were made of the hydrogen-ion displacement and adsorption of barium ion on titrating a sol containing 18 g. of cupric ferrocyanide per liter with 0.02 *N* barium chloride. The results are shown in table 1 and are reproduced graphically in figure 1. It is apparent that the displacement of hydrogen ions is less than the amount of barium added and of barium adsorbed. The displacement is complete somewhat below the precipitation value, indicated by a vertical line cutting the displacement curve. Most of the added barium is adsorbed at concentrations just above the precipitation value.

TABLE 2

Titration of sol II

0.02 *N* $BaCl_2$ ADDED TO 20 CC. OF SOL. TOTAL VOLUME, 25 CC.	$[H^+] \times 10^3$ IN SOLUTION	$[H^+] \times 10^3$ DISPLACED	$[Ba^{++}]$ ADDED	$[Ba^{++}] \times 10^3$ ADSORBED
0.0	0.85	0.0	0.0	
0.5	0.98	0.13	0.4	
1.0	1.10	0.25	0.8	
1.5	1.34	0.49	1.2	
2.0	1.34	0.49	1.6	
2.5	1.34	0.49	2.0	1.65
5.0	1.34	0.49	4.0	2.31

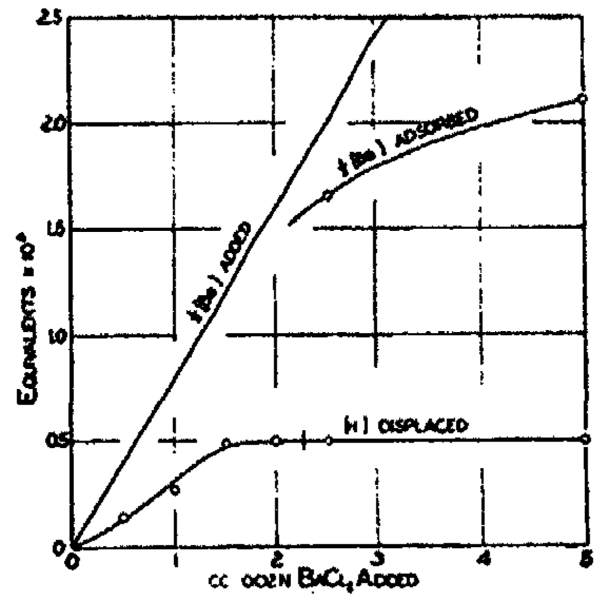

FIG. 2. Curves for adsorption of Ba^{++} and displacement of H^+ in the titration of cupric ferrocyanide sol II with barium chloride.

Experiments with sol II. A second sol was prepared using but one-half the amount of hydroferrocyanic acid to effect the peptization as was used in sol I; it contained 13 g. of cupric ferrocyanide per liter. The observations of displacement of hydrogen and adsorption of barium on titrating with barium chloride are given in table 2 and figure 2. As was to be expected, the hydrogen-ion concentration of the sol at the start was less than for sol I and the amount of hydrogen ion displaced by the added electrolyte was correspondingly less.

Experiments with sol III. For the purpose of comparing the action of different electrolytes, a third sol of hydrogen-ion concentration intermediate between I and II and containing 16 g. of cupric ferrocyanide per liter was titrated with the chlorides of barium, strontium, and potassium; and the adsorption of barium and strontium was determined. The data are given in table 3 and figure 3. It is apparent that the coagulating power, displacing power for hydrogen ion, and the adsorption of strontium and barium are similar, but the values for strontium are somewhat less in every case than for barium. The univalent potassium ion has a definitely

TABLE 3

Titration of sol III

ELECTROLYTE ADDED TO 20 CC. OF SOL. TOTAL VOLUME, 25 CC.	$[H^+] \times 10^3$ IN SOLUTION	$[H^+] \times 10^3$ DISPLACED	EQUIVALENTS $\times 10^3$ ADDED	EQUIVALENT $\times 10^3$ ADSORBED
0.02 *N* $BaCl_2$			$\frac{1}{2}[Ba^{++}]$	$\frac{1}{2}[Ba^{++}]$
0.0	0.97	0.0	0.0	
1.0	1.15	0.18	0.8	
1.5	1.19	0.22	1.2	
2.0	1.26	0.29	1.6	
2.5	1.29	0.32	2.0	
2.8			2.24	1.74
3.0	1.29	0.32	2.4	
5.0	1.29	0.32	4.0	2.07
0.02 *N* $SrCl_2$			$\frac{1}{2}[Sr^{++}]$	$\frac{1}{2}[Sr^{++}]$
0.0	0.97	0.0	0.0	
1.0	1.08	0.11	0.8	
1.5	1.13	0.16	1.2	
2.0	1.22	0.25	1.6	
2.5	1.24	0.27	2.0	
2.8			2.24	1.55
3.0	1.26	0.29	2.4	
4.0	1.26	0.29	3.2	
5.0			4.0	1.72
0.033 *N* KCl			$[K^+]$	
0.0	0.97	0.0	0.0	
1.0	1.08	0.11	1.33	
2.0	1.15	0.18	2.67	
3.0	1.19	0.22	4.00	
4.0	1.19	0.22	5.33	
5.0	1.19	0.22	6.67	

lower coagulating power than the divalent ions, and the power of the former to displace hydrogen ions is lower at the same concentration.

DISCUSSION OF RESULTS

The behavior of cupric ferrocyanide sols towards electrolytes is so much like that of the hydrous oxide and sulfur sols, that it can be explained by a similar mechanism. Cupric ferrocyanide gel peptized by hydroferrocyanic acid is negatively charged, owing to preferential adsorption of the common ferrocyanide anion. Since the ionization constant of the fourth hydrogen ion is so small (2), it is probable that even in the dilute solutions employed, the anion is chiefly $HFe(CN)_6^{---}$ (represented by R^{---} in figure 4) rather than $Fe(CN)_6^{----}$. In any event, the negative ions may be assumed to form the inner portion of a double layer surrounding the hydrous particles of cupric ferrocyanide, as represented diagrammatically in figure 4a. The counter ions are hydrogen ions which form the diffuse outer portion of the double layer. Some of the hydrogen ions are held so strongly (adsorbed) by the attractive force of the inner layer that they are not detected by a hydrogen electrode, whereas others, because of a relatively higher kinetic energy, exert sufficient osmotic repulsive force against the attraction of the adsorbed ferrocyanide ions so that they are a part of the intermicellar solution and thus influence the hydrogen

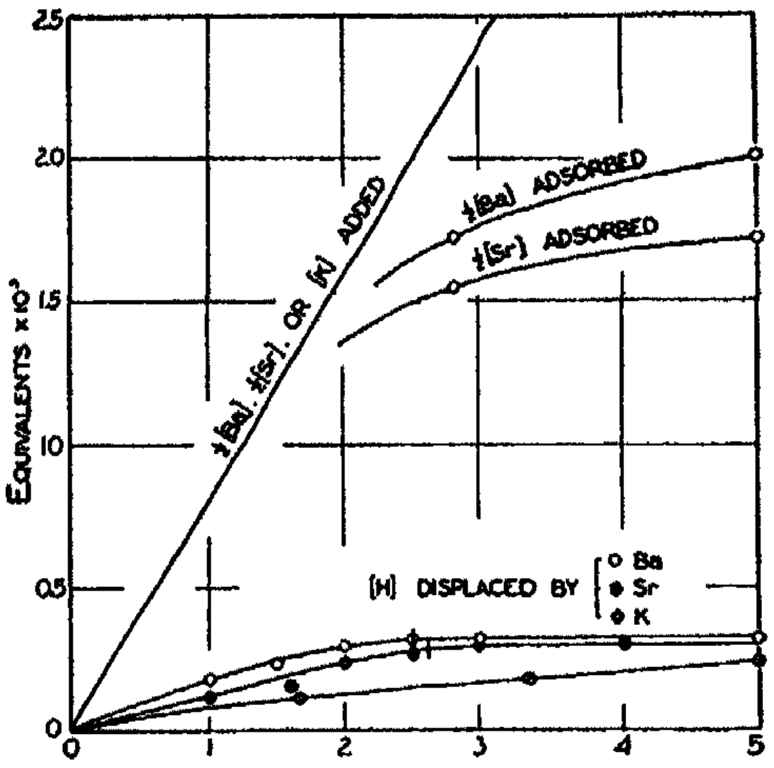

FIG. 3. Curves for adsorption of precipitating cations and displacement of H^+ in the titration of cupric ferrocyanide sol III with the chlorides of barium, strontium, and potassium.

electrode. These are represented in the diagram beyond the dotted line. On adding an electrolyte such as barium chloride to the sol, the divalent barium ions are attracted more strongly by the inner layer than the counter hydrogen ions, as shown diagrammatically in figure 4b, and the thickness of the double layer is reduced. At the same time, some adsorbed hydrogen ions are displaced and are detected in the intermicellar solution. This contraction of the double layer or compression of the outer layer resulting from stronger adsorption of barium ions than hydrogen ions under the prevailing relative concentrations, causes a lowering of the ζ-potential

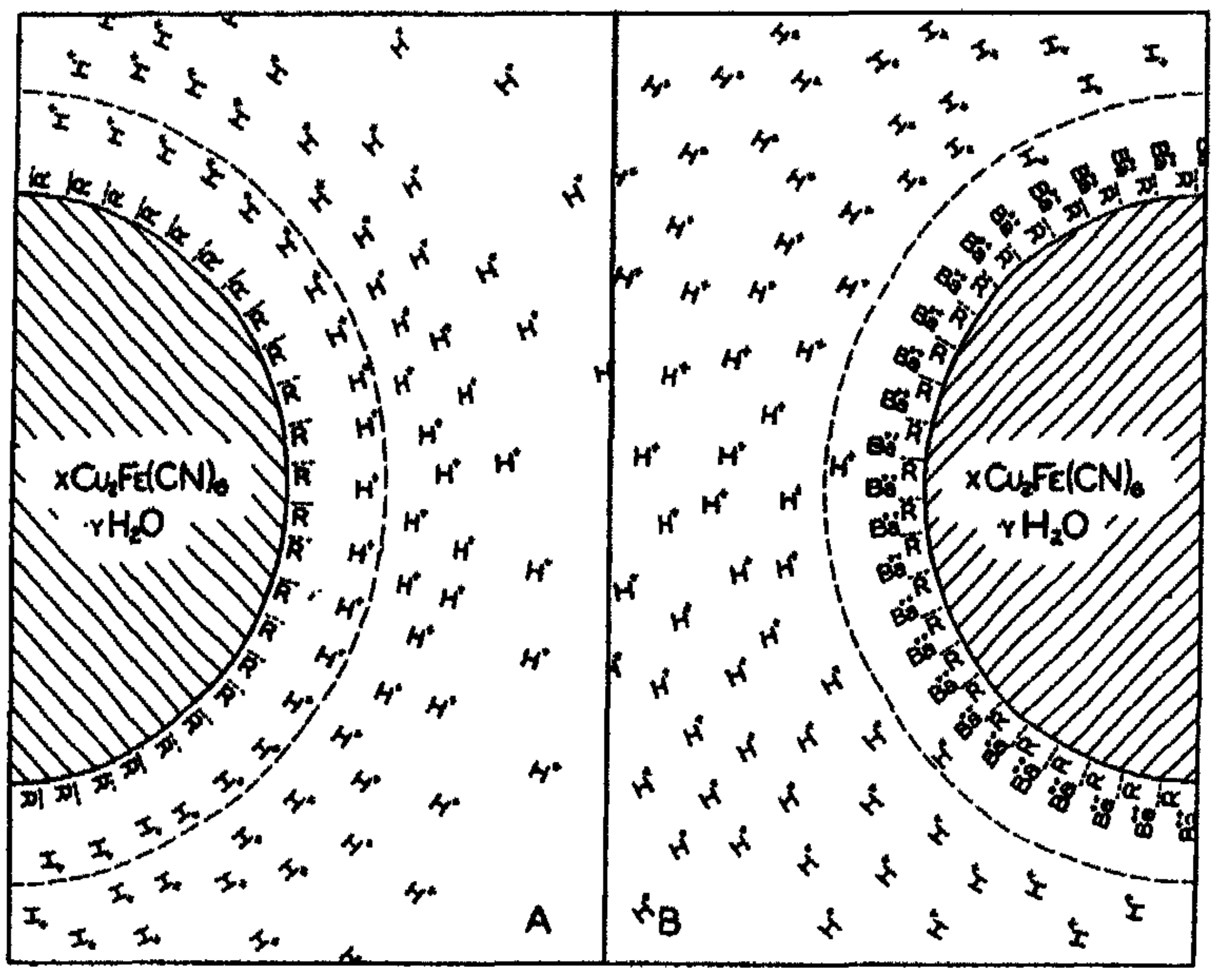

FIG. 4. Diagrammatic representation of the constitution of a particle of colloidal cupric ferrocyanide before and after the addition of Ba^{++}.

on the particles; when this is reduced sufficiently, coagulation takes place. The displacement of adsorbed hydrogen ions by adsorbed barium ions is far from an equivalent displacement, since most of the adsorbed barium ions correspond to hydrogen ions which are in the intermicellar solution and so are measurable potentiometrically in the original sol. It is not at all surprising that in certain cases all the adsorbed hydrogen ions are displaced before sufficient barium ions are adsorbed to reduce the ζ-potential to the coagulation point.

Since most of the added barium ions are adsorbed at concentrations slightly *above* the coagulation value, it would follow that most if not all the added barium ions are adsorbed *below* the coagulation value. Since the total barium adsorbed above the coagulation value is somewhat greater than the total hydrogen ions in the sol, it follows that, to a certain extent, both barium ions and chloride ions are adsorbed in equivalent amounts from the barium chloride solution. The observed phenomena are almost identical with those using the positive hydrous oxide sols of iron, aluminum, and chromium in which the counter ions are chloride ions, and the precipitating electrolyte is potassium sulfate (11). The behavior of strontium chloride is similar to that of barium chloride, whereas potassium chloride has a lower precipitating power, because potassium ions are less strongly adsorbed and displace hydrogen less strongly than the divalent ions at the same concentration.

From the above observations it is concluded that the action of electrolytes on cupric ferrocyanide sol is similar to that previously observed on five other sols. The lowering of the ζ-potential of the cupric ferrocyanide particles on the addition of electrolytes is due to the contraction of the double layer or, if preferred, to a compression of the outer layer resulting from adsorption of the added cations. At all concentrations the cation adsorption is much greater than the hydrogen-ion displacement, since most of the counter ions in the diffuse layer are in the intermicellar solution. The adsorption is for the most part an exchange adsorption, in which the cations carried down are in exchange with the counter hydrogen ions of the diffuse outer layer. The apparent difference in behavior between the sols investigated in this laboratory and the silver iodide sol studied by Verwey and Kruyt, is that in the former the potential reduction results from adsorption of precipitating ions, whereas in the latter, adsorption may not be essential for all the potential reduction. It is a matter of opinion whether the behavior of the six sols which we have studied should be regarded as special, whereas that of the silver iodide sol typifies the general behavior as claimed by Verwey and Kruyt, or whether the reverse is true.

SUMMARY

1. A study has been made of the adsorption of cations and of the displacement of hydrogen ions during the electrolyte coagulation of negative cupric ferrocyanide sol prepared by peptization of cupric ferrocyanide gel with hydroferrocyanic acid.

2. At concentrations both above and below the precipitation value, the adsorption of cations is much greater than the displacement of hydrogen ions, since most of the hydrogen ions, which constitute the diffuse outer portion of the double layer surrounding the particles, are in the intermicellar solution.

3. The adsorption of cations is largely an exchange adsorption, in which the cations carried down by the precipitated gel are in exchange with

the counter hydrogen ions of the diffuse outer portion of the double layer.

4. The lowering of the ζ-potential of the cupric ferrocyanide particles on the addition of electrolytes is due to the contraction of the double layer, or, if preferred, to a compression of the outer layer resulting from adsorption of the added cations.

5. The behavior of cupric ferrocyanide sol toward electrolytes is similar in essential respects to that of hydrous oxide sols, sulfur sol, and arsenic trisulfide sol investigated in this laboratory.

6. The apparent difference in behavior between the six sols studied by us and the silver iodide sol studied by Verwey and Kruyt, is that in the former the potential reduction results from adsorption of precipitating ions, whereas in the latter, adsorption may not be essential for all the potential reduction.

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ERRATUM

Vol. 40, p. 988: Reference 12 should read "Harkins and Brown: J. Am. Chem. Soc. **41**, 499 (1919)."

THE ADSORPTION CONDENSER AND ELECTROMOTIVE FORCE[1]

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The controversies concerning the origin of electromotive force have offered a great stimulus for the development of electrochemistry (14). The existence of a metal-surface work function in the surface of metals immersed in water is either denied or ignored by a number of electrochemists (18). Others, reasoning from the behavior of metals in the highest vacuum obtainable, consider that a condenser must exist with or without a chemical reaction at the surface. To date no important tool for the complete understanding of electrochemistry has been evolved from either the chemical-reaction or the contact-potential theory, although the latter has the advantage.

The pioneering work of Butler (3) pointed the way for development. Shortly after Butler's work the picture of a metal became much more complicated. The Sommerfeld (16) and Bloch (1) theories of metals gave a much clearer picture of the energy relationships at the metal surface. These theories divided the total metal-surface work function into two parts, the internal and the external work function. Gurney (9) modified the external work function by introducing a division termed the "interface" potential to account for the resultant condenser in the interface of a metal in a solution. The "interface" potential seemed absolutely new, but in reality Gurney merely used the concepts and language of molecular spectroscopy to describe the forces that cause the adsorption of ions on an electrode, and named the potential of the adsorption condenser the "interface" potential. He showed that the energy which produces the adsorption of ions can be represented as the difference between two electron energy levels,—the electron energy level of the metal and the electron energy level of the ion in solution. After he had proved the necessity for an increased adsorption of ions during the passage of current across a metal interface, he explained the overvoltage data of Bowden (2). Bowden adjusted his electrodes until their potentials were that of the equilibrium hydrogen or oxygen electrode at the start of the experiment.

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The hypothesis of ion adsorption on the surface of metals has been a very important part of a large number of theories of the phenomena of metal surfaces. Helmholtz (10) in 1879 suggested an ion adsorption condenser to explain a number of characteristics of metals, including electrokinetic potentials. His theory has been modified and extended by a large number of theorists, including Debye and Hückel (5), Gouy (8), Stern (17), and Freundlich (7). Langmuir pointed out that an ion adsorption condenser furnishes the only true potential of an electrode. The structure of the adsorption condenser is in dispute, but there is general agreement that the adsorbed layer must be mobile enough to participate in electrokinetic phenomena and it must be sensitive enough to the concentration of the ions in the solution so that its contribution to the electrode potential will be in accord with the thermodynamic equation of Nernst.

Our (4) recent experiments on the rapid motion of metals through solutions indicate that electrokinetic potentials at crystalline metal surfaces are produced by the disturbance of a layer of adsorbed colloidal particles. The rate of build up and decay of the potential is too slow for the phenomenon to be due to the behavior of simple ions (12). Metallic colloids have a characteristic effect on the potential. The chemical reaction theory is eliminated. In other experiments we (11) produced very large electrokinetic potentials at noble metal electrodes during overvoltage measurements at low current densities. It seems still more obvious that the latter are due to the disturbance of a layer of colloidal particles in the interface. If the very important principle of Butler and Gurney, that "the passage of a certain current across an electrode interface necessitates a certain overpotential," is to be accepted, any great disturbance of the overvoltage at low current densities by movement of the interface through the solution indicates (1) that a part of the hypothetical equilibrium condenser has been disturbed, and (2) that this part of the equilibrium potential is made up not of the ions of the solution whose concentration is established by the current, but of colloidal particles of hydrogen and metal.

In the experiments on overvoltage another very interesting phenomenon was observed. The metals copper, silver, gold, and platinum, when polarized cathodically in pure dilute aqueous sulfuric acid solutions at current densities of less than 10^{-5} ampere per square centimeter, showed electrode potentials in the platinum direction from the equilibrium hydrogen electrode. The solutions were very carefully freed from traces of oxygen by boiling and cooling in a stream of purified hydrogen; purified hydrogen was bubbled through the solution during the measurements. Previous cathodic polarization at high current strengths and moving the metal rapidly through the solution cause the potentials to go farther in the platinum direction. Long periods of polarization in an apparatus where the hydrogen gas could be collected proved that hydrogen was not liberated.

Weighing the cathodes before and after the individual experiments and spectroscopic analyses of the anodes showed that colloidal particles of metal carrying a negative charge were plated off of the cathodes.

Examples of the plating of metals off of cathodes are quite numerous in the experience of electroplaters; the phenomenon is most baffling in the light of the principles accepted at present. Kohlschütter (13) has ultraphotomicrographic evidence that there are colloidal particles in the electrode interface and claims that they play an important part in the electroplating process. Our experiments establish "the solution-of-the-negatively-charged-cathode-colloids" as the explanation of plating-off processes and indicate most clearly the need for a theory in which colloidal particles play a very important part.

The point from which we think the theory should start is indicated by the results of the recent experiments on electron diffraction from pure polished metal surfaces. Attempts to secure an indication of structure in a polished metal surface using electron methods always fail. The beam is diffused into broad lines. Since it is possible to get an indication of structure from natural crystal surfaces that are essentially plane, the results of the experiments on polished metals indicate quite definitely that such a surface is made up of particles of finely divided metal. Such a premise leads logically to the conclusion that finely divided particles are an intrinsic part of the metal surface, and that polishing a surface merely thickens the layer.

During the rest of this discussion we shall outline a theory of electrode potentials in which we consider a single electrode potential as being composed of the metal-surface work function and a colloidal adsorption condenser.

THE METAL

The conception of a metal which we shall use is essentially that originated by Sommerfeld and modified by Bloch. For some purposes all of the electrons of the metal atoms may be considered as being free to move from one end of a perfect lattice to the other without resistance. Electrical resistance is produced by a disturbance of this lattice. For the purposes of the quantum statistics, the electrons may be considered as bound in energy levels to which they are assigned according to the Pauli exclusion principle. The outermost electrons, the so-called valence electrons, behave like a very highly compressed or degenerate gas, obeying the Fermi-Dirac statistics. They are the only ones that can respond to an external electric field, make transitions to higher energy levels of the electron gas, change direction under influence of an electric field, and hence participate in the electronic conduction process.

These principles apply only as long as the perfect lattice exists. Local irregularities, such as the surface of the perfect crystal, introduce new levels. For example, some space charge barrier must balance the maximum kinetic energy of the electrons, from 2 to 20 volts, so that the only effective electron barrier is the external work function. Such a space charge barrier might be formed by an impurity that, being stuck to the surface, becomes charged by induction and so affects the periodicity of the field near the boundary that the lower energy levels are damped out. The external metal-surface work functions, however, are measured when the possibility of impurities being present is at a minimum. At any rate it is not desirable to develop a theory of an ideal metal surface assuming the existence of an impurity. As has already been pointed out, there has accumulated an appreciable amount of direct and deductive evidence for the existence of a layer of finely divided metal in the metal surface. Therefore our theory assumes the adsorption on a pure metal surface of a layer of finely divided metal particles that are charged with excess negative charges (electrons) sufficient to balance the maximum kinetic energy of the metal electrons.

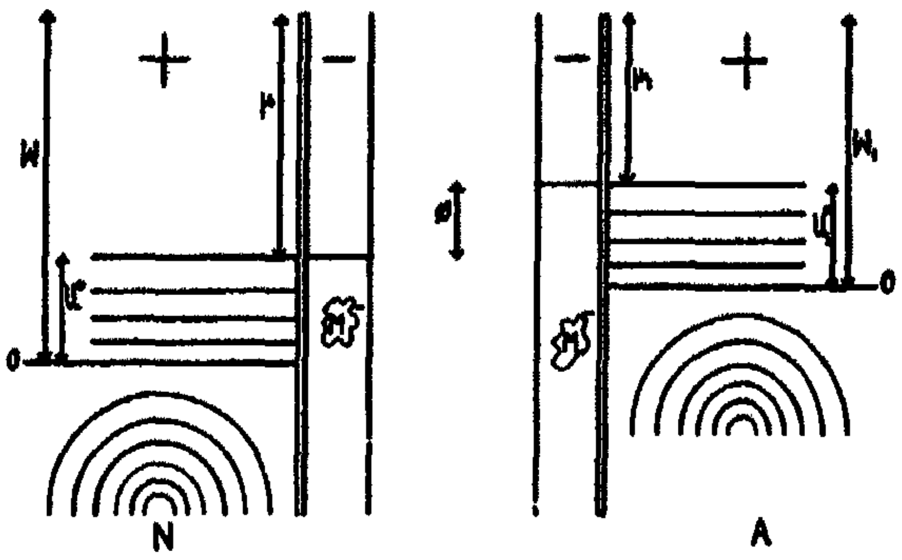

FIG. 1. The energy relations at the surface of a noble (*N*) and an active (*A*) metal in a vacuum

The energy relations at the surface of a noble and an active metal in a vacuum are represented by *N* and *A*, respectively, in figure 1. W and W_1 are the total metal-surface work functions, or the potential barriers for an electron of zero kinetic energy; μ and μ_1 are the external metal-surface work functions, or the potential barriers for an electron of maximum kinetic energy; U^0 and U_1^0 are the maximum kinetic energies of the electrons at 0°K. U^0 is given by the equation,

$$U^0 = \left(\frac{h^2}{2m}\right)\left(\frac{3n}{8\pi}\right)^{2/3} \tag{1}$$

where h is Planck's constant, m is the mass of the electron, and n is the number of electrons per unit volume. The energy distribution function expressing $\mathrm{d}n_w$, the number of electrons per unit volume whose total kinetic energies lie between w and $w + \mathrm{d}w$, is

$$\mathrm{d}n_w = \frac{A w^{1/2}\,\mathrm{d}w}{e^{\frac{-(U^0 - w)}{kT}} + 1} \qquad . \qquad (2)$$

It is possible to show from this distribution function that U^0 may be used as the approximate value of the maximum kinetic energy of the electrons at room temperature. The relatively enormous velocities of the electrons are counteracted at the metal surface by a layer of negatively charged metal particles, while the crystalline metal assumes a positive charge as a result of the particles being negatively charged (see figure 1). Any electron that gets inside of this layer will be accelerated enormously toward the crystalline metal, and an electron emerging from the metal surface with the maximum velocity will have its velocity reduced to zero by the time it reaches the particle layer. Therefore it is necessary to give the electron the additional energy, μ, in order that it may overcome the force due to the attraction of the electric image and the force due to the attraction of the electrostatic environment and escape.

THE SOLUTION

We shall consider the solution in which the metal is immersed from the energy level point of view in much the same way that Fowler (6) has. Positive ions and dissolved oxidizing agents are regarded as possessing empty electron energy levels. In the gas phase, positive ions have rather low energy levels (large ionization potentials), but when they dissolve in a polar solvent such as water, ions of the metals above hydrogen lose considerable energy so that their energy levels are raised, while ions of the metals below hydrogen gain energy so that their energy levels are lowered. When the positive ion is stable its empty energy level must be equal to or above any full electron energy level in the metal, such as the maximum kinetic energy level, or the full energy level of a negative ion. The energy level of a positive ion in solution can be raised, with respect to a metal energy level, by diluting the salt furnishing the positive ion or by giving the solution a negative charge with respect to the metal. The energy level of a positive ion in solution can be raised with respect to a negative ion only by dilution.

The negative ions and dissolved reducing agents are regarded as possessing full electron energy levels in the solution. The negative ions in the gas phase have energy levels that are not as low, on the energy scale, as the energy levels of the positive ions. The two kinds of ions neutralize each other on collision. When the negative ions are dissolved in a polar solvent like water their energy level is lowered until both positive and negative ions exist as separate ionic species. It is necessary for the energy level of a negative ion to be lower than the metal energy level because the metal furnishes the electron supply. The energy level of the negative ion can be lowered with respect to a metal energy level by dilution, or by giving the solution a positive charge with respect to the metal. The energy level of a negative ion can be lowered with respect to a positive ion only by dilution.

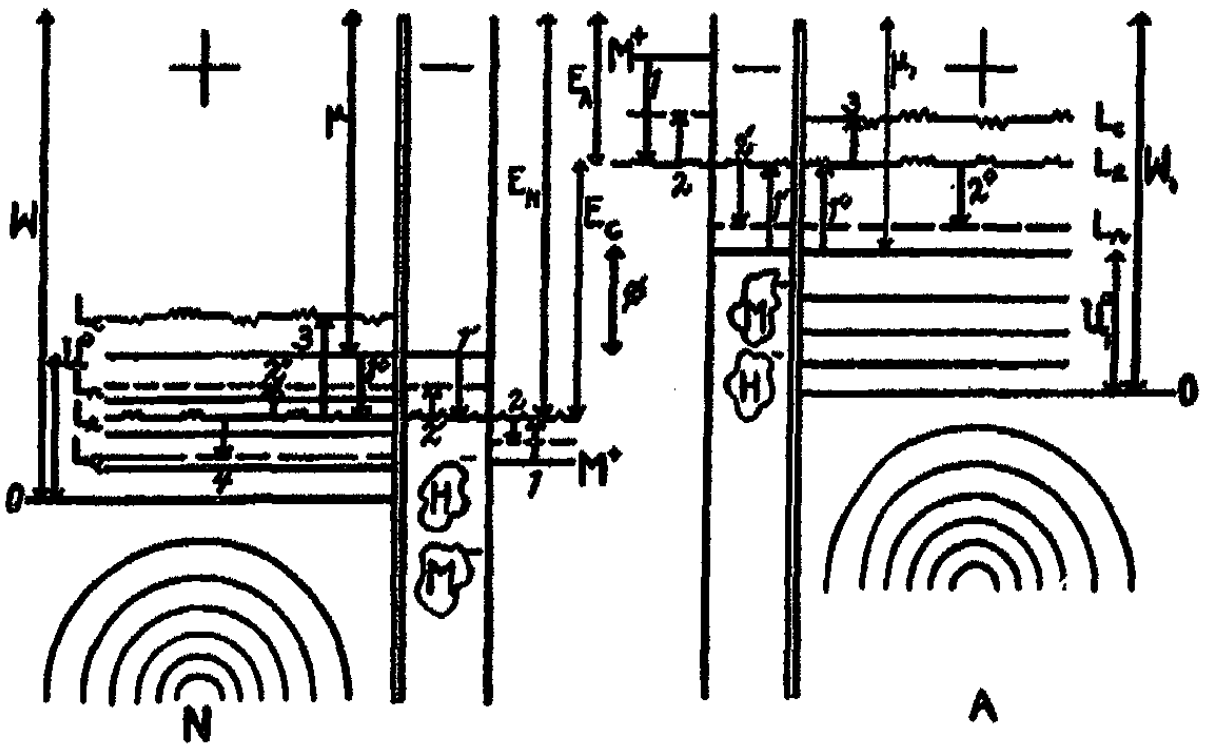

FIG. 2. The result of the raising of the energy level of the positive ions of an active (*A*) and of a noble (*N*) metal

If the electron energy level of an ion is occupied by an electron it is a full level; if it is not occupied it is an empty level. For any ion species that participates in the reactions at an electrode interface the full and the empty energy levels tend to be the same.

THE ELECTRODE

When a metal is placed in an aqueous solution of its salt the energy relations in the surface are changed. The colloidal particles become identified with the electrical surface of the solution, so that any charge on the colloidal particles is now the net charge on the solution. The instantaneous effect is the raising of the electron energy level of the solution ions in the surface of the layer, owing to the charge the colloid had in a vacuum. The result of the raising of the energy level of the positive ions of an active metal is shown in figure 2(*A*) at M^+. The empty positive ion level is higher than the metal energy level. The colloidal layer will have metal atoms on the surface of the particles that can be considered as solution ions possessing full energy levels. These full energy levels must lose electrons to the crystalline metal, producing a decrease in the negative charge on the solution, a decrease in the positive charge on the metal, and a positive ion in the solution. As a final result when equilibrium is reached the metal energy level is raised and the empty positive ion energy level is lowered until the two levels are the same. This situation is shown at L_e, figure 2(*A*).

The immediate result of the raising of the energy level of the ions of a noble metal is represented in figure 2(*N*) at M^+. The empty energy level of the solution ion is below the energy level of the electrons in the metal. Electrons can flow from the metal into the ion level, producing a full positive ion level or a neutral metal atom that deposits on the crystalline metal. This process charges the solution more negatively and the crystalline metal more positively, so that the metal energy level is lowered while the energy level of the solution ion is raised until the two levels are the same and equilibrium is established. This latter situation is represented at L_e, figure 2(*N*).

When equilibrium is reached at an electrode the energy barrier for the electrons in the metal is changed from μ to $\mu - fV = fE$, where V is the interface potential for the electrode, $\mu = W - U^0$, the external metal-surface work function, E is the electrode potential, f is the charge on the electron, and fV is the energy of transformation 1′, shown in figure 2. Any lack of definition of the energy levels is matched on the inside and outside of the metal. The current of electrons leaving the perfect lattice of the metal and neutralizing solution ions of the colloidal layer is given by the expression

$$i_1 = K_1(M^+)Te^{\frac{-(W_1-U^0-nFV)}{2RT}} \tag{3}$$

where M^+ is the activity of the metal ions. The current of electrons, from the full energy levels in the colloidal layer, that flows into the metal leaving ions to be hydrated in the solution is given by the expression

$$i_2 = K_2(P)Te^{\frac{+(W_2-U^0-W_h-nFV)}{2RT}} \tag{4}$$

where P is a constant characteristic of the metal and W_h is the energy of hydration of the ions. When the electrode is in equilibrium, the currents i_1 and i_2 are equal. Equating equations 3 and 4 gives

$$nFE = \frac{W_h}{2} + RT \ln \frac{K_1(M^+)}{K_2(P)} \tag{5}$$

or

$$E = E_0 + \frac{RT}{nF} \ln (M^+) \tag{6}$$

which is the thermodynamic equation of Nernst.

A cell made up of the two different types of electrodes such as those shown in figure 2 can be represented by a solution connection between the two interfaces. The electromotive force of the cell, measured on a potentiometer, would be $E_c = E_A - E_N$, or the difference between the energy levels of the solution ions in the colloidal layers of the two electrodes. The contribution of the metals to the electromotive force is the contact difference of potential, ϕ (figure 1). The contribution of the solution to the electromotive force is $EV - EV_1$.

ELECTROKINETIC POTENTIALS AT METAL SURFACES

The importance of the rôle played by the colloidal particles in supplying either empty or full energy levels (metal atoms) to the positive ions in solution is emphasized by a consideration of what happens when an electrode is moved rapidly through a solution. It is obvious that the large frictional and centrifugal forces will throw the particles out into the solution. This removal of the colloidal particles removes the source of full electron energy levels to a position where the tendency of the electrons to leak to the metal is reduced, and if the instantaneous energy level of the solution ions, M^+, is any above or below the metal energy level in a vacuum the effective electrode potential changes.

Let us consider an active metal in pure water first. The removal of the colloidal particle makes it possible to set up only a false equilibrium. The positive ion level will return toward its instantaneous position, M^+, and the metal energy level will return toward its position in vacuum, transformations 2,2′, and 2″ (figure 2). The solution gets a more negative charge in order to balance the kinetic energy of the metal electrons at L_n, and the chemical reaction fills empty hydronium ion levels. The electrode potential of the metal changes in the platinum direction. If the above experiment on the electrokinetic potential of an active metal is repeated in solutions of its salts, the electrokinetic potential of the metal is not so large. The decrease in the electrokinetic potential is not dependent upon the increased activity of the salt in the solution alone, but also upon the effect of the colloidal particle in solution upon the energy levels of the ions. It is not very easy to predict the shape of the electrokinetic potential-concentration of electrolyte curve, so it will not be attempted here.

Violent motion of the noble metal in water wipes off the colloidal particles. The energy level of these particles is below the energy level of the hydronium ion, and since the negative charge on the solution is too great to balance the maximum kinetic energy of the metal electrons, electrons are forced into the metal. The energy level of the metal in vacuum tends to be restored and the electrode potential changes in the sodium direction, L_r. If the solution contains positive ions into which the electrons can flow, an added salt, then the potential of the electrode may change in the platinum direction.

The predictions that have been made concerning the electrokinetic potentials at metal surfaces, using the colloidal layer theory, are in very good agreement with the facts. The magnitude and sign of the electrokinetic potentials of metals in pure water are correct for improving the agreement between metal-surface work functions and molal electrode potentials.

THE HYDROGEN ELECTRODE

According to the general description given of an equilibrium electrode, the hydrogen electrode must be an electrode whose potential is dependent upon the energy level of the hydronium ions in solution. The hydronium ions in solution must have a supply of both empty and full energy levels, the hydronium ion level must be the same as the metal energy level, and the metal energy level must be in equilibrium with the hydrogen gas molecules when equilibrium is reached. The metal must supply a large amount of colloidal metal to adsorb the monatomic hydrogen. The colloidal layer must possess monatomic hydrogen or ions with full energy levels. The height of the full energy levels of the hydronium ions is determined by the partial pressure of the hydrogen gas. The base metal must not be capable of reacting with hydrogen ions. When these conditions are fulfilled the equilibrium processes that take place at a hydrogen electrode can be described exactly as those of the pure metals. Any increase in the height of the full level in the colloidal layer due to the neutralization of positive ions or increase in the hydrogen gas pressure causes a flow of electrons to the metal. These electrons arriving at the metal raise the energy level of the metal until the electrons flow back to an empty level of the colloidal layer, thereby reëstablishing the original condition.

THE OXYGEN AND CHLORINE ELECTRODES

The contact-potential theory of electromotive force has been difficult for many chemists to accept, because it has not given a clear picture of an equilibrium oxidizing gas electrode such as the oxygen or chlorine electrodes. The colloidal adsorption theory eliminates this difficulty when it shows that the energy levels of the empty ion (monatomic gas) and the full ion are the same as the energy level of the metal. The energy level of the metal must be largely established by the oxidation potential of the oxidizing gas, and the height of the level of the empty ion must be sensitive to changes in the partial pressure of the gas. The only difference between these electrodes and the ordinary metal electrodes is that the full energy level of the solution ion is represented by a negative ion, while the empty level is represented by a monatomic gas. In the case of oxygen and chlorine the potential at equilibrium is quite far in the positive direction.

The practical difficulty encountered in producing an equilibrium electrode for an oxidizing gas is due to the difficulty in finding a metal whose colloidal layer will produce ions with an empty energy level from the gas molecules. It is naturally easier to produce an equilibrium chlorine electrode than an equilibrium oxygen electrode, because in the first case the empty level that must be supplied is monatomic chlorine, while in the latter case the empty level is the free hydroxyl radical, whose energy level is below the energy level of monatomic oxygen, owing to hydration.

AN ELECTRODE CARRYING A CURRENT

In treating an electrode that carries a current we use the principle proved by Gurney. The probability of the passage of the excess electrons in the current direction (as a result of the quantum mechanical tunneling principle) must account for the current density. The equation for the net current across the interface is given by the equation

$$\pm i = K_1(M^+)Te^{\frac{-(W_1-U^0-nFV)}{2RT}} - K_2(P)Te^{\frac{-(W_2-U^0-W_h-nFV)}{2RT}} \tag{7}$$

which is a combination of equations 3 and 4. Excess electrons can pass in one direction only when a full electron energy level is higher on one side of the electrode interface than an empty level on the other, as we have emphasized before. The full energy levels are higher on the metal side at a cathode, L_c, and on the solution side at an anode, L_a.

When the positive solution ions are the ions of a noble metal, a slight increase in the negative potential of the electrode causes electrons to leak through the condenser and neutralize the metal ions in the colloidal layer (see L_c, figure 2 (*A*)). The metal atoms crystallize onto the perfect crystal. The increase in potential determines the current density according to equation 7. If the positive solution ions are hydronium ions or the ions of some active metal, the potential of the electrode must be raised until the energy level of the metal is above that of the other metal ions in the colloidal layer of the solution. While the potential is being raised the current across the interface is carried into the solution by the colloidal particles accepting more electrons and then leaving the interface, owing to the applied potential. After the energy level of the metal reaches that of the solution ions, the electrons fall into these empty levels and the metal plates out of solution. If the solution ions are of two different species, the one whose empty energy level is exceeded first by the metal level is neutralized. When the two different species have the same energy level the two plate out together.

The active metals show the same type of behavior, except for the fact that the change in potential, produced by violent motion of the metal, is of the opposite sign. Consequently equation 7 can not be used to predict the shape of the current density–overvoltage curve when there is active gas evolution. On account of the well-known lack of smoothness of metal surfaces and on account of the fact that the surface smoothness is constantly changing, there is a theoretical reason for both the lack of definite meaning for and the lack of reproducibility of the current density–overvoltage curves for the deposition of electrolytic gases at high current strengths.

In the case of high current densities, rotation redistributes the colloidal metal on the crystalline surface as well as the lines of force, so that the overvoltage will always be sent in the platinum direction. In the case of oxygen overvoltage these same factors will naturally send the potential in the sodium direction.

SUMMARY

An explanation of overvoltage and electrokinetic potentials is offered. The origin of electromotive force is described as well as the mechanism for conduction processes at a metal–solution interface. The explanation is based upon a colloidal layer of metal on the crystalline metal surface.

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THE DIRECT EXAMINATION OF SOLS BY X-RAY DIFFRACTION METHODS[1]

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The application of x-ray diffraction methods to the determination of the constitution of sols has usually been indirect. X-ray diffraction studies have been made on the dry powder or moist gel obtained from the sol by precipitation with electrolytes, ultrafiltration, or centrifuging. In previous papers (10, 12) it was shown that, in general, the moist gels obtained by ultrafiltration of sols give the same x-radiograms as the dry powder. Thus with alumina, stannic oxide, and indium hydroxide sols, the moist gels obtained by ultrafiltration give the pattern of γ-$Al_2O_3 \cdot H_2O$, SnO_2, and $In_2O_3 \cdot 3H_2O$ or $In(OH)_3$, respectively. Although it is often assumed that the sol particles have the same constitution in the sol state as in the moist precipitate, the direct examination of sols by x-ray diffraction methods should prove whether or not this is the case.

Very little work has been published on the direct examination of sols by x-ray methods. Kraemer (5) in discussing the application of x-ray methods to colloids states, "this technic [x-ray method] yields no results for the surface of particles, nor is it effective (as yet) in dealing with colloidal solutions." Björnståhl (3) examined gold and silver sols by allowing them to flow through a tube of gold-beaters' skin centered in the camera and obtained patterns which agreed with those for metallic gold and silver, respectively. The important investigations of Böhm and Niclassen (1) on the gels of various hydrous and hydrated oxides and hydroxides, has been supposed by some people to include investigations of sols in the sol state. Professor Böhm in a private communication states, "Die Aufnahem für die Arbeit in der Z. f. anorganische Chemie, 132, 1 (1924) wurden, wie Sie richtig vermuten, an den meist feuchten *Ruckstanden* von Solen nach dem Koagulieren oder Eindampfen (so beim Crum'schen Sol) gemacht." Böhm and Ganter (2) examined *liquid sols* by flowing aged ferric oxide and vanadium pentoxide sols through a Mark tube and observed some indication of orientation of the needle-like particles. Our first work (10, 12) on the direct examination of a sol was

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[1] Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

carried out on a thixotropic stannic oxide sol, which gave the pattern of stannic oxide. More recently Heller, Kratky, and Nowotny (4) examined various ferric oxide sols in thin glass capillary tubes. These investigators obtained the patterns of FeOCl, β-FeOOH (11), and γ-FeOOH, only; no indication of the formation of complexes was observed.

In this paper will be given the results of an x-ray study of a number of representative sols with the object of obtaining direct evidence concerning the constitution of the colloidal particles.

EXPERIMENTAL

The chief difficulties in the direct examination of sols are (a) the relatively low concentration of the dispersed phase, (b) the scattering of x-rays by the water in the samples, and (c) the possibility of coagulation of the sol by the x-rays. The first and second difficulties may be obviated by using fairly concentrated sols; and the third by flowing the sols through the camera. Some objections may be raised to flowing the sol through a tube of any kind. For this reason, in most cases the sol was allowed to flow in an uninclosed column, in the same way that Debye originally examined liquids.

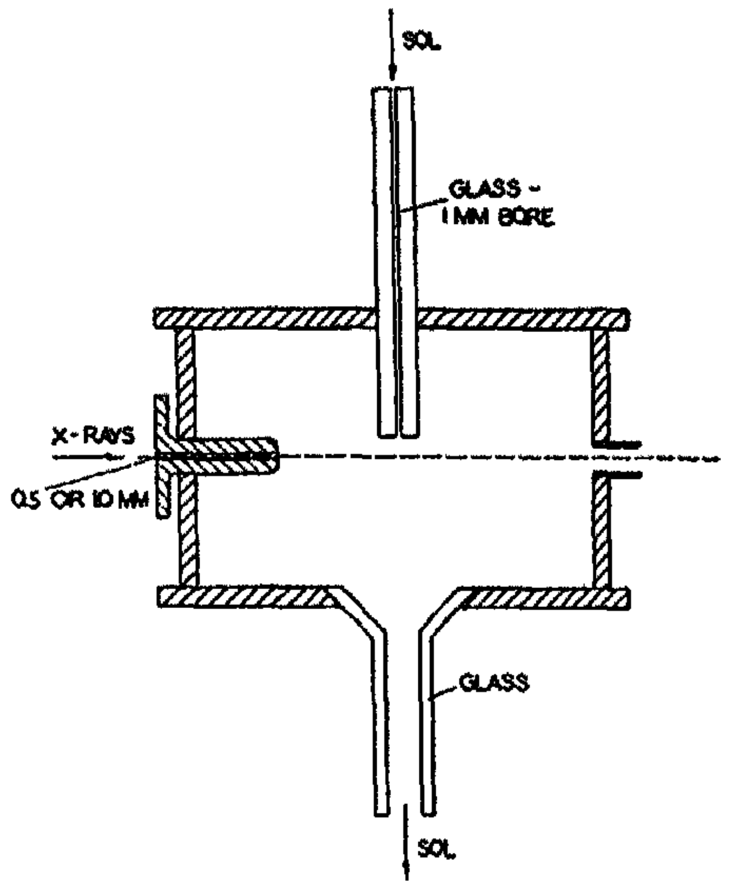

FIG. 1. X-ray diffraction camera for the direct examination of sols

THE CAMERA

A Debye-Scherrer type of camera was employed, a diagram of which is shown in figure 1. The sol (or liquid) was allowed to flow into the capillary tube. By maintaining a suitable head the rate of flow was adjusted so that a smooth, uninclosed column was obtained. In some cases a thin Mark tube was inserted in the capillary tube, giving a column of sol inclosed in glass. The scattering from the Mark tube is so small that it causes little or no difficulty. A possible objection to the use of the Mark tube is that solid particles might deposit on the walls and give the x-radiogram. However, there was no indication of this. A blank x-radiogram, obtained for a used but unwashed Mark tube as a sample, gave the same result as a new Mark tube. Furthermore, the same patterns were obtained using the inclosed and the uninclosed column of sol.

PREPARATION OF SOLS

Ferric oxide sol. A hydrous ferric oxide sol was prepared by the addition of a slight excess of ammonium hydroxide to a solution of ferric chloride. The resulting gel was washed rapidly by decantation until almost free from chloride, and a few drops of hydrochloric acid were added. Peptization and aging were brought about by warming for several hours at 60–65 C., while stirring vigorously with a mechanical stirrer. It has been shown (9) that the freshly precipitated hydrous ferric oxide gives no x-ray diffraction lines or bands, but that the material aged as described above gives the α-Fe_2O_3 pattern. This sol contained about 90 g. of ferric oxide per liter of sol.

Alumina sols. The two alumina sols examined were made by methods already described in detail (10). Sol I was prepared according to the method of Thomas (7) by peptization with hydrochloric acid. Sol II was prepared by the peptization of precipitated alumina with hydrochloric acid. The gels from these sols gave the γ-$Al_2O_3 \cdot H_2O$ pattern (10, 12). Alumina sol I, which contained 11.0 g. of alumina per liter originally, was concentrated by evaporation to 55.0 g. of alumina per liter. Alumina sol II was concentrated by evaporation to 41.2 g. of alumina per liter.

Stannic oxide sol. The method of preparation of this Zsigmondy stannic oxide sol has already been described (10, 12). The concentration of the sol was 33.4 g. of stannic oxide per liter.

Indium hydroxide sol. A hydrous indium hydroxide gel was prepared by the interaction of a slight excess of indium chloride solution and a solution of ammonium hydroxide. The gel was washed by centrifuging until peptization began, after which a few drops of hydrochloric acid were added. The sol contains 22.1 g. of indium oxide (In_2O_3) per liter.

Beta ferric oxide monohydrate sol. The gel formed by the interaction of solutions of ferric chloride and ammonium carbonate was repeptized with an excess of ferric chloride. The sol was purified by dialysis in the cold for three months, and was concentrated by boiling on a hot plate. It would be expected (9) that β-FeOOH would form under these conditions, since this material results from the slow hydrolysis of ferric chloride solution. But since the sol is dark red, and β-FeOOH is yellow, the dispersed particles must not be all β-FeOOH. The sol contains 89.6 g. of ferric oxide per liter.

Titanium dioxide sol. This sol was prepared by the slow hydrolysis of titanium tetrachloride solution. A slightly acid solution of the salt was hydrolyzed by heating to boiling; the resulting gel of hydrous titanium dioxide was centrifuged to remove excess acid, and repeptized by suspending in water to which a few drops of hydrochloric acid were added. The sol contained 30.8 g. of titanium dioxide per liter. From the method of preparation, one would expect (8) the particles to consist of the rutile modification of the dioxide.[2]

FIG. 2. X-ray diffraction pattern for a hydrous ferric oxide sol (α-Fe_2O_3)

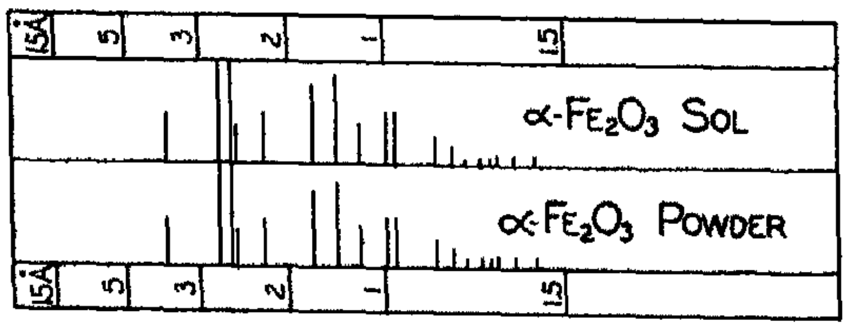

FIG. 3. X-ray diffraction patterns

Silver sol. The silver sol used was a commercial protected silver sol ("Argyrol") containing approximately 40 per cent silver.

Silver iodide sol. A silver iodide sol was prepared by mixing solutions of silver nitrate and hydriodic acid of such concentration that the resulting sol contained 80 millimoles silver iodide and 8 millimoles hydriodic acid per liter. The sol concentration was therefore 18.7 g. of silver iodide per liter.

X-RAY EXAMINATION

A hydrous ferric oxide sol was prepared and examined first in February 1934. The sol was not examined in the camera described in this paper, but

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[2] Investigations which will be reported later are in progress on the preparation of gels of the rutile modification of titanium dioxide.

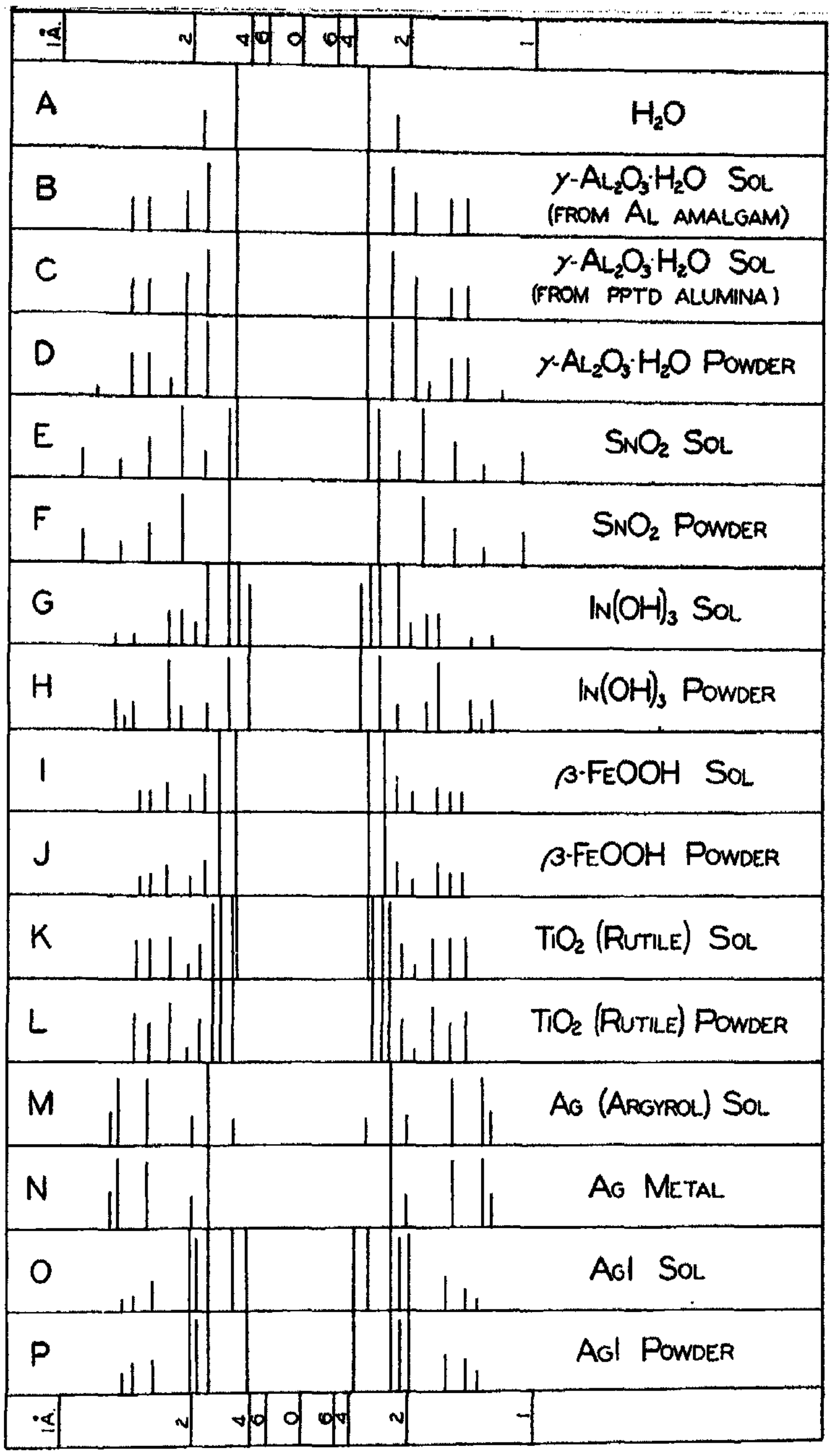

Fig. 4. X-ray diffraction patterns

was flowed through a "nonex" glass tube in the General Electric diffraction apparatus, using Mo K_α radiation. The pattern obtained after ninety-six hours exposure is reproduced in figure 2. The results compared with

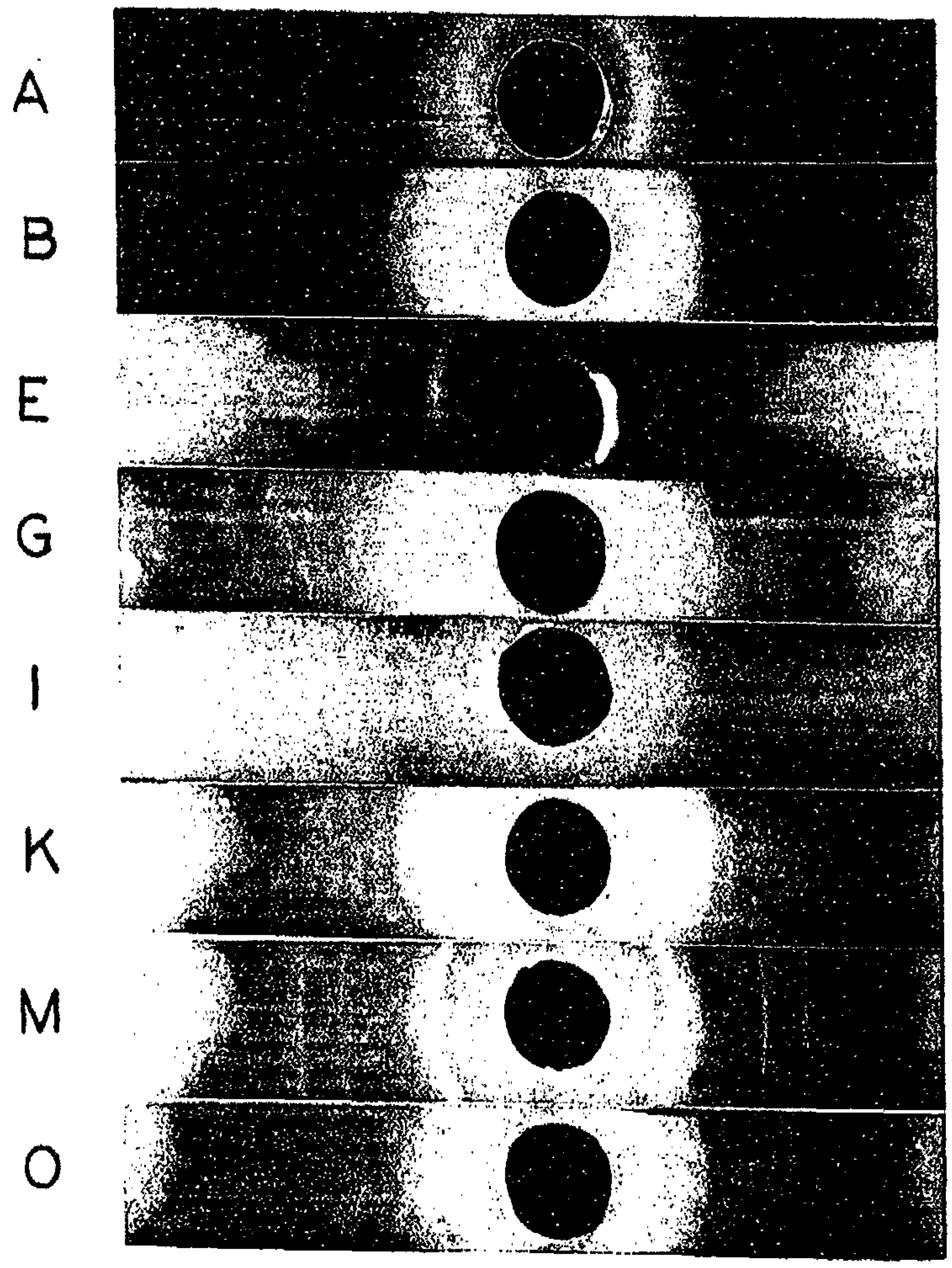

FIG. 5. X-ray diffraction patterns. A, H_2O; B, γ-$Al_2O_3 \cdot H_2O$; E, SnO_2; G, $In(OH)_3$; K, β-FeOOH; K, TiO_2(rutile); M, Ag; O, AgI.

α-Fe_2O_3 powder are shown diagrammatically in figure 3. The pattern obtained with the sol is identical with that from crystals of α-Fe_2O_3.

The other sols described above were examined in the special camera shown in figure 1, using a Philips cross-focus tube with Cu K_α radiation (nickel foil filter). The exposure time was 30 minutes in all cases reported. While working with the ferric oxide sols a filter of aluminum foil was placed between the sample and the film to prevent fogging of the film by fluorescent x-radiation from the iron. For purposes of comparison, the pattern of distilled water was also obtained. To identify the patterns from the sols, x-radiograms were made from the corresponding powders, using the same camera. This was done by placing the solid in a Mark tube attached to the capillary tube in the camera. The results obtained from pure water, the various sols, and the various solid materials are given in chart form in figure 4. Reproductions of some of the negatives are given in figures 5. Alumina sol I containing 11.0 g. of alumina per liter (not included in figures 4 and 5) gave the pattern of γ-$Al_2O_3 \cdot H_2O$.

DISCUSSION OF RESULTS

From inspection of figures 4 and 5 it is apparent that in every case the sol pattern is a composite of the patterns from pure water and the material making up the sol particles. Thus in the case of the weak indium hydroxide sol the water bands are relatively intense, whereas in the case of the strong silver sol the water bands are hardly visible.

Only a slight indication of fibering in the pattern of the α-Fe_2O_3 sol was observed. This sol was probably not aged as long as the one examined by Böhm and Ganter (6), who reported definite indications of orientation.

As pointed out under the method of preparation, the β-FeOOH sol is red in color, whereas pure β-FeOOH is definitely yellow. The results indicate that the sol consists of two portions: (a) yellow β-FeOOH particles which give the lines in the x-radiogram, and (b) dark red particles of α-Fe_2O_3 which are too fine to give a definite x-ray pattern (9). This conclusion is supported by an earlier observation (9) of the slow settling out of some β-FeOOH particles during the aging of dark red sols.

The results confirm the previous conclusions of the authors (10, 12) based on the examination of moist gels, namely, that typical hydrosols of oxides, elements, or inorganic salts consist essentially of aggregates of minute crystals of the respective hydrous oxides or simple hydrates, simple elements, or simple salts. There is no indication of the presence in the sols of complexes such as postulated by Pauli (6), Thomas (7), and others.

SUMMARY

The following is a brief summary of the results and conclusions reported in this paper:

1. For the first time, a number of representative hydrosols have been examined directly by x-ray diffraction methods, taking precautions so that the resulting x-radiograms are for the actual sol particles.

2. A Debye-Scherrer type of camera has been designed especially for the direct examination of a completely uninclosed, flowing column of sol.

3. Alumina sols prepared (a) by the action of amalgamated alumina on water, and (b) by the peptization of precipitated alumina gave the pattern of γ-$Al_2O_3 \cdot H_2O$.

4. Ferric oxide sols were found to consist of particles of α-Fe_2O_3 or β-FeOOH, depending on the method of preparation.

5. A stannic oxide sol (Zsigmondy), a protected silver sol ("Argyrol"), an indium hydroxide sol, a negative silver iodide sol, and a titanium dioxide sol gave respectively the patterns of SnO_2 (cassiterite), metallic silver, $In(OH)_3$, AgI, and TiO_2 (rutile).

6. It is concluded, in agreement with previous x-ray studies on moist gels, that the common inorganic hydrosols consist in general of particles of simple oxides or simple hydrates, elements, or salts, and not of complexes as postulated by some investigators.

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THE POLYMERIC CHARACTER OF BITUMINOUS COAL[1]

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The bituminous coals occupy an intermediate position in what has been called (15) the "coal band" (figure 1). Such organic substances as lignin and humic acids lie at one end of this band, and anthracite coal and graphite at the other. Whether lignin or cellulose is looked upon as the essential progenitor of bituminous coals, it appears that in the coalification process the simple linear polymeric structure, which is generally accepted for cellulose and which has been proposed (11) for lignin, is modified in the sense of the formation of a tridimensional polymer by linkages between the linear units. Whatever the mechanism, there is no doubt that the process is characterized by increasing enrichment in ring structures (6). The higher the rank of the coal, the more complete is the condensation to such structures, until graphite, the limiting member of the series, is reached. The establishment of a building unit in such a polymer obviously presents great difficulties, and we can perhaps never obtain as satisfactory a picture for the structure of such a substance as we have for cellulose and the polymeric esters, lactones, and anhydrides.

The essentially "chemical" character of polymerization has been emphasized in recent years (7), and in those cases where the energetics of the process have been investigated, the reactions have been shown to be exothermic; hence, one would expect elevated temperatures to displace the equilibrium toward depolymerization. Many such cases have long been known among the addition polymers such as styrene and rubber, and more recently the ready thermal reversibility of such purely condensation types as the polymeric lactones and anhydrides has also been pointed out (8).

A typical bituminous coal from the Pittsburgh seam contains carbon, hydrogen, and oxygen in approximately the same ratio as coumarone, C_8H_6O, which has a normal boiling point of 170°C.; the coal contains somewhat less oxygen and more hydrogen and such polar groups as hydroxyl and carboxyl are present, if at all, in very small amounts. Thus on the basis of composition alone, one would expect bituminous coal to distill completely at moderate temperatures. Its low volatility is ob-

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[1] Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

viously due to high molecular weight, but thermal decomposition would be expected to give some clue to the nature of the building units as it has in the case of other high molecular weight substances. That the ordinary distillation processes do not, appears to be due to the fact that in coal the primary unit itself has a very low vapor pressure. Hence in pyrolysis the rate of decomposition of this primary unit into secondary products, some of greater molecular weight (coke) and some of less (gaseous and liquid hydrocarbons and low-boiling phenolic bodies), is faster than its rate of evaporation. Certain methods of degradation, some purely thermal in character and others combining thermal and chemical effects, which yield significant information as to the nature of the building units in bituminous coal, have, however, been developed. These are (1) pyrolysis in the molecular still, (2) thermal decomposition in solvents at elevated temperatures, (3) hydrogenation, and (4) mild oxidation.

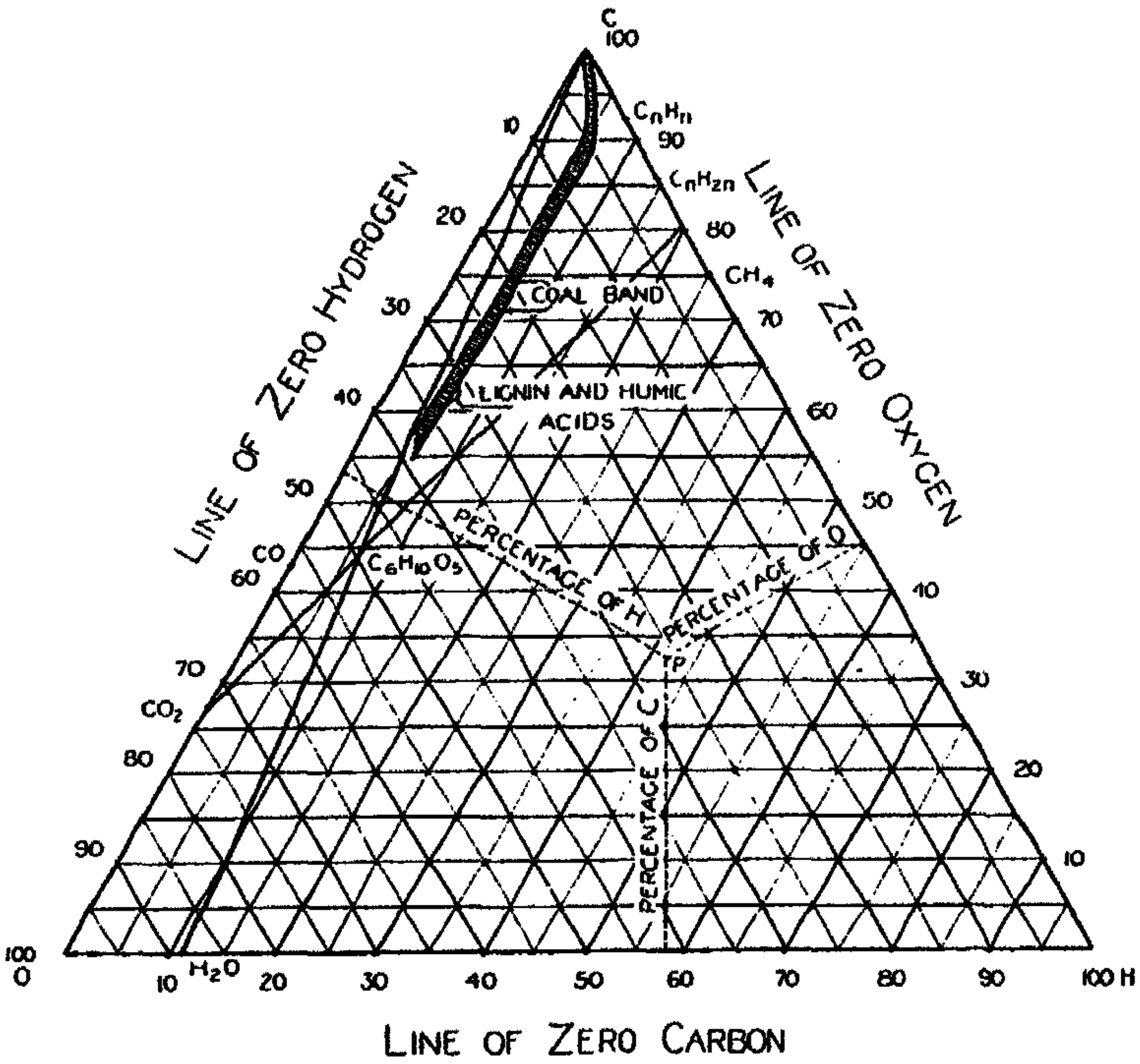

FIG. 1. The "coal band" and some typical carbon, hydrogen, and oxygen compounds

PYROLYSIS IN THE MOLECULAR STILL

When a bituminous coal is heated to 500–550°C. at pressures of 1 micron or less in a molecular still, where the distance between evaporating and condensing surfaces is very much less than the mean free path of the evaporating molecules, and where the possibility of collision with surfaces hotter than the evaporating surface is eliminated, secondary thermal decomposition is largely avoided (13). The condensate obtained under these conditions contains, along with the usual liquid hydrocarbons and phenolic substances, appreciable amounts of brown, amorphous solids, *neutral in character and readily soluble in such polar aromatic solvents* as phenol, but almost completely insoluble in petroleum ether or ethyl ether. These substances have been designated "bitumens" by coal investigators. They can not be redistilled, even in the molecular still, without some decomposition, yielding gaseous and liquid hydrocarbons, phenolic bodies, bitumens, and a coke residue. The point of view that these neutral, ether-insoluble substances, the bitumens, constitute an important primary thermal degradation product of bituminous coal, is supported by the experimental facts that in the thermal decomposition of a given coal a reduction in pressure, an increase in heating rate, and a decrease in particle size of the coal all tend to increase the yield of bitumens. The effects of reduction in pressure and the use of coal ground to particles less than 2 μ, designated μ-coal, are illustrated by the data of table 1. The increase in the amount of bitumen recovered in the condensate when the μ-coal was employed is very striking and shows that in a 20- to 40-mesh coal particle considerable secondary decomposition takes place before the evaporating substances can escape. Since phenolic bodies have been shown (14) to be secondary decomposition products of the bitumens, the decreased yield of the former with increased recovery of the latter is to be anticipated.

TABLE 1

Composition of condensates from atmospheric and vacuum distillations

Temperature, 525°C.

	ATMOSPHERIC	VACUUM	
	20-40 Mesh coal	20-40 Mesh coal	μ-Coal*
	per cent	*per cent*	*per cent*
Neutral			
Ether-insoluble (bitumens)	2.78	7.11	17.10
Ether-soluble	7.51	8.61	8.20
Phenolic and acidic	2.45	2.56	1.37
Basic	0.40	0.20	0.16
Water and loss	3.98	2.32	1.50
Total	17.12	20.80	28.33

* Prepared by grinding in a Szegvari pebble mill; particle size less than 2μ.

THERMAL DECOMPOSITION IN SOLVENTS

That resinous or bituminous substances could be extracted by solvents from bituminous coals at a temperature much below that at which they could be recovered by distillation has been known for many years. The early experimenters, working at low temperatures and recovering a few per cent of material, regarded the process as a simple solvent extraction, and considered the materials extracted to have been present as bodies which were of significantly different chemical constitution from, and hence much more soluble than, the bulk of the coal substance. With the development of pressure extractors and the use of new solvents (17) and of temperatures ranging from 250° to 350°C., the yield of "extract" rose as high as 80 per cent, thus showing that products at present not distinguishable from the resins and bitumens of the early investigators could be formed by thermal decomposition of the bulk of the coal substance. The point of view that solvent extraction at elevated temperatures should be looked upon as a mild thermal decomposition has been emphasized by Lowry (15); Peters and Cremer (16) point out that the small variation in chemical composition between extract and residue can not account for their marked physical differences, and hence one must assume that polymerization is involved. A recent study (3) of extract and residue from a bituminous coal from the Pittsburgh seam has shown that insofar as present knowledge permits these substances to be characterized, there is little difference between extract and residue other than in molecular weight, and that the extract can properly be considered a primary building unit in the coal polymer, depolymerization having been effected by the elevated temperature and the action of the solvent.

To what extent the degradation of coal by solvents at elevated temperatures involves the formation of colloidal dispersions rather than molecular solutions is not certain. Dark-field examination of these solutions at room temperature reveals colloid particles. The extracts, however, contain very little inorganic residue and it seems probable, if the phenomenon were chiefly peptization, that the peptized material would be of ash content similar to the coal. It appears more likely that the substances extracted are molecularly dispersed at the temperatures of the extraction process and associate or polymerize to the colloid units on cooling. Also, as will be seen later, all these products formed by solvent action at elevated temperatures give freezing-point depressions in phenolic solvents which correspond to molecular units of moderate size.

The yields of soluble products recovered by thermal decomposition of a bituminous coal from the Pittsburgh seam in benzene (1), phenol, and tetralin (2) at temperatures of 250–350°C. are shown in table 2. The much greater effectiveness of this type of degradation as compared with vacuum distillation is strikingly illustrated, as is also the specific action of such a polar solvent as phenol, with which, at corresponding temperatures, a fivefold yield of soluble products over that with the non-polar benzene is obtained. Unfortunately attack by this method at still higher temperatures is limited by the thermal instability of the solvents themselves.

MILD HYDROGENATION

The effectiveness of mild hydrogenation in the primary breakdown of bituminous coal was demonstrated by F. Fischer, Peters, and Cremer (9), who found that by prolonged reaction at temperatures as low as 260°C., a German bituminous coal, ground to a particle size of less than 2 μ, yielded 85 per cent of material soluble in hot benzene. It is significant that these investigators designated the products recovered by this mild hydrogenation as "pseudo-bitumens."

TABLE 2

Decomposition in solvents at elevated temperatures

SOLVENT	TEMPERATURE	TIME	COMPOSITION OF EXTRACTS				
			Neutral		Phenolic and acidic	Basic	Total
			Ether-insoluble	Ether-soluble			
	°C.	*hours*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Benzene	260	44	10.26	4.93	0.16	0.10	15.45
Tetralin	250	136	20.0	12.90	0.71	0.17	33.8
	300	126	12.3	4.34	0.32	0.15	17.0
	350	108	20.2	9.65	0.74	0.18	30.8
			52.5	26.89	1.77	0.50	81.6
Phenol	250	44	57.6	7.0	0.80	0.13	66.7

Work with a coal from the Pittsburgh seam has led to similar results, but a higher temperature, 350–400°C., has been found necessary. Under these conditions approximately 80 per cent of the American coal can be recovered in the form of high-boiling oils and bitumens.

MILD OXIDATION

When a bituminous coal is refluxed with dilute nitric acid, e.g., 1 *N*, it is rapidly converted to organic acids, some of which are of low enough molecular weight to be soluble in water or dilute acid, and others, the so-called regenerated humic acids, which are soluble in or peptized by alkali, but precipitate on acidification. The humic acids formed in this way usually represent not less than 60 per cent of the carbon of the original coal, although this is a function of the period of oxidation, since these acids are the primary oxidation product and the water-soluble acids of lower molecular weight are secondary products (21). The rate of formation of both types of acids is a function of the rank of the bituminous coal, lower rank coals reacting with greater velocity.

The humic acids obtained by oxidation of bituminous coal dry to brownish-black or jet-black scales. They do not melt and on pyrolysis yield only low molecular weight volatile products, carbon dioxide, and water, and a carbonaceous residue. They form brown solutions with dilute alkalies, in which dark-field examination discloses many colloid particles. Their aqueous alkaline solutions diffuse only partially through parchment.

The alkali humates formed from coal show certain analogies to soaps: both form colloidal aggregates in aqueous solution; both are molecularly dispersed in solvents of the type ROH, where R is aliphatic in the case of soaps and aromatic in the case of the humates; both are dispersing agents in aqueous solution; and both furnish aqueous solutions of high viscosity, although this is much less marked in the case of the humates because of plate-shaped rather than thread-like particles.

TABLE 3

Ultimate composition of bitumens and original coal

SOURCE	CARBON	HYDROGEN	OXYGEN	NITROGEN	SULFUR	ASH
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Molecular still, 525°C	81.15	5.69	11.56	1.16	0.44	0.0
Pressure extraction:						
Benzene, 250°C	84.70	6.32	5.71	1.59	0.68	1.08
Tetralin, 300°C	82.21	5.06	10.00	1.16	0.43	1.14
Phenol, 250°C	81.15	4.88	9.32	1.52	0.89	2.24
Hydrogenation*	85.25	7.27	4.88	1.88	0.42	0.30
Original coal	78.27	5.19	5.53	1.63	0.98	8.39
Ash-free	85.50	5.66	6.03	1.78	1.03	

* Hydrogenation of the residue from a benzene extraction at 250°C.

COMPOSITION OF THE BITUMENS AND THE HUMIC ACIDS

Ultimate compositions of bitumens obtained by different methods of degradation are shown in table 3. All contain, along with carbon and hydrogen, significant amounts of oxygen and small quantities of nitrogen and sulfur. Group tests indicate the absence of carboxyl, ester, carbonyl, or alkoxyl groups. Determinations of hydroxyl oxygen have given variable results depending upon the sample of bitumen employed and the method of methylation. Usually not more than half of the oxygen can, however, be accounted for as hydroxyl groups, and the balance must be assumed to be in ether linkages or heterocycles. Hydrogenation at 425°C. of bitumens obtained by benzene pressure extraction, followed by dehydrogenation to aromatics and isolation of the crystalline picrates of the aromatics has resulted in evidence for the presence of condensed cyclic structures as large as four or five rings (4). Drastic oxidation of coal bitumens is reported (5) to result in high yields of benzene polycarboxylic acids. There thus appears little doubt that the nucleus of these bitumens consists of condensed C_6 ring structures with occasional heterocyclic rings containing oxygen, nitrogen, or sulfur.

The ultimate compositions and equivalent weights of humic acids prepared by mild oxidation of: (1) the whole coal, (2) bitumens extracted by heating with benzene at 250°C., and (3) the insoluble residue from the benzene extraction are shown in table 4. Carboxyl and hydroxyl groups can be determined by methylation; the latter are present in smaller amounts than reported for "humic acids" from other sources. There is also evidence for the presence of isonitroso groups, but not more than one-half to two-thirds of the total oxygen can be accounted for in all functional groups together, indicating the presence of ether or heterocyclic oxygen. Little information is available as to the nature of the nucleus of these humic acids. Hydrogenation of the alkali humates by heating with sodium formate (10) at 360°C. results in simultaneous decarboxylation and conversion of the nucleus to high-boiling oils and bitumens. The latter are not distinguishable from bitumens obtained by degradation of the original coal.

TABLE 4

Ultimate composition and equivalent weights of humic acids

SOURCE	CARBON	HYDROGEN	OXYGEN	NITROGEN	SULFUR	ASH	EQUIVALENT WEIGHT
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
Original coal	61.46	3.21	30.4	3.36	0.65	1.1	240
Bitumen*	57.17	3.71	34.7	3.09	0.34	0.9	192
Residue†	60.17	3.89	31.4	3.04	0.55	1.0	244

* By oxidation of soluble material from benzene pressure treatment at 250°C.

† By oxidation of insoluble residue from benzene pressure treatment at 250°C.

MOLECULAR WEIGHT MEASUREMENTS

These preparations of primary degradation products of coal are, of course, not homogeneous. Determinations of average values of molecular weight have, however, led to interesting results. As has been pointed out, the bitumens are readily soluble in polar aromatic solvents such as phenol and catechol, and much less soluble in aromatic non-polar types such as benzene and diphenyl. Only two solvents suitable for cryoscopic measurements on the regenerated humic acids have been found, namely, catechol (20) and *p*-nitrophenol.

The results of cryoscopic molecular-weight determinations on bitumens and regenerated humic acids, prepared in a number of ways from a coal from the Pittsburgh seam, are shown in table 5.

The significant feature of these data is the low and relatively constant values obtained in the solvents, catechol and *p*-nitrophenol. Considering the different methods of degradation employed, the relative constancy of these values argues strongly for the presence in this bituminous coal of some fundamental unit of the order of magnitude indicated. Wherever solubility permitted, measurements were made in several solvents. In such cases a rough correlation was observed between dipole moment of the solvent and apparent molecular weight, solvents of higher moment giving lower molecular weights. The differences noted between different solvents are much greater than has been found for known cases of molecular association. Two explanations appear possible to the writer: (1) association to colloid particles in the non-polar solvents or (2) actual degradation of a polymer by the polar solvents.

TABLE 5

Molecular weights of bitumens and humic acids

SOLUTE	SOLVENT					
	Catechol	*p*-Nitrophenol	*p*-Bromophenol	Tribromophenol	Pyrene	Diphenyl
Bitumen from:						
Molecular still	250	220	320	360	(a)	(a)
Benzene extract	285		550	650		>1000
Tetralin extract	335		540			
Phenol extract	360		440			
Hydrogenation of residue(b)	320	320	550		960	>1000
Hydrogenation of humic acids(c)	260			510		>1000
Humic acid from:						
Original coal	235	230				
Bitumen(d)	215					
Residue(e)	240	280				

(a) Incompletely soluble. (b) Insoluble residue from benzene pressure extraction, hydrogenated at 350–400°. (c) Humic acids from original coal, hydrogenated at 350–400°. (d) Bitumen from benzene pressure extract. (e) Residue from benzene pressure extract.

Such physical properties as vapor pressure and solubility indicate that both bitumens and regenerated humic acids are bodies of high molecular weight. It is known, however, that polar groups in certain positions reduce volatility to a surprising degree. *p*-Hydroxybenzoic acid, for example, of molecular weight 138, is stated (19) to have a vapor pressure of 0.3 micron at 100°C., a value a thousandfold less than that for the *o*-hydroxy acid, salicylic acid. Further, while an average molecular weight of 300 appears low, an aromatic hydrocarbon of seven closely condensed rings has a molecular weight of only 302, and it should be noted that the molecular weight of the largest condensed aromatic structures which have been actually isolated from coal or pitch is smaller than this. It is also of interest that Fuchs (12), in picturing a hypothetical humic acid molecule, suggests a structure containing five condensed rings as the building unit, while Schrauth's (18) building element contains four six-membered and three five-membered condensed rings.

The presentation of the picture of bituminous coal as a polymer, built up of units of moderate molecular weight, naturally arouses the question as to how these units are in turn held together to form the high molecular weight body we know as coal. Unfortunately, very little can be said on this point at the present time. Considering the probable method of genesis of coal, many of the known types of polymeric structure could conceivably be present. Its relatively great resistance to hydrolytic agents appears, however, to render improbable some of these, such as ester, anhydride, acetal, or lactone. An ether-linked structure, such as has been suggested for lignin, a Bakelite type, or an addition polymer formed from unsaturated units seems more likely.

The determination of the exact character of the building units in bituminous coal and the nature of the forces which hold these units together present problems which as yet have been scarcely touched and offer a fertile field for chemical and physical investigation.

SUMMARY

Evidence is presented for the point of view that bituminous coal is a polymer. Cryoscopic measurements in catechol on the degradation products of a typical coal from the Pittsburgh seam indicate that the unit is of moderate molecular weight, 250 to 350. Significant yields of this fundamental building unit are obtained by thermal decomposition in the molecular still, by the action of solvents such as benzene, tetralin, or phenol at elevated temperatures, by hydrogenation, and by mild oxidation. The chief difference between the primary degradation products obtained by mild oxidation, the regenerated humic acids, and those recovered by thermal decomposition or hydrogenation, the bitumens, appears to lie in the presence in the humic acids of carboxyl groups, which confer alkali solubility and hydrophilic properties. The probable chemical nature of these primary degradation products and the possible methods by which the units combine are discussed.

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MOLECULAR PROPERTIES OF LIGNIN SOLUTIONS[1]

FROM VISCOSITY, OSMOTIC PRESSURE, BOILING-POINT RAISING, DIFFUSION, AND SPREADING MEASUREMENTS

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Recent chemical researches (2, 12) indicate that lignin, as isolated from previously extracted wood by several different methods, is a reproducible material with rather definite properties. It has ten polar groups, methoxyl and hydroxyl, for each empirical molecular weight unit of approximately 900, the proportion of each varying somewhat with the source of the lignin and the means of its isolation (12). The presence of unsaturated groups has also been demonstrated. An uncertainty still exists as to whether the basic part of the molecule is made up of aromatic or furan units.

The work reported here was undertaken with the hope that physical data on lignin solutions would aid in the further characterization of lignin. Previous measurements of the molecular weight of lignin are meager and have been made chiefly on lignin derivatives which, because of the nature of the preparations and the drastic solvents used, must have been degraded. These values range from 200 to 2000 (1, 6, 7, 9, 11, 17, 26, 27, 28, 29, 36). The most reliable value seems to be that of Samec (30) who, using a static osmotic pressure method, reported a value of 4000 for the molecular weight of Willstätter lignin dissolved in ammonium hydroxide. Spreading measurements have also been made to determine the thickness of lignin films on a water surface. Wedekind and Katz (37) obtained 10 A. U. for phenol lignin and Freudenberg (5) reports 20 A. U. for the sodium salt of the diazobenzenesulfonic acid derivative of cuprammonium lignin.

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[1] Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11–13, 1936.

Abstracted from a thesis submitted by D. L. Loughborough to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] Maintained at Madison, Wisconsin, in coöperation with the University of Wisconsin.

PREPARATION OF MATERIAL

The lignin used in this investigation[3] was prepared from maple and spruce wood. The sawdust was extracted with alcohol-benzene mixture for two or three days to remove resins and fatty substances. This was followed in consecutive order by a thorough extraction in hot water, cold water, and ether. The lignin was isolated from the extracted sawdust in three different ways: (a) by the modified sulfuric acid method of the Forest Products Laboratory (31); (b) by extracting the lignin directly with methyl alcohol acidified with hydrochloric acid (6); and (c) by extracting in a sodium hydroxide–ethyl alcohol mixture (25). The soluble portions of the isolated lignin preparations were purified by alternate solution in alcohol and precipitation in water three or four times. In some cases the product was also precipitated in ether. The measurements reported here were made on the product after different numbers of precipitations, and in some cases the final product was electrodialyzed for forty-eight hours at 230 volts. The material was dried in a vacuum oven at 50°C. for more than forty-eight hours and stored over phosphorus pentoxide until needed. The solvents were of reagent quality, dried by standard drying methods.

The completely nitrated and methylated lignins were prepared from methyl alcohol–hydrochloric acid lignin. The nitrated lignin was prepared according to the method of Gilman (10) for nitrating furfural; the methylated lignin was prepared by the ordinary methylation process with dimethyl sulfate.

SOLUBILITY OF LIGNIN

The solubility of lignin in organic solvents depends to a large extent on the method used for isolating the lignin. When isolated by the sulfuric acid method, only about 12 per cent of maple lignin and less than 2 per cent of spruce lignin is soluble in methyl alcohol. Since the sulfuric acid method removes the lignin quantitatively, these fractions represent the fraction of the total lignin that may be brought into solution by this method. Both the alkali and methyl alcohol–hydrochloric acid methods yield from one-third to one-half of the total lignin content of the wood. Virtually all the yield is soluble in methyl alcohol after precipitation and washing free of alkali and acid. No chemical difference, however, has been found between the soluble and insoluble fractions of the isolated lignins. Thus the solubility differences are probably due to polymerization.

Since all the physical measurements considered in this study were made

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[3] Acknowledgment is made to E. E. Harris of the Forest Products Laboratory for the preparation of a number of the lignin samples and lignin derivatives used in this investigation. To him also are due thanks for many suggestions and advice on the chemical aspects of this problem.

on solutions of lignin, no definite conclusion can be drawn regarding the total isolated lignin, or the lignin as it occurs in the tree.

Lignin is somewhat soluble in many solvents, among which are the aliphatic alcohols and acids, methyl and ethyl acetate, acetone, and chloroform. Lignin that is air-dried after precipitation in water is insoluble in water, ether, benzene, or carbon tetrachloride. Although the solubility is not very great in most of these solvents, the amount that can be put into solution can be greatly increased by evaporation of the solutions. It is almost impossible to dissolve all the dry material added to the solvent, since some of the lignin almost invariably forms a tarry insoluble mass.

The solubility in chloroform is greatly increased by removing every trace of water. In the alcohols, on the other hand, the solubility is increased considerably by the addition of small amounts of water. For example, the direct solubility of alkali lignin in methyl alcohol was found to increase to a water content of approximately 18 per cent by volume and then to decrease with a further increase in water content.

All the solutions of dry lignin were clear. They showed no Tyndall cone unless treated in a way that causes precipitation, as when appreciable amounts of water are added. Solutions have been kept as long as two years without showing any cloudiness. Lignin dissolved in the foregoing solvents can thus be considered as forming true solutions.

VISCOSITY

A Bingham viscometer, flow time 1,164 sec. for water under 6 cm. of mercury, was rigidly mounted in a thermostated water bath held at 25° ± 0.02°C. The applied pressure was controlled from an auxiliary tank of 70 liters capacity. This tank could be filled to the desired pressure, closed from the air line, and held at this pressure for long periods of time. The pressure was read with a cathetometer to a tenth of a millimeter of mercury. Several measurements of the efflux time for flow in both directions were made at each pressure.

Poiseuille's law, in which the reciprocal of the efflux time is proportional to the pressure, was obeyed over the complete pressure range used. Over the concentration range used (0.2 to 8.0 per cent) there was no great deviation from the modified Einstein law

$$\frac{100\,\eta_{sp}}{CV} = 2.5\,\theta \tag{1}$$

where η_{sp} is the specific viscosity (increase in relative viscosity of the solution over that of the solvent), C is the concentration in grams per 100 cc. of solution, V is the specific volume of the solute, and θ is a constant, which is unity for the ordinary Einstein equation. The expression $\frac{100\ \eta_{sp}}{CV}$ has been designated by Kraemer (15) as the specific hydrodynamic volume. V was determined pycnometrically at 25°C. for sulfuric acid lignin and methyl alcohol–hydrochloric acid lignin dissolved in methyl alcohol and acetic acid. The values were in fairly good agreement, and average 0.75. The change in the specific viscosity per unit concentration with concentration for methyl alcohol-hydrochloric acid lignin in different solvents is given in figure 1. The curves are practically horizontal over an appreciable concentration range, with the expected upward curvature at higher concentrations in the case where higher concentrations were obtainable. It is uncertain if the curvatures in either direction at extremely low concentrations have any significance, though the deviations seem to be greater than the experimental error. The linear portions of the curves have been extrapolated to zero concentration in order to calculate the limiting values of θ, without regard to the curvature at low concentrations, as has been done by other investigators (16, 34). These values, as shown in table 1, are practically constant for all the solvents. Values of θ for sulfuric acid and alkali lignins are also given. These measurements were not made over a sufficient concentration range to make extrapolation advisable, so that they represent the directly calculated values. They are not in so good agreement as the values for methyl alcohol-hydrochloric acid lignin, but they do represent the order of magnitude of θ.

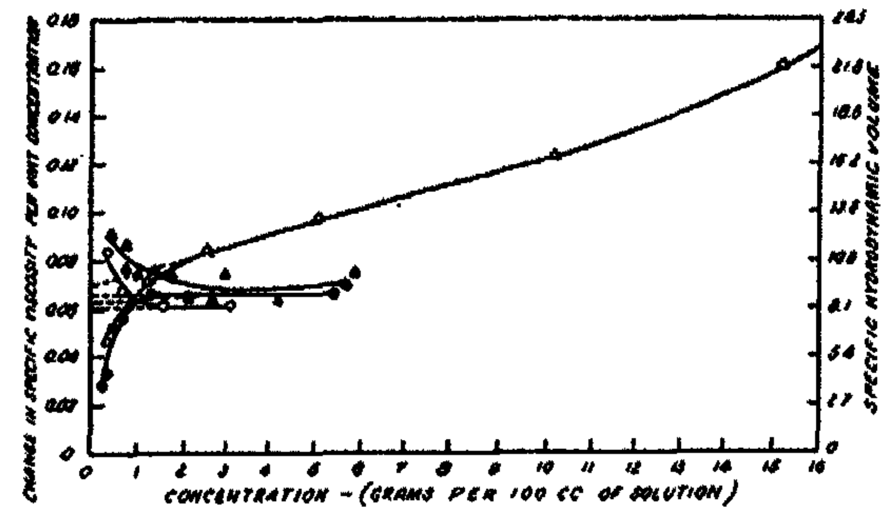

FIG. 1. Change in the specific viscosity per unit concentration with concentration for methyl alcohol–hydrochloric acid lignin. △, chloroform; ▲, acetone; ●, methyl alcohol; ○, ethyl alcohol.

Three explanations are possible for the deviation of the data from the simple Einstein equation in which θ is unity. The first is that the departure may be due to solvation of the solute particle. The method of measuring the specific volume used does not give a true measure of the volume of the solvated particle. The constancy of θ, however, for quite different solvents makes this factor, in all probability, of minor importance. The second explanation is that the equation is derived on the basis of no interaction between particles, a condition which would occur only at infinite dilution. Unfortunately, the extrapolation to zero concentration can not be definitely made until more accurate measurements at extremely low concentrations are available. The third explanation is that if the particles were not spherical, they would not be expected to obey the original Einstein equation derived on that basis. The equation has been extended to include differently shaped particles by Eisenschitz (4), Jeffery (13), and Kuhn (17, 18). The Eisenschitz equation for appreciably elongated elliptical particles when substituted in the modified Einstein equation gives the shape factor l/a of the elliptical particles in terms of the multiple of the Einstein constant θ, thus

TABLE 1

Multiples of Einstein constant obtained for various lignin preparations from viscosity data at 25°C.

SOLVENT	VALUES OF $\frac{1}{2.5} \cdot \frac{100\eta_{sp}}{CV}$		
	Methyl alcohol-hydrochloric acid lignin*	Sulfuric acid lignin†	Alkali lignin†
Methyl alcohol	3.36	3.00	4.90
Ethyl alcohol		4.12	
Ethyl alcohol (few per cent water)	3.26		
n-Butyl alcohol		4.50	
n-Propyl alcohol		4.20	
Acetone	3.30	2.08	
Methyl acetate		2.60	
Chloroform	3.46		

* By extrapolation to zero concentration.

† From single measurements below 1 per cent concentration, by assuming η_{sp}/C as constant.

$$0.159 \frac{l}{a} \frac{1}{\log 2 \frac{l}{a}} = 2.5\,\theta \qquad (2)$$

This gives a shape factor for lignin of approximately 7.5. Although this shape factor is in a range for which there is no apparent reason for the validity of the equation, Theis and Bull (34) have found the relationship to be obeyed by stearic acid which, from x-ray and spreading measurements, has been shown to have a shape factor of this order.

If the specific viscosity is a function of the shape of the molecule, it should vary with the temperature. At the higher temperatures the frequency of rotation about even the longest axes will be large in terms of the collision frequency, and a molecule will offer nearly spherical collision volume. The values of the specific viscosity should tend more and more toward that predicted by the Einstein equation. The plot of θ as a function of temperature over a small range is shown in figure 2. The extension of this curve could readily give a value of unity for θ at high temperatures.

Direct application of the Staudinger method (33) of determining the molecular weight from viscosity to these data is impossible, since no information is available on the lower molecular-weight homologues of lignin, if there are any. An idea of the magnitude of the molecular weight

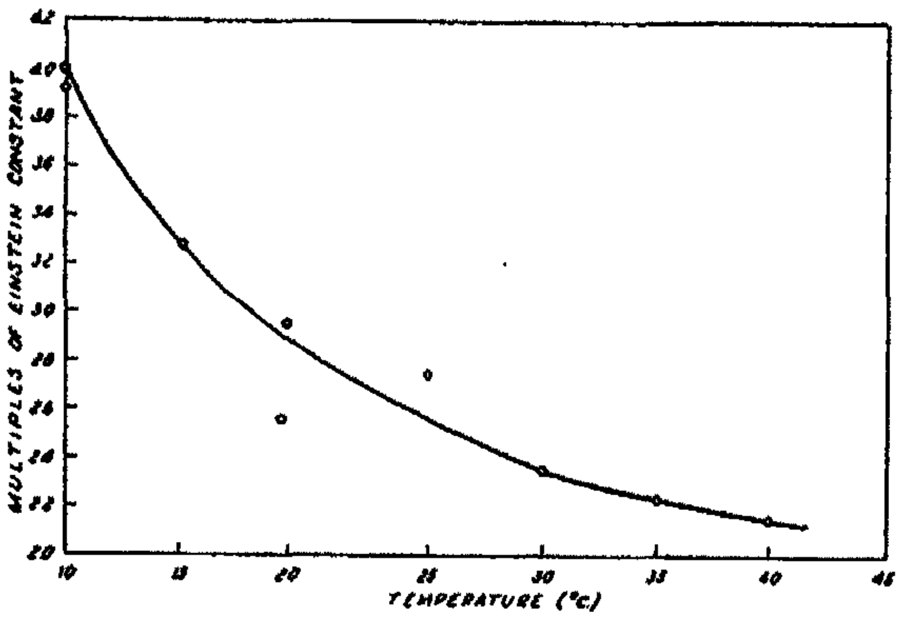

FIG. 2. Variation of the specific hydrodynamic volume of a sulfuric acid lignin in methyl alcohol with temperature.

m may be obtained by choosing a representative value for the constant in the equation

$$\frac{\eta_{sp}}{C} = Km \tag{3}$$

in which C is the concentration in terms of the weight of the repeating basic group and K is a constant. Taking the basic chemical molecular weight of lignin (900) as the repeating group and a value of K equal to that for rubber, 3×10^{-4} (33), the molecular weight obtained is 18,000. If the value of K of 10×10^{-4} for cellulose (33) is used, the molecular weight is 6000. These values can be thought of merely as an interesting speculation.

The viscosity data on lignin show conclusively that lignin is not a linear polymer such as cellulose, which has a value of θ of 280 to 400 (21). The lignin molecule, however, deviates definitely from spherical, a probable shape factor being about 7.5. The approximate constancy of θ for different solvents indicates that lignin is probably not differently associated in the different solvents. Differences in solvation in the different solvents also appear to be small.

OSMOTIC PRESSURE

The measurement of molecular weight by osmotic pressure provides a method that is less affected by impurities than any of the other thermodynamic methods, such as freezing-point lowering or boiling-point raising. The method used was a modification of the dynamic method of Sørensen (3, 32, 35), altered to give a better support to the membrane and to make possible the use of less material.

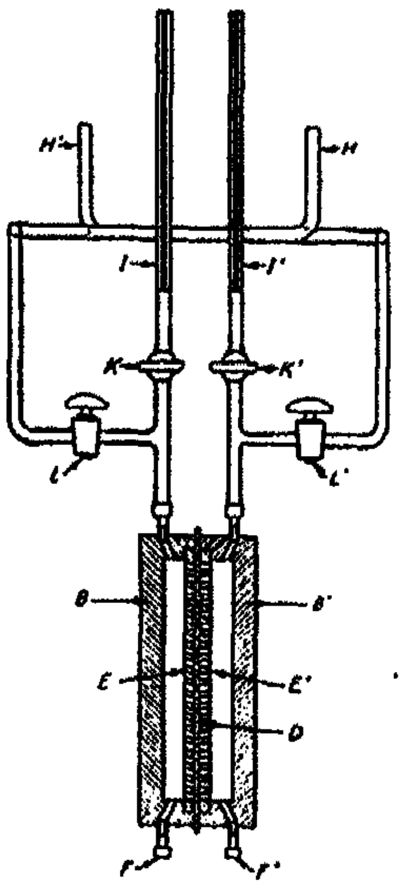

FIG. 3. The osmometer

The osmometer (figure 3, side view) consists of two brass cells, B and B′, 4 in. in diameter and 1 in. thick, with a hole 3 in. in diameter turned to a depth of ½ in. in each. The cavities between the cells are separated from each other by two perforated brass disks, E and E′, which rest on the circular flanges. The membrane D is held securely between these two disks. The rest of the apparatus serves in filling, applying the pressure, and measuring the flow. The osmometer is filled through F and F′ (the primed letters indicate solution and the unprimed letters the solvent) by suction applied at H and H′, the level of both solution and solvent being raised, free from bubbles, to the horizontal part of H. F and F′ are securely closed with brass screw caps. All stopcocks are closed and the system allowed to stand for eight or ten hours. This procedure allows any material of very small molecular weight to come to equilibrium before the measurements are made. The whole apparatus, with the stopcocks open, is then placed in a constant-temperature bath held at 25° ± 0.05°C. When thermal equilibrium has been established, stopcocks K′ and L are closed, the pressure applied at H′, and the flow measured in the capillary tube I by means of a cathetometer. If the applied pressure is greater than the osmotic pressure, the liquid will be forced across the membrane and up the capillary tube I. The rate of flow is proportional to the pressure in excess of the osmotic pressure, so that when the flow is zero, the applied pressure equals the osmotic pressure. Readings of the height of the meniscus in I were measured every half-minute for 20 minutes, and these values were plotted against the time to determine the rate of flow. The rates of flow obtained under different applied pressures were plotted against the pressure and the curves extrapolated to zero flow, the intercept being the osmotic pressure.

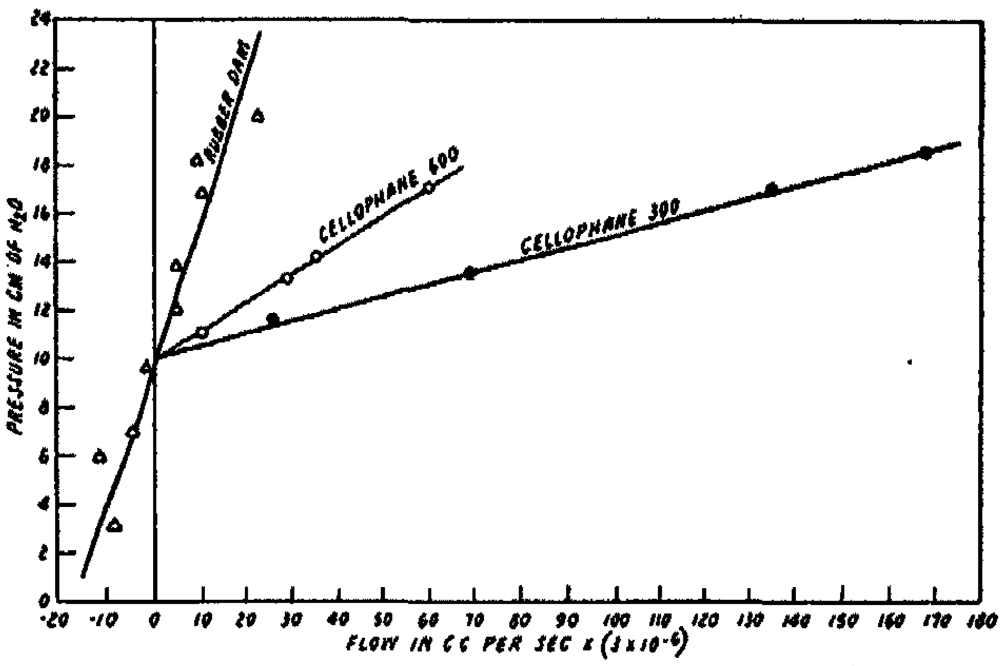

FIG. 4. Dynamic means of determining the osmotic pressure from the rate of flow under different hydrostatic pressures for methyl alcohol-hydrochloric acid lignin (0.00142 g. per cubic centimeter) in methyl alcohol.

Rubber dam and cellophane membranes were used. The cellophane membranes were of 600 and 300 gage. The cellophane was swollen in water, and the water replaced by the solvent. The fact that the osmotic pressure is independent of the membrane may be noted in figure 4, in which a typical plot of flow against pressure for a solution of methyl alcohol-hydrochloric acid lignin in methyl alcohol is given for all three membranes.

The molecular weights, as tabulated in table 2, were calculated from the osmotic pressure on the basis of the van't Hoff law. The average molecular weight is, within experimental error, unchanged by the solvent, the method by which the lignin was isolated, the number of reprecipitations after the second in the purification, the fractionation, the temperature at which the measurement was made, the presence of small amounts of water or small amounts of salt, or the concentration.

The fact that elevation of the temperature does not affect the molecular weight indicates that the lignin molecule is not a loose aggregate of smaller molecules subject to thermal dissociation. No dissociation or polymerization occurs when small amounts of water are added. When sufficient salt is added to overcome any Donnan effect that might be present, the molecular weight is unchanged, indicating that there can not be any appreciable Donnan effect in the case of the electrolyte-free systems. Acetone and ethyl alcohol solutions of methyl alcohol–hydrochloric acid lignin were poured through a filter containing a small amount of activated charcoal. When this process was carried out rapidly, it was possible to halve the concentration. Molecular weights calculated from the osmotic pressure exerted by these solutions were definitely of the same order of magnitude as those calculated from the total fraction. Both the difficulty of performing the fractionation and the similar molecular weights measured indicate strongly that lignin forms monodisperse solutions. This is not in agreement with the results of Fuchs (8) for phenol lignins.

The most probable molecular weight from the measurements on maple lignin prepared by the three methods previously mentioned is 3900 ± 300. This is very close to the value reported by Samec (30), and also approximately four times the empirical molecular weight (4 × 900). Completely methylated and nitrated lignins show increases in molecular weight that can be accounted for on the chemical basis. The fact that the different lignin preparations, which represent different portions of the total lignin, give similar molecular weights is a strong indication that the lignin is not a mixture of molecular species with appreciable variation in molecular weight, for it is highly improbable that each of the preparations should contain the same molecular distribution.

BOILING-POINT RAISING

A few measurements of the boiling-point raising of lignin in chloroform and acetone were made. In this work two sets of the modified[4] Cottrell boiling-point raising apparatus were used so as to require only 10 cc. of solution. They were heated on an electric hot plate by inserting the end of each into a form-fitting brass thimble so that only the part beneath the inverted funnel was heated. The tubes were inserted through holes in an

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[4] This was done by H. D. Tyner of the Forest Products Laboratory.

TABLE 2

Molecular weight of various lignin preparations from osmotic pressure measurements at 25°C.

TYPE OF LIGNIN	SOLVENT	CONCENTRATION	MEMBRANE	REMARKS	MOLECULAR WEIGHT
		grams per cc.			
Maple lignin (methyl alcohol-hydrochloric acid)	Methyl alcohol	0.001-0.01	Cellophane 600	In various states of purification	3800* ± 300
	Methyl alcohol	0.01824	Cellophane 600	Electrodialyzed	4050
	Methyl alcohol	0.00125	Cellophane 600	At 39.6°C.	3500
	Methyl alcohol	0.00166	Cellophane 600	+10 per cent water	3840
	Methyl alcohol	0.00237	Cellophane 600	+10 per cent water	4200
	Methyl alcohol	0.00142	Rubber dam		3600
	Methyl alcohol	0.00142	Cellophane 600		3850
	Methyl alcohol	0.00142	Cellophane 300		3750
	Methyl alcohol	0.00075	Cellophane 300		3900
	Methyl alcohol	0.00125	Cellophane 300		3900
	Ethyl alcohol	0.00274	Cellophane 600		4900
	Ethyl alcohol	0.00120	Cellophane 600	Charcoal fractionated	4000
	Acetone	0.00268	Cellophane 600		3600
	Acetone	0.00235	Cellophane 600	Charcoal fractionated	3720
	Chloroform	0.00504	Cellophane 600		4050
	Total average				3870
Maple lignin (sulfuric acid)	Methyl alcohol	0.00913	Cellophane 600		4560
	Methyl alcohol	0.00754	Cellophane 600		3920
	Methyl alcohol	0.00913	Cellophane 300		4100
	Methyl alcohol	0.00408	Cellophane 300	0.045 *N* with NaCl	3930
	Ethyl alcohol	0.0960	Cellophane 300		3420
	Total average				3985

Maple lignin (alkali)	Methyl alcohol	0.00717	Cellophane 600		4500
	Ethyl alcohol	0.00105	Rubber dam		3680
	Total average				4090
Fully methylated maple lignin (alcohol-hydrochloric acid)	Methyl alcohol	0.00245	Cellophane 600		4500
	Acetone	0.00459	Cellophane 600		4300
	Acetone	0.00240	Cellophane 600		4200
	Total average				4300
Fully nitrated maple lignin (alcohol-hydrochloric acid)	Ethyl alcohol	0.00450	Cellophane 600		3940
Spruce lignin (alcohol-hydrochloric acid)	Methyl alcohol	0.00242	Cellophane 600		3520
	Methyl alcohol	0.00242	Cellophane 600		3500
	Total average				3510

* Average of ten determinations.

asbestos board up to the liquid level to eliminate the heating of the upper part of the apparatus by other than the boiling liquid and vapor. Measurements of the temperature were made with Beckmann thermometers when solvent was in both tubes and when solvent was in one and solution in the other. Thermometer readings were taken after different lengths of time, and the values obtained after experimental constancy was attained were averaged. The molecular weights calculated from the boiling-point raising, together with the probable error due to fluctuations of the temperature, are given in table 3. Considerable difficulty was encountered in making the measurements upon spruce lignin, because it separated from solution in higher concentrations. Even in the comparatively low concentration reported the solution showed a slight Tyndall cone. Similar difficulty in obtaining consistent results was encountered with the sulfuric acid lignin. Only the value most consistent with the other data is given. All the measurements on methyl alcohol-hydrochloric acid lignin are given, however. In general, the agreement with the osmotic-pressure values is good, although the experimental error seems to be somewhat greater. The data give a further indication that temperature does not affect the

TABLE 3

Molecular weight of various lignin preparations from boiling-point raising measurements

TYPE OF LIGNIN	SOLVENT	CONCENTRATION	MOLECULAR WEIGHT	ERROR
		grams per gram of solvent		
Maple lignin (methyl alcohol-hydrochloric acid)	Chloroform	0.0672	3780	±100
	Chloroform	0.0336	3620	±400
	Chloroform	0.0308	3760	±200
	Chloroform	0.0154	3670	±500
	Acetone	0.0952	3180	±300
	Acetone	0.0472	3460	±500
Maple lignin (sulfuric acid)	Chloroform	0.00605	3160	±1000
Maple lignin (alkali)	Chloroform	0.0432	3510	±400
	Chloroform	0.0216	3810	±300
	Chloroform	0.0093	3410	±500
Fully methylated maple lignin (methyl alcohol-hydrochloric acid)	Chloroform	0.0101	4220	±700
Spruce lignin (methyl alcohol-hydrochloric acid)	Chloroform	0.00598	3640	±1000

molecular weight and that it is inappreciably affected by the concentration.

DIFFUSION

The measurement of the diffusion constant was carried out by the method of Lamm (19, 20), in which the rate of change of concentration is measured by following the rate of change of index of refraction. The latter is determined by measuring the displacement of the lines of a uniform, transparent scale placed behind the diffusion cell, the displacement being caused by the index of refraction gradient in the cell. Photographs of the scale, using the monochromatic light from a sodium vapor lamp for illumination, were taken every half-hour for a period of about four hours with a long focus camera to avoid distortion of the image.

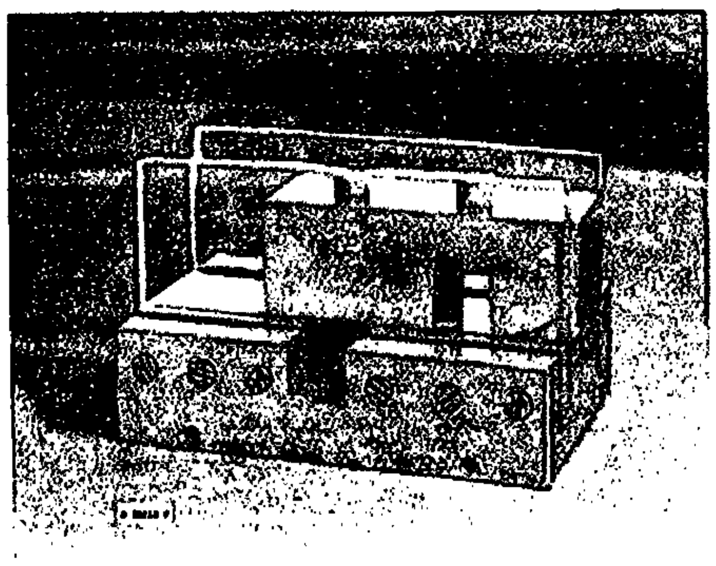

FIG. 5. The diffusion apparatus

The diffusion apparatus was constructed of two blocks of monel metal. The larger of two blocks had two grooves 3/4 in. deep and 3/8 in. wide running the length of the block, 1/4 in. from the edge. Plate glass windows were securely fastened in these grooves by means of a brass spring arrangement, the pressure of which was adjusted by set screws (figure 5). Slots 1/2 in. wide and 1/2 in. deep were cut across each of the blocks, serving as the cells when the faces are closed by the plate glass. The apparatus was put together in the position shown in the figure, the upper cell being filled with solvent and the lower with solution by means of openings in the top of the smaller block, after which they were closed with corks as shown in the illustration. In the case of the chloroform solutions the procedure was reversed, since the solvent is more dense than the solute. The apparatus was fastened securely to the bottom of a brass air bath that had plate glass windows at each end. The air bath was surrounded completely by a water bath held at 25° ± 0.02°C. The apparatus was allowed to reach

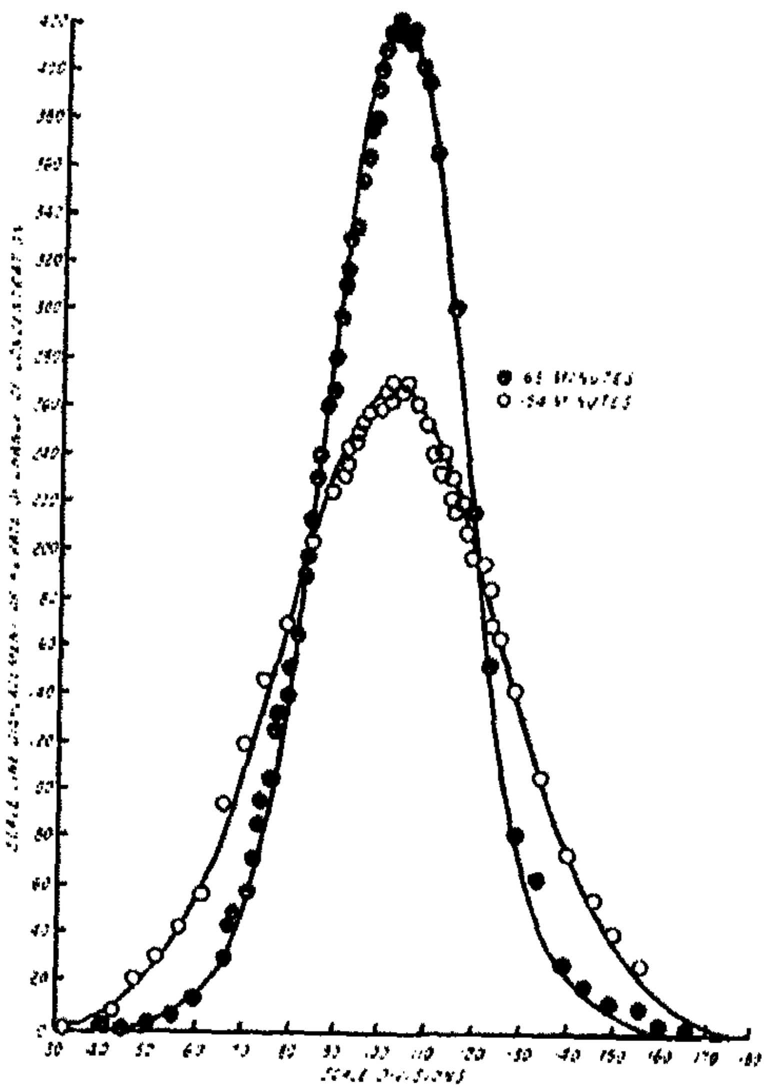

Fig. 6. Diffusion curves for sugar solutions. Scale displacement as a function of the height in the diffusion cell.

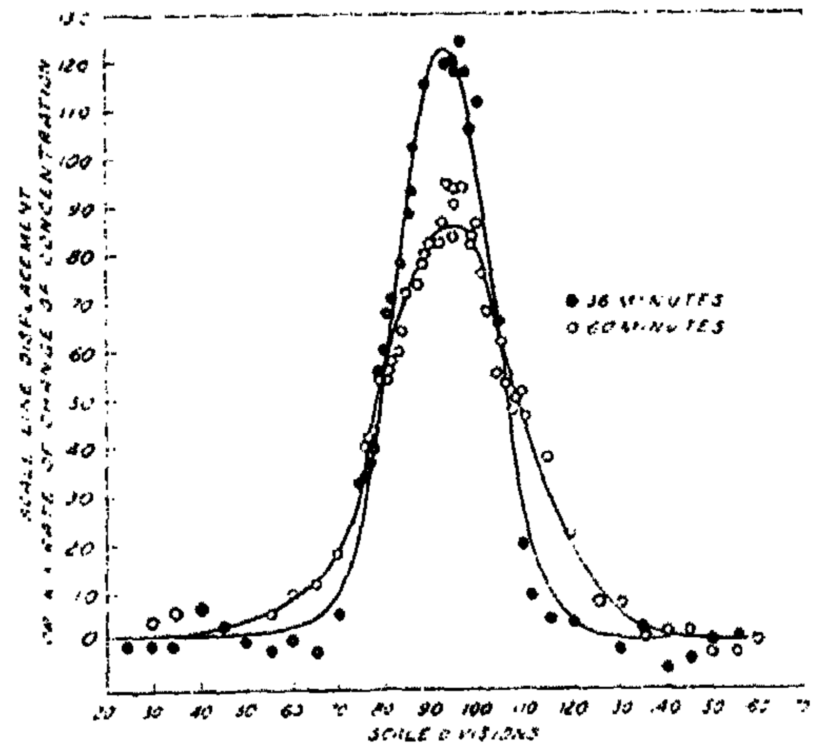

Fig. 7. Diffusion curve for methyl alcohol-hydrochloric acid lignin in methyl alcohol. Scale displacement as a function of the height in the diffusion cell.

thermal equilibrium, for which two hours usually was considered sufficient, the air being stirred constantly. Then the upper cell was pushed over the lower by a steadily moving screw. The boundary formed between them was very sharp, as may be noted by the fact that the diffusion constant measured was independent of the time, even for times as short as half an hour.

The displacement of each line on the photographs was measured with a comparator to 0.002 cm., and the displacement plotted against the height in the cell. Representative plots for sugar and for lignin are shown in figures 6 and 7. On the basis of the index of refraction being proportional to the concentration, these graphs are, except for a scale factor, a plot of the rate of change of concentration against the height in the cell. The solution of Fick's law for diffusion taking place under these conditions is a normal probability curve, the standard deviation σ of which is related to the diffusion constant D through the following equation:

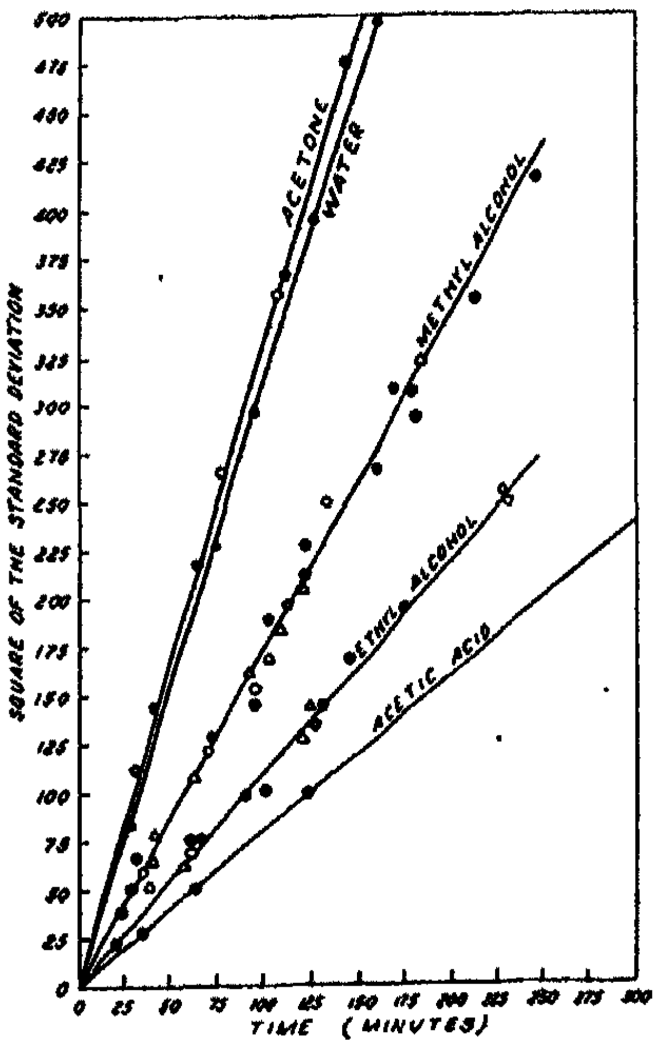

FIG. 8. Diffusion data in terms of the relationship between the square of the standard deviation and the time for sugar in water solutions and various lignin preparations in several organic solvents. ○, sulfuric acid lignin (0.2-0.4 per cent); ●, methyl alcohol-hydrochloric acid ligin (0.1-0.6 per cent); △, alkali lignin (0.3 per cent); ▲, sugar (0.5 per cent).

$$\frac{K\sigma^2}{2t} \tag{4}$$

where t is the time. The standard deviation was determined by finding the normal curve of known standard deviation that most closely matched the experimental points. The lines in figures 6 and 7 represent the normal curves chosen to represent those data. The squares of the standard deviation were plotted against the time, and the diffusion constant was determined from the slope. When the concentrations were of the order of one-half of 1 per cent or more, the displacement of the lines was so great as to make accurate determinations impossible. Only those curves were used to determine the standard deviation for which most of the scale lines could be read with certainty. A plot for sugar and the various lignin preparations in several of the solvents is shown in figure 8. The diffusion constant obtained for sugar is 4.58×10^{-6} sq. cm. per second, which is in good agreement with the accepted values found in the literature.

The determination of the molecular weight of lignin was made from the diffusion constant by means of Einstein's diffusion equation

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \qquad (5)$$

The molecular weights so determined are shown in table 4. A single run with a McBain–Northrup diffusion cell (22, 23) was made on a solution of methyl alcohol–hydrochloric acid lignin in methyl alcohol at a concentration of 0.00248 g. per cubic centimeter. The cell constant was determined with sugar. A molecular weight of 9500 was obtained. The molecular weights for all the lignins in all the solvents are nearly identical, but they are considerably higher than the molecular weights determined by osmotic-pressure data. There are two reasons that might account for this difference. First, the lignin solution might be a mixture of different molecular species. The osmotic pressure gives a molecular weight that depends upon the number of particles in the solution, whereas the diffusion constant gives a molecular weight that depends upon a weight average of the particles. Any appreciable deviation from monodispersion would result in higher calculated molecular weights from diffusion than from osmotic pressure, because the larger particles would have the dominating effect in the former measurements and the smaller particles in the latter (21). Several reasons have already been given to indicate that the lignin solutions approach monodispersion. The diffusion data also give further evidence of monodispersion. If the solutions were polydisperse, each species would diffuse at its own rate and its data would fall on a normal curve whose shape would depend on the weight and the number of particles of that particular species. The measured curve would be a weighted sum of these separate curves. This sum would probably not be normal, though it might approach normal if there were a great many particles of nearly equal molecular weights. The fitting of the data to a normal curve can not be done with enough accuracy to show small departures from normal, but the agreement, as shown in figures 6 and 7, is very good. Also the plot of the square of the standard deviation against the time is linear over long periods. If the system were polydisperse this would not be true. Thus appreciable deviations from monodispersity are highly improbable.

If the molecules were not spherical, the use of the Einstein equation would be unjustified. Though the departure from spherical, as indicated by viscosity data, is small for the lignin molecule, the difference between the molecular weights obtained by osmotic pressure and by diffusion increases rapidly with increasing ellipticity. Perrin (24) has developed a theory for the rotary diffusion of elliptical particles. The result is expressed in terms of the ratio of the time of relaxation for an elliptical particle (τ_1) and for a sphere (τ_0). The ratio of τ_1/τ_0 for a prolate spheroid rotating about its minor axis is

TABLE 4

Molecular weight of various lignin preparations from diffusion measurements at 25°C.

TYPE OF LIGNIN	SOLVENT	MOLECULAR WEIGHT	ERROR
Maple lignin (methyl alcohol-hydrochloric acid)	Methyl alcohol	10,000	±200
	Ethyl alcohol	10.000	±200
	Acetic acid	9.500	±500
	Chloroform	10,500	±500
Maple lignin (sulfuric acid)	Methyl alcohol	11,000	±1000
	Methyl alcohol (0.045 *N* with NaCl)	11.000	±500
	Methyl alcohol (+11 per cent water)	10,000	±500
	Ethyl alcohol	12,000	±1000
	Acetone	12.000	±600
Maple lignin (alkali)	Methyl alcohol	10.000	±500
	Ethyl alcohol	9,000	±500
Spruce lignin (methyl alcohol-hydrochloric acid)	Methyl alcohol	7,350	±300
Fully methylated maple lignin (methyl alcohol-hydrochloric acid lignin)	Acetone	9,500	±500

$$\frac{\tau_1}{\tau_0} = \frac{2}{3}\,\frac{1 - \rho^4}{(2 - \rho^2)\,\dfrac{\rho^2}{\sqrt{1 - \rho^2}}\,\log\dfrac{1 + \sqrt{1 - \rho^2}}{\rho} - \rho^2} \tag{6}$$

where ρ is the ratio of minor to major axis. If a somewhat similar relationship holds for linear diffusion, it should be possible to determine a shape factor for the lignin molecule. If the true molecular weight of lignin is taken as 3900, the diffusion constant, considering the molecule to be spherical, can be calculated. This diffusion constant is three-quarters of the measured values and, according to Perrin's theory, gives a shape factor of approximately 8. This is in as good agreement with the shape factor found from viscosity data as could be expected.

It is thus quite definite that the deviations of the molecular weight obtained by diffusion from the values obtained from osmotic pressure are due to a deviation of the molecule from a spherical shape rather than to the system being polydisperse.

Measurements, to be published later, made on the dispersion of the dielectric constant of chloroform solutions of lignin gave molecular weight values that were in good agreement with the values calculated from the diffusion constant. This was to be expected, since the dispersion of the dielectric constant is a measure of the rotary diffusion constant.

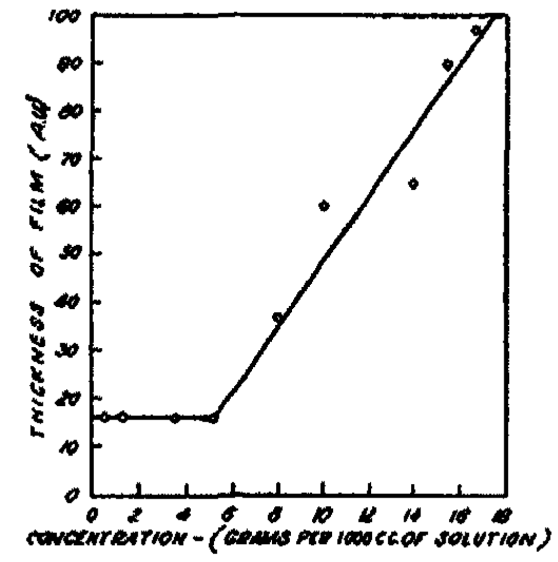

FIG. 9. Area covered per unit weight of methyl alcohol-hydrochloric acid lignin in chloroform as a function of the concentration.

SPREADING MEASUREMENTS

Some concept of the dimensions of large organic molecules can be obtained from the measurement of the area covered by a material when spread on a liquid in which it is insoluble. If the molecular weight and density are known, the area per molecule as well as the thickness of the film can be determined.

Lignin was dissolved in chloroform and spread on water against the pressure of a thin film of lycopodium powder. When the area covered per gram of lignin was plotted as a function of the concentration, a limiting concentration of 0.005 g. per cubic centimeter was obtained, below which the area covered per gram was a constant. This constant value corresponds to a film thickness of 16 A. U. (figure 9). If the molecular weight is taken as 3900, the area per molecule is 318 sq. A. U.

Spreading measurements were also made with a modified Langmuir film balance. The pressure exerted was practically zero until an area of 308 sq. A. U. per molecule, using several different concentrations, was reached. If the area was decreased slightly below this value the pressure rose very rapidly, the film collapsed, and the measurements were no longer reversible. Measurements upon 0.1 *N* hydrochloric acid solution gave similar results, and also measurements with nitrated lignin. If the two surface dimensions were equal, they would be equal to 17.6 A. U. and the molecule would be practically spherical. This is in disagreement with the previous findings reported here, which indicate a length from six to eight times the effective cross-sectional diameter. If the dimensions are taken as 16 A. U. by approximately 100 A. U. by 3 A. U., all the known data may be correlated.

SUMMARY AND CONCLUSIONS

Lignin isolated by three different methods and dissolved in a number of different organic solvents gives molecular weights of two magnitudes, one of which is 3900 ± 300 and the other 10,000 ± 1,000. The lower value was obtained by the osmotic-pressure and boiling-point raising methods, both of which give number average values and are independent of shape. The higher value was obtained by diffusion measurements, which give weight average values and are affected by shape. Two explanations for this difference are offered, one depending on the concept of polydispersity and the other depending on the departure of the molecules from a spherical shape. A number of reasons are given to show that the latter explanation is probably correct. The viscosity data indicate that the lignin dispersion approaches monodispersion, because of the practical constancy of the multiples of the Einstein constant at infinite dilution in the different solvents. The constancy of the molecular weight of all the lignin preparations in all the solvents, the nearness with which the actual diffusion data approach the theoretical standard deviation curves, and the nonvariation of the diffusion constant with time are also given as evidence that the isolated lignin is a single molecular species. On the other hand, the magnitude of the multiple of the Einstein constant obtained from viscosity data and the deviation of the molecular weight calculated from the diffusion constant from the molecular weight from osmotic pressure both indicate that lignin has a shape factor of the order of 6 to 8. It thus appears that the true molecular weight is of the order of 3900 ± 300, which is four times the empirical molecular weight. A possible set of molecular dimensions based on the film thickness obtained from spreading measurements and the shape factor is of the order of 3 × 16 × 100 A. U.

The lignin preparations prepared by methods which deviate so appreciably and which give soluble fractions representing such different portions of the total lignin all approached monodispersion and gave identical molecular weights within experimental error. These phenomena certainly indicate that the soluble fractions of isolated lignin are similarly associated, namely, four times the empirical molecular weight of 900.

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THE COLLOIDAL NATURE OF ASPHALT AS SHOWN BY ITS FLOW PROPERTIES[1]

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Although our knowledge of the physicochemical state of asphalt is quite incomplete, the notion of the colloidal nature of bituminous materials has been advanced by various authors. Richardson (21) did considerable pioneer work at a time when the modern conception of the colloidal state was just beginning to take form. Recently Nellensteyn (16, 17) and his coworkers have described asphalts as protected lyophobe sols in which the micelles, forming the dispersed phase, are composed of high molecular weight hydrocarbons of high carbon content, presumably enveloping nuclei of free carbon. It is generally assumed that the dispersed phase is composed of those substances, called asphaltenes, which are insoluble in 86° Baumé naphtha. The continuous or dispersing phase contains low molecular weight hydrocarbons which are soluble in 86° Baumé naphtha and are called petrolenes. Mack (14) considered asphalts as sols of asphaltenes in a mixture of asphaltic resins and oily constituents (petrolenes), and investigated the viscosity of various combinations of these phases. From his data he drew conclusions concerning the causes for the high viscosities shown by asphaltic materials.

Although there is some information in the literature regarding the viscosity of asphalt, there has been little work done in the direction of determining the presence and degree of the abnormal flow properties such as thixotropy, quasi-viscousness, and elastic effects which frequently prevail in, and are characteristic of, colloidal systems. On the basis of limited data some workers have asserted that asphaltic bitumen is truly viscous, while others have stated that it exhibits non-Newtonian flow characteristics. It is the purpose of the present paper to discuss the flow properties of asphalts of widely different source and type of processing, and to show how a knowledge of these properties substantiates the theory that asphalts are colloidal. The authors intend to show that the existence and magnitude of the anomalous flow characteristics depend not only on the type of bitumen, but also on the temperature at which the measurements are made,

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and on the method and degree of processing to which the asphalt has been subjected.

VISCOUS ASPHALTS

In our laboratory a number of asphalts have been studied in order to ascertain the effect of temperature and shearing stress on the experimentally determined viscosities. Measurements have been made from 15° to 130°C. by means of the modified Bingham–Murray plastometer (6, 19), the Bingham–Stephens alternating-stress method (7), the falling coaxial cylinder viscometer (20), and the conicylindrical rotation viscometer (15). All of these instruments as used in our laboratory have been described and discussed elsewhere (28). To complete the study of temperature effects, viscosities at temperatures as high as 190°C. have been measured by means of a Saybolt–Furol viscometer and the values in Furol seconds converted to poises (12).

TABLE 1

Identification of asphalts

DESIGNATION	SOURCE (TYPE)	PROCESS	PENETRATION AT 25°C., 100 G., 5 SEC.	RING AND BALL SOFTENING POINT
				°C.
A	Californian	Vacuum	55	47.2
B	Mexican	Vacuum	55	52.2
C	Mexican	Batch steam	62	52.2
D	Refined Trinidad native lake asphalt		4	96.7
E	Venezuelan	Batch steam	53	53.3
F	Venezuelan	Batch steam	41	61.9
G	Venezuelan	Air-blown	65	68.9
H	Venezuelan	Air-blown	94	57.2
I	Venezuelan	Air-blown	132	51.1

The viscosities of many steam- and vacuum-refined asphalts of paving consistency prepared from Californian, Venezuelan, Mid-Continent, and Mexican petroleums showed no dependence on the shearing stress employed over the large range of stresses studied at low (atmospheric) temperatures. However, with certain types of these asphalts deviations from viscous flow appear in the region of 40 penetration (3) at 25°C., 100 g., 5 sec., and are more exaggerated as the asphalt becomes harder. Vacuum-refined Californian asphalt exhibited Newtonian flow at atmospheric temperature even when it had been processed to as low as 35 penetration at 25°C., 100 g., 5 sec. (viscosity = 25 × 10^6 poises at 25°C.).

Table 1 serves to identify the various asphalts discussed in this paper with regard to source, method of processing, penetration, and Ring and Ball softening points.

In table 2 data on asphalts A and B, both of 55 penetration at 25°C., 100 g., 5 sec., are presented as typical examples of asphalts exhibiting truly viscous flow properties at both high and relatively low (atmospheric) temperatures.

The viscosities at the higher temperatures were measured in the Bingham–Murray apparatus, while the Bingham–Stephens alternating-stress method was used for the determination of the viscosities at low temperatures. The reproducibility of the above viscosity values is within ±5 per cent. Within this limit the data in table 2 are typical of numerous asphalts whose viscosities are independent of the shearing stress employed.

TABLE 2

Data showing Newtonian flow for asphalts A and B

SHEARING STRESS	VISCOSITY	SHEARING STRESS	VISCOSITY
Asphalt A at 100°C.		Asphalt B at 110°C.	
dynes per cm.²	*poises*	*dynes per cm.²*	*poises*
367.8	42.6	426.9	56.9
306.7	41.6	371.0	57.0
263.0	42.0	332.3	56.9
233.8	42.0	300.9	57.4
211.0	41.6	274.9	56.5
194.8	41.5	253.1	57.2
181.0	41.8	234.5	56.7
		218.4	57.2
Asphalt A at 20°C.		Asphalt B at 30°C.	
149,800	11.5×10^6	17,000	2.16×10^6
135,700	11.6×10^6	15,200	2.29×10^6
123,600	11.9×10^6	13,300	2.35×10^6
110,000	11.7×10^6	11,500	2.40×10^6
93,500	11.8×10^6	9,900	2.38×10^6
80,300	11.8×10^6	8,400	2.34×10^6

EFFECT OF TEMPERATURE ON VISCOUS ASPHALTS

It is generally assumed that asphalt is a system in which the solubility of the dispersed phase (asphaltenes) in the oily continuous phase (petrolenes) is influenced by temperature. At high temperatures the solubility is increased, except for free carbon if it is present. As the temperature is progressively lowered the two phases become more distinct and the colloidal properties of the system become more exaggerated. However, even at low temperatures the system usually is stable, the asphaltenes remaining dispersed owing to the protective action of the asphaltic resins. Various investigators are divided in their opinions as to whether this system has the form of a suspensoid or of an emulsoid. The opinion has been expressed that the temperature-viscosity curves for asphaltic bitumen should have two marked points of transition, one where the system passes from the liquid to the semiliquid state, and the other where a transition occurs from the semiliquid to the solid state. From the rheological standpoint, this latter statement is ill-defined for, as far as flow properties are concerned, a transition from the true liquid state to anything approximating the solid state means a change from purely viscous properties to definitely plastic behavior, involving yield values and mobilities rather than viscosities. From the numerous data collected in our laboratory no asphalt has been found to possess plastic properties as defined above.

Nellensteyn and Roodenburg (18) have shown points of inflection in the relation between surface tension and temperature, while Klinkmann (13) and Spiers (26) have shown such transition points in their temperature-viscosity relationships for bitumen and tar. On the other hand, there is an abundance of data which shows that there is a distinct continuity throughout the viscosity-temperature curves. Evans and Pickard (9), Eymann (10), Pochettino (20), and Rodiger (22) have all given data supporting the latter statement. Saal (24) has recently shown that there is no break in the relation between temperature and surface tension for asphaltic bitumen.

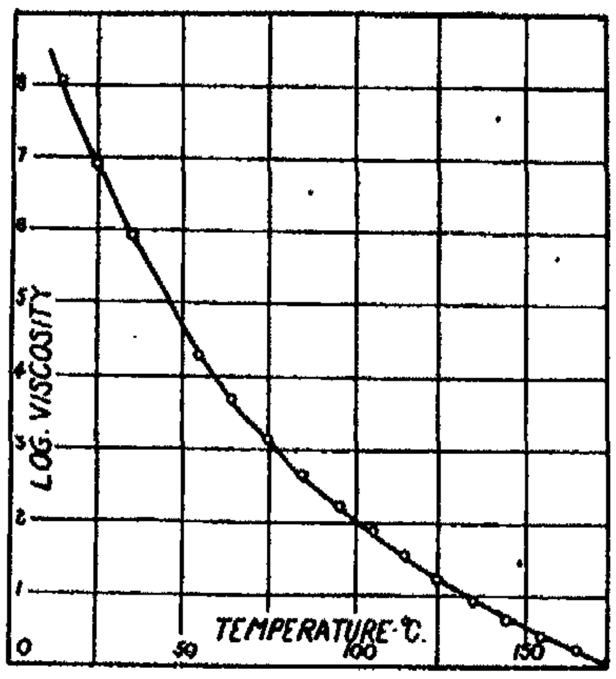

FIG. 1. Variation of viscosity of asphalt C with temperature

In our laboratory the viscosities of fourteen asphalts of widely different origins, processed differently and to various degrees, have been measured from 15° to 190°C. Some of these data have been reported elsewhere (19, 25). The viscosities from 15° to 35°C. were measured by the alternating-stress method (7), from 40° to 130°C. by the modified Bingham-Murray apparatus (19), and above 130°C. with a Saybolt-Furol viscometer (2). The Furol seconds were converted to absolute C.G.S. units (poises) (12). The type of data obtained is illustrated by figure 1, which shows the logarithm of the viscosity for asphalt C plotted against the temperature in degrees Centigrade. In none of the fourteen asphalts is there any indication of a sudden break in the viscosity–temperature relationship.

The fact that no sudden changes occur in the log viscosity versus temperature (°C.) relation does not discount the notion that as the temperature is lowered, the asphaltenes gradually separate from true solution with the petrolenes to give rise to a stable system whose colloidal properties become more pronounced as the temperature decreases. The facts indicate that the transition from a condition approximating true solution to a distinctly colloidal state is so gradual that no sudden change in physical properties occurs. From a plot such as that shown in figure 1 it is evident that the so-called "softening point", which is of value to bituminous technologists, does not represent a temperature at which the viscosity changes sharply. It has already been pointed out (1) that the Ring and Ball softening point (4) is merely the temperature at which any asphalt attains a particular viscosity (approximately 12,000 poises). Saal (23) states that the Ring and Ball softening point may correspond to a viscosity value somewhere between 10,000 and 20,000 poises.

At atmospheric temperatures (15° to 40°C.), a range to which paving asphalts are subjected in use, a plot of the logarithm of viscosity against temperature in degrees Centigrade is a straight line within the limits of experimental error. Therefore, for this range, viscosity and temperature may be related by the expression

$$\log \eta = mt + b \qquad (1)$$

where η = viscosity in poises, t = temperature (°C.), and m and b are constants. For the higher temperatures where the viscosities vary from 1 to 5 poises, a consistency range in which asphalts are usually processed, the same type of equation applies.

An asphalt viscosity index, which evaluates the susceptibility of asphalts to temperature changes in terms of percentage decrease of viscosity (in poises) for a 1°C. rise in temperature, has been derived (27), using the slope m of equation 1. This index is expressed as

$$\text{A.V.I.} = 100\ (10^{m} - 1) \qquad (2)$$

Experimentally, it is only necessary to measure the viscosities η_a and η_b at two temperatures t_a and t_b (°C.) within the range where equation 1 is valid. Then,

$$\text{A.V.I.} = 100\left[\left(\frac{\eta_a}{\eta_b}\right)^{1/(t_a\ -\ t_b)} - 1\right]^{*} \qquad (3)$$

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* In actual practice the A.V.I. is most readily calculated from the expression 100 (antilogarithm of the slope "m" − 1).

Since the viscosity of asphalt diminishes with increasing temperature the values of the A.V.I. are negative, but from the definition given above the sign may be ignored. For asphalt C, shown in figure 1, the A.V.I. changes from 20.5 at the low service temperatures to 4.4 at the high processing temperatures. Thus, a great decrease in both viscosity and susceptibility to temperature change occurs with a large rise in temperature.

THIXOTROPY IN ASPHALTS

Numerous cases have been found where an initial working of the asphalt sample at a high stress was required before a constant viscosity value was obtained. After a variable amount of structure, depending on the nature of the asphalt, was removed from the sample by the application of mechanical shear, the viscosity values for all stresses less than that initially used were constant. This phenomenon of thixotropy or breakdown of structure under the influence of mechanical working has been observed in many colloidal systems, especially when the concentration of the dispersed phase is appreciable. A typical case of thixotropy is found in the viscosity data for asphalt D given in table 3. The measurements on this asphalt were made using the alternating-stress method.

TABLE 3

Viscosity data showing presence of thixotropy in asphalt D at 50°C.

DIRECTION OF MOVEMENT*	SHEARING STRESS	VISCOSITY
	dynes per cm.^{2}	*poises* $\times 10^{-4}$
In	145,000	23.6
Out	144,000	21.0
In	144,000	18.9
Out	144,000	18.2
In	144,000	17.4
Out	143,000	17.1
In	143,000	16.8
Out	143,000	16.0
In	143,000	16.0
Out	143,000	16.7
In	143,000	15.9
Out	124,000	16.4
In	124,000	15.6
Out	113,000	16.7
In	113,000	15.7
Out	92,800	16.5
In	92,800	15.9
Out	82,300	16.3
In	82,300	16.0

* The first "out" movement is never recorded because of difficulties in focusing, etc.

It will be noted that after the initial "working" period, the viscosity of this asphalt decreases to a value which remains essentially constant over a range of decreasing shearing stresses. The viscosity value corresponding to the "in" movement, for a given shearing stress, is always lower than that corresponding to the "out" movement. This behavior probably is caused by the elasticity of the material.

AGE-HARDENING OF ASPHALTS

An interesting and important manifestation of thixotropy is the phenomenon of age- or time-hardening of asphalts. Asphalt technologists know that if the penetration of a sample of asphalt is obtained immediately after cooling and again on the same undisturbed sample at intervals of several days, the asphalt will be found to have become harder with the passage of time. Remelting the sample causes the asphalt to return to its original consistency.

TABLE 4

Increase in viscosity of asphalt E with time

TIME	VISCOSITY	TIME	VISCOSITY
hours	*poises* × 10^{-6}	*hours*	*poises* × 10^{-6}
4	7.54	317	9.38
25	7.80	820	11.0
52	8.21	2232	12.1
77	8.56	4455	12.7
148	8.89	9100	14.2
		5*	8.3

* Remelted sample.

Measurement of viscosity in absolute units offered a sensitive method of evaluating this age-hardening phenomenon (29). The falling coaxial cylinder viscometer (20, 28) was particularly well adapted to such an investigation, because several instruments could be filled simultaneously with the same asphalt and stored at a constant temperature, and determinations of the viscosity could be made at any desired intervals of time. Ten or twelve instruments were usually filled with a particular asphalt. The viscometers and contents were stored in a cabinet maintained at 25° ±0.5°C. At increasing intervals of time samples were removed from the cabinet and the viscosities measured at 25°C., using a rather low shearing stress (7200 dynes per cm.^{2}). After each measurement was completed the sample was discarded. Table 4 gives the data obtained using asphalt E.

The first value obtained (at the end of four hours) is unaccountably high, but the remaining nine values fall very close to a straight line when log viscosity is plotted against log time. The sample which had aged for 9100 hours was remelted in the viscometer, cooled, and the viscosity determined at the end of five hours, with the result shown at the bottom of table 4. It is evident that after aging for over one year a large percentage of the structure which had developed could be destroyed by heat.

The phenomenon of age-hardening is apparently thixotropic in its nature, because by the application of a high shearing stress in a rotating-cylinder viscometer the viscosity of an aged asphalt can be reduced just as is done by heating.

TABLE 5

"Equilibrium viscosities" of quasi-viscous asphalt F at 25°C.

APPROXIMATE TIME OF WORKING	MEAN SHEARING STRESS	RATE OF SHEAR	"EQUILIBRIUM VISCOSITY"
minutes	*dynes per cm.*^{2}	*reciprocal seconds* × 10^4	*poises* × 10^{-6}
35	11,600	5.72	20.3
30	34,800	17.6	19.9
60	69,600	40.6	17.3
100	138,700	114.	12.2

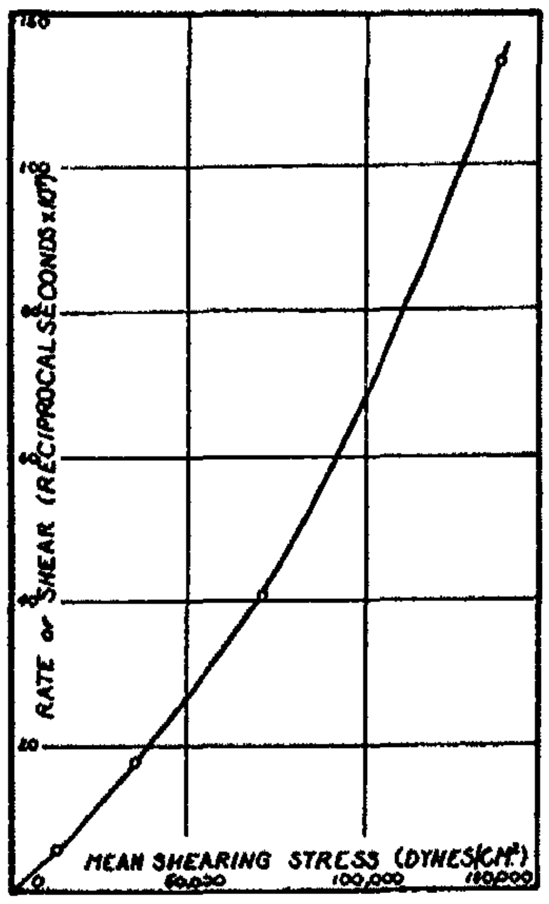

FIG. 2. Non-Newtonian flow of asphalt F at 25°C.

NON-NEWTONIAN FLOW

When a system possesses sufficient internal structure to cause the appearance of marked thixotropic effects, other anomalous flow characteristics often become apparent. At a particular shearing stress such a system must be worked in a given direction until a constant rate of movement is obtained. From this an "equilibrium viscosity" may be calculated.

However, the "equilibrium viscosity" decreases with increasing shearing stress, and a plot of the rate of shear versus shearing stress yields a curvilinear relationship passing through the origin. This phenomenon has been called non-Newtonian flow, and the materials are said to be quasi-viscous.

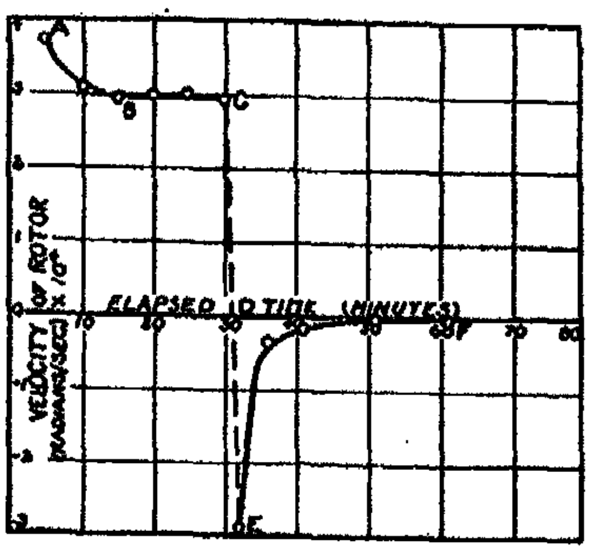

Fig. 3. Elastic effects in asphalt F at 25°C. Mean shearing stress = 34,800 dynes per square centimeter.

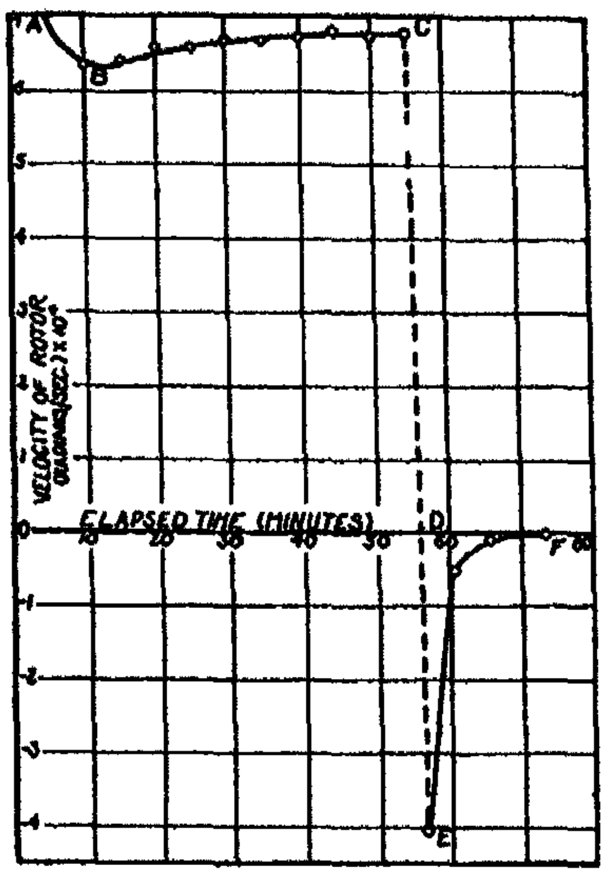

Fig. 4. Elastic and thixotropic effects in asphalt F at 25°C. Mean shearing stress = 69,600 dynes per square centimeter.

This type of flow indicates that the system possesses some rigidity, but the material cannot be called a plastic solid in the sense in which Bingham (5) uses the term. A "yield value" would have little physical significance since it would depend completely on the shearing stress at which it would be determined. Further, the "yield value" would be zero when the rate of shear is zero.

Table 5 and figure 2 show data for asphalt F, a steam-refined asphalt of paving consistency, which exhibits a marked quasi-viscous nature. The measurements were made in the conicylindrical rotation viscometer (15, 28) at 25°C. Only the final "equilibrium viscosities" are recorded.

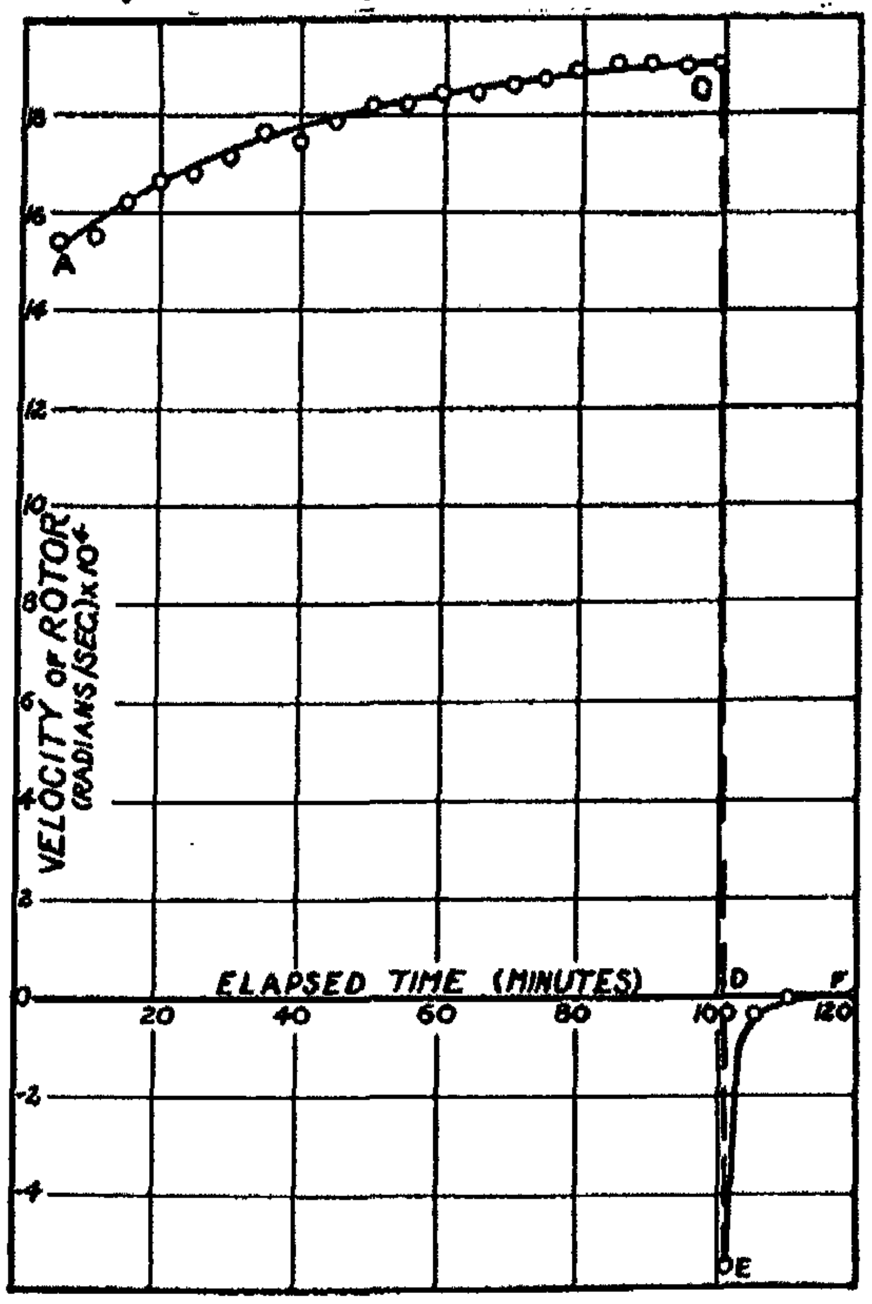

FIG. 5. Elastic and thixotropic effects in asphalt F at 25°C. Mean shearing stress = 138,700 dynes per square centimeter.

ELASTIC EFFECTS

Figures 3, 4, and 5 give some additional information concerning the flow properties of asphalt F. The rate of movement of the inner cylinder (radians per second × 10^{-4}) is plotted against time in minutes for the last three shearing stresses given in table 5. If the material were purely viscous, the rate of movement would be independent of the period of working. However, it is observed (figure 3) that at the low stress (34,800 dynes per cm.^{2}) the rate of movement of the inner cylinder is initially high and with time decreases asymptotically to a constant value. The same behavior was noted for a shearing stress of 11,600 dynes per cm.^{2} Such a phenomenon has been recognized in other materials as an elastic fore-effect by Braunbek (8) and by Ferry and Parks (11), et al. The initial elastic displacement is gradually obscured by the viscous deformation, and the rate of movement eventually becomes constant. The "equilibrium viscosity" given in table 5 is calculated from this constant rate. At point *C* in figure 3 the stress is suddenly removed from the sample and an elastic return is effected, the inner cylinder of the viscometer rotating in the reverse direction of its own accord. The rate of reverse movement is shown by curves *DE* and *EF*.

At a higher stress (69,600 dynes per cm.^{2}) the same elastic fore- and aftereffects are noted (figure 4). However, this stress is high enough so that the initial elastic fore-effect is partially masked by the breaking-down of structure within the sample. As the internal structure is destroyed by the mechanical shearing the rate of movement of the inner cylinder increases and finally becomes essentially constant. This constant rate is again used to calculate the "equilibrium viscosity" recorded in table 5.

When the high stress (138,700 dynes per cm.^{2}) is used (figure 5), the initial elastic effect is entirely obscured by the viscous deformation and breakdown of structure within the asphalt. However, it is evident that the system still possesses some structure, even after being subjected to a high stress for 100 minutes, because an elastic return is noted when the shearing stress is removed from the sample.

DEPENDENCE OF ANOMALOUS FLOW PROPERTIES ON THE DEGREE OF PROCESSING

It is known that as the processing of an asphalt continues the material becomes harder, resulting in a lower penetration and an increased percentage of asphaltenes (dispersed phase). In conjunction with this fact we have found that in air-blown asphalts of the type represented by asphalts G (65 penetration), H (94 penetration), and I (132 penetration), the harder the asphalt, the greater the deviation from Newtonian flow. Comparisons of these asphalts were made at approximately equal ranges of *rate of shear,* for it seems reasonable that the magnitude of thixotropic and quasi-viscous effects should depend on the rate at which the samples are sheared. If, on the other hand, we had compared these asphalts of widely different "viscosities" at a given range of shearing stresses, the low viscosity asphalt (132 penetration) would have been subjected to much higher rates of shear than the asphalt of highest viscosity (65 penetration). Thixotropic and quasi-viscous effects in the higher viscosity asphalts, as evidenced from a comparison of the final "equilibrium viscosities" of these three different asphalts, would therefore have been underestimated.

For a complete study of elastic effects, however, all samples should be run at exactly the same shearing stresses. Since we are interested primarily in the thixotropic and quasi-viscous characteristics of these materials in the present work, we have used approximately equal ranges of rates of shear.

In all of the determinations low shearing stresses were employed so as to insure the absence of slippage of the samples at the walls of the viscometer.

In table 6 are given the "equilibrium viscosities" of the air-blown asphalts G, H, and I, as measured in the conicylindrical rotation viscometer at 25°C.

TABLE 6

"Equilibrium viscosities" of air-blown asphalts G, H, and I at 25°C.

ASPHALT	MEAN SHEARING STRESS	TIME OF WORKING	TIME FOR ATTAINMENT OF EQUILIBRIUM "η"	RATE OF SHEAR	EQUILIBRIUM "η"	BREAKDOWN OF STRUCTURE BY CONTINUED WORKING
	dynes per cm.^{2}	*minutes*	*minutes*	*reciprocal seconds* $\times 10^4$	*poises* $\times 10^{-4}$	
G (65 penetration)...	21,900	1,260	100	1.16	188	None
	43,800	805	615	5.21	84.0	Slight
	76,800	10	*	13.9*	55.2*	Considerable*
	76,800	545	*	30.0*	25.7*	Considerable*
H (94 penetration)...	1,060	400	50-400†	0.434	24.4	None
	2,150	770	40-700†	0.870	24.7	None
	4,340	445	35-425†	1.74	24.9	None
	8,730	690	30-630†	3.77	23.1	None
	32,900	10	*	20.3*	16.2*	Considerable*
	32,900	645	*	38.6*	8.52*	Considerable*
I (132 penetration)...	1,060	260	150-240†	0.231	4.58	None
	4,340	790	50-740†	1.00	4.34	None
	10,900	10	*	27.8*	3.92*	Some*
	10,900	440	*	35.2*	3.09*	Some*

* An equilibrium velocity was not attained during the time allotted to the experiment; the viscosity continued to decrease on further working.

† The time could not be ascertained more accurately because the equilibrium state was attained in the sample during the absence of the observer.

At low shearing stresses the samples were worked for long periods of time to make certain that "equilibrium viscosities" had really been attained. It is evident from table 6 that at the lowest stresses none of these asphalts shows thixotropic behavior in this instrument, although they are quasi-viscous (i.e., the "equilibrium viscosity" is dependent on the shearing stress employed). At the highest stress employed in each case, however, the breakdown of structure is very evident, since the "viscosities" diminish with time at constant shearing stress. These experiments substantiate the results shown in figures 3, 4, and 5 for asphalt F in indicating that there is a critical shearing stress at which the structure of the asphalt sample is broken down to some extent in this instrument with continued working in a given direction. At all stresses above this threshold value thixotropy is manifested.

TABLE 7

"Equilibrium viscosities" of air-blown asphalt G (65 penetration)

TEMPERATURE	MEAN SHEARING STRESS	TIME OF WORKING	TIME FOR ATTAINMENT OF EQUILIBRIUM "η"	RATE OF SHEAR	EQUILIBRIUM "η"	BREAKDOWN OF STRUCTURE BY CONTINUED WORKING
°C.	*dynes per cm.^{2}*	*minutes*	*minutes*	*reciprocal seconds × 10^4*	*poises × 10^{-6}*	
25.0	21,900	1,260	100	1.16	188	None
	43,800	805	615	5.21	84.0	Slight
	76,800	10	*	13.9*	55.2*	Considerable*
	76,800	545	*	30.0*	25.7*	Considerable*
35.0	1,060	360	300	0.434	24.4	None
	6,530	170	70	2.61	25.0	None
	10,900	970	100–820†	4.19	26.0	Slight
	32,900	10	*	19.7*	16.7*	Considerable*
	32,900	420	*	51.4*	6.40*	Considerable*
45.0	511	840	20	1.00	5.07	None
	1,170	540	320	2.60	4.50	None
	3,240	260	30	6.65	4.87	None
	8,730	10	*	22.0*	3.96*	Some*
	8,730	235	*	29.5*	2.95*	Some*
55.0	504	240	90	6.96	0.724	None
	1,050	130	20	15.0	0.696	None
	2,490	130	30	32.5	0.766	None

* An equilibrium velocity was not attained during the time allotted to the experiment; the viscosity continued to decrease on further working.

† The time could not be ascertained more accurately because the equilibrium state was attained in the sample during the absence of the observer.

If the "equilibrium viscosities" of asphalts G, H, and I are compared at equal ranges of rate of shear, it is noticed that the harder the asphalt (i.e., the more it has been processed), the greater is the deviation from Newtonian flow. This is true even if we omit from this comparison the "equilibrium viscosity" values at the highest stresses, where breakdown of structure causes marked decreases in the "viscosities."

The anomalous flow properties of the blown asphalts G, H, and I were similar to those of the batch steam-refined asphalt F, but more pronounced.

No means has been found for expressing the "degree of deviation" from Newtonian flow as a function of the amount of dispersed phase. In the first place, there is no method of expressing the amount of divergence from purely viscous flow. Secondly, the percentage of asphaltenes is not an absolute measure of the colloidality of the asphalt. Although asphaltenes are defined by a solubility test, they vary appreciably in molecular weight and probably in composition for different types of asphalt. Also, the continuous phase (petrolenes) may differ greatly in various asphalts. The natures as well as the amounts of the continuous and dispersed phases are undoubtedly responsible for the colloidal characteristics of asphalts.

INFLUENCE OF TEMPERATURE ON ANOMALOUS FLOW PROPERTIES

As the temperature increases, the high molecular weight constituents of asphalt (asphaltenes) become more soluble in the continuous oily phase (petrolenes), and a gradual transition occurs in the nature of the flow exhibited by the system. With increasing temperature, the elastic and thixotropic properties of the asphalt system, as well as its quasi-viscous character, are less pronounced; at a high enough temperature the system exhibits truly viscous flow. Table 7 presents the "viscosity" data of the air-blown asphalt G at various temperatures. At 55°C. this sample exhibited viscous flow within the range of shear rates used in these experiments. As the temperature was lowered, the anomalous flow properties became more exaggerated. Determinations were made at approximately equal ranges of rate of shear for the reason stated in the previous section.

CONCLUSION

The flow characteristics of asphalts are frequently complex, indicating that their physical structure and chemical composition are exceedingly involved. Some asphalts appear to be truly viscous, whereas others exhibit varying degrees of anomalous flow (thixotropy, age-hardening, quasi-viscousness, and elasticity). The magnitude of these characteristics depends largely on the source of the asphalt, the degree of processing, and the temperatures and rates of shear at which the measurements of flow are made. It is generally believed that the source, processing, and temperature of test influence the nature and amount of dispersed material present (i.e., the colloidality of the asphalt). Of course, the rate of shear has a profound influence on the physical structure of the system at the time of measurement. The presence of flow properties which are generally characteristic of colloidal systems lends strong support to the concept that asphalts are distinctly colloidal. In the case of truly viscous asphalts, the change of viscosity with decreasing temperature is continuous and there is no evidence of a sudden change from a sol to a gel condition, or from a semisolid to a solid state, as some workers have erroneously concluded from insufficient data.

The gradual formation of an internal secondary structure unstable to heat and mechanical working has been noted in all types of asphalt, whether viscous or not. This occurrence of age-hardening is another conclusive proof that asphalts are colloidal in nature.

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PARTICLE SIZE AND OPTICAL PROPERTIES OF EMULSIONS[1]

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Numerous efforts have been made to calculate theoretically the dependence of the light-scattering power of suspensions upon the size and refractive index of the particles, the refractive index of the medium, and the wave length of light used. For infinitely small, non-absorbing particles in a non-absorbing medium, Rayleigh's treatment (9) is generally judged satisfactory, but if the particle size approaches the order of magnitude of the wave length of light, or if the particle is colored, the theoretical calculation of scattering becomes much more difficult and a matter of approximation (1, 4, 5, 6, 8, 9, 11). On the other hand, the empirical correlation of experimental data on light scattering with relevant physical factors has on the whole been unsatisfactory, owing to insufficiently accurate information on particle size. As a rule, investigators have had to be satisfied to assume their suspensions to contain particles of uniform size, although as a matter of fact, any artificial and practically all natural suspensions contain particles of definitely non-uniform size.

Fortunately, the Svedberg ultracentrifuge can under favorable conditions provide the required information, but rather involved calculations are required to extract the desired relations between light scattering and particle size, owing to the fact that the ultracentrifuge does not give directly a particle-size distribution. Specifically, a particle-size distribution may be expressed as a relationship between dc/dr and r, where dc/dr is proportional to the weight of particles having a radius between r and $r + dr$. The ultracentrifuge, however, gives the relation between $d(kc)/dr$ and r, where k is the apparent absorption coefficient of a suspension of particles of radius r. For a suspension of colorless particles in a colorless medium, the "absorption" is of course entirely due to scattering, and the "absorption coefficient" in such cases provides a measure of the light-scattering

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power of the suspension. The relation between $d(kc)/dr$ and r we call a "weight-optical distribution," and since k in general varies with r, the "weight-optical distribution" normally is not identical with the true "weight distribution" curve (7).

In this paper, a method will be described for calculating, with the aid of a simple mechanical product-integraph, the relationship between the "absorption coefficient" k and the radius from a series of weight-optical distribution curves. In addition, the light-scattering powers of a series of emulsions of constant particle-size distribution but different refractive index relations are reported in terms of apparent absorption coefficient k, and a general relation connecting the apparent absorption coefficient with particle size, the refractive indices of particles and medium, and the wave length is deduced by means of the product-integraph.

THE PRODUCT-INTEGRAPH AND ITS USE

The most direct way of determining the relation between absorption coefficient (as a measure of light scattering) and radius for a certain kind of particle in a medium of specified refractive index is by the analysis of a series of weight-optical distribution curves for suspensions with different particle sizes.

If a given weight-optical distribution be represented by the equation

$$d(kc)/dr = f_n(r)$$

and the variation of the absorption coefficient k with r be represented by

$$1/k = F(r)$$

then, in general, it follows that

$$\int_{r_{\text{min.}}}^{r_{\text{max.}}} f_n(r) \cdot F(r) = 1$$

Each weight-optical distribution is represented by a particular $f(r)$, and our task is to calculate $F(r)$ from the series of simultaneous integral equations equal in number to the experimentally determined weight-optical distributions. Since the solution of such equations with the required accuracy is impractical by algebraic means, a mechanical product-integraph based upon the principles of a two-dimensional moment balance was devised for the purpose.

The moment balance was simply a drawing board supported on a fulcrum and carrying a system of coördinates. The r-axis (or abscissa) coincides with the fulcrum. The $f_n(r)$ functions are divided into a number of equal areas (e.g., 10) and are represented by a series of equal weights (for instance, 10 g. each). Each weight is placed at the mean r value for the area it represents. On the left-hand side of the board, 10 cm. from the fulcrum, a weight of 100 g., representing unit moment, is placed. On the right-hand side of the board, perpendicular to the fulcrum, $F(r)$ is measured along the ordinates.

When the weights representing any $f(r)$ are placed at their appropriate r-positions and their ordinates adjusted until the board balances, the corresponding equation of the set is satisfied, and $F(r)$ is the curve drawn through the positions of the weights. Each of the experimental functions $f(r)$ is put on the moment balance separately, and $F(r)$ is adjusted until, by a process of trial and error, an $F(r)$ curve is found which will satisfy all of the equations. The resulting curve represents the relation between $1/k$ and radius, which of course can be readily converted, if desired, into a curve of k versus radius. With a moment balance sensitive to differences in moments of 0.3 per cent, an $F(r)$ curve can be found that satisfies the experimental data to 3 to 4 per cent.

A specific example of the use of this product-integraph for determining the relationship between "absorption coefficient" and particle radius has previously been presented (3), and a more detailed description of the theory of the product-integraph is published elsewhere (2).

THE EFFECT OF REFRACTIVE INDEX AND PARTICLE SIZE UPON ABSORPTION COEFFICIENT (LIGHT SCATTERING)

Inasmuch as the light-scattering efficiency of a particle is affected by particle shape and is complicated by double refraction in solid particles, emulsions were chosen as representing ideal conditions. A stock emulsion of Nujol in 76 per cent glycerol containing 1 per cent of Castile soap was prepared and thoroughly homogenized. From this stock emulsion, a series of emulsions of the same particle-size distribution but with markedly different light-scattering properties was prepared by reduction of the refractive index of the medium by dilution with various proportions of glycerol and water. Six emulsions with the dispersion medium varying from 15 to 76 per cent of glycerol were so prepared, corresponding to a range in refractive index of the medium from 1.359 to 1.444 at a wave length of 444 millimicrons, where the absorptions and weight-optical distributions were measured. At the same wave length, the refractive index of the Nujol is 1.488.

The weight-optical distribution curves of the six emulsions were determined with the Svedberg low-speed ultracentrifuge in the usual manner and are presented in figure 1. The areas of these curves are equal to the light absorptions, measured also in the ultracentrifuge within an aperture of about 4°, with a parallel beam of incident light (see table 1). The "absorption coefficients" are defined in the conventional way and refer to a suspension containing 0.01 cc. of particles per 100 cc. of suspension.

In contrast to the case described above, the $F(r)$ function is different for each of these emulsions, owing to the differences in the refractive indices, but the function relating concentration and radius (i.e., dc/dr versus r) is the same. It was found that the differences in light-scattering efficiency

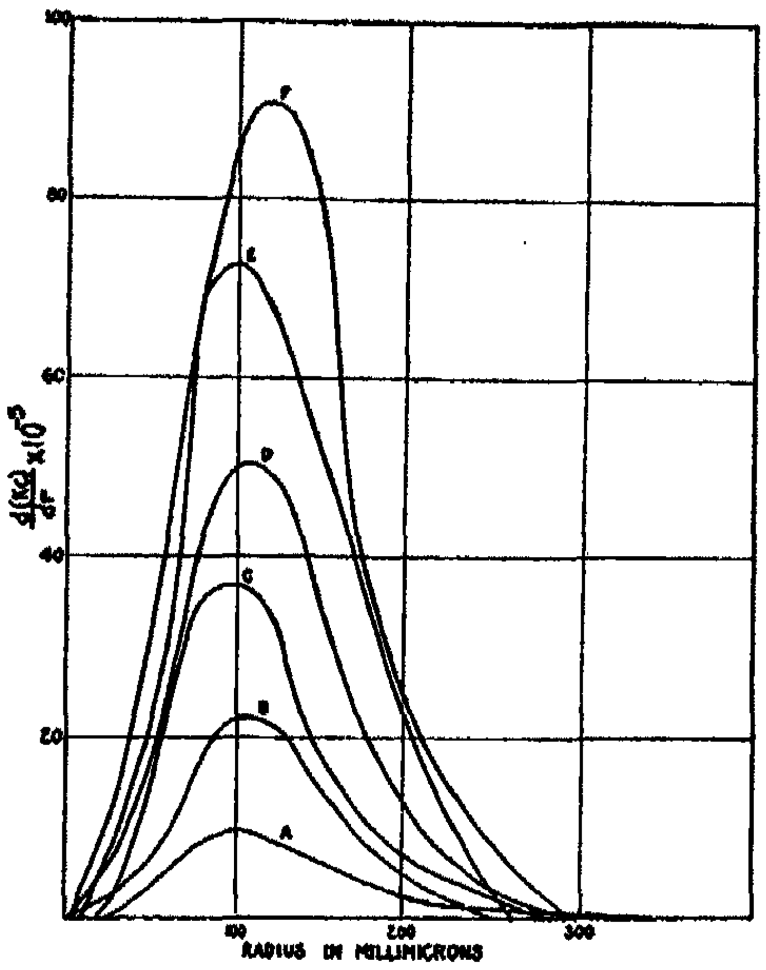

FIG. 1. Weight-optical distribution curves of series of emulsions with the same particle-size distribution but different refractive index of the medium.

TABLE 1

Absorption coefficients of Nujol emulsions

EMULSION	ABSORPTION COEFFICIENT	EMULSION	ABSORPTION COEFFICIENT
NE-2A	0.0293	NE-2D	0.162
-2B	0.0656	-2E	0.236
-2C	0.110	-2F	0.300

as determined by the refractive indices could be reduced to a common denominator, as it were, by use of the dimensionless factor

$$\frac{m^2 - 1}{m^2 + 2} \cdot \frac{n_0}{\lambda} \cdot r$$

where m is the ratio of the refractive index of the particle to that of the medium, n_0 is the refractive index of the medium, λ is the wave length of the light used in vacuum, n_0/λ is therefore the wave length of the light used in the medium, and r is the particle radius. This factor we call the "relative optical radius." The abscissa values of the weight-optical curves were converted to a "relative optical radius" basis.

The ordinates of the weight-optical distributions were in turn multiplied by the corresponding radii. The resulting curves (figure 2) could then be treated in the same fashion as the f(r) functions discussed in the section on the product-integraph and its use, and a curve obtained with the product-integraph relating $1/(kr)$ and the "relative optical radius." Figure 3 presents kr versus "relative optical radius." k in this case refers to the absolute "absorption coefficient" of a suspension containing 0.01 cc. of particles per 100 cc. of suspension measured under the specified conditions of illumination and angle of collection. kr we refer to as the "absorption coefficient per unit projected area."

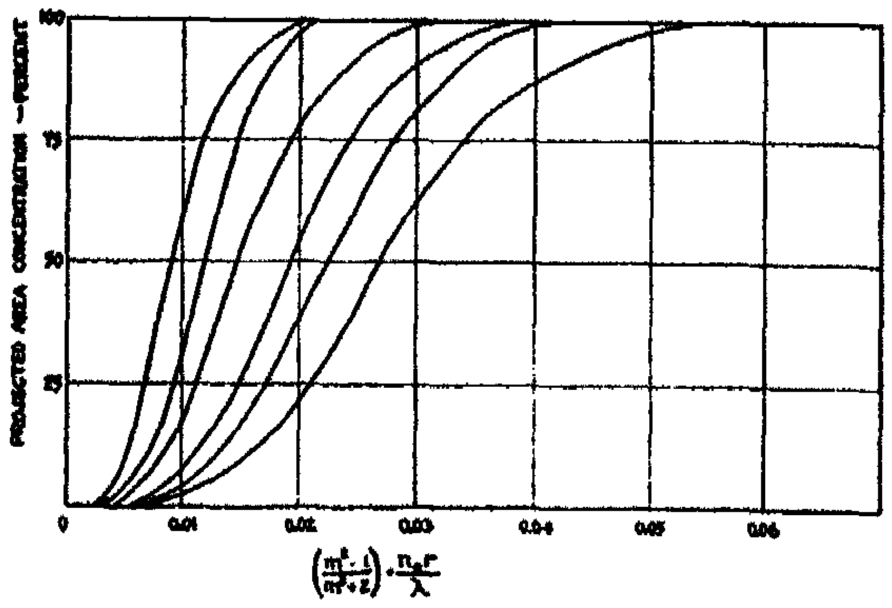

FIG. 2. Projected area concentration in per cent versus relative optical radius

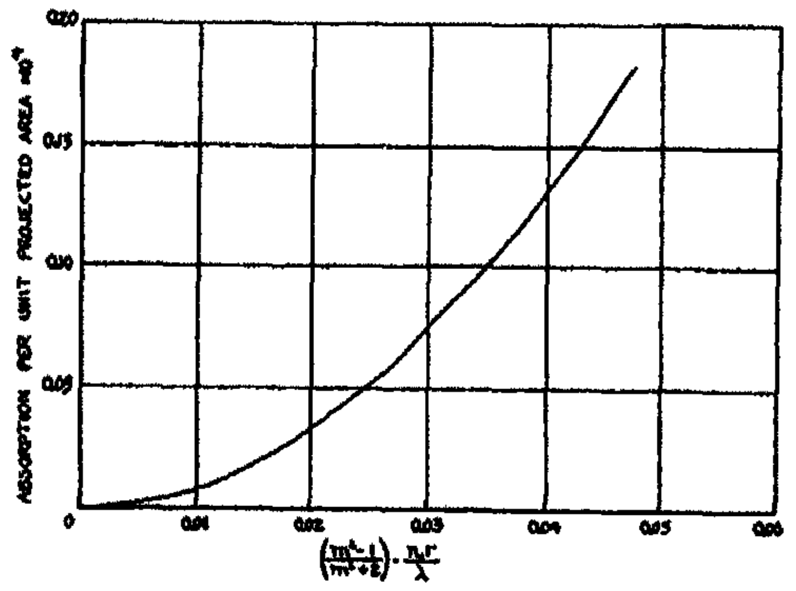

FIG. 3. Generalized curve relating the absorption constant of a suspension with the concentration, particle size, refractive indices of particle and medium, and the wave length.

Presumably, figure 3 should describe the light absorption for the indicated range of relative optical radius, regardless of the values of the individual quantities entering into the relative optical radius. Experimentally, however, the actual range in values covered is as follows:

$$r = 20 \text{ to } 270 \text{ m}\mu$$
$$m = 1.03 \text{ to } 1.94$$
$$n_0 = 1.359 \text{ to } 1.444$$
$$\lambda = 444 \text{ m}\mu$$

Further work will be required before we can be sure that the method here employed for correlating the various factors involved is really as generally valid as it now appears.

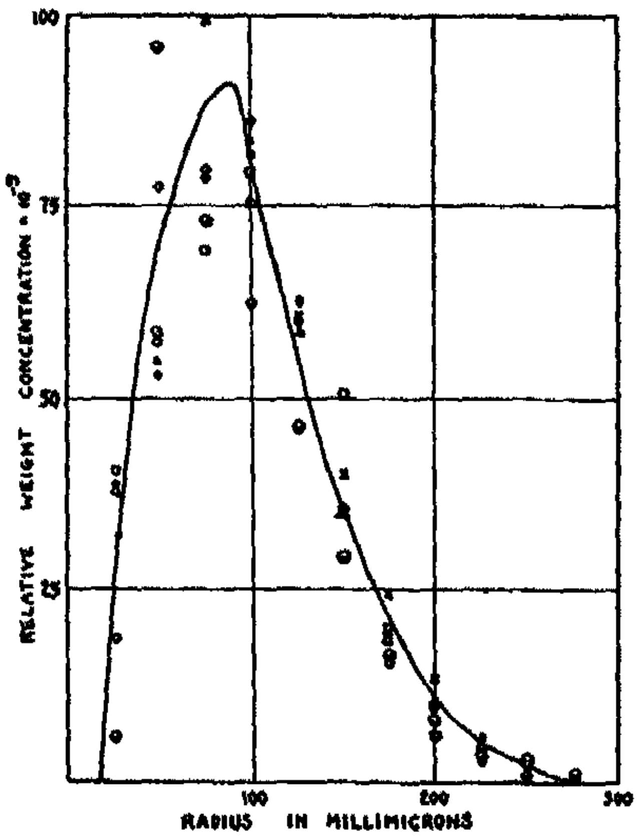

FIG. 4. The weight-distribution curve for the series of emulsions, as calculated from the weight-optical curves of figure 1 and the generalized curve of figure 3.

Figure 4 presents the weight-distribution curves for the emulsions used, as calculated from the experimental weight-optical distribution curves by means of the generalized curve of figure 3.

The relation of these experimental results to theoretical calculations of light scattering will be discussed in a later publication.

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ULTRAFILTRATION THROUGH CELLOPHANE OF POROSITY ADJUSTED BETWEEN COLLOIDAL AND MOLECULAR DIMENSIONS[1]

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Some years ago we found that the pores of commercial Cellophane swollen in water happened to be of such size that ordinary molecules, such as sucrose or anthracene, passed through freely, while all known colloids were partially or wholly held back (5). Now we find that Cellophane, Sylphrap, and Viscacelle, as at present manufactured, possess distinctly finer pores, so that a portion even of sucrose or potassium chloride is held back on ultrafiltration.

Such cellulose membranes possess the great advantage that they are chemically indifferent and that the same membrane can be used for a series of different solutions or solvents without noticeable change in porosity, provided that the transition from one solvent to another is made by washing through with mutually miscible liquids. Such Cellophane serves as a most useful test to prove the presence or absence of colloidal matter, or as a means of measuring the amount of crystalloid present in the colloidal solution. It was very convenient that unlimited supplies of such uniform material were commercially available, requiring no troublesome laboratory preparation. Naturally, care had to be taken to obtain Cellophane, etc., which had not been waterproofed in any way.

Formerly we were interested in the problem of adjusting the size of pores down to finer and finer molecular dimensions, so as to separate the ordinary large molecules, such as sucrose or potassium chloride, from small molecules, such as methyl alcohol and water. This was readily achieved by deposition of collodion or viscose in the pores by filtering the necessary amount of their solutions through the Cellophane, thus producing molecular sieves of any desired fineness. Cellophane which has not been swollen in water is practically air-tight.

Now that commercial membranes are denser, we are faced with the opposite problem of finding some simple method of restoring them to the invaluable position they formerly occupied, intermediate between ordinary

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[1] Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11–13, 1936.

recognized molecules and the finer colloidal particles. In a paper on dyeing Morton (6) reported that the permeability of Viscacelle is greatly increased by a treatment with sodium hydroxide. In the present investigation, we have found that solutions of zinc chloride of particular concentration are most satisfactory for achieving our purpose. We are greatly indebted to the manufacturers of Cellophane, Sylphrap, and Viscacelle for samples and even for a specimen of Cellophane that never had been allowed to dry.

The subject of ultrafiltration is not quite simple. This was well brought out in a valuable and careful study by Ershler (1), who studied the effect of stirring upon the apparent permeability of a collodion membrane.[2] We have been led to investigate systematically the effects of pressure and of stirring upon the simplest case, that of a non-electrolyte such as sucrose. Other observations refer to the effect of molecular size and of the electrical effects with salt solutions or charged colloidal sols. We have also taken occasion to measure the hydration of pectin.

I. CONTROL OR ADJUSTMENT OF THE POROSITY OF CELLULOSE MEMBRANES

Not only is modern sheet cellulose (Cellophane, etc.) denser than formerly, but, as was pointed out in previous communications, Cellophane swells less after aging, or at higher temperature (3). Freshly manufactured Cellophane may swell as much as threefold in thickness (not in length, nor more than a few per cent in width), but after keeping for several years it may swell to less than double its thickness. The change in thickness goes parallel with change in porosity. Dry No. 300 Cellophane and Sylphrap are 0.0009 in. or 0.023 mm. thick; this was the material chiefly used in the present investigation. No. 600 Cellophane, previously used, filters more slowly. It also retains distinctly (at least three-halves) more solute.

Swelling in water

With a new and an older sample of Cellophane No. 600, the thickness in inches upon swelling in water for fifteen minutes and for twenty-four hours at three different temperatures was as shown in table 1.

With No. 300 Cellophane swollen in water the dimensions were the same at fifteen minutes as after three hours, as shown in table 2. Thus the Cellophane swollen at room temperature very slowly shrinks again at 100°C.

The porosity and the rate of ultrafiltration also depend upon the tem-

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[2] We are in agreement with his main conclusions except for a few sentences in the first two paragraphs of his paper in which, since his membranes were of unsuitable porosity and were, of course, not suitable for distinguishing between molecules and particles, he stated the *non sequitur* that Kistler's coarse ones likewise were not.

perature of swelling in water. Thus, at 200 pounds pressure, when 3 per cent sucrose was filtered through 24 sq. cm. of filter:

CELLOPHANE SWOLLEN AT	RATE OF ULTRAFILTRATION	SUCROSE RETAINED[3]
°C.	*grams per minute*	*per cent*
25	0.38	13
100	0.22	22.0

Swelling in sodium hydroxide solution

The porosity of membranes swollen in sodium hydroxide is dependent upon both temperature and concentration. In general, an optimum concentration exists for each temperature, the optimum being more pronounced and the swelling greater at low than at high temperatures. Membranes swollen at low temperatures are more permeable than those swollen first at high temperatures and then brought to lower temperatures, although lowering the temperature after the initial swelling does cause an increase.

TABLE 1

Swelling of No. 600 Cellophane in water

TREATMENT OF CELLOPHANE	NEW SAMPLE (DRY 0.0016 IN.)		OLD SAMPLE (DRY 0.0016 IN.)	
	15 min.	24 hrs.	15 min.	24 hrs.
	inches	*inches*	*inches*	*inches*
Water at 0°C.	0.0035	0.0035	0.0033	0.0034
Water at room temperature	0.0035	0.0035	0.0032	0.0034
Water at 100°C.	0.0030	0.0030	0.0028	0.0029

TABLE 2

Swelling of No. 300 Cellophane in water

TREATMENT OF CELLOPHANE	DIMENSIONS
Original	40 x 76 x 0.023 mm.
Water at room temperature (25°C.)	46.5 x 76 x 0.051 mm.
Water at 100°C.	45 x 76 x 0.038 mm.
Water at 100°C., then 2 days at 25°C.	45 x 76 x 0.038 mm.
Room temperature, then 3 hours at 100°C.	45 x 76 x 0.045 mm.

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[3] For the method of calculation and definition of per cent sucrose retained, $1 - \phi$, see part II, below. All ultrafiltrations were carried out with the apparatus previously described, similar to that supplied by Vereinigung Göttinger Werke, Göttingen, with electrical stirrer, which was always used except when otherwise mentioned. The interior was silver-plated, and such parts as the stirrer and filter bed were replaced by pure silver. When electrolytes were present, the plated parts were coated with paraffin. Pressures were obtained from a cylinder of nitrogen.

Conversely, swelling initially at low temperatures and then heating causes a decrease, but not of sufficient magnitude to give the same result as is obtained with the reverse procedure.

Membranes swollen in sodium hydroxide have a tendency to become very brittle, especially when the swelling is large, and so are not satisfactory over a wide range of porosity.

Neale (7) has discussed the swelling of viscose cellulose sheets and presents a plausible theory as to the mechanism. The hysteresis effects just pointed out cannot, however, be explained on the basis of osmotic and Donnan effects.

Swelling in zinc chloride solution

Zinc chloride is a remarkable swelling agent in that its effectiveness is almost confined to the range 60 to 65 per cent. Kahlbaum's best grade of anhydrous zinc chloride was employed, and analysis confirmed its purity and freedom from water.

Detail of procedure for swelling in zinc chloride. The membranes were swollen by first pouring enough of the solution into a flat dish to cover the bottom, then putting in the Cellophane, and finally pouring on the remainder of the solution. Sufficient solution was used to cover the membrane completely, and care was exercised to prevent its adhering to the bottom of the dish. This was accomplished by simultaneously tilting and rotating the dish for the first ten minutes. A coating of paraffin on the bottom of the dish is desirable, but not necessary. At the completion of swelling, i.e., after fifteen to twenty minutes, the excess liquid was carefully pipetted off so as to leave the membrane lying flat. Wrinkling of the surface may lead to cracking of the membrane upon removal of the swelling agent. After removal of the excess liquid, water was poured in and the dish was rotated to speed up diffusion. After a few minutes the membrane was removed and washed free from zinc chloride by means of dilute hydrochloric acid. The acid was then washed out with distilled water. Determination of the ash left upon burning the treated membrane indicated that satisfactory removal of zinc had been effected.

Effect of zinc chloride. As criteria of the extent and effectiveness of swelling we have used the thickness, the rate of filtration, and the per cent of sucrose retained when a 3 per cent sucrose solution is filtered through the membrane. Thickness is significant except at the higher concentrations of zinc chloride, where the surface of the membrane tends to slough off in layers and the softening likewise renders the result uncertain. If insufficient time is allowed for swelling, the sloughing may be uneven. Swelling for long periods instead of fifteen minutes increases sloughing. Sylphrap swells more than Cellophane, and its surface remains smooth. Viscacelle swells less and sloughs more than Cellophane. The swelling increases steadily with lowering of temperature from 40° down to 10°C., but 3°C. is too low for appreciable swelling in fifteen minutes.

Table 3 shows the degree of reproducibility of swelling in particular concentrations of zinc chloride as judged by the rate of flow of water in grams per minute.

TABLE 3

Effect of swelling No. 300 Cellophane in zinc chloride solutions upon the rate of filtration of water at various pressures (pounds per square inch)

CONCENTRATION OF $ZnCl_2$	RATE OF FILTRATION AT PRESSURES OF			
	40 lbs.	80 lbs.	120 lbs.	200 lbs.
per cent				
60		0.267	0.375	0.558
60		0.285	0.397	0.580
63.0	0.467	1.037	1.408	
63.0	0.450	1.009	1.403	
63.8	1.011	1.968	2.850	
63.8	0.698	1.298	1.782	
64.0	2.125	4.31	5.97	
64.0	1.56	3.13	4.24	

TABLE 4

Increase of thickness on swelling

CONCENTRATION OF $ZnCl_2$	THICKNESS OF		
	Cellophane	Sylphrap	Viscacelle
per cent	*inches*	*inches*	*inches*
Original dry	0.0009	0.0009	0.0009
60	0.0030	0.0035	0.0030
61	0.0040 (after use 0.0035)	0.0043	0.0037
62	0.0046	0.0054	0.0045
63	0.0060*	0.0082**	
64	0.0060* (after use 0.0050)	0.0080**	(0.0055)
65	>0.0060		

* Increase in all dimensions; surface slightly roughened.

** Surface still smooth after 15 minutes. However, after 17 hours the surface is sloughed off.

The thickness increases on swelling as shown in table 4. With the membranes swollen in 63 per cent and 64 per cent solution, filtration of a 3 per cent sucrose until two-thirds or three-quarters had passed through left a residue not more concentrated than 3.01, 3.06, and 3.02 per cent, respectively. Likewise, 3 per cent potassium chloride and 3 per cent potassium iodate passed through unaltered, within the error of analysis. The Cellophane swelled distinctly, both in length and breadth. The rate of filtration for Sylphrap was about three-fifths, and for Viscacelle about twofifths that for Cellophane, but the pressure relations were similar to those in table 3. The pressure of 200 pounds appears to compact the membranes, so that the rates are no longer proportional to the pressure, either with water or with solutions.

The effect of pressure upon the retention of sucrose as shown in table 5 will be discussed in part II. Figure 1 shows the pressure dependence of the rates for Cellophane taken from table 5.

As is ordinarily the case with gels, the swollen membranes shrink upon drying and do not regain their original porosity. Experiments upon Cellophane which had never been dried in the course of manufacture were run to determine to what extent the structure might be allowed to collapse without this collapse becoming permanent. Accordingly, strips of the Cellophane were weighed, soaked in glycerol solutions of various concentrations, and then dried and reweighed. The glycerol was then washed out and the strips were weighed, dried, and weighed for a fourth time. The percentages of free space occupied by the glycerol and the percentage of space regained upon reswelling were calculated as follows:

TABLE 5

Effect of swelling No. 300 Cellophane in zinc chloride solution upon the rate of filtration (R in grams per minute) and per cent of sucrose retained from 3 per cent sucrose solution

CONCENTRATION OF $ZnCl_2$	THICKNESS	PER CENT OF SUCROSE RETAINED AND RATE OF FILTRATION AT PRESSURES OF							
		40 lbs.		80 lbs.		120 lbs.		200 lbs.	
		Per cent	R	Per cent	R	Per cent	R	Per cent	R
per cent	*inches*								
0	0.0009	4.3	0.06	9.2	0.14	13.7	0.20	14.5	0.35
61	0.0040	3.7	0.17	5.8	0.34	7.1	0.51	7.3	0.65
64	0.0060	0.0	1.14	0.0	2.10	0.0	2.62	0.0	3.24
65		0.0	1.53	0.0	3.12	0.0	3.97	0.0	

Per cent of space kept filled while dry..	0.0	9.0	20.3	30.3	41.4	51.5
Per cent of space regained on swelling..	36.9	53.3	84.6	94.4	96.0	98.2

It is apparent that essentially complete recovery of the original form results if 30 per cent or more of the free space is filled while dry. This affords a means of preserving membranes of this type, if it is necessary to dry them. They may be kept in glycerol solution for some time without change also. In water decomposition takes place after a few days.

When membranes were soaked in 50 per cent glycerol and then dried, after seven weeks the glycerol was washed out and the membranes were found to have retained at least nine-tenths of the previous rate of filtration and to have recovered from previous higher pressures.

The experiment also shows that the swelling process with zinc chloride probably does not consist merely in a breaking down of the old structure, but in a setting up of a new structure. That is, the gel particles have not been torn apart, owing to strains within the gel, but rather have been allowed to orientate in such a manner as to relieve the stress. Upon washing out the zinc chloride the ability to orientate is lost, and the new orientation becomes the preferred one. Thereafter the tendency is to return to this form after compression.

The advantages of the method of preparing membranes may be briefly stated. Assuming that no new pores are opened, one may conclude that in a series of membranes the number of pores and the relative pore sizes may be readily calculated from areas before and after swelling, and from rates of flow of water.

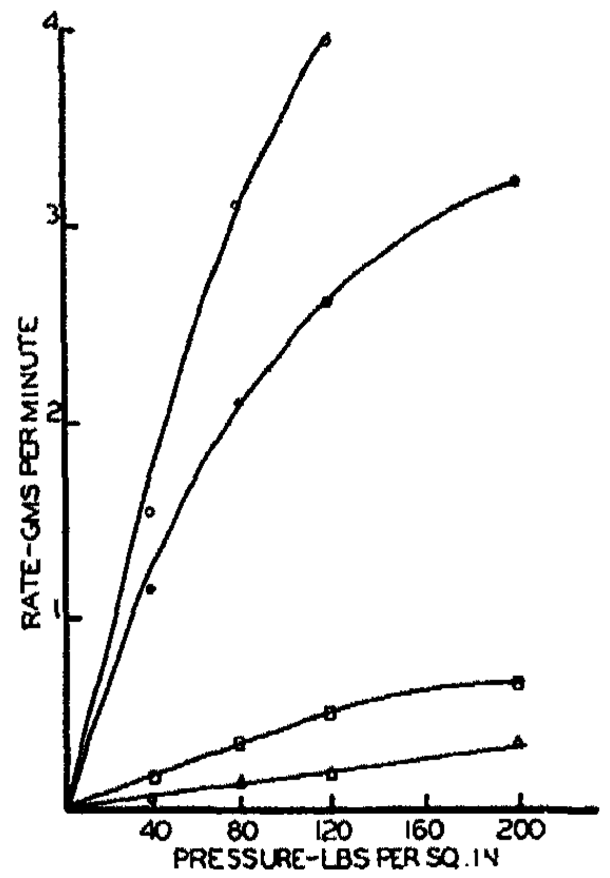

FIG. 1. Effect of zinc chloride on porosity of Cellophane. □, water; △, 61 per cent zinc chloride; ●, 64 per cent zinc chloride; ○, 65 per cent zinc chloride.

The convenience of the method makes it especially applicable when only a few membranes of varying pore sizes are desired.

II. THE DEPENDENCE OF RETENTION OF ELECTROLYTES AND OF NON-ELECTROLYTES UPON MOLECULAR SIZE, CONCENTRATION, RATE OF STIRRING, PRESSURE, AND OTHER FACTORS

The retention or sieving constant $(1-\phi)$ is defined by Manegold (2) as the constant proportion of solute held back throughout a given filtration,

ϕ being set equal to the ratio between the concentration of original solution and residue for a small amount of filtration. If x_1 and x_2 are the concentrations of successive samples of residue of solution remaining above the filter whose volumes are v_1 and v_2, it is readily shown that $x_1/x_2 = (v_1/v_2)\phi$, where ϕ is identical with that deduced in Manegold's more complicated expression. Retention will therefore be expressed as $100(1-\phi)$ per cent. In all cases approximately 50 g. was placed in the filter, which had been previously rinsed with several portions of the same solution. After standing a small sample was removed for analysis immediately before filtration began. The residue after filtration was also analyzed.

Effect of size of molecule

Table 6 is of interest in showing how ordinary Cellophane swollen in water discriminates between molecules of progressively larger size. At 350 pounds pressure the rate for the first three was 0.47 g. per minute per 24 cm.^{2}; for raffinose at 200 pounds, 0.35 g.

TABLE 6

Percentage of different molecules held back by ordinary Cellophane

SOLUTE	INITIAL CONCENTRATION	FINAL CONCENTRATION	PER CENT RETAINED
	per cent	*per cent*	
Glycerol (C_3)	2.96	3.02	2.2
Dextrose (C_6)	2.86	3.20	7.0
Sucrose (C_{12})	2.96	3.53	14.9
Raffinose (C_{18})	2.96	3.58	18.1

Effect of concentration, and the contrast between electrolytes and non-electrolytes

Table 7 shows how sucrose compares with a number of electrolytes, and also shows the enormous effect of dilution upon electrolytes first discovered by Ershler for collodion membranes of slightly greater porosity. All these solutions were filtered through the same actual piece of Cellophane at 200 pounds per square inch, except for the viscous 48 per cent sucrose, where 340 pounds were used. The calculation of ϕ is necessarily inaccurate for the dilute potassium iodate, because of the change in ϕ with concentration.

Figure 2 contrasts the relative constancy of retention of sucrose with the great effect of dilution upon an electrolyte such as potassium iodate. Two hundred pounds pressure and the same rate of stirring were used throughout. The most dilute solution of sucrose was 0.05 per cent, where the accuracy of analysis is impaired.

The high retention of very dilute electrolytes is probably due to the charges upon the walls of the pores of the membrane, in accordance with the principle of Donnan equilibrium,[4] the effect being suppressed by sufficient concentration of any electrolyte, as is shown at the end of table 7.

TABLE 7

Per cent retained, 100(1 − φ), for a series of solutions filtered through the same piece of Cellophane

DATE	RATE	SOLUTION	PER CENT RETAINED
December 7, 1935	0.39	2.94% KCl	1.92
December 7, 1935	0.38	3.01% KIO_3	1.78
December 14, 1935	0.33	3.01% sucrose	14.50
December 14, 1935	0.37	0.97% KIO_3	3.06
December 24, 1935	0.35	0.083% KIO_3	48.
December 24, 1935	0.35	0.92% CdI_2	3.45
December 24, 1935	0.29	24.3 % CdI_2	7.55
December 26, 1935	0.31	5.30% $NaIO_3$	4.08
December 27, 1935	0.043	48.23% sucrose	8.59
January 7, 1936	0.27	2.99% HIO_3	5.54
January 18, 1936	0.27	3.01% sucrose	14.16
January 22, 1936	0.27	2.94% KCl	3.57
January 23, 1936	0.29	2.97% KIO_3	4.5
Another specimen		0.087% KIO_3 + 0.74% NaCl	7.1
Another specimen		3.0% $NaIO_3$ + 10% NaCl	6.1
Another specimen		17.7% KCl	0.9

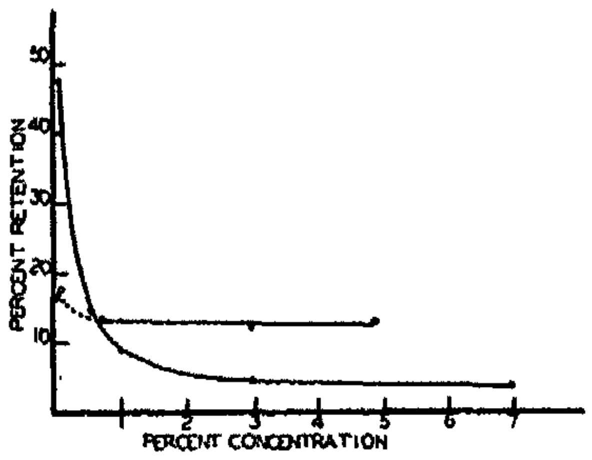

Fig. 2

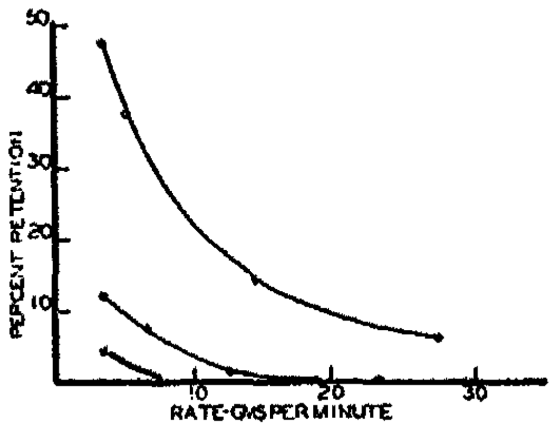

Fig. 3

Fig. 2. *Dependence of retention on solute concentration.* ○, sucrose; ●, potassium iodate.

Fig. 3. Dependence of retention on porosity; retention of sucrose and of potassium iodate of two concentrations by membranes of different porosities. ●, 3 per cent sucrose; ○, 0.08 per cent potassium iodate; ×, 3 per cent potassium iodate.

The effect of the charge in keeping dilute electrolytes away and thus simulating a reduced size of pore may be compared with the similar effect in

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[4] Other influences of Donnan distribution in ultrafiltration were pointed out and discussed by J. W. McBain and W. McClatchie (J. Am. Chem. Soc. 55, 1315 (1933)). For its suppression see reference 3.

dyeing. If so, the rôle of added salt in dyeing is not that of a dispersing agent, as has often been suggested, but rather that the effective pore size is restored.

Effect of varying porosity on retention

Figure 3 exhibits for sucrose and potassium iodate the effect of steadily increasing porosity, as measured by rate of flow at 200 pounds and 140 R.P.M., in permitting more and more complete passage of the solute. It is evident that long after sucrose is passing completely, there is still a marked effect upon the very dilute potassium iodate. For higher ionic concentration the potassium iodate curve lies wholly below that of sucrose. In other words, the exaggerated effect in the dilute electrolyte is a Donnan effect.

Use of membranes for detecting presence of colloid

The data in this paper clearly show that membranes must be suitably chosen and employed if they are to detect and measure the presence of colloid with certainty. It must be shown that the particular membrane is sufficiently porous to pass quantitatively all ordinary molecules, including electrolytes in which the ionic concentration is sufficiently high to suppress Donnan effects. In a previous communication (4) it was concluded that nearly saturated solutions of sodium and potassium iodates contained a distinct proportion of colloid. However, reëxamination of the original records shows that the experiments assembled in that communication were spread over a series of years, and that although the original Cellophane was indeed tested for its complete permeability to electrolytes and non-electrolytes, the much later experiments on the iodates had been carried out with a later and evidently much denser sample of Cellophane. There therefore remains no definite evidence for the presence of appreciable colloid in these solutions, although it may be significant that the retention of cadmium iodide in concentrated solution is twice that in more dilute solution.

Effect of pressure and rate of stirring

Ershler has convincingly pointed out that complete absence of stirring must soon suppress all minor differences between the composition of filtrate and original solution, because of the automatic building up of the compensatingly high concentration in the layer of liquid resting upon the upper surface of the filter.

We extend this to point out in the data here deduced that it is always a race between the rate at which the solution is being bodily thrust through and the rate at which any molecule or particle which cannot freely pass through all portions of the membrane is escaping from its neighborhood, through electrical influences (Donnan effect), through diffusion, and through convection. Hence, the higher the pressure and the higher the viscosity, and the higher the molecular weight, the greater must be the rate of stirring in order to allow the membrane to exhibit its selective action. Even for a non-electrolyte such as sucrose, these effects are intriguing, as is shown in figure 4. It is quite clear that unless the pores are large enough to pass all similar molecules freely ($1 - \phi = 0$), great care must be taken in interpreting quantitatively the retentions observed under the actual conditions of the filtration.

In figure 4 it is evident that maximum retention occurs when the pressure is 200 pounds per square inch (rate of filtration is 0.44 g. per minute) at the fastest practicable rate of stirring, a rate faster than that for which

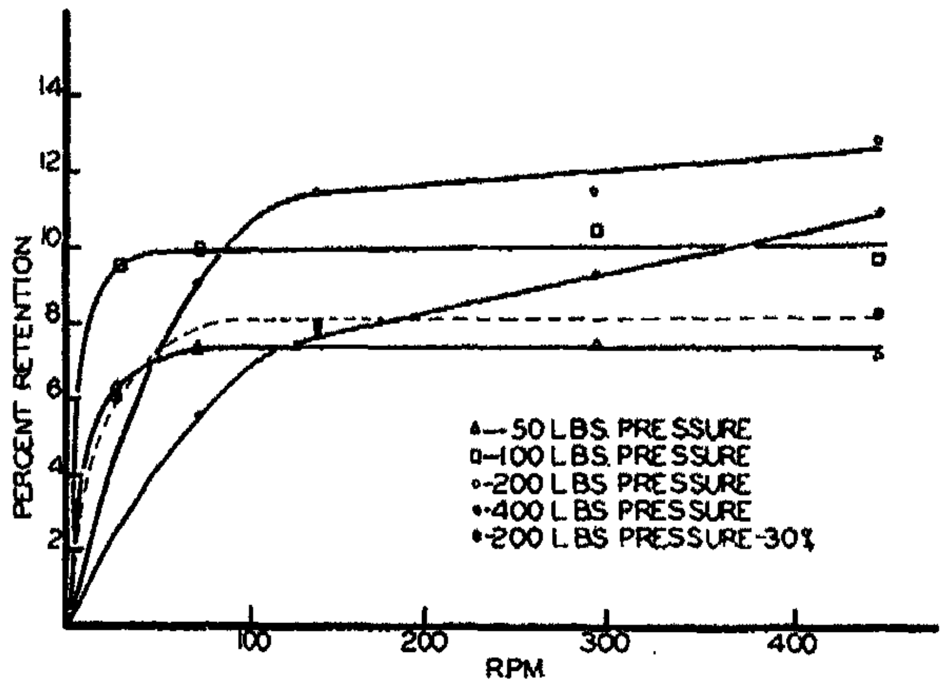

FIG. 4. Dependence of retention on pressure and rate of stirring; percentage of sucrose retained in filtration through ordinary Cellophane at various pressures and rates of stirring. Full lines refer to 3 per cent sucrose; the dashed line to 30 per cent sucrose at 200 pounds pressure.

the instrument is commercially supplied. The position of the curve for 30 per cent sucrose is predictable from the ratio of viscosities or of rates of filtration when compared with 3 per cent sucrose, except at the lowest rate of stirring. Some of the effects are similar to those discussed in the theory of dependence of heterogeneous reaction upon rate of stirring.

SUMMARY

1. Commercial sheet cellulose is much less porous than formerly. It is now necessary to swell in zinc chloride solutions exceeding 63 per cent zinc chloride (37 per cent water), in order to make these membranes freely permeable to all ordinary molecules. Further, the ionic concentration must be sufficient to suppress Donnan effects in the case of very dilute electro-

lytes, including colloids. Contrary to a previous intimation, owing to this change in a commercial membrane there remains no certain evidence for colloid in iodate solutions, although some is indicated in very concentrated aqueous cadmium iodide.

2. With incompletely permeable membranes such as ordinary cellulose, interesting influences of size of molecule, concentration, rate of stirring, pressure, viscosity, and diffusion are observed.

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STUDIES IN THIXOTROPY. I

DEVELOPMENT OF A NEW METHOD FOR MEASURING PARTICLE-SIZE DISTRIBUTION IN COLLOIDAL SYSTEMS[1]

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INTRODUCTION

In spite of their wide occurrence throughout colloid chemistry, calling forth many investigations, our knowledge of the mechanism of sol–gel transformations and of the structure of the gel state may be described as very rudimentary. This is particularly true in the case of the isothermal reversible sol–gel transformation known as thixotropy.

Thixotropy was first formally observed in iron oxide sols (17), but it has since been reported in many of the hydrous oxide sols as well as in systems as diverse as clay suspensions and heather honey.

For a complete exposition in English of the work on thixotropy we refer the reader to a recent comprehensive monograph by Freundlich (3). Pryce-Jones (11) offers a much shorter review in connection with his studies on the thixotropy of paint.

The characteristic property of a thixotropic system is an increase in its viscosity with time, immediately following mechanical action upon it, all other conditions being constant. Loosely speaking, as long as the system retains those properties ordinarily ascribed to a liquid, it is considered a sol and when it becomes more or less rigid, owing to its constantly increasing viscosity, it is termed a gel. The exact meaning to be attached to the terms "sol" and "gel" will be discussed in a future paper in this series.

Since this isothermal transition from sol to gel appears to be continuous, and since the only difference found to date between sol and gel is mechanical, it is reasonable to conclude that during the period of gelation some type of structure with mechanical resistance to shear is being built up out of the constituent particles of the sol. This picture would postulate a two-phase system, but the type of structure and its mode of formation are subject to discussion.

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[1] Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

Despite the fact that the chief difference between sol and gel is mechanical and is due to the formation of a structure of some kind out of the constituent particles, there has as yet been no systematic investigation of the effect of particle size upon thixotropy. The importance of this variable has been recognized by Freundlich (3), Russell (12), and Bradfield (1). In idealized form, an investigation of the effect of particle size upon thixotropy should start with a polydispersed system which exhibits the phenomenon, separate the particles into several fractions depending upon their size, and determine the velocity of the sol–gel transformation upon each particle-size fraction at various values of concentration of the dispersed phase, concentration of electrolyte, pH, temperature, etc. The results should be of importance in furthering our interpretation of the mechanism involved and in picturing the final structure. It is the purpose of the present series of articles to describe such an investigation.

The system chosen should first of all exhibit thixotropy to a high degree, exist over a suitable range of particle sizes, and be very stable and reversible, showing a minimum of aging effects. No other system meets these requirements to the same remarkable extent as the clay mineral bentonite of the Wyoming variety.

It became apparent at the start that the initial phase of the investigation would have to concern itself with the development of a rational method for separating a polydispersed system into various particle-size fractions and in turn measuring the distribution of particle sizes in each of these fractions, since no satisfactory method is available at present for such a fractionation in the colloidal range. The remainder of the present paper will describe the method which has been developed for this purpose, and following papers in the series will disclose experimental results and discuss their significance to thixotropy and gel structure in general.

PREVIOUS MEASUREMENT OF PARTICLE-SIZE DISTRIBUTION CURVES

Although a dozen or more methods may be used to determine absolute particle size in a polydispersed system (4), sedimentation rate and sedimentation equilibrium methods are the only ones known for determining the form and value of the particle-size distribution function in a given suspension.

Odén (10) gives the most elaborate description of sedimentation methods. Unfortunately these become increasingly difficult to employ as the dispersed phase approaches colloidal size. Svedberg and Estrup (15) measured particle-size distribution directly in the ultramicroscope by noting rates of fall, but such a method is tedious and needs the questionable assumption that all particles are visible. Westgren (18) combined sedimentation rate with sedimentation equilibrium and presented distribution curves on gold sols, but his measurements were complicated by unavoidable diffusion effects. The basket-type centrifuge used by Marshall (7) to determine distribution curves by essentially the same procedure used in gravity fields cannot exert a strong enough field to settle colloidal particles with equivalent spherical diameters of less than 100 mμ.

Ultracentrifugal methods as developed by Svedberg and associates (16) are probably the best methods in use at the present time for determination of the distribution function by sedimentation rate or sedimentation equilibrium methods. Unfortunately, the equipment is complicated and so expensive that at present it is enjoyed by but few laboratories in the whole world. A further disadvantage of the ultracentrifuge in the present instance is that it possesses no capacity for making fractionations upon a large quantity of material. McBain (8) has recently been developing the air-driven spinning top as an ultracentrifuge, but while this device is less expensive than a Svedberg machine, it appears to possess no capacity for fractionations.

Of all standard centrifuges on the market the so-called supercentrifuge alone possesses the ability to settle out the finest particles in colloidal sols. Although the supercentrifuge has been used before in colloidal research in clays, notably by Moore, Fry, and Middleton (9) and Bradfield (2), it has never been adapted to the quantitative measurement of distribution curves. Lenoir (6) investigated the use of a laboratory supercentrifuge of the Sharples type for this purpose. The Sharples machine is reasonably priced, and if a technique of evaluating the distribution function by its use could be developed, a valuable tool would be available to many workers. A further advantage of the supercentrifuge in the present instance is its adaptability to fractionations. Lenoir's results indicated that the supercentrifuge had possibilities, but, owing to certain theoretical objections to his calculations, his distribution curves are only of relative significance. While retaining the essential features of the Lenoir experimental technique, the present authors have developed a new method of calculation.

DEVELOPMENT OF THEORY UNDERLYING THE USE OF THE SUPERCENTRIFUGE IN DETERMINING DISTRIBUTION CURVES

The most convenient method for describing a polydispersed system of spherical particles is that proposed by Odén (10). In a given weight of sol let there be T grams of dispersed phase. Since these T grams consist of a great many sizes we can in general plot a curve of percentage of total weight (P) of particles of size below a given diameter (D) against that diameter. Figure 1 represents a system, the largest particle of which is $D_{\text{max.}}$, 100 per cent of the total weight of dispersed phase being below this diameter. It is often more convenient to represent the system by a curve obtained by plotting a new function $f(D)$ against D where $f(D)$ is defined as dP/dD obtained as the slope of the curve in figure 1. Figure 2 represents the same system as figure 1, with the distribution function dP/dD plotted against D. The area under this curve on figure 2 between D_1 and D_2 represents the percentage of a given weight of dispersed phase having diameters between D_1 and D_2. The differential percentage of total weight having a given diameter D is $\left(\frac{dP}{dD}\right) dD$ taken at the value of D in question, and the weight of particles having a given diameter D is $T\left(\frac{dP}{dD}\right)\frac{dD}{100}$. In dealing with anisotropic particles such as are met in the case of clays, the concept of "equivalent spherical radius" must be employed. The geometric significance of this equivalent spherical radius has been described for the important case of discs by L. Squires and W. Squires (13), and found to be a function of the diameter and thickness of the disc. The significance of this anisotropy in the present work will be discussed in a later article.

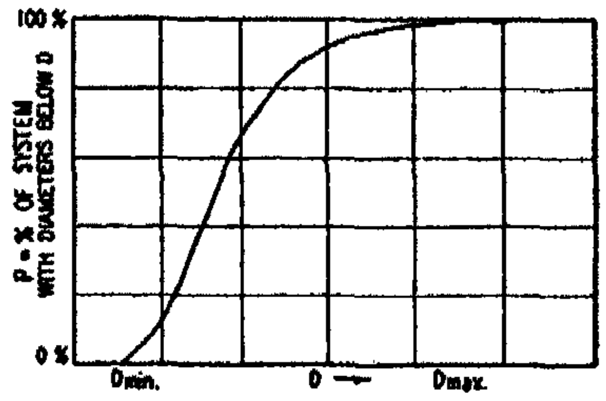

Fig. 1

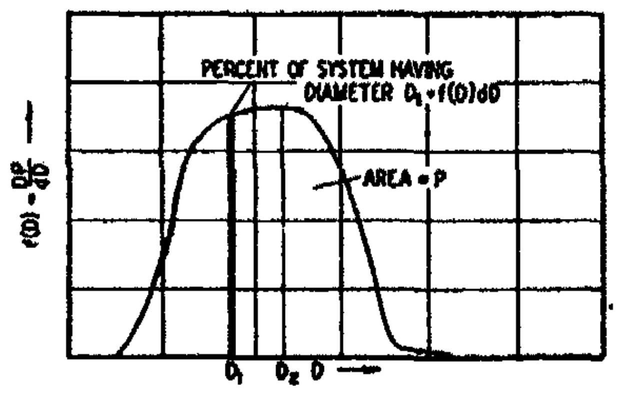

Fig. 2

Fig. 1. Representation of a system, the largest particle of which is $D_{max.}$, 100 per cent of the total weight of dispersed phase being below this diameter.

Fig. 2. Representation of the same system as in figure 1, with the distribution function dP/dD plotted against D.

The supercentrifuge consists of a balanced vertical bowl coupled to an electric motor drive. Figure 3 is a schematic cross section of the bowl, emphasizing the essentials of the flow. The suspension is fed into the rapidly rotating bowl at the point marked "liquid feed". It then passes two straightening vanes at right angles to each other and flows up the sides of the bowl in a film and out of the bowl over the edge of the weir marked "exit". The thickness of the film on the walls is determined by the diameter of the weir at the top.

Under the influence of centrifugal force the particles settle out onto the walls of the bowl, which are covered with a removable celluloid liner. When a convenient amount of suspension has flowed through the bowl, the feed is cut off and the liner removed. The settled particles are scraped off at definite distances up the bowl and weighed. From these data, and knowing the rate at which the suspension was fed, the rotational velocity of the bowl, the temperature, the densities of the dispersed phase and dispersing medium, and the dimensions of the bowl, the distribution curve for the suspension is calculated.

Figure 3 also shows the path of settling of the particle. In general this will be a curve, since the particle has a velocity parallel to the axis of rotation due to the flow through the bowl and a velocity perpendicular to the axis of rotation due to the centrifugal force. Any particle p of diameter D starting to settle at a distance of X_0 from the axis of rotation will come to rest upon the wall of the bowl at some definite point A at a distance y from the entrance. Under constant settling conditions (temperature, angular velocity of bowl, rate of feed) the relation between X_0, y, and D is definite and may be expressed as

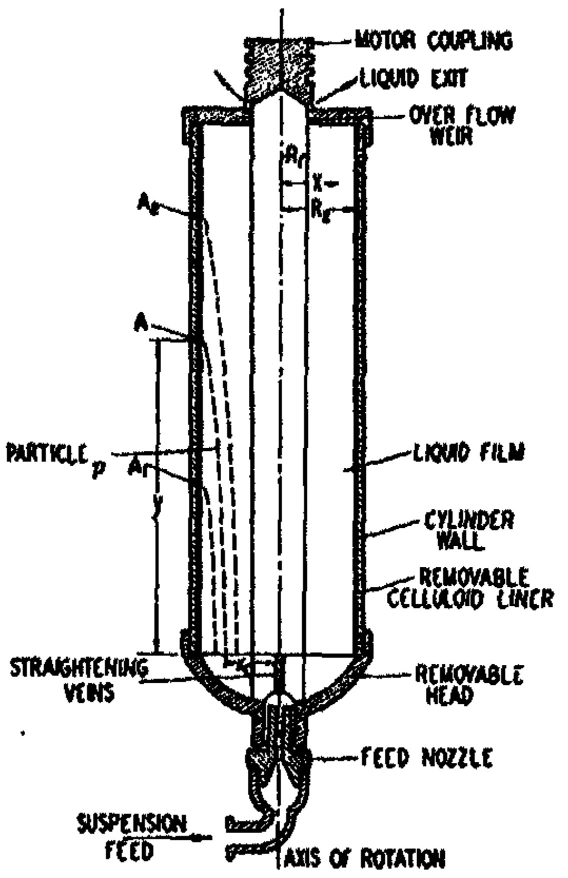

Fig. 3. Section through supercentrifuge cylinder

$$F(X_0, y, D) = 0 \tag{1}$$

or

$$X_0 = \phi(y, D) \tag{2}$$

It is important to note that any particle similar to p starting to settle at some larger value of X_0 (i.e., at a point nearer the wall) will settle out on the wall at some point A_1 before point A is reached. On the other hand, a particle similar to p starting to settle at a smaller value of X_0 will come to rest at some point A_2 beyond A.

If the suspension contains a number of particles, N_D, similar to p flowing into the bowl, and if we consider the suspension uniformly mixed at the time settling begins, the number of these particles N'_D which have settled out onto the wall before point A is reached is given by the product of N_D and the ratio of the total volume of suspension flowing across the area enclosed by the concentric circles of radii X_0 and R_1 to the total amount of suspension fed into the bowl.

$$N'_D = N_D \frac{\int_{X_0}^{R_1} u\mathrm{d}A}{Q} = N_D \frac{\int_{X_0}^{R_1} u2\pi X_0\mathrm{d}X_0}{Q} \tag{3}$$

A = cross-sectional area of film in square centimeters,
u = local velocity of flow parallel to the axis of rotation at any point X_0 in the film in centimeters per second,
Q = volumetric rate of feed in cubic centimeters per second, and
R_1 = radius of the bowl less the thickness of the celluloid liner.

The weight of the particles settled out is proportional to their number so that

$$W'_D = W_D \frac{\int_{X_0}^{R_1} u2\pi X_0\mathrm{d}X_0}{Q} \tag{4}$$

where W'_D is the weight of particles similar to p which have settled out onto the wall and W_D is the total weight of particles similar to p which have flowed into the bowl.

Consider now feeding into the centrifuge T grams of a polydispersed system the distribution function of which is known. Then up to any point, y, on the liner, that portion of the cumulative weight due to particles of diameter D similar to p which have settled out will be:

$$W'_D = T\left[\frac{\int_{X_0}^{R_1} u2\pi X_0\mathrm{d}X_0}{Q}\right]\left(\frac{\mathrm{d}P}{\mathrm{d}D}\right)\frac{\mathrm{d}D}{100} \tag{5}$$

The total weight due to particles of all diameters settled out up to a point y will be denoted by $W_{(y)}$ and is equal to the sum of the W_D terms due to every particle size.

$$W_{(y)} = \sum_{D=D_{\text{min.}}}^{D=D_{\text{max.}}} W'_D = T\sum_{D=D_{\text{min.}}}^{D=D_{\text{max.}}}\left[\frac{\int_{X_0}^{R_1} u2\pi X_0\mathrm{d}X_0}{Q}\right]\left(\frac{\mathrm{d}P}{\mathrm{d}D}\right)\frac{\mathrm{d}D}{100} \tag{6}$$

The summation can be expressed as a definite integral.

$$W_{(y)} = T\int_{D=D_{\text{min.}}}^{D=D_{\text{max.}}}\left[\frac{\int_{X_0}^{R_1} u2\pi X_0\mathrm{d}X_0}{Q}\right]\frac{f(D)}{100}\,\mathrm{d}D \tag{7}$$

In this equation X_0 is calculated as a function of D at any value of y by equation 2.

Having obtained experimentally values of W at various values of y, knowing u as a function of X_0, and knowing the form of ϕ in equation 2, we can establish the form of $f(D)$ from this integral equation.

To simplify the first calculations it was decided to neglect the effect of variation in the local velocity of flow of the suspension over the cross section of the film at the entrance to the bowl, but to take this into account when considering the settling path of the particles.

As equation 3 stands it is perfectly general and would apply to any kind of a velocity gradient found in the film. With the simplification mentioned N_D' will be given by the product of N_D and the ratio of the area enclosed by the concentric circles of radii X_0 and R_2 to the total cross-sectional area of the film. It may be seen that the result expressed in equation 8 is equivalent to assuming that at the entrance to the bowl where settling starts a constant amount of dispersed phase flows across every increment of area. Under these conditions equation 3 reduces to:

$$N_D' = N_D \left[\frac{R_2^2 - X_0^2}{R_2^2 - R_1^2} \right] \tag{8}$$

where R_1 = inner radius of liquid film. Where equation 7 reduces to:

$$W_{(y)} = T \int_{D=D_{\min.}}^{D=D_{\max.}} \left[\frac{R_2^2 - X_0^2}{R_2^2 - R_1^2} \right] \left[\frac{f(D)}{100} \right] \mathrm{d}D \tag{9}$$

No success was experienced in trying to obtain $f(D)$ from this equation in an analytically rigorous manner, the necessary transformation being unknown to mathematicians. Fortunately the form of solution may be approximated to any desired degree of accuracy. Assume that the suspension is made up of particles of diameters $D_1, D_2, D_3 \ldots D_n$, each of fractional amounts $F_1 + F_2 + F_3 + \ldots F_n = 1$. Then at any value of y, for example y_1, we know $W_{(y_1)}$ and can evaluate $\phi(y, D)$ for every value of D. $W(y)$ may be taken at n different values of y because there are n different diameters $D_1, D_2, \ldots D_n$. Thus we have at all values of y

$$\begin{aligned} \frac{W_{(y_1)}}{T} = {} & \left[\frac{R_2^2 - \phi^2(y_1, D_1)}{R_2^2 - R_1^2} \right] F_1 + \left[\frac{R_2^2 - \phi^2(y_1, D_2)}{R_2^2 - R_1^2} \right] F_2 \\ & + \cdots \left[\frac{R_2^2 - \phi^2(y_1, D_n)}{R_2^2 - R_1^2} \right] F_n \end{aligned} \tag{10}$$

$$\frac{W_{(y_2)}}{T} = \left[\frac{R_2^2 - \phi^2\,(y_2\,, D_1)}{R_2^2 - R_1^2}\right] F_1 + \left[\frac{R_2^2 - \phi^2\,(y_2\,, D_2)}{R_2^2 - R_1^2}\right] F_2$$

$$\vdots \qquad + \cdots \left[\frac{R_2^2 - \phi^2\,(y_2\,, D_n)}{R_2^2 - R_1^2}\right] F_n$$

$$\frac{W_{(y_n)}}{T} = \left[\frac{R_2^2 - \phi^2\,(y_n\,, D_1)}{R_2^2 - R_1^2}\right] F_1 + \left[\frac{R_2^2 - \phi^2\,(y_n\,, D_2)}{R_2^2 - R_1^2}\right] F_2$$

$$+ \cdots \left[\frac{R_2^2 - \phi^2\,(y_n\,, D_n)}{R_2^2 - R_1^2}\right] F_n$$

The unknowns in this set of n simultaneous equations in n unknowns are the fractional values which can be determined, F_1, F_2, F_3, etc. Knowing the fractional amounts of all particles present we can plot a curve similar to figure 1 and from it determine the distribution function. In practice it is possible to get a first approximation to the true value of the distribution function by considering the system as being composed of some small number of particles, for example, five. The set of five equations which can then be written can be solved for the fractional amounts of each of the particles and figures 1 and 2 constructed. The form of the distribution function is then varied until it gives values of W at every value of y corresponding to the experimental data. If the form of $f(D)$ is known, W at any value of y is calculated from equation 7 by graphically evaluating the corresponding line integral over all values of D.

To evaluate W at any value of y by this method of graphical integration, it is necessary to plot values of the quantity

$$\left[\frac{R_2^2 - \phi^2\,(y, D)}{R_2^2 - R_1^2}\right] \frac{f(D)}{100}$$

against D for all values of D. The area under this curve is proportional to W at the value of y in question.

It is recognized that the solution proposed is in fact one of successive approximation. Assumption of the suspension's being composed of a small number of different particles and solution of the corresponding equations simply provides a rational method of making a first approximation as to the form of $f(D)$. The labor involved in solution of the above integral equation may be considerably shortened if a proper integrating machine is available.

It remains now to show how the form of the function ϕ is derived. The necessity for and physical meaning of the equation $X_0 = \phi(y, D)$ has been discussed above. Before the form of the equation may be determined, we must know the nature of the velocity components of a settling particle both parallel to and perpendicular to the axis of rotation.

It is first necessary to establish the type of flow of the suspension itself through the centrifuge. The film of liquid suspension moves up the walls of the bowl by virtue of the hydrostatic head, due to the fact that the film is slightly thicker at the bottom than at the top. At the high speeds of rotation and low rate of feed, it can be shown that this difference is negligible and that no great error will result if the suspension is considered to flow up the walls of the bowl in stream-line flow with the stream lines parallel to the axis of rotation. On this basis it is possible to describe the velocity component parallel to the axis of rotation of a particle settling at any distance from the axis of rotation. The derivation follows that of Lamb (5) with the exception that the boundary conditions for integration are those of a concentric film of fluid rather than a solid tube of fluid. The final equation is

$$\frac{dy}{dt} = VK_1\left[R_1^2 \ln \frac{X}{R_2} + \frac{R_2^2 - X^2}{2}\right] = u \tag{11}$$

In this equation dy/dt is the velocity parallel to the axis of rotation at any distance X from the axis of rotation. V is the average velocity over the cross section of the entire film calculated from the relation

$$V = \frac{Q}{(R_2^2 - R_1^2)\pi} \tag{12}$$

where Q is the volumetric rate of feed.

K_1 is a function of the construction of the bowl and is given by:

$$K_1 = \frac{R_2^2 - R_1^2}{\frac{3R_1^4}{4} + \frac{R_2^4}{4} - R_2^2R_1^2 - R_1^4 \ln \frac{R_1}{R_2}} \tag{13}$$

It is recognized that this idealized picture of the flow may be complicated by end effects in the bowl used in the present work, where the ratio of length to diameter was about 10. An experiment was performed to see the magnitude of these end effects.

Essentially, the experiment consisted in filling the centrifuge bowl with salt solution and at a definite time starting to feed in at a definite rate sodium hydroxide solution of the same density and of known normality. Samples of the effluent were taken at various times and titrated with standard hydrochloric acid to determine their sodium hydroxide content. A curve of total equivalents of sodium hydroxide flowing out versus time was then plotted and compared with the theoretical curve calculated on the basis of the above velocity distribution. The results indicated good agreement between theory and experiment.

By designing a centrifuge bowl especially for this work, such errors could be eliminated still further.

The velocity component perpendicular to the axis of rotation is given by Stokes' law (14):

$$\frac{dX}{dt} = \frac{D^2 \Delta\rho \omega^2 X}{18\eta} \tag{14}$$

where $\Delta\rho$ is the difference in density between dispersed phase and dispersing medium, ω is the angular velocity of rotation, and η is the viscosity of the dispersion medium at the temperature of settling.

Dividing equation 11 by equation 14 we obtain the slope of the settling curve for any particle at any point. We obtain:

$$\frac{dy}{dX} = \frac{18\eta V K_1}{D^2 \Delta\rho \omega^2 X}\left[R_1^2 \ln \frac{X}{R_2} + \frac{R_2^2 - X^2}{2}\right] \tag{15}$$

During any one run at constant values of η, V, and ω, we may integrate this equation for any value of D between the limits:

$$\begin{aligned} y &= 0 \qquad & X &= X_0 \\ y &= y \qquad & X &= R_2 \end{aligned}$$

since the particle has just come to rest upon the wall at some point y.

Integration gives:

$$y = \frac{18\eta V K_1}{\omega^2 \Delta\rho D^2}\left[\frac{R_2^2}{2} \ln \frac{R_2}{X_0} - \frac{R_1^2}{2}\left(\ln \frac{R_2}{X_0}\right)^2 + \frac{X_0^2 - R_2^2}{4}\right] \tag{16}$$

If the rate of feed, temperature, and velocity of rotation are kept constant, this equation is of the form

$$X_0 = \phi(y, D) \tag{2}$$

but is unfortunately implicit in X_0, for which we wish to solve. Solution of equation 16 for X_0 may be accomplished either through a family of curves or by representation on an alignment chart.

An error in equation 16 arises in the variation of the term R_2, owing to a layer of particles building up on the wall. This is minimized by using only a small amount of suspension in any one run and thus building up a relatively thin layer of particles. The average deviation of R_2 from its value represented by the diameter of the bowl less the thickness of the removable liner is very slight.

The method which has just been described is well suited for making a particle-size fractionation upon a polydispersed system like bentonite and measuring the distribution curves of the resulting fractions.

The solid line in figure 4 represents the experimental data in a run upon a sample of bentonite from which all large particles had been removed by gravity settling over a period of three months. The distribution curve calculated from these data is shown as the solid curve in figure 5. The rate of feed was held constant during the run to a value of 7.5 cc. per minute by a constant-level siphon. A total of 282 cc. of suspension of concentration 0.46 per cent were fed through, followed by 300 cc. of distilled water. The centrifuge was operated at a speed of 20,200 R.P.M. (ω = 2115 radians per second) measured by a stroboscope. Speed control was by voltage regulation and the temperature was 21.5°C., corresponding to a viscosity of water of 0.009695 poise. The density of the bentonite was determined by a pyknometric method as 2.8. This figure, however, is subject to revision, as work is in progress to determine the density under settling conditions more accurately. In the present machine R_1 = 1.07 cm. and R_2 = 2.117 cm.

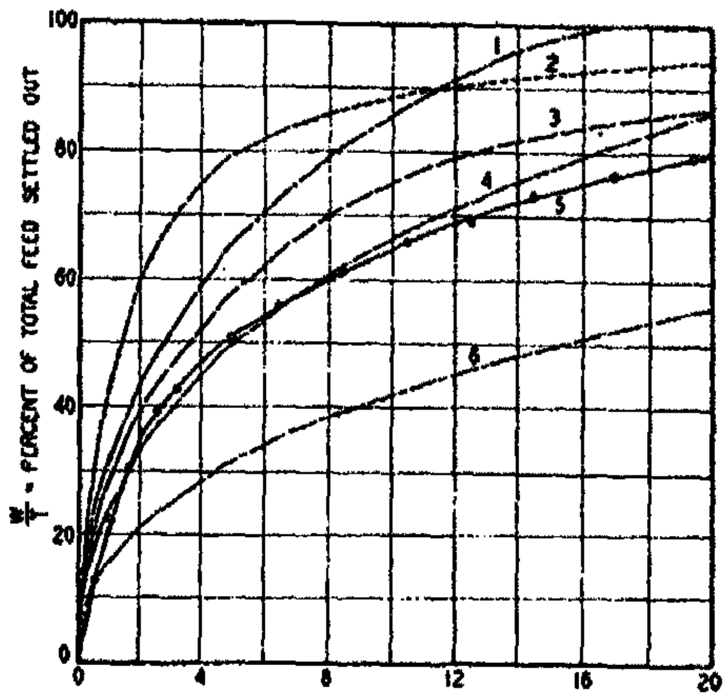

Fig. 4. Data used in calculating distribution curves

1. — - — monodispersed system; D = 35mμ.
2. ········· polydispersed system isodistributed between D = 12.5 mμ and D = 90 mμ; $f(D)$ = 1.29 × 10^6.
3. —— —— polydispersed system isodistributed between D = 12.5 mμ and D = 48.8 mμ; $f(D)$ = 2.75 × 10^6.
4. ·—·—· monodispersed system; D = 25 mμ.
5. ———— experimental curve; run No. 4.
6. —··— monodispersed system; D = 15 mμ.

At the conclusion of the run the liner was removed from the bowl and the precipitate allowed to dry. The precipitated clay was then scraped off at definite distances from the bottom of the liner, dried in an oven, and weighed in ground glass stoppered weighing bottles. Curve 5 of figure 4 was plotted from these data.

The condition imposed upon the distribution function calculated from these data is that integration of equation 7 over all values of D at any value of y, for example y_1, must give the experimentally determined value of W, that is W_1, at y_1. Figure 6 shows such a graphical integration at the point $y = 10$ cm. The area under the curve is proportional to the total weight of particles $W_{(y)}$ which settled out on the liner up to $y = 10$ cm. The proportionality factor is T, the total weight of dispersed phase fed into the machine during the run (see equation 7).

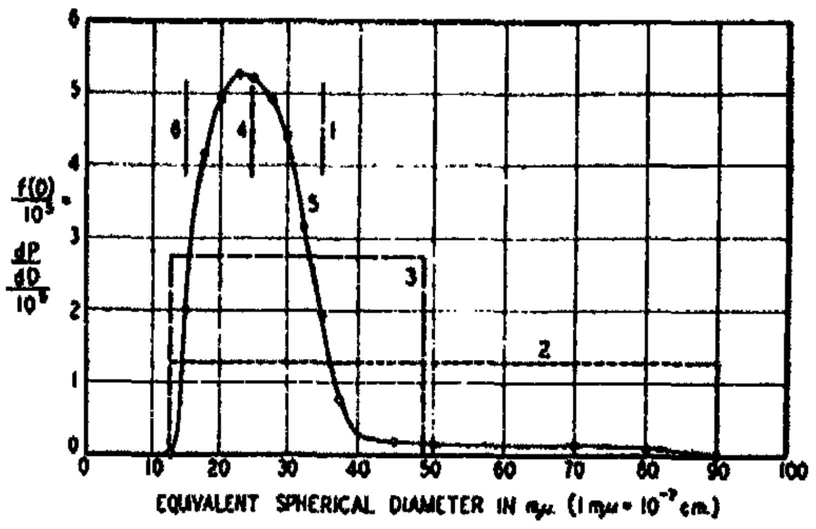

FIG. 5. Distribution curve calculated from curves of figure 4. P = per cent of sample by weight having diameters below D.

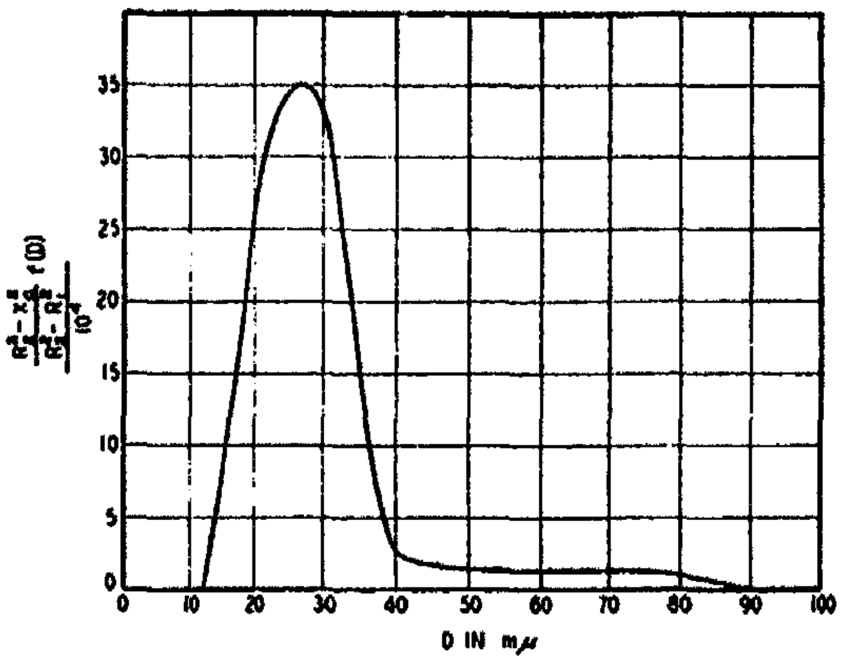

FIG. 6. Evaluation of line integral over $f(D)$ at $y = 10$ cm.
Area = W at $y = 10$ cm.

The distribution curve shows that the majority of the particles in this highly colloidal bentonite have equivalent spherical diameters, the majority of which range from 15 to 35 mμ with both larger and smaller sizes present. For comparison calculated curves are presented showing how the experimental data should have looked if the distribution function had taken one of the other forms indicated. Corresponding curves on figures 4 and 5 are represented by the same number.

By systematically centrifuging samples similar to the one whose distribution curve is shown, as well as those heavier portions taken off by gravity settling, a series of fractions of different average particle sizes will be obtained for the gelation tests.

CONCLUSION

In connection with a new series of studies regarding the effect of particle size on thixotropy and gel structure in general, it was necessary to develop a new method for making particle-size fractionations and measuring particle-size distribution curves of systems existing in the true colloidal range of matter. The new method employing the supercentrifuge has been described and should prove useful in many lines of colloidal research, since it employs relatively inexpensive equipment compared to other methods in use at present.

Future improvements in the accuracy of this method will probably have to come in the design of a supercentrifuge especially adapted for measurements of particle size. At the present time the purpose was to develop the theory necessary to the measurement of distribution curves in truly colloidal systems with a machine standard on the market and well within the financial reach of many laboratories. It is felt that the general theory as embodied in equation 7 is satisfactory, and that curves obtained with the present machines are reasonably accurate. Future experimental work now in progress will show to what extent the simplification introduced by equation 8 is justified. Finally it must be remembered that the supercentrifuge is the best means available at the present time for making rational particle-size fractionations in systems containing the very finest colloidal particles.

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ADSORPTION OF IONS AND THE PHYSICAL CHARACTER OF PRECIPITATES. II

FERRIC OXIDE AND BENTONITE PRECIPITATES[1]

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Among the various factors which influence the physical nature of a precipitate, the specific effect of adsorbed ions is often one of the most important. The importance of choosing the proper medium for the formation of precipitates in analytical work is too familiar to require discussion here.

The experiments here recorded were suggested by previous observations made by Cunningham in collaboration with Weiser (5) on sulfur precipitates formed by salting Odén's sulfur sol. Stingl and Morawski (4) and Odén (3) had recorded various salts as giving precipitates ranging macroscopically from gelatinous through flocculent, slimy, and fine-grained to plastic in character, depending upon the precipitating ion used. The work of Weiser and Cunningham showed that, in the last analysis, these precipitates were either gelatinous or non-gelatinous, depending upon the degree of hydration of the ions adsorbed. In the case of the formation of plastic sulfur, the neutralizing ions did not carry with them sufficient protective water to prevent complete coalescence of the particles. In the case of a gelatinous precipitate, the neutralizing ions not only carried sufficient water to form a protective coating about the micelles and prevent contact of sulfur to sulfur, but the protective water at the same time usually acted as an adhesive, loosely binding the precipitated particles together. Ions of intermediate hydration gave intermediate types of precipitates.

Weiser and Cunningham made motion pictures[2] through the ultramicroscope which showed the outflow of dense, adsorbed water into ordinary supernatant water as a slightly adsorbed, highly hydrated ion was displaced by a highly adsorbed, slightly hydrated ion added to the supernatant liquid. At the same time the sulfur micelles usually coalesced,

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[1] Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11–13, 1936.

[2] Presented at the Sixth Colloid Symposium, held at Toronto, Canada, June, 1928.

forming a particle of plastic sulfur very much smaller than the original clump. In an extreme case, the shrinkage was to less than 0.5 per cent of the original volume.

Some views taken from the motion pictures are reproduced from the original article (5) in figure 1.

In view of the results obtained with sulfur, it seemed reasonable to expect that precipitates of substances not exhibiting the coalescing tendency of amorphous sulfur would be more or less gelatinous, depending upon the degree of hydration of adsorbed ions. Since the bulk of the sulfur clumps varied so greatly with the amount of adsorbed water, it seemed feasible to compare various precipitates on a basis of their bulk.

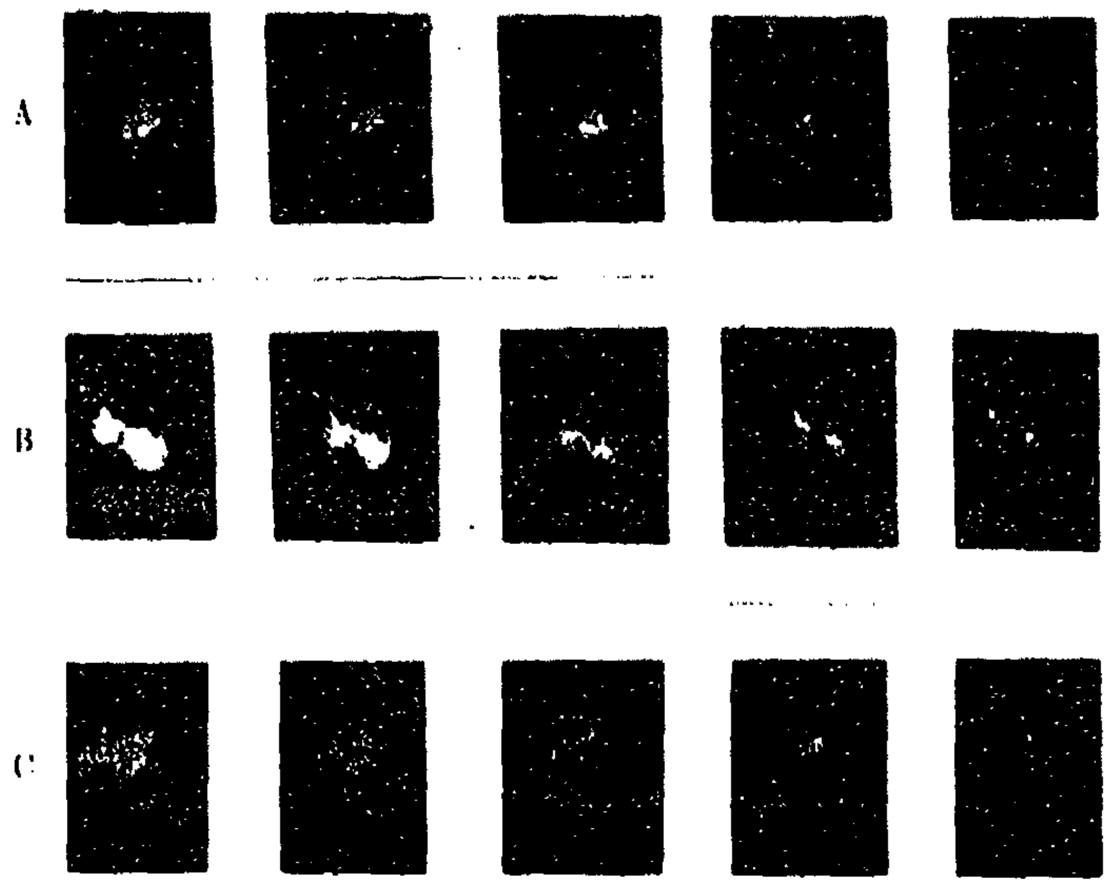

Fig. 1. Ultramicroscopic views of the shrinkage of sulfur clumps on displacing a slightly adsorbed, highly hydrated ion by a highly adsorbed, slightly hydrated ion. A, Li^+ displaced by K^+; B, Li^+ displaced by Cs^+; C, Li^+ displaced by Ba^{++}.

The effects of varying both positive and negative adsorbed ions on both a positive colloid, ferric oxide, and a negative colloid, bentonite, were studied.

EXPERIMENTAL PROCEDURE

For the purpose of forming the precipitates under uniform conditions, the Weiser mixing device (6) was used in all cases. This device consists of a smaller test tube sealed in the bottom of a larger one. One of the two liquids to be mixed is placed in each compartment, the larger tube is then stoppered, and the apparatus is shaken quickly and vigorously.

After forming the precipitates in the above manner, they, together with their supernatant liquids, were poured into 5 x ½ in. test tubes, centrifuged for five minutes, and allowed to stand. After at least two days, the depths of the precipitates were measured with a millimeter scale. The actual volumes were not recorded, but the capacity of the test tubes of the size used is about 1 cc. per 6-mm. depth. The data are recorded in the charts, figures 2 to 5.

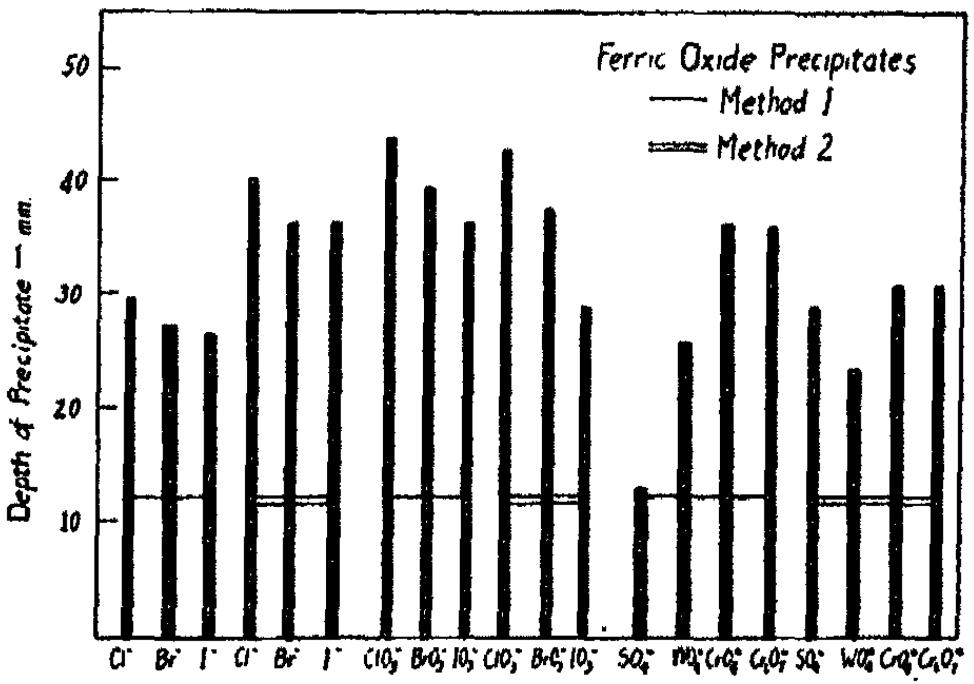

FIG. 2. Comparison of the bulks of ferric oxide precipitates obtained by varying the precipitating ion

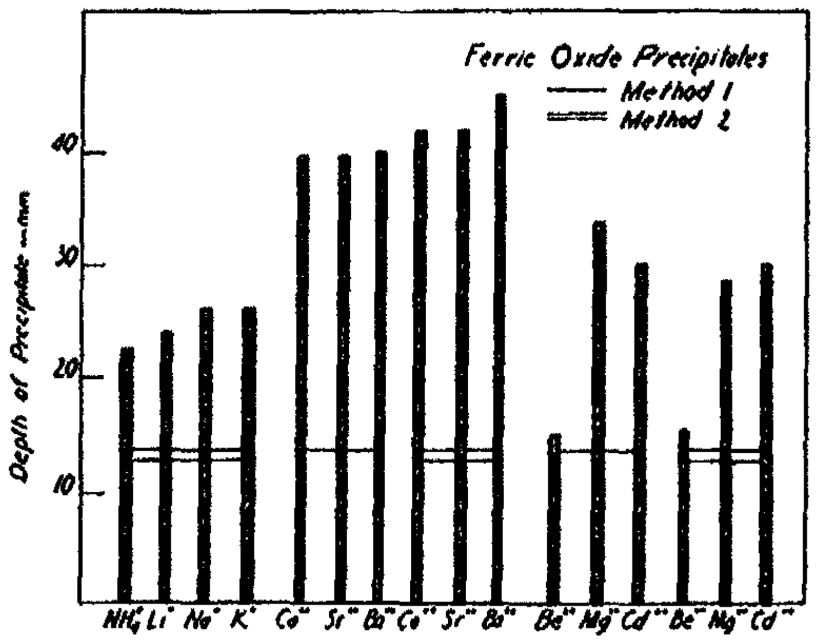

FIG. 3. Comparison of the bulks of ferric oxide precipitates obtained by varying the stabilizing ion

The individual procedures are described more fully in the following paragraphs.

Ferric oxide precipitates

Method 1. Each precipitate was formed separately by placing 1 cc. of N ferric chloride in the inner compartment of the mixing device and 1 cc. of N sodium hydroxide plus 15 cc. of a normal solution of the salt supplying the ion to be studied in the outer compartment. The calculated mass of the ferric oxide was in each case 0.036 g. The results are indicated in figures 2 and 3.

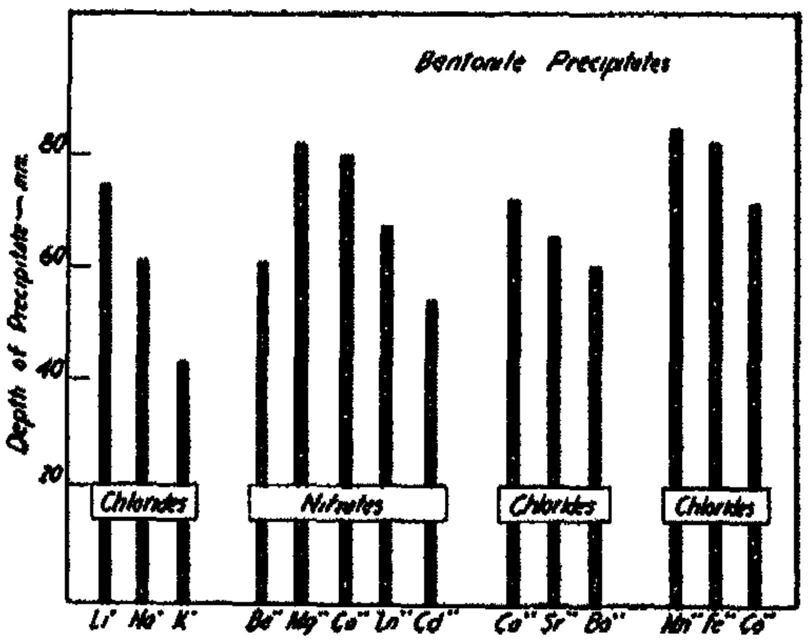

FIG. 4. Comparison of the bulks of bentonite precipitates obtained by varying the precipitating ion

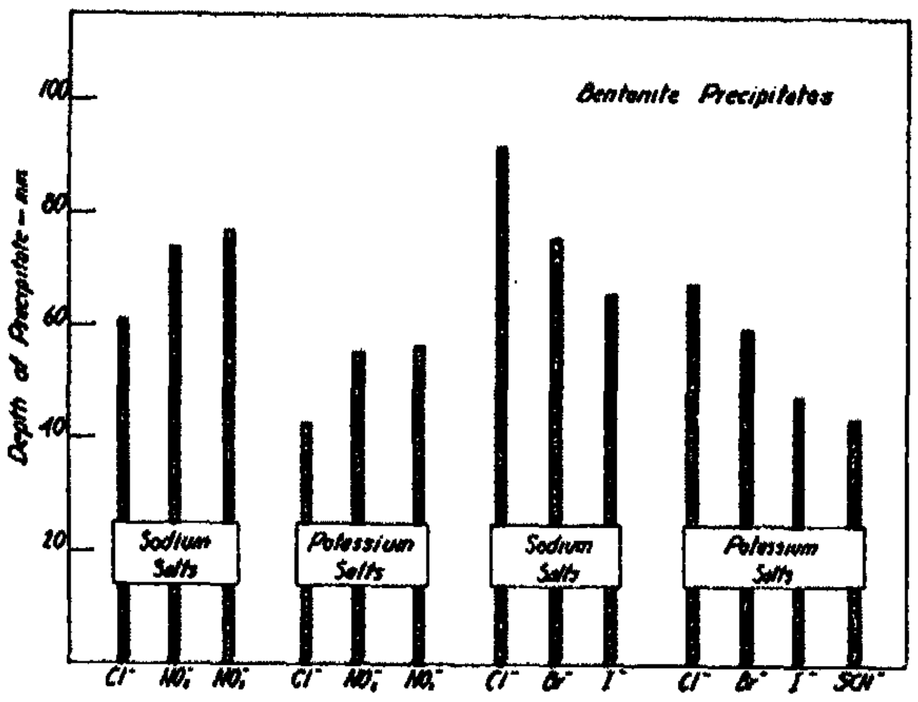

FIG. 5. Comparison of the bulks of bentonite precipitates obtained by varying the stabilizing ion

Method 2. A ferric oxide sol was prepared by adding 100 cc. of N sodium hydroxide to 900 cc. of ⅔ N ferric chloride, while stirring. This procedure resulted in a ferric oxide sol in 0.5 *N* ferric chloride. The sol was dialyzed for ten days, until the dialyzate, on evaporation to one-tenth its volume, showed no test for chloride.

To form the precipitates, 2-cc. portions of this sol were placed in the inner compartment of the mixer and 15-cc. portions of *N* salt solutions were placed in the outer compartment. By evaporation of 25-cc. portions of the sol, it was found that the mass of solid contained in 2 cc. of sol was 0.045 g. The results are indicated in figures 2 and 3.

All the values plotted in figures 2 and 3, for ferric oxide precipitates, were measured after the precipitates had been standing six months.

Bentonite precipitates

A bentonite sol was prepared by adding 4 parts of powdered bentonite to 100 parts of boiling water, with stirring, and allowing to stand at least two days before using. To form the precipitates, 10 cc. of sol and 10 cc. of 2 *N* salt were mixed in the mixing device. Each precipitate contained 0.4 g. of bentonite. The results are indicated in figures 4 and 5. All bentonite precipitates stood at least two days before being measured.

DISCUSSION OF RESULTS

There is no good agreement among various workers or methods as to the actual degree of hydration of ions. In fact, there is some disagreement as to their order of hydration. Recent investigators (1, 2) have claimed that the degree of hydration is a linear function of the electrostatic charge on the ion. In general, the degree of hydration decreases as the atomic weight increases, for the ions of elements in a given family in the periodic classification.

As far as possible, the ions in the charts (figures 2 to 5) have been grouped according to the periodic classification. Runs plotted on vertical depth-lines tied together by horizontal tie-lines were made simultaneously. Results not tied together by horizontal lines in the charts are not to be compared with one another for the reason that, since they were made at different times, the sols were in different stages of ageing.

With ferric oxide, the bulks of the precipitates obtained with halogen-containing ions by the first method (metathetical formation of ferric oxide in the presence of various salts) were in the order $Cl^- > Br^- > I^-$ and $ClO_3^- > BrO_3^- > IO_3^-$. By the second method (salting out the dialyzed sol), the order was $Cl^- > Br^-, I^-$, and $ClO_3^- > BrO_3^- > IO_3^-$. In each case the order is as predicted.

The bulks of the ferric oxide precipitates obtained by the first method with the divalent ions studied were in the order CrO_4^{--}, $Cr_2O_7^{--} > WO_4^{--} > SO_4^{--}$. By the second method, the order was CrO_4^{--}, $Cr_2O_7^{--} > SO_4^{--}$ WO_4^{--}, the order of SO_4^{--} and WO_4^{--} being reversed. No information was available to the authors as to the findings of other workers with regard to the hydration of these ions.

The bulks of the ferric oxide precipitates obtained with various cations by the first method were in the order $Ba^{++} > Sr^{++}$, Ca^{++} and $Mg^{++} > Cd^{++} > Be^{++}$. By the second method, the order was: K^+, $Na^+ > Li^+ > NH_4^+$; $Ba^{++} > Sr^{++}$, Ca^{++}; $Cd^{++} > Mg^{++} > Be^{++}$. With the exception of the case $Mg^{++} > Cd^{++}$ by the first method, the positions of the ions in these series are all the reverse of those expected on a basis of their positions in the periodic classification. However, since ferric oxide is a positive sol, these are stabilizing ions, and the heavier ions are much more highly adsorbed than the lighter ones. It is believed that the heavier stabilizing ions are so highly adsorbed as to bring about the adsorption of a sufficiently larger quantity of negative precipitating ions to account for the increased bulk of the precipitate. No attempt has been made to prove this hypothesis but, in the absence of evidence to the contrary, it seems reasonable.

With bentonite, a negative sol, the bulks of the precipitates obtained with various cations were in the order: $Li^+ > Na^+ > K^+$; $Mg^{++} > Ca^{++} > Zn^{++} > Be^{++} > Cd^{++}$; $Ca^{++} > Sr^{++} > Ba^{++}$; and $Mn^{++} > Fe^{++} > Co^{++}$. With the exception of Be^{++}, these ions all fall in the order predicted.

The bentonite precipitates obtained in the presence of various stabilizing ions ran in the order $NO_3^- > NO_2^- > Cl^-$ and $Cl^- > Br^- > I^- > SCN^-$. As far as predictable from the periodic classification, the positions of these ions are in agreement with the theory.

In practically all the above cases, the order of the ions is in agreement with the familiar Hofmeister series for their effect on the swelling of gelatin. That is, those ions which, in these experiments, gave precipitates of least bulk are the ones which make gelatin the least gelatinous, or most fluid, and *vice versa*. The indication is that in the case of the thinner gelatin gel there is less bound water and more lubricating water than in the thicker gel.

The results of these experiments could not be duplicated with arsenious sulfide sol, for the reason that the arsenious sulfide itself is not gelatinous enough to give precipitates of sufficient bulk to show the differences in bulk. This does not mean that the adsorbed ions have no effect on the character of the micelles, however.

It is hoped that the results of these experiments may be found of practical use in the control of the nature of precipitates and the consistency of pastes.

SUMMARY

1. A study has been made of the effect of adsorbed ions on the bulks of ferric oxide and bentonite precipitates.

2. The bulk of the precipitate is symbatic with the degree of hydration of the adsorbed ions.

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COACERVATION OF AMYLOPHOSPHORIC ACID AND PROTEINS[1]

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When hydrophilic colloids of opposite electric charge are mixed in solution, separation of a complex may be observed over a range of concentration of the components. In most cases this complex is of a liquid nature, separating out in the form of microscopic droplets. After some time these drops may unite to form a viscous liquid layer at the bottom of the container. This phenomenon has been observed before, but its underlying principles have been recognized lately by Bungenberg de Jong and Kruyt (3, 1), who have given the name "coacervation" to this separation of a liquid phase from solutions of hydrophilic colloids ("complex coacervation" when two or more colloid components are involved). They assume that the difference in sign of the charge causes the micelles to approach, their double layers partly discharging each other. Owing to this approach the outer and less firmly bound water of hydration will be removed, but ultimately the approach will come to a halt, when the force of attraction, due to the contrast in charge, will be balanced by the resistance of the more rigidly bound water of hydration. They therefore consider the resulting droplet to be a conglomerate of positive and negative micelles which remain individually next to each other, each retaining part of its water of hydration (*acervus* = swarm, heap). They showed that this phenomenon occurs generally in solutions of hydrophilic colloids, even when only one colloid is involved, the opposition in charge being located in this case on one and the same surface (either naturally as in the proteins or brought about artificially by adsorption of polyvalent ions of a charge opposite to that of the colloid).

From measurements of viscosity it could be shown that partial dehydration takes place, the viscosity of the mixtures of the two colloid solutions being considerably lower than that calculated from additivity. On the other hand, these authors showed that every influence which diminishes the electric charge of the micelles and therefore lowers the attraction of the colloid particles, prevents the formation of the coacervate

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or disperses the complex again after it has formed. As two opposite potentials are involved, this influence is found for both cations and anions, the concentrations required being lower the higher the valency of the ion (double Schulze–Hardy rule).

These coacervates may separate out in any form ranging from a fairly liquid fluid to a more or less plastic mass. The better the opposite charges are balanced, the higher the contrast in charge, and the greater will be the mutual dehydration. On the other hand, the effect of the attraction can be increased by the addition of dehydrating agents. It was found by these authors that the tendency of a hydrophilic colloid to enter into coacervation depends on its density of charge. Nucleic acid, having a high density of charge, combines readily with other biocolloids, and the resultant coacervate is highly resistant to electrolytes. No coacervates could, however, be obtained with the carbohydrate amylose as a component, a fact which may perhaps be significant in connection with the position of amylose as a reserve substance in nature.

The negative electric charge of amylose is probably due, at least in part, to the dissociation of the hydroxyl groups in the surface of the micelle. This dissociation is a function of the hydrogen-ion concentration of the solution. The charge is small in comparison to that of other hydrophilic colloids as agar or gum arabic, where more strongly dissociated groups resulting from sulfuric acid esters or from the carboxyl group contribute to it. In alkaline medium the dissociation of the hydroxyl groups of amylose is favored and, eventually, a completely developed double layer can be built up. In neutral or slightly acid solution, however, the negative charge of amylose is too small to bring about coacervation with positive proteins, the mutual attraction being too small to overcome the repelling force of the micelle hydration.

The character of amylose can now be changed completely by introducing strongly negative groups into the surface of the micelle, for instance, by esterification with phosphoric acid. The resulting amylophosphoric acid shows an appreciable anodic migration and possesses a sufficiently high density of charge to be able to combine with positively charged proteins to droplets and floccula, which in their general behavior show the character of coacervates.

We prepared amylophosphoric acid following the method described by Kerb (7, 21). Six grams of "amylum soluble Merck," free from nitrogen, were dissolved in the usual way in 150 cc. of hot water. After cooling, the vessel was placed in ice and 24 g. of pure calcium carbonate was stirred in. In the course of two hours a solution of 5 g. of phosphorus oxychloride in 10 cc. of chloroform was gradually added under continuous vigorous stirring. An equal amount of water was then added and the precipitate centrifuged off after it had settled overnight. From the clear solution calcium amylophosphate was precipitated by addition of an equal volume of alcohol; the precipitate was washed with 50 per cent alcohol and redissolved in water. The solution was then electrodialyzed until free from calcium. In the mean the amylophosphoric acid so prepared contained 0.5 per cent of phosphorus pentoxide, calculated on the dry substance.

When solutions of amylophosphoric acid and of a protein are mixed in different proportions at a pH below the isoelectric point of the protein, a pronounced turbidity, caused by the formation of microscopic droplets, may be observed in a distinct region of proportions of the two colloids. Gradually, the liquid droplets change to solid floccula and settle to the bottom of the vessel. Addition of alkali in small quantities causes the turbidity to disappear as the charge on the protein is reduced and ultimately reversed. Addition of acid has the same effect, as the charge of both colloids is diminished.

In order to establish further the coacervate nature of the new phase, we measured the viscosities of the mixtures in comparison to those of the two components. When two solutions of hydrophilic colloids are mixed and no interaction of the micelles takes place, the viscosities of the mixtures can be calculated from those of the two components by the rule of additivity. In the case of oppositely charged colloids a deviation from additivity is observed, which is greater the more completely the opposite charges balance each other (2, 4).

AMYLOPHOSPHORIC ACID-GELATIN

We used a 0.12 per cent solution of amylophosphoric acid and a 0.12 per cent solution of a pure gelatin (isoelectric point, pH = 5.0). The viscosities were measured in an Ostwald viscometer at 40°C. The required pH values of the solutions were obtained by adding the necessary amounts of sodium hydroxide or hydrochloric acid, and were controlled by means of a quinhydrone electrode and by color indicators. The results are collected in table 1 and represented in figure 1. The fourth column of the table gives the relative viscosities as found experimentally; the fifth, those calculated for additivity of the viscosities of the two unmixed solutions and their proportion in the mixture.

The results are in complete accord with what may be expected in the case of a coacervate. The lower the pH, that is the farther the gelatin is removed from its isoelectric point (and therefore the larger its positive charge), the less is the total amount of gelatin necessary to bring about the minimum in the additivity curve. The optimum of attraction of the opposite charges of the micelles is found at a pH of approximately 3.5.

Separation of coacervate droplets is found not only at the colloid proportions denoted by the minima, but also at some distance on either side of the minima. The droplets which separate at the conditions of the minimum are electrically neutral, and they show practically no cataphoretic movement. On either side of the minimum, however, the droplets show an outward electrophoretic charge of the sign of the colloid which predominates in the complex. At the proportion of exact balance, the micelles can approach each other to a maximum extent and the hydration is therefore at a minimum. When there is a preponderance of either of the two charges in the complex, the mutual repulsion of these excess charges causes the system to be less condensed and more hydrated.

TABLE 1

Viscosities of mixtures of amylophosphoric acid and gelatin sols

pH	AMYLOPHOSPHORIC ACID SOL	GELATIN SOL	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{exptl.}}$	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{calcd.}}$	PER CENT OF ADDITIVITY
	cc.	cc.			
2.6	100		0.075		100
	95	5	0.023	0.082	28.1
	80	20	0.027	0.102	26.5
	50	50	0.079	0.143	55.4
	20	80	0.165	0.184	89.7
		100	0.211		100
3.5	100		0.109		100
	95	5	0.022	0.113	19.5
	80	20	0.019	0.126	15.1
	50	50	0.052	0.151	34.4
	20	80	0.118	0.176	67.0
		100	0.193		100
4.2	100		0.111		100
	90	10	0.064	0.108	59.3
	80	20	0.041	0.105	39.0
	50	50	0.023	0.094	24.4
	20	80	0.043	0.085	50.6
		100	0.078		100
4.6	100		0.113		100
	80	20	0.064	0.104	61.5
	50	50	0.028	0.090	31.2
	30	70	0.028	0.081	34.6
	20	80	0.035	0.076	46.1
		100	0.067		100
4.9	100		0.115		100
	80	20	0.099	0.105	94.3
	50	50	0.066	0.090	73.3
	30	70	0.059	0.080	73.7
	20	80	0.061	0.075	81.3
		100	0.065		100

AMYLOPHOSPHORIC ACID-LEUCOSIN

The viscosities of mixtures of a sol of amylophosphoric acid and of one of leucosin, prepared from wheat, were determined at 30°C. The results are tabulated in table 2 (figure 2). The phenomena are similar in all respects to those described for the system amylophosphoric acid-gelatin.

AMYLOPHOSPHORIC ACID-POTATO ALBUMIN

An albumin from potato was obtained by saturating the juice, squeezed out by means of a hydraulic press, with ammonium sulfate. The precipitated impure proteins were shaken with cold water, and the filtered solution again saturated with ammonium sulfate. This was repeated four times. The original deep-green color of the juice had then largely disappeared. The solution of the last precipitate in water was submitted to electrodialysis. Some globulin which separated out during this last process was removed by filtration. The viscosities of the sol mixtures were measured at 30°C. The results are represented in table 3 (figure 3).

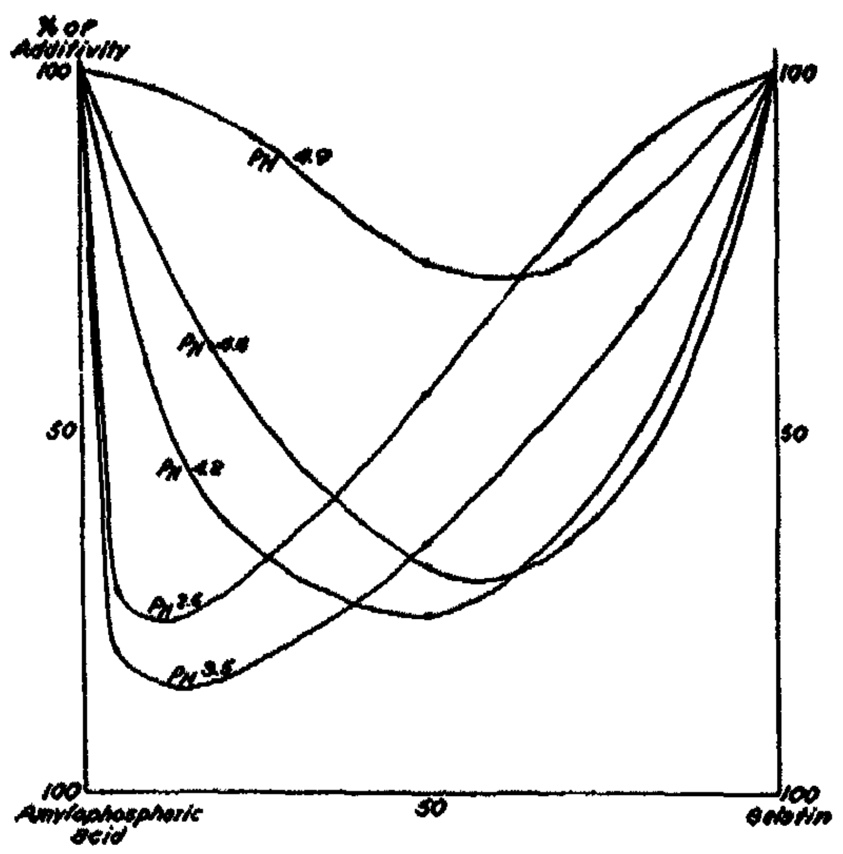

FIG. 1

The following general characteristics which these coacervates have in common may be mentioned. Immediately after mixing of the solutions, when the coacervate still exists in the form of liquid drops, it can be dissolved again completely by addition of either alkali, or acid, or neutral electrolytes. In the case of peptization with neutral salts in small quantities, the coacervate can be made to reappear by addition of alcohol or

TABLE 2

Viscosities of mixtures of amylophosphoric acid and leucosin sols

pH	AMYLO-PHOSPHORIC ACID SOL	LEUCOSIN SOL	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{exptl.}}$	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{calcd.}}$	PER CENT OF ADDITIVITY
	cc.	cc.			
2.7	100		0.111		100
	95	5	0.049	0.107	45.8
	80	20	0.035	0.096	36.4
	50	50	0.039	0.073	53.5
		100	0.035		100
3.0	100		0.111		100
	95	5	0.065	0.107	60.7
	80	20	0.030	0.096	31.3
	50	50	0.032	0.072	44.5
	20	80	0.037	0.049	75.5
		100	0.033		100
4.0	100		0.112		100
	80	20	0.049	0.095	51.6
	50	50	0.034	0.070	48.5
	20	80	0.033	0.044	74.9
		100	0.027		100
4.5	100		0.114		100
	80	20	0.076	0.095	80.1
	50	50	0.044	0.067	65.7
	20	80	0.027	0.038	76.1
		100	0.020		100

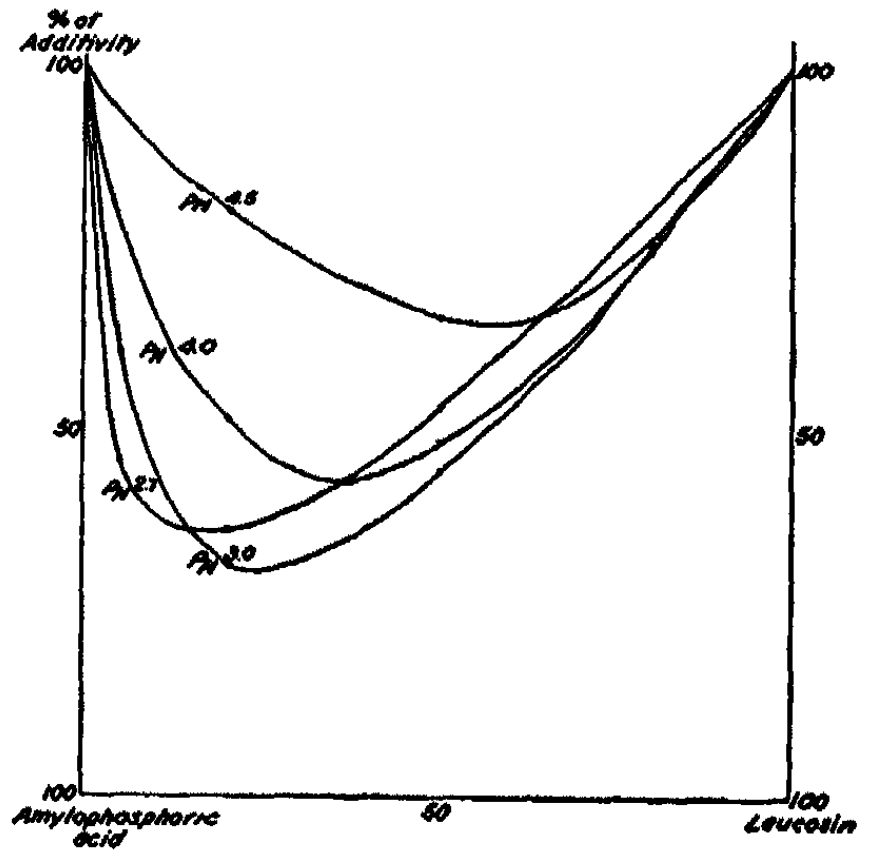

Fig. 2

TABLE 3

Viscosities of mixtures of amylophosphoric acid and albumin sols

pH	AMYLO-PHOSPHORIC ACID SOL	ALBUMIN SOL	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{exptl.}}$	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{calcd.}}$	PER CENT OF ADDITIVITY
	cc.	*cc.*			
2.6	100		0.115		100
	90	10	0.071	0.107	66.3
	80	20	0.055	0.098	56.1
	50	50	0.040	0.072	55.5
	25	75	0.034	0.050	68.0
		100	0.028		100
3.5	100		0.120		100
	95	5	0.085	0.115	73.9
	75	25	0.037	0.096	38.6
	50	50	0.023	0.073	31.5
	25	75	0.021	0.049	42.8
		100	0.025		100
4.4	100		0.122		100
	80	20	0.069	0.101	68.4
	50	50	0.031	0.070	44.3
	25	75	0.024	0.044	54.5
		100	0.018		100

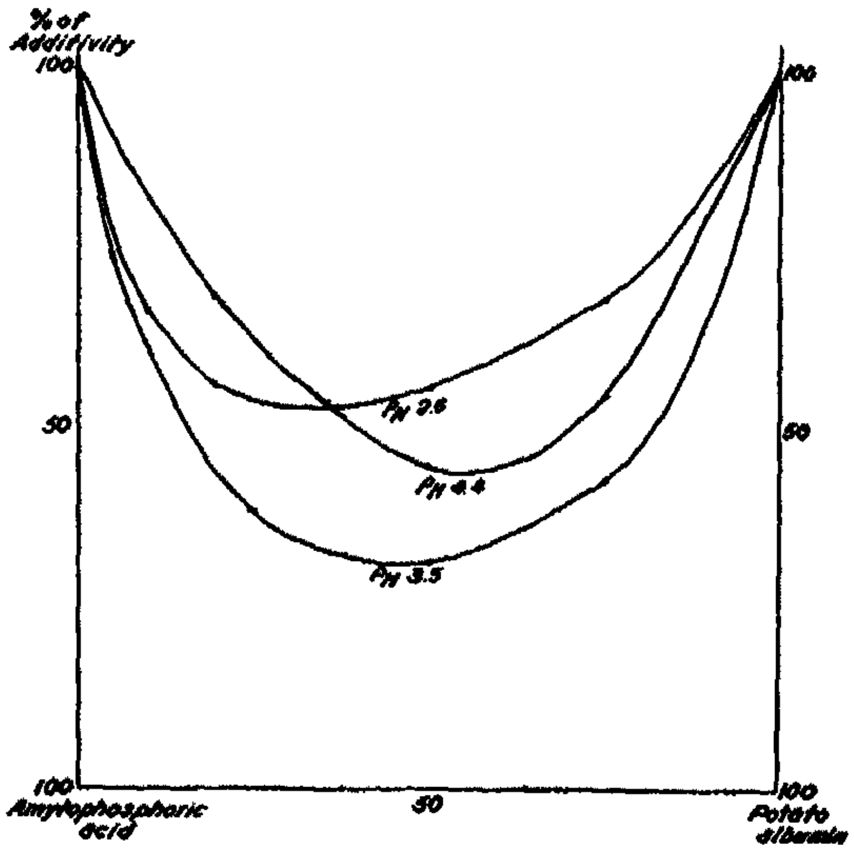

Fig. 3

another dehydrating agent. The droplets of these coacervates have, however, a pronounced tendency to change to floccula on standing. They then become, at the same time, more resistant to dispersion; peptisation may sometimes be obtained by potassium thiocyanate or alkali.

AMYLOPECTIN

The observation that amylose can enter into coacervation with proteins only after its density of charge has been increased, for instance, by esterification with phosphoric acid, leads to some new speculations on the nature of amylopectin. It is to the presence of amylopectin that the high viscosity and the paste-forming qualities of a starch solution are ascribed. A solution of native starch in water is, however, not a true colloidal solution. Its viscosity does not follow Poiseuille's law, indicating the presence of micelle conglomerates or gel fragments in the solution (12, 6). In the ultracentrifuge the amylopectin settles quickly and long before the amylose (8); even in the ordinary centrifuge, the amylopectin fraction can be separated from the bulk of the solution (22).

We may consider a solution of native starch to be a solution of amylose in which amylopectin, in the form of gel fragments, is more or less finely suspended.

Samec (18, 14, 20, 17) showed that amylophosphoric acid is a component of the amylopectin and that, apart from silicic acid and fatty acids, it contains nitrogenous substances often to a considerable extent. In potato starch the nitrogen content is small compared to that of phosphoric acid; from wheat, amylopectin fractions can be obtained in which the nitrogen content is equal to or even greater than the content of phosphoric acid. Samec assumed that protein and amylophosphoric acid are bound "salt-like" in amylopectin, but later he himself showed this view to be unsatisfactory (16).

We suggest that it may be of advantage to consider amylopectin to be of the nature of a coacervate as described in the first part of this paper, that is to say, that the binding of the components is not one of classical chemical mass stoichiometry, but rather a balancing of the opposite charges of the colloid micelles involved, these micelles largely retaining their individuality in the complex.

It has been shown that the ultimate electrophoretic charge of the coacervate drops will depend on the proportions of two colloids present. In potato starch the negative component largely predominates over the positive protein. In accordance with the above theory one would expect the resulting coacervate to have a negative charge and to move cataphoretically to the anode, as is found experimentally. Similarly Samec and Antonovic (19) found fractions of wheat amylopectin which differed in their cataphoretic behavior, those in which phosphoric acid is in excess moving to the anode, and those in which protein is in excess actually moving or at least having a tendency to move to the cathode. Samec's original assumption that the high viscosity of starch solutions is solely due to the phosphoric acid content of the amylopectin has been the subject of controversy (13, 23, 6, 5). Indeed the viscosity of a solution of amylophosphoric acid, obtained from pure amylose, is not very much higher than that of a solution of amylose. The excessively high viscosities originally mentioned by Samec may be explained by the fact that the amylose which he esterified with phosphoric acid was obtained from amylopectin fractions from which the phosphoric acid had been removed previously by saponification. The nitrogenous substances probably remained in solution and were able to give rise to new coacervates as soon as amylophosphoric acid was formed again. These complexes, remaining dispersed in solution as gel fragments, could then cause a high viscosity. Indeed we found that the complexes of amylophosphoric acid and proteins described in this paper can be dispersed by boiling in a solution of pure amylose, from which they do not separate again on cooling. The viscosity of a solution so obtained shows an appreciable increase compared to that of an equally concentrated amylose solution.

Samec distinguished amylopectin fractions according to the color produced with an iodine–potassium iodide solution, the color changing from blue to red the higher the nitrogen content of the fraction. Whereas a solution of amylophosphoric acid gives a blue color with this reagent, we found that the color obtained with the coacervates previously described turned from blue to violet and red, the more the protein content was increased.

Many experiments have been recorded in which the properties of native starch have been changed by treatment with either dilute hydrochloric acid or potassium hydroxide. From our point of view, removal of protein from wheat amylopectin in larger proportion than phosphoric acid (15) must necessarily lead to a product resembling potato amylopectin (the coacervate, by removal of the positive component, changing to a complex in which the negative amylophosphoric acid micelles predominate), and ultimately to a product having the properties of a soluble starch (the system being incapable of coacervation owing to the absence of one of the components).

Considering potato amylopectin to be a coacervate complex with a large negative surplus charge, one may expect it to be able to undergo renewed coacervation with positively charged protein, ultimately leading to a product resembling wheat amylopectin, as has indeed been found (16, 11). Many authors have described amylopectin as differing only from amylose by being more interlocked (more dense) and less hydrated (24, 9, 10, 5). These properties are inherent in coacervate complexes, the opposite charges causing the micelles to approach more closely to each other and to be less hydrated than in free colloidal solution.

In conclusion the author wishes to express his thanks to Prof. H. R. Kruyt, in whose laboratory this investigation was carried out, for his continual interest.

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KELVIN SINGLE-POTENTIAL DIFFERENCES

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In 1802 Volta (18) expressed the belief that most of the electromotive force of a voltaic cell was generated at the junction of the two metals which dipped into the solution or solutions. This could not be the whole truth, because cases are known in which we can reverse the flow of current through the cell, and because it is possible to make a cell having quite an electromotive force out of one metal and two suitably chosen solutions. Volta's theory was known as the contact theory and has been held from that day to this by most physicists, with Lodge as the outstanding exception.

The chemists felt that the chemical reaction furnished the electrical energy and that consequently most of the potential difference was set up where the chemical change took place,—at the metal-liquid and liquid-liquid interfaces. Some potential difference must be set up at the metal-metal interface because of the behavior of thermocouples. Since the thermoelectric force is very small, the chemists hoped that the contact potentials between metals were also very small,—which does not follow at all. A few chemists, Ostwald among them, claimed that the Peltier effect was a measure of the potential difference between two metals, but this delusion did not last long. If the argument had been valid (9), people would have devised some method of determining the potential difference between metal and solution from the Peltier effects for the metal-solution junctions. The so-called chemical theory of the voltaic cell has been held by most chemists, Sir Humphry Davy and Langmuir being two conspicuous exceptions.

When it was shown by Helmholtz that there was a definite relation between the electromotive force of a reversible cell, the heat of reaction, and the temperature coefficient of the electromotive force, it seemed to most chemists that the century-old contest was over, because there was nothing left for the metal-metal contact except values so small that they were lost in the errors of determination of the three important terms (4). It does not seem to have struck any chemist as curious that Helmholtz (13) should continue to believe in the contact theory and should develop it in his Faraday Lecture. Since there is no transport of ponderable matter in metallic conduction, it is a mistake to talk about the heat of formation of brass in connection with the Daniell cell, as Lodge does (17).

If the heat-equivalent of the contact potential is contained in the heat of reaction as determined by the chemist, there is no difficulty and the metal-metal potential may have any value in reason. This was seen clearly by Gurney (11). "A chemical change such as

$$CuSO_4(aq) + Zn \rightarrow ZnSO_4(aq) + Cu$$

carried out as a test-tube reaction, does not appear to be connected with any electrical Volta potential difference; hence the parallelism between the chemical series and the Volta series appears to be merely fortuitous, or else spurious. The only method of reconciling the contending views would be to prove that by some concealed relation the heat evolved in the test-tube reaction is itself determined by the Volta potential difference characteristic of the reacting metals. If the proof of this unsuspected relation could be obtained, then certainly the controversial deadlock would disappear."

Gurney's conclusion is right, but his premises are wrong. In 1906 one of us (1) said that "the most striking characteristic of an electrolytic reaction is that it occurs in two places,—at the anode and at the cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction. Any chemical reaction therefore, which can be made to take place electrolytically, must consist (22) of an anode and a cathode process." Consequently the same amount of heat will be generated regardless of whether one carries out the reaction in the test-tube or in a voltaic cell; and consequently the heat equivalent of whatever metal-metal potential there may be will occur in both cases.

What Gurney was really trying to say was that most chemists do not realize clearly that the heat-equivalent of any metal-metal potential appears in the heat of reaction as determined by the chemist. Helmholtz would never have accepted Gurney's statement that "it is not the chemical energy which determines the value of the electromotive force."

As far back as 1847 Helmholtz (12) explained the contact potential between zinc and copper on the assumption that zinc has a higher attracting force to positive electricity. So far as we know (4), Langmuir (16) was the first physical chemist to go over to the camp of the Voltaists and, nearly seventy years after Helmholtz, he wrote that "the Volta series of the elements is determined by the magnitude of φ, the electron affinity." Langmuir pointed out also that recent work in physics on electron emission from heated metals, thermal effects accompanying the electron emission, photoelectric effects from metals, measurements of contact potentials, ionizing potentials of metal vapors, single-line spectra of metal vapors "affords conclusive proof that contact potentials exist independently of chemical reactions and are of the same order of magnitude as those observed by Volta."

In the laboratories (14, 6) of Kelvin and of J. J. Thomson experiments have been performed to show that an ionized-air gap tends to eliminate the potential difference between the phases adjoining it. These experiments seem of the utmost importance. If an ionized-air gap eliminates the potential difference completely, it becomes a simple matter to take any cell and to put in an ionized-air gap at one junction after another and thereby determine all the single-potential differences. If the elimination is not complete, there will be an error in each determination of a single-potential difference, but we shall be nearer the true value than ever before. It will be a simple matter to apply the method to reversible electrodes, and the physicists (8) of the Kelvin school have always fought shy of measuring reversible electrodes.

METHOD OF MEASUREMENT

To measure the electromotive force of a cell containing metallic or solution electrodes separated by an ionized-gas gap, the conducting phases on the two sides of the ionized-gas gap must present a large enough area to each other so that sufficient ion-current can flow to equalize their potentials in a reasonable time. The grounded electrode must surround almost completely the one which is connected with the electrometer; otherwise the potential of the latter is changed more rapidly by induction from external objects than it can be equalized by the ion current.

Following Greinacher (10) and others, a compensation method was used. A potentiometer furnished the compensating potential difference, and the null instrument was a modified form of the Dolezalek electrometer, loaned us by Professor Richtmyer. It was used at a sensitivity of about 150 mm. per volt, thus enabling electromotive forces to be read to 0.01 volt. Most of the electrodes studied were difficult to reproduce to better than 0.05 volt. It is believed that the results as given are probably right to ± 0.1 volt.

In the mounting finally developed for the electrodes, the lead from the electrometer is shielded by a brass tube filled with paraffin until it approaches the paraffin base of the electrodes. It then passes into a glass tube bent in a U-shape and ends in a mercury well at the bottom of the U. The glass tube, coated with paraffin to diminish leakage of charge over its surface, passes under the grounded outer electrode, touching neither the electrode nor the table top. Its extreme end is bent horizontal to keep out occasional drippings when the electrode is covered with a solution. A platinum or copper wire attached to the bottom of the inner electrode is bent into such a shape that it can be inserted into the mercury well in order to make connection with the electrometer. The inner electrode rests on two paraffin pillars and is held upright by the wire running into the mercury well. To minimize leakage over the surface of the insulation, the path over the paraffin is made as long as practicable.

The air gap was ionized by means of radium furnished to us by Professor Papish. When in use the radium was enclosed in a lead block having a narrow slit which permitted radiation between, and parallel to, the electrodes.

The preparation of the various electrodes is described later. Solutions were applied to the electrodes simply by flowing them over the surface, the electrodes being removed from their supports and held horizontal. It was found possible to dispense with the agar which was used in earlier experiments.

The ordinary voltaic cells, which were measured for comparison with the ionized-air cells, were set up in beakers or in calomel half-cell vessels. The electromotive forces were measured with the potentiometer and a galvanometer, no special pains being taken to get the third decimal place, since they were to be compared with the electromotive forces of the much less reproducible ionized-gas cells.

SILVER CHLORIDE CONCENTRATION CELLS

Ordinary voltaic cells without ionized-air gaps were measured first. The electrodes were platinum foil, plated with silver from a cyanide bath. They must be washed free from cyanide or they will give erratic and worthless results. One of the electrodes chloridized by anodic treatment in concentrated hydrochloric acid gave nearly the same potential (within about 5 mv.) in dilute hydrochloric acid saturated with silver chloride as an unchloridized electrode in the same solution. Hence in all of the following cells hydrochloric acid saturated with silver chloride was relied upon to form a chloride film upon the silver electrode.

The hydrochloric acid solutions were of the following concentration:

$$c_1\text{HCl} = 0.00976\,N$$
$$c_2\text{HCl} = 0.484\quad N$$

They were saturated with silver chloride by adding freshly precipitated silver chloride and stirring mechanically for several hours. The solutions were stored in carefully cleaned bottles provided with siphons so that grease-free solution could be drawn off. This precaution seems to be important when the solutions are used in ionized-air cells.

The electrodes for the ionized-air cells were made of platinum foil and were plated with silver from a cyanide bath. After a preliminary rinsing, they were washed exhaustively by boiling in repeated changes of distilled water. The electrodes acquired a grease film particularly readily, but this could be removed by boiling in alcohol.

In making the measurements, as many cross-checks as possible were obtained. For example, both the inner and the outer electrodes were moistened with the dilute hydrochloric acid (c_1), inserted in the supports, and the electromotive force measured. It was about 0.01 volt. Then the solution on the inner electrode was replaced by c_2HCl. After making a measurement, both solutions (which tended to drain off and to evaporate) were renewed and the measurement repeated. If the values did not agree within 0.02–0.03 volt, the solutions were renewed again. Then c_2HCl was flowed over both electrodes and the electromotive force was found to be within 0.01 volt of zero. The solution on the inner electrode was replaced with c_1HCl; the electromotive force was very nearly the same as it was when the outer electrode was wetted with c_1HCl and the inner electrode with c_2HCl. This shows that the geometric asymmetry of the cell does not affect the results. Numerous checks of this sort were made. The electromotive forces were satisfactorily reproducible on the whole, provided the electrodes were washed thoroughly after plating and were free from grease.

After the electrodes have been in use for an hour or two, they no longer hold a coherent film of liquid and the results become more erratic. Occasionally, even before this happens, the electromotive force will fall for no apparent reason as much as 0.04 volt below what preceding measurements led one to expect. The great majority of the values, however, agree within ± 0.02 volt, and the cross-checks are so consistent that we believe we may disregard the few erratic ones.

As stated before, $c_1\text{HCl} = 0.00976\ N$ hydrochloric acid saturated with silver chloride and $c_2\text{HCl} = 0.484\ N$ hydrochloric acid saturated with silver chloride. We use the symbol ||| throughout this paper to denote an ionized-gas gap. All silver chloride electrodes were formed by dipping a silver electrode into one of these hydrochloric acid–silver chloride solutions. In the three cells where the silver chloride electrode is dry, the film was prepared by dipping the silver electrode into one of the solutions and allowing it to dry. The electromotive force is given the sign of the left-hand electrode, and the positive current flows from right to left through the cell when the electromotive force is positive. This is the international custom and not the one still maintained by G. N. Lewis. The arrow denotes the direction of flow of current. A summary of the data is given.

$$\text{(1)}\quad \underset{+}{\text{Ag}} \mid \underline{\text{AgCl}}\ \underset{\leftarrow}{c_1\text{HCl}} \mid c_2\text{HCl}\ \underline{\text{AgCl}} \mid \underset{-}{\text{Ag}} \qquad E = 0.162 \text{ volt}$$

$$\text{(2)}\quad \underset{+}{\text{Ag}} \mid \underline{\text{AgCl}}\ \underset{\leftarrow}{c_1\text{HCl}} \mid \text{sat. KCl} \mid c_2\text{HCl}\ \underline{\text{AgCl}} \mid \underset{-}{\text{Ag}} \qquad E = 0.0995 \text{ volt}$$

$$(3)\quad \underset{+}{\mathrm{Ag}} \mid \underline{\mathrm{AgCl}}\ \underset{\longleftarrow}{c_1\mathrm{HCl}\ |||\ c_2\mathrm{HCl}}\ \underline{\mathrm{AgCl}} \mid \underset{-}{\mathrm{Ag}} \qquad E = 0.07 \text{ to } 0.09 \text{ volt}$$

$$(4)\quad \underset{-}{\mathrm{Ag}} \mid \underline{\mathrm{AgCl}}\ \underset{\longrightarrow}{|||\ c_1\mathrm{HCl}}\ \underline{\mathrm{AgCl}} \mid \underset{+}{\mathrm{Ag}} \qquad E = -0.20 \text{ to } -0.22 \text{ volt}$$

$$(5)\quad \underset{-}{\mathrm{Ag}} \mid \underline{\mathrm{AgCl}}\ \underset{\longrightarrow}{|||\ c_2\mathrm{HCl}}\ \underline{\mathrm{AgCl}} \mid \underset{+}{\mathrm{Ag}} \qquad E = -0.14 \text{ volt}$$

$$(6)\quad \underset{+}{\mathrm{Ag}}\ \underset{\longleftarrow}{|||\ c_2\mathrm{HCl}}\ \underline{\mathrm{AgCl}} \mid \underset{-}{\mathrm{Ag}} \qquad E = 0.30 \text{ volt}$$

$$(7)\quad \underset{+}{\mathrm{Ag}}\ |||\ \underset{\longleftarrow}{\underline{\mathrm{AgCl}}} \mid \underset{-}{\mathrm{Ag}}\ . \qquad E = 0.42 \text{ volt}$$

The saturated potassium chloride solution takes out much of the potential difference between the solutions, but not all. Since the value for cell 3 is a little less than that for cell 2, we can say that the ionized-air gap takes out most of the potential difference and perhaps all. We cannot say that all the potential difference has been eliminated experimentally until the technique is improved to the point where we can measure with a sufficient degree of accuracy to examine solutions so dilute that we can calculate potential differences with the same degree of accuracy. We can show, however, that the measured results are consistent among themselves.

From cell 7 we have $\underline{\mathrm{AgCl}} \mid \mathrm{Ag} = 0.42$. From the difference between cells 5 and 6 we have $\underline{\mathrm{AgCl}} \mid \mathrm{Ag} = 0.44$, which is inside the experimental error. From cell 6 we have $c_2\mathrm{HCl}\ \underline{\mathrm{AgCl}} \mid \mathrm{Ag} = 0.30$, while the algebraic sum of Nos. 5 and 7 gives 0.28. On standing No. 6 changes slowly from +0.30 to −0.18, which is not far different from the value for No. 5 and indicates that the silver had been chloridized by vapor of hydrogen chloride from the solution.

As the most probable values for the present we take: $\underline{\mathrm{AgCl}} \mid c_1\mathrm{HCl} = 0.21$, $\underline{\mathrm{AgCl}} \mid c_2\mathrm{HCl} = 0.14$, and $c_1\mathrm{HCl} \mid c_2\mathrm{HCl} = 0.082$, which adds up to 0.152 instead of 0.162. By taking the value for No. 3 as 0.07 complete agreement could be obtained.

ZINC-COPPER CELLS

The copper sulfate and zinc sulfate solutions were made up to be 0.25 *M* (0.5 *N*) with an accuracy of about 1 per cent, and were kept in bottles with siphons. The cuprocyanide solution was made 0.25 *M* in cuprous cyanide and 2.5 *M* in sodium cyanide. The sodium zinc cyanide solution was made from sodium cyanide and zinc sulfate, and was approximately 0.1 *M* with respect to zinc cyanide and 1.0 *M* with respect to excess sodium cyanide.

The copper electrodes, cut from sheet copper and cleaned in nitric acid, were plated with copper from a cyanide bath, washed thoroughly in running tap water, and then rinsed in distilled water. The zinc electrodes were cut from a heavy sheet of zinc. After cleaning in hydrochloric acid solution, they were amalgamated by dipping in mercuric chloride solution and then rubbing with mercury until bright. The object of amalgamation is to prevent the formation of a coherent coating of zinc oxide. This effect is well-known and very striking in the case of amalgamated aluminum.

For the ionized-air cells both an inner and an outer electrode of each metal were provided, so that cross-checks could be made. The amalgamated zinc electrodes were reproducible within about 0.05 volt without great difficulty. The copper electrodes required more care; but approximately the same reproducibility was attained, provided the same general method of preparation was followed. A summary of the data is given.

(1) $\underset{-}{\mathrm{Zn}}\,|\,0.5\,N\ \underset{\longrightarrow}{\mathrm{ZnSO_4}}\,|\,0.5\,N\ \mathrm{CuSO_4}\,|\,\underset{+}{\mathrm{Cu}}$ $E = -1.106$ volts

(2) $\underset{+}{\mathrm{Zn}}\,|\,0.5\,N\ \underset{\longleftarrow}{\mathrm{ZnSO_4}}\,|\,\text{sodium cuprocyanide}\,|\,\underset{-}{\mathrm{Cu}}$ $E = 0.32$ volt

(3) $\underset{-}{\mathrm{Zn}}\,|\,\underset{\longrightarrow}{\text{sodium zinc cyanide}}\,|\,\text{sodium cuprocyanide}\,|\,\underset{+}{\mathrm{Cu}}$ $E = -0.13$ volt

(4) $\underset{+}{\mathrm{Zn}}\,|\,0.5\,N\ \mathrm{ZnSO_4}\,|\,\underset{\longleftarrow}{\text{sodium zinc cyanide}}\,|\,\underset{-}{\mathrm{Zn}}$ $E = 0.45$ volt

(5) $\underset{-}{\mathrm{Zn}}\underset{\rightarrow}{|||}\underset{+}{\mathrm{Cu}}$ $E = -1.05$ to -1.30 volts. The values obtained on the same days as the other measurements of this series were mostly grouped around -1.2 volts; but, previously and subsequently, more divergent values were found.

(6) $\underset{+}{\mathrm{Cu}}\,|\,0.5\,\underset{\longleftarrow}{N}\ \mathrm{CuSO_4}\,|||\,\underset{-}{\mathrm{Cu}}$ $E = 0.02$ volt

(7) $\underset{-}{\mathrm{Cu}}\,|\,\underset{\longrightarrow}{\text{sodium}}\ \text{cuprocyanide}\,|||\,\underset{+}{\mathrm{Cu}}$ $E = -1.4$ to -1.50[1] volts

(8) $\underset{-}{\mathrm{Zn}}\,|\,0.5\,\underset{\longrightarrow}{N}\ \mathrm{ZnSO_4}\,|||\,\underset{+}{\mathrm{Zn}}$ $E = -0.03$ volt

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[1] When the first measurements on the Daniell cell with ionized air were made in 1935, the solutions were held on the electrodes with an agar gel. Re-design of the apparatus has made this unnecessary and all these measurements except No. 7 were made with only a thin film of solution covering the electrodes. When this was attempted with the cuprocyanide solution, cell 7 gave only about -0.5 to -0.7 volt and was very unsteady, presumably owing to oxidation of the cuprocyanide. Covering the electrode with filter paper, however, and wetting this with the solution caused the electrode to give the value tabulated. Complications, apparently due to some substance dissolved from the filter paper, will be discussed at a future time.

(9) Zn | 0.5 N $ZnSO_4$ ||| Cu $E = -1.16$ volts
− → +

(10) Zn | 0.5 N $ZnSO_4$ ||| 0.5 N $CuSO_4$ | Cu $E = -1.10$ volts
− → +

(11) Zn ||| sodium zinc cyanide | Zn $E = 0.40$ volt
+ ← −

The values are not as consistent as those for the silver chloride concentration cells, though the discrepancy is not large. To make Nos. 4 and 11 consistent, we should have zinc 0.05 volt positive against zinc sulfate, whereas it is 0.03 volt negative according to No. 8, a discrepancy of nearly 0.1 volt. If we consider the potential difference between equimolecular zinc sulfate and copper sulfate solutions as zero and subtract 0.03 for zinc–zinc sulfate and 0.02 for copper–copper sulfate from the 1.106 for the cell as a whole, we get 1.056 volts for the contact potential between zinc and copper. This corresponds only with the lowest value given in No. 5; but it is quite probable that the copper was oxidized somewhat by the ionized air, in which case the observed values would be too high. This would apply also to No. 9.

As the most probable values for the present we may take $Zn|ZnSO_4$, $ZnSO_4|CuSO_4$, and $CuSO_4|Cu$ as approximately zero ± 0.1 volt, in which case the Volta potential for zinc and copper becomes 1.1 volts ± 0.1 volt.

Within the present limits of experimental error the electromotive force of the typical Daniell cell is due practically completely to the contact potential difference between zinc and copper. If we decrease the concentration of copper ions sufficiently, as by adding sodium cyanide solution to the copper sulfate solution, the direction of the current reverses (15) and the potential difference between copper and solution changes from approximately zero to approximately 1.4 to 1.5 volts, with the copper charged negatively. If we take Zn|sodium zinc cyanide|sodium cuprocyanide|Cu, the electromotive force is approximately zero (−0.13), the metal-electrolyte potential differences are approximately 1.45–0.32 volt (arithmetical sum is 1.8 volts), while the metal–metal potential difference is approximately 1.1 volts.

In Erskine-Murray's experiments (7), using a modified form of Volta's method with no ionized-air gap, the contact potential for zinc-copper would usually be from 0.7 to 1.0 volt, though occasional values as high as 1.2 volts were obtained (6). Similarly, Langmuir and others (20) report about 0.75 volt for the difference between the electron attractions of zinc and copper. The discrepancy between these results and ours is due to the fact that the physicists used pure zinc instead of amalgamated zinc. When we used pure zinc with an ionized-air gap we got values several tenths of a volt too low. The invisible oxide film is coherent in the case of pure zinc and not coherent in the case of amalgamated zinc.

When zinc or copper is oxidized intentionally, the oxidized metal becomes more cathodic. Erskine-Murray has even oxidized zinc to the point where it gave no potential difference against copper. We have confirmed his result by carrying the value down 0.8 volt with a less intensive oxidation. It is quite evident that no physicist who has studied Volta potentials has ever had a zinc surface that was not coated with a film, usually an oxide film. To that extent the chemists have always been right in their criticisms of the measurements of the physicists. Where the chemists slipped up was in not seeing that the presence of an oxide film on the zinc would decrease the apparent contact potential, and the presence of an oxide film on the copper would increase it. Not knowing the conditions under which an electromotive force is set up, they postulated that the oxidation of zinc in an air gap would set up a current.

Sir Humphry Davy (5) changed from the chemical theory to the contact theory in 1806 because "iron burnt in oxygen gas, properly connected with a condensing electrometer, gives no charge to it during the process. Nitre and charcoal deflagrated in communication with the same instrument do not by their agencies in the slightest degree affect the gold leaves." Ostwald (19) pointed out that there should be no electrification under these conditions, and yet he considered that the Volta fundamental experiment was merely an oxidation phenomenon.

The confusion that has arisen between the physicists and the chemists is brought out clearly in some comments by Kelvin on a letter by Lodge. Lodge said: "There is a true contact-force at a zinc-copper junction, which on a simple and natural hypothesis (equivalent to taking an integration constant as zero) can be measured thermoelectrically and is about one-third millivolt at 10°C. A voltaic force, more than a thousand times larger, exists at the junction of the metals with the medium [solutions] surrounding them; and in an ordinary case is calculable as the difference of the oxidation-energies; but it has nothing to do with the heat of formation of brass."

Kelvin said: "What would be the efficacy of the supposed oxygen bath in the experiments with varnished plates of zinc and copper? or in Erskine-Murray's experiment, described in his paper communicated last August to the Royal Society, in which metallic surfaces, scraped under melted paraffin so as to remove condensed oxygen or nitrogen from them, and leave fresh metallic surfaces in contact with a hydrocarbon, are subjected to the Voltaic experiment? or in Pfaff's and my own and Pellat's experiments with different gases, at ordinary and at low pressures, substituted for air? or in Bottomley's high vacuum and hydrogen and oxygen experiments above?"

"The anti-Voltaists seem to have a superstitious veneration for oxygen. Oxygen is entitled to respect because it constitutes fifty per cent of all the chemical elements in the earth's crust, but this gives it no title for credit as coefficient with zinc and copper in the dry Volta experiment, when there is none of it there. Oxygen has more affinity for zinc than for copper; so has chlorine and so has iodine. It is partially true that different metals—gold, silver, platinum, copper, iron, nickel, bismuth, antimony, tin, lead, zinc, aluminium, sodium—are for dry Volta contact-electricity in the order of their affinities for oxygen; but it is probably quite as nearly true that they are in the order of their affinities for sulphur, or for oxy-sulphion (SO_4) or for phosphorus or for chlorine or for bromine. It may or may not be true that metals can be arranged unambiguously in order of their affinities for any of these named substances; it is certainly true that they cannot be arranged *definitely and surely* in respect to their dry Volta contact-electricity. Murray's burnishing, performed on a metal which has been treated with Pellat's washing with alcohol and subsequent scratching and polishing with emery, alters the quality of its surface far more than enough to change it from below to above several metals polished only by emery; and, in fact, Pellat had discovered large differences due to molecular condition without chemical difference, before Murray extended this fundamental discovery by finding the effect of burnishing."

While we agree with Lord Kelvin's conclusion that there is a real potential difference between two metals in contact, we cannot endorse all of his arguments. Bottomley (3) found a value of a little over 0.74 volt for the Volta potential between zinc and copper. Reducing the pressure to less than 0.002 mm. had no effect on the measured potential difference, nor did the substitution of hydrogen for air. These experiments prove nothing nowadays, because the low pressure would not decompose a zinc oxide film and gaseous hydrogen would not touch it at ordinary temperatures. Erskine-Murray scratched a copper plate under melted paraffin wax so as to get a presumably clean surface, allowed the wax to cool, and found that there was little or no change relative to a plate exposed to air but not covered with wax. This sounds very convincing until one remembers that air is quite soluble in melted paraffin, 15 to 20 volume per cent, and that consequently the copper plate was always exposed to oxygen and undoubtedly always had an oxide film on it.

Kelvin lays special stress on the fact that the order of metals as determined by oxygen, chlorine, sulfur, etc., are much the same; but this does not prove anything. Unless special complexes are formed, the heats of reaction and the free energies will vary approximately in the same order. The question of the effect of burnishing and scratching is of no importance today, because we know that changing the crystal size and straining the crystals have definite effects on the potential differences at electrode surfaces.

LEAD STORAGE CELL

The lead electrodes were made from sheet lead. To prepare a peroxide electrode, a lead electrode was made anode in 20 per cent sulfuric acid with a current density of about 1 ampere per dm.[2] Almost at once it turned dark brown with a coppery sheen, and then oxygen was given off. After a few minutes the electrode was removed, rinsed well with distilled water, and dried quickly over a heater. It must not be allowed to stand wet more than ten or twenty minutes, otherwise the film breaks down. The peroxide film is purposely left thin to facilitate the removal of acid and water. When this was not necessary, a thicker film was prepared by forming the electrode. The ionized-air cells showed occasionally a marked tendency to change with time.

$$(1)\ \underset{-}{\text{Pb}} \mid \underset{\longrightarrow}{\text{H}_2\text{SO}_4\ (\text{sp. gr. } 1.20)}\ \underline{\text{PbO}_2} \mid \underset{+}{\text{Pb}} \qquad E = -2.07 \text{ volts}$$

$$(2)\ \underset{+}{\text{Pb}} \mid \underset{\longleftarrow}{\underline{\text{PbO}_2}} \ |||\ \underset{-}{\text{Pb}} \qquad E = 1.26 \text{ volts}$$

$$(3)\ \underset{+}{\text{Pb}} \mid \underline{\text{PbO}_2}\ \underset{\longleftarrow}{\text{H}_2\text{SO}_4\ (\text{sp. gr. } 1.20)}\ |||\ \underset{-}{\text{Pb}} \qquad E = 2.05 \text{ volts}$$

$$(4)\ \underset{-}{\text{Pb}}\ |||\ \underset{\longrightarrow}{\text{H}_2\text{SO}_4\ (\text{sp. gr. } 1.20)}\ \underset{+}{\text{Pb}} \qquad E = -0.06 \text{ volt}$$

To make 1, 3, and 4 consistent, 4 should have been 0.02 instead of −0.06. The most probable values at present are:

$$\text{Pb} \underset{\rightarrow}{\mid} \text{H}_2\text{SO}_4 = 0.02 \pm 0.1$$

$$\text{H}_2\text{SO}_4 \underset{\rightarrow}{\mid} \underline{\text{PbO}_2} = 0.80 \pm 0.1$$

$$\underline{\text{PbO}_2} \underset{\rightarrow}{\mid} \text{Pb} = 1.20 \pm 0.1$$

This makes the total for the cell 2.07, as it should be; but the data are not really anywhere near as accurate as this. There is always the probability of an oxide film on the lead.

To get away from this to some extent a few experiments were made with an amalgamated zinc anode in zinc sulfate.

$$(1)\ \underset{-}{\text{Zn}} \mid 0.5\ N\ \text{ZnSO}_4 \mid \underset{\longrightarrow}{\text{H}_2\text{SO}_4\ (\text{sp. gr. } 1.20)}\ \underline{\text{PbO}_2} \mid \underset{+}{\text{Pb}} \qquad E = -2.47 \text{ volts}$$

$$(2)\ \underset{-}{\text{Zn}}\ |||\ \underset{\longrightarrow}{\text{H}_2\text{SO}_4\ (\text{sp. gr. } 1.20)}\ \underline{\text{PbO}_2} \mid \underset{+}{\text{Pb}} \qquad E = -2.50 \text{ volts}$$

$$(3)\quad \underset{-}{\mathrm{Zn}} \;|||\; \underset{\rightarrow}{\underline{\mathrm{PbO_2}}} \mid \underset{+}{\mathrm{Pb}} \qquad E = -1.60 \text{ volts}$$

$$(4)\quad \underset{-}{\mathrm{Zn}} \underset{\rightarrow}{\;|||\;} \underset{+}{\mathrm{Pb}} \qquad E = -0.41 \text{ volts}$$

This means in round numbers:

$$\mathrm{H_2SO_4} \underset{\rightarrow}{\mid} \underline{\mathrm{PbO_2}} = 0.90 \pm 0.1$$

$$\mathrm{PbO_2} \underset{\rightarrow}{\mid} \mathrm{Pb} = 1.20 \pm 0.1$$

No matter what set of figures one takes, the peroxide electrode gives rise to practically all the electromotive force of the cell, and the potential differences on the two sides of the peroxide film are of the same general magnitude. That will undoubtedly remain true even though the absolute values be shifted.

PLATINUM-HYDROGEN ELECTRODE

It seemed probable that platinum in the presence of hydrogen would behave differently from platinum in air, contrary to what Bottomley and others believed. Consequently a few preliminary experiments were made to test this.

A smooth, bright-platinum inner electrode was used with silver, copper, and amalgamated zinc outer electrodes (prepared as before) as references. Tests showed that the potentials of zinc and of silver measured against copper were not affected appreciably by substituting ionized hydrogen for ionized air. The platinum was cleaned either by glowing in a flame or by treating with warm chromic-acid cleaning solution (bichromate and sulfuric acid).

The hydrogen was from a commercial cylinder and was, at first, passed through alkaline pyrogallol and concentrated sulfuric acid to purify it; but later, in order to avoid explosions, it was found necessary to pass it into the electrode chamber too rapidly to permit washing. No significant differences in the potentials were observed when purification of the hydrogen was discontinued. Behavior similar to that of a poisoned hydrogen electrode in a liquid solution was noticed on one occasion, but did not occur again.

To confine the hydrogen around the electrodes a copper box was made. In use, this was inverted on the desk top near the electrode and filled with hydrogen through a tube at the top. Then, with the hydrogen still flowing, it was picked up carefully and lowered quickly over the electrodes displacing the air. The excess hydrogen escaped round the bottom. This method was preferable to placing the copper box over the electrodes and then passing in hydrogen at the top to displace the air downwards, since the latter procedure resulted occasionally in explosions, due apparently to catalysis at the platinum surface.

The reproducibility of cells with platinum electrodes is not very good as yet. We had hoped that the hydrogen cells would behave more consistently than they did, but the general results show up fairly well. It made little difference whether the platinum was activated by flaming or in a chromic-acid cleaning solution.

In the following data H denotes ionized hydrogen.

(1) Ag ||| Pt $E = -0.17$ volt
− → +

(2) Ag | H | Pt $E = 0.83$ volt
+ ← −

The values in 1 and 2 are based on a single measurement each.

(3) Ag ||| Cu and Ag | H | Cu $E = 0.30$ volt, the same in the two cases.
+ ← − + ← −

(4) Cu ||| Pt $E = -0.76$ volt
− → +

(5) Cu | H | Pt $E = 0.35$ to 0.50 volt
+ ← −

(6) Zn ||| Pt $E \doteq -1.4$ volts
− → +

(7) Zn | H | Pt $E = -0.33$ volt
− → +

These results are not consistent among themselves. Since we know that Zn|H|Cu is about the same as Zn ||| Cu and that Zn|H|Ag is about the same as Zn ||| Ag, we conclude that ionized air and ionized hydrogen behave about alike with zinc, copper, and silver, whereas ionized hydrogen makes platinum 1.0 to 1.2 volts less noble. This is another way of saying that platinum activates hydrogen—which we know happens—whereas zinc, copper, and silver do not activate it appreciably under these conditions. Spiers (21) obtained very different values for iron-platinum in air and in hydrogen, but he attributed this chiefly to changes in the iron. He may have been right in this, because his treatment was a bit heroic.

BEHAVIOR OF ALLOYS

In order to get a preliminary idea of how alloys might be expected to behave, a crude, synthetic alloy was prepared by covering a zinc electrode more or less completely with pieces of copper. These alloy substitutes replaced the zinc electrode in our standard Daniell cell and were also measured against copper with an ionized-air gap between. The two systems behaved entirely differently, rather to our surprise. In the solution the composite electrode gave low values for a short time and then came back approximately to the value for the Daniell cell. The composite electrode is a short-circuited cell and precipitates zinc on the copper. One measures, therefore, the potential due to the less noble phase in the alloy.

With the ionized-air gap against copper, the composite electrode gave a value nearly equal to that of zinc when the amount of attached copper was very small and nearly equal to that of copper when the zinc surface was covered nearly completely by copper. With the composite electrode and the ionized-air gap, there is no change in surface if we assume that oxidation is negligible under the conditions of the experiments, and consequently the observed electromotive force is a function of the nature and relative masses of the two phases in a binary alloy.

This explains why an electrode is so much more sensitive to polishing and scratching when determining the single-potential differences by Kelvin's methods than when the same electrode is in contact with a solution. If the scratching or polishing makes the surface more or less homogeneous, it will change the observed potential difference, whereas the electrode in solution changes only when one changes the less noble phase.

PASSIVE IRON

It was expected that we could measure the Kelvin single-potential difference between iron and passive iron, thereby getting an independent confirmation of our previous proof (2) that passive iron owes its peculiarities to an adsorbed film of the instable oxide, FeO_3. To eliminate the effect of oxidation as much as possible, the iron electrode was amalgamated with sodium amalgam and the sodium washed out. The iron was made passive in concentrated nitric acid, sp. gr. 1.42, and was washed and dried carefully to avoid damaging the film. After the measurement, it was tested for passivity by dipping into nitric acid of sp. gr. 1.20.

Against amalgamated iron, iron which has stood in the air for several days after being cleaned, iron which has been made passive and dried carefully, active iron dried in the same way, and iron freshly cleaned in acid, rinsed and wiped dry, all give approximately the same values. They are approximately 0.1 volt cathodic. To make matters worse, a piece of iron which has been heated in the air until it has a thick film of oxide on it is approximately 0.6 volt cathodic to amalgamated iron. At present the Kelvin method gives no information in regard to passive iron. We do not know whether this is because the oxide film is too thin, too porous, or both. We do know that a thin film of oxide on zinc lowers the potential 0.3-0.4 volt, while a thick one may lower it 0.8-1.0 volt. We have also shown that an unspecified iron oxide film, presumably ferric oxide, will change the

Kelvin potential against iron 0.1–0.6 volt, perhaps more. More study of the oxide films is evidently called for.

SUMMARY

The general results of this paper are as follows:

1. Both Kelvin and Helmholtz evidently saw that a term for the Volta potential is included in the heat of reaction as determined by the thermochemist, though they seem not to have mentioned it specifically. The chemist has not been clear on this point because he has postulated that the Volta potential is negligible. Gurney (1932) is apparently the man who brought the matter into the open.

2. A pure zinc surface in air is always coated with a coherent film of oxide which makes the metal appear more noble. Amalgamated zinc does not form a coherent film on the surface. Since the physicists, from Volta down to the present, have not understood about amalgamated zinc, they have never had a surface corresponding at all to pure zinc.

3. Scratching a zinc or copper surface under molten paraffin is merely a beautiful gesture, because air is soluble in the hydrocarbon. A further proof is that the results thus obtained are those of the slightly oxidized metal.

4. By using amalgamated zinc we have been able to confirm the contention of Kelvin and of J. J. Thomson that an ionized-air gap removes most, and probably all, of the potential difference between the adjoining phases.

5. By putting in an ionized-air gap successively at each junction in a voltaic cell it is possible now to measure the Kelvin single-potential difference at that junction to at least ±0.1 volt. There is no apparent reason why the measurements should not be made much more accurate.

6. In the ordinary Daniell cell, Zn|0.5 N $ZnSO_4$|0.5 N $CuSO_4$|Cu, practically all the electromotive force arises at the zinc–copper junction, the potential differences at the other junctions being each approximately zero.

7. On adding sodium cyanide to both sides of the ordinary Daniell cell the electromotive force may be dropped from 1.106 volts to 0.13 volts, in which case the arithmetical (not algebraical) sum of the metal–electrolyte potentials increases from approximately zero to approximately 1.8 volts, which is nearly double the Volta potential difference between the metals.

8. In the lead storage cell with sulfuric acid of sp. gr. 1.20, practically all of the electromotive force is developed at the lead peroxide electrode, the potential differences at the two sides of the peroxide film being roughly of the same order of magnitude.

9. The Kelvin single-potential difference for platinum–hydrogen and

platinum-air is apparently about 1.0-1.2 volts. The change from air to hydrogen has no marked effect with zinc, copper, and silver.

10. With two-phase binary alloys the Kelvin single-potential difference is a function of the nature and relative masses of the two phases.

11. It is not possible at present to get information about passive iron with an ionized-air gap.

12. We have used the term "Kelvin single-potential difference" because it is not yet known whether the ionized-air gap removes all the potential difference between the adjoining phases and gives the true or Volta potential differences.

13. The important thermodynamic developments by Helmholtz, Gibbs, Nernst, and Planck are not affected by these measurements. Their validity is the same now that it was before. The calculations of so-called solution pressures are now worthless, because they depended on the explicit assumption that the contact potential difference between metals was negligible.

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SEDIMENTATION VOLUME, DILATANCY, THIXOTROPIC AND PLASTIC PROPERTIES OF CONCENTRATED SUSPENSIONS

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Concentrated paste-like suspensions of fine powders in liquids manifest certain properties, which depend strongly on the degree of packing. The rule given in table 1 was put forward, and was shown to hold in a few cases (2, 3). This rule was considered to be rather a rough guide, since factors such as particle shape, etc., were not taken into account. It would obviously be necessary to investigate the physical side of each of these phenomena more thoroughly, because very little is known about them. But, before doing so, it seemed desirable to compare the behavior of a large number of powders of different kinds to see whether the rule really was a first approximation to the truth, and to detect cases which might be specially fit for more exact investigation. This was the aim of the following paper.

The substances used, most of which are minerals, are listed in table 2. The objection could be raised that they might be impure, and that this would impair the results. We selected the minerals in as pure a condition as possible, and any obvious foreign matter was removed; there were two mixtures,—chalk and Solnhofen slate. In addition, the results seemed to show that small amounts of impurities, less than 1 per cent or so, did not change fundamentally the properties under investigation.[1] Minerals have, on the other hand, several advantages. Many of them are highly insoluble, and they are harder than the solid products of the same constitution chemically which have been precipitated from solution.

A thixotropic and plastic behavior was observed only if the solid particles in the suspension were sufficiently fine. There should be present a fairly high percentage with a diameter of between 1 and 10 μ.

The original substances were first coarsely ground in a porcelain mortar, or in an iron percussion mortar in the case of hard substances. These powders were then ground to the correct size, in most cases in a porcelain

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[1] Cf. the discussion on the behavior of different forms of calcium carbonate, at the end of this paper.

ball-mill, containing 55 hard porcelain balls of a diameter of 1.50 cm.; generally, about 200 g. of the coarse powder was put into the mill with 0.25 l. of water, the lid then clamped on, and the whole lot rotated at 60 to 80 R.P.M. until the powder was sufficiently fine, as determined by sedimentation. Very hard substances, such as quartz and rutile, were powdered finely in a mechanical agate mortar, because they would be contaminated to a large extent with porcelain powder if the ball-mill were used.[2]

The powders were fractionated by sedimentation in water, and the fraction with particles of diameters between 1 and 10 μ was selected for the experiments. In some cases the particles stuck together in water; then they sedimented in a clear line, either because they were actually homodisperse, or because the larger particles formed a network which enmeshed the smaller ones, and caused the whole lot to sediment together. Since such powders could not be fractionated under these conditions, they were ground in the ball-mill until the rate of fall of the sedimenting level corresponded to the correct particle size. The diameter of the particles, as calculated from the sedimentation velocity, according to Stokes' law, agreed in a satisfactory way with the value observed in microscopic measurements.

TABLE 1

Properties of paste-like suspensions

PROPERTIES DEPENDENT UPON CLOSE PACKING	PROPERTIES DEPENDENT UPON LOOSE PACKING
Small volume of sedimentation	Large volume of sedimentation
Dilatancy	No dilatancy
No thixotropy	Thixotropy
No plasticity	Plasticity

Four liquids were used,—pure water, and N aqueous solutions of hydrochloric acid, sodium hydroxide, and sodium chloride. The measurements with the electrolyte solutions were clearly not sufficient to show how changes in the nature and concentration of the electrolytes influenced the properties under investigation, but it seemed desirable to use these solutions in order to gain some idea of the kind and amount of the change caused by the presence of electrolytes.

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[2] This contamination might falsify the results also with other powders, especially those of harder substances. To test this a sample of a fairly hard substance, hematite (hardness 5.5–6.5 in Mohs' scale) was ground to the same size (about 5μ diameter) in the ball-mill, another in the agate mortar. The two samples behaved identically as to dilatancy, thixotropy, and plasticity. Hematite pastes are not dilatant, but are strongly thixotropic and plastic; a small difference as to sedimentation volume was insignificant. It was shown further that finely powdered porcelain could not be expected to behave in a very active way as an impurity. Its pastes turned out to be closely packed; they were dilatant, but neither thixotropic nor plastic.

TABLE 2

Description of substances studied

SUBSTANCE	CHEMICAL COMPOSITION	HARDNESS	CRYSTALLINE STRUCTURE
1. Diamond	C	10	Cubic
2. Graphite	C	0.5–1	Hexagonal
3. Jet	(C)[*]		Amorphous
4. Corundum	Al_2O_3	9	Hexagonal
5. Hematite	Fe_2O_3	5.5–6.5	Hexagonal
6. Pyrolusite	MnO_2	2–2.5	Rhombic
7. Litharge	PbO	5–5.5	Amorphous
8. Quarts	SiO_2	7	Hexagonal
9. Rutile	TiO_2	6–6.5	Tetragonal
10. Titanium dioxide	TiO_2		Tetragonal
11. Vanadium pentoxide	V_2O_5		Rhombic
12. Tin pyrites	$SnS_2 \cdot Cu_2S \cdot FeS$	3–4	Tetragonal
13. Galena	PbS	2–3	Cubic
14. Mosaic gold	SnS_2		Hexagonal
15. Fluorspar	CaF_2	4	Cubic
16. Barytes	$BaSO_4$	3–3.5	Rhombic
17a. Gypsum (oven-dried)	$CaSO_4 \cdot xH_2O$[†]	1.5–2	Rhombic
17b. Gypsum (air-dried)	$CaSO_4 \cdot 2H_2O$	1.5–2	Monoclinic
18. Selenite	$CaSO_4 \cdot 2H_2O$	1.5–2	Monoclinic
19. Calcium carbonate (pure)	$CaCO_3$		Hexagonal
20. Aragonite	$CaCO_3$	3.5–4	Rhombic
21. Iceland spar	$CaCO_3$	3	Hexagonal
22. Limestone	$CaCO_3$	3	Hexagonal
23. Marble	$CaCO_3$	3–4	Hexagonal
24. Mica (muscovite)	Complex silicate	2.5–3	Monoclinic
25. Monax glass	Complex silicate	6	Amorphous
26. Porcelain	Complex silicate	7	Amorphous
27. Kaolin	Complex silicate	2–2.5	Monoclinic
28. Steatite	Complex silicate ($H_2Mg_3Si_4O_{12}$)	1	Monoclinic
29. Chalk	$CaCO_3$, mixed with clay		Hexagonal
30. Solnhofen slate	$CaCO_3$, mixed with clay		Hexagonal

[*] Jet is an intermediate compound between wood and coal, formed from petrified wood under high pressure, and it contains vegetable structures. It is homogeneous, and contains carbon, some 8 per cent of water, and 20 per cent of hydrocarbons, which appear on distillation. It shows a subconchoidal fracture, and is amorphous.

[†] After the gypsum had been ground to the correct size in water in the ball-mill, the excess water was removed by filtration and half of the residue was dried at about 90°C. in a steam oven, and half by exposure to the air for several days. The oven-dried sample had lost some of its water of crystallization.

SEDIMENTATION VOLUME

This was determined by allowing a known weight of powder to sediment uniformly in a known volume of water or aqueous solution, in graduated tubes having an internal radius of 0.58 cm., calibrated in cubic centimeters up to 20 cc., and fitted with ground glass stoppers. The weight of the substance taken, in all cases, was that weight, as calculated from the density of the material, which had the same volume as had 3.00 g. of quartz, i.e., 1.13 cc. By using a constant volume, the results for the individual substances could be directly compared.

The tubes were first carefully cleaned. Then a small known volume of the liquid was poured in, and this was followed by the weighed quantity of the powder, and finally the rest of the liquid was admitted, and the whole lot shaken up until all the solid was in suspension. When the sediment had commenced to settle, and a layer of clear liquid had appeared on the surface, the solid which remained on the walls of the tube above the liquid was pushed down into the liquid by means of a rubber plunger. Then the tube remained undisturbed for at least twenty-four hours, and the volume of the sediment was read at the end of that time. The sediment was shaken into suspension again after this, and the experiment repeated until the sedimentation volume had reached a constant figure.

The sedimentation volume proved to be a most intricate phenomenon, depending strongly upon many factors; it evidently needs a thorough examination. The absolute value of the volume of sedimentation was less in wider tubes, and, in consequence, all the tubes had to be of the same internal cross section, in this case, 1.06 sq. cm., and of constant bore. It also depended, to a certain extent, on the volume of the liquid; it decreased slightly as the volume of the liquid decreased below a certain limiting liquid volume, which in this case was about 9.0 cc., so that 15.0 cc. of liquid was used in all cases, in order to be well above this limiting volume.

In many cases, as the determinations were repeated, the sedimentation volumes decreased gradually until the final value was reached. This was probably due to the removal of entrapped air by repeated shaking. This behavior, or when there was only a very small change at all, was considered to be the normal behavior. An increase in sedimentation volume which was observed in a number of cases was anomalous, and most likely due to a chemical action between solid and liquid.

VELOCITY OF SEDIMENTATION

Measurement of the sedimentation volume naturally led to a determination of the velocity of sedimentation, this being obtained by observing the limiting line between sediment and clear liquid a short time after shaking, and at intervals of a few minutes until there was practically no further fall; the time for the fall of the majority of particles was from two to three hours. Sedimentation velocity proved to be valuable in characterizing the behavior of the different suspensions.

With many substances, the sedimentation volume decreased markedly if the tube was rolled to and fro between the palms of the hands after the solid had settled, and the particles allowed to settle without any further shaking. The standard time of rolling was 30 sec., the time of settling was, as before, about twenty-four hours, and this procedure was repeated until a constant volume was reached. A strong decrease, more than 25 per cent, was only observed with particles which were expected to be anisometric, i.e., plates or needles; for instance, mosaic gold in water (decrease 33 per cent), mica in water (decrease 40 per cent), and graphite in *N* hydrochloric acid solution (decrease 30 per cent). So the effect was probably due to the fact that the particles were oriented by the gentle movement. They were able to settle after orientation to a smaller sedimentation volume, the plates lying like sheets of a book on each other, while so long as they were lying irregularly, they enclosed a much larger volume of liquid, as was the case when they settled at random without being oriented (9).

DILATANCY

Dilatancy (8) was investigated only in a qualitative way, by mixing known amounts of the powders and liquids in a small basin into pastes, and observing the effect of a disturbance with a spatula. Normal or strong dilatancy was shown, for example, by a mixture of 5.0 g. of quartz and 2.25 cc. of water. This paste, if left to itself, appeared quite fluid, but when it was disturbed with a spatula, it immediately became dry and very resistant to the spatula. It was extremely difficult to pick up a portion of the paste on the spatula, but, once there, it became fluid again, and ran off in the manner of a treacly liquid. After the disturbance, if the paste was left alone again, it rapidly became liquid, and this could be accelerated by tapping the basin.

Non-dilatant pastes showed no change in consistency when they were disturbed with a spatula. No liquid exuded when they were spread out, nor when they were left to themselves, nor when the basin was tapped.

An intermediate behavior was observed between these extreme cases in a number of pastes, best described as a passive or weak dilatancy. The pastes concerned did not show any obvious change in consistency on mechanical treatment, nor did liquid exude when they were left to themselves, or at least, this happened very slowly. But when the vessel containing the paste which had been mixed with the spatula was gently tapped, liquid was soon seen to come out in quantity.

THIXOTROPY

Thixotropy was also observed in somewhat of a qualitative fashion, in a tube 18.0 cm. long and 0.93 cm. in internal diameter, fitted with a ground glass stopper. A series of pastes of increasing liquid concentrations was made, beginning, frequently, with a mixture of 3.0 g. of the solid powder and 1.0 cc. of liquid, and the liquid content was increased in increments of 0.25 cc. at a time.

For each thixotropic paste, there was a region of concentrations where the mass became liquid on shaking, but solidified when left to rest. With a certain minimum amount of liquid, the paste could not be heard or felt to move when shaken; the only change was a change in its position in the tube before and after shaking. This concentration of solid was taken as the upper limit of the thixotropic region. As more liquid was added, the state was reached where the paste could be heard to flow when the tube was shaken, but it solidified immediately after shaking ceased. With still more liquid, the time of solidification became finite, and increased gradually; determinations ceased after it had reached ten minutes. The lower limit of the thixotropic region was generally chosen as that when the time of solidification was about a minute or so. On adding an excess of liquid, the paste did not solidify at all, but separated into two phases on standing.

In non-thixotropic pastes, the liquid masses did not solidify at all. As soon as the amount of liquid was sufficiently large, generally the whole mass flowed down when the tube was inverted, and the liquid separated from the solid when the tube was allowed to remain undisturbed, the sediment not being thixotropic. In some cases, mostly with coarser powders, when the tube was inverted, the solid remained as a hard clod at the top, and clear liquid ran down the walls of the tube.

Quite a number of pastes were found to be rheopectic, that is, they solidified more quickly if they were subjected to a regular gentle motion, as, for instance, by tapping the tube on the bench, or by rolling it to and fro between the palms of the hands. Rheopexy could only be observed in a region of concentrations where the time of thixotropic solidification was fairly long.[3]

PLASTICITY

Plasticity has not, so far as we know, been determined by any standard method. In order to compare plasticity with the other properties under consideration, an isothermal method of characterizing plastic behavior was essential. The method used was practically identical with that used for investigating flow pressure (6). The pastes were pressed against a disc, through the center of which was a small hole. The shearing took place at the hole. If the paste issued from the hole unchanged and well deform-

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[3] In some pastes a stable foam was formed, which was liable to cause apparent thixotropy and rheopexy by preventing the liquid part from flowing in the tube. This foam could be broken by a gentle tap on the outside of the tube, and then it could be seen whether thixotropy or rheopexy existed or not.

able, it was plastic;[4] it was not plastic if it was changed in any way by the shearing forces.

This "plastometer" is shown in figure 1. The brass cylinder, AA, 7.6 cm. long, and 1.91 cm. in internal diameter, was fitted with a brass screw cap B at one end, to which was attached an inextensible rubber tube to convey the air pressure from a cylinder of air; and with another cap C on the other end with a hole in its center, 0.91 cm. in diameter. The jet, abcd, was housed in a piece of brass, whose vertical cross section was T-shaped, and which fitted through the hole in C, and could be clamped tight by screwing C on to the cylinder, and an air-tight joint obtained by interposing a lead washer. The jet was 0.16 cm. in diameter, drilled centrally and ground smooth with emery paste; the top, ab, was slightly countersunk, and the bottom edges were rounded off, else the threads tended to curl up and stick to the brass and so form a loop instead of a nice straight thread. It was found necessary to communicate the air pressure to the paste by means of a brass piston E, of weight 60.6 g. The paste was put into the space F.

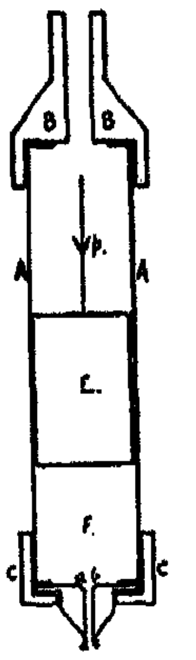

Fig. 1. The plastometer

Air pressure was applied on to the piston from a cylinder of compressed air. The pressure was controlled by means of a reducing valve on the cylinder. Pressure was measured by means of a simple mercury manometer in centimeters of mercury, and all pressures are given as such. This valve also controlled the rate of rise of pressure.

The requisite amounts of liquid and powder were mixed in a small basin

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[4] We would thus agree with the following definition of plasticity: "Plasticity is that property which enables a material to be deformed continuously and permanently without rupture during the application of a force which exceeds the yield value of the material" (H. Wilson, *Ceramics; Clay Technology*, p. 55. New York (1927).)

with a flat spatula for a measured time, usually 30 seconds, and the homogeneous paste was transferred to the cylinder, also by means of the spatula, in a measured time, again usually 30 seconds. Then the cylinder and its ends were screwed together. After noting whether the weight of the piston alone was sufficient to cause any extrusion, pressure was applied slowly. The reducing valve was opened slightly to give a rate of rise of pressure of 1 or 2 cm. per minute, and this was continued for a few centimeters rise. Then the pressure was allowed to rise more quickly, and so on, in stages, always keeping the rate constant for a few centimeters rise before the next stage, and observing the effect of the pressure on the paste, until the final pressure rise of from 50 to 70 cm., which took place at about 60 cm. per minute.

TABLE 3

Behavior of a plastic paste of chalk

EXPERIMENT	PRESSURE	RATE OF RISE OF PRESSURE	RESULT	THREAD LENGTH
	cm.	*cm. per minute*		*cm.*
No. 1. 5 g. of chalk was mixed with 2.0 cc. of water by means of a flat spatula, in a small basin, for 30 sec., and transferred to the cylinder in 40 sec.	0		Nothing	
	1–3	1	Threads	1–2
	3–6	1–2	Threads	2–3
	6–10	6	Threads	3–4
	10–20	20	Threads	5–6
No. 2. 5 g. of chalk was mixed with 2.0 cc. of water by means of a flat spatula, in a small basin, for 30 sec., and transferred to the cylinder in 40 sec.	0		Nothing	
	1–2	1	Threads	1–2
	2–3	2	Threads	2–3
	3–9	7	Threads	3–5
	9–22	24	Threads	6–7

In each experiment all the paste was expressed.

If the paste was plastic, the mass was extruded in threads, which broke off as soon as they had reached a certain well-defined length. This length was measured on a scale below the jet.

Table 3 gives an example of the behavior of a plastic paste of chalk.

The measurements on the plasticity of these pastes were remarkably reproducible, provided that the above-mentioned precautions were taken.

The behavior of the pastes in this plastometer classified them very definitely and very simply into three groups: (*i*). *Plastic pastes*, which were extruded in threads of characteristic lengths. *Non-plastic pastes*, in which the extrusion took the nature of: (*ii*). Drops of clear liquid, there being left in the cylinder a hard and rather dry cake of the solid powder. (*iii*). Sticky or pasty drops, consisting of a mixture of the solid and liquid phases, containing an excess of liquid compared with the original mixture.

The rule mentioned above was found to hold for a great number of pastes.

Firstly, there are the cases agreeing with close packing; these are the suspensions which showed a small sedimentation volume, generally less than 4.0 cc. for the standard amount of substance (cf. page 1229), normal dilatancy, no thixotropy, and no plasticity, the extrusion in this case being sticky drops of liquid. (The figures in the ensuing tables are the final volumes of sedimentation in cubic centimeters, previous to any intentional orientation.) The pastes shown in table 4 belong to this group.

TABLE 4

Sedimentation volumes in cubic centimeters of closely packed pastes which are not thixotropic

SUBSTANCE	LIQUID PHASE			
	Water	*N* HCl	*N* NaOH	*N* NaCl
Jet	4.0	4.6		4.6
Corundum		3.75		
Quartz	2.0	2.7		
Vanadium pentoxide	3.35			
Fluorspar	3.1	2.1	3.1	3.2
Monax glass	2.0	2.65		
Porcelain	2.0	2.7	3.65	3.4

TABLE 5

Sedimentation volumes in cubic centimeters of loosely packed pastes, which are strongly thixotropic and plastic

SUBSTANCE	LIQUID PHASE			
	Water	*N* HCl	*N* NaOH	*N* NaCl
Graphite	6.55	6.3	7.1	6.6
Jet			10.4	
Hematite	7.3	5.85	8.3	9.5
Titanium dioxide	9.6	7.0	10.1	9.75
Vanadium pentoxide		8.6		
Tin pyrites	7.55	10.6	5.4	7.5
Galena	8.8	8.8		5.95
Kaolin	6.3	6.5	6.8	7.4
Chalk			9.5	5.9
Solnhofen slate	5.9		11.2	5.9

Then there are cases agreeing with loose packing; these are the suspensions which showed a large sedimentation volume, generally greater than 6.0 cc., no dilatancy, strong thixotropy over a broad range of concentrations (for instance, thixotropic pastes of graphite in water contained from

32 to 52 per cent of solid and thixotropic pastes of hematite in water from 38 to 67 per cent of solid), and plasticity, the paste being extruded in well-defined long threads. To this group, the pastes listed in table 5 belong.

In addition to these cases in which the rule holds in its entirety, a number of examples were found where portions of the rule held quite strictly; generally, the properties connected in these cases were correlated in one direction only, and could not be reversed:

(*1*). There was practically no case of normal dilatancy which did not correspond to a small volume of sedimentation, that is, less than 4.0 cc. In this respect, there may be added to the pastes mentioned in table 4, those in table 6. These differ from those in table 4 by being weakly thixotropic; the range of thixotropy for corundum in water was from 63 to 67 per cent of solid, and that for Monax glass in *N* sodium chloride was from 57 to 63 per cent of solid. These pastes were not plastic.

TABLE 6

Sedimentation volumes in cubic centimeters of closely packed pastes which are dilatant, but also weakly thixotropic[6]

SUBSTANCE	LIQUID PHASE			
	Water	*N* HCl	*N* NaOH	*N* NaCl
Diamond	4.1	3.2		
Corundum	4.45		4.4	4.15
Quartz			3.4	3.3
Monax glass			3.5	3.5

The reverse does not hold true. Pastes with a very small volume of sedimentation need not show normal dilatancy; they may be passively dilatant. Examples of this are aragonite in water and *N* sodium chloride solution, and marble in water and *N* sodium chloride solution (see table 9).

(*2*). Suspensions which showed a large volume of sedimentation were also thixotropic. Examples are those in table 5, and to these, those in table 7 can be added. Table 7 contains pastes which have a large volume of sedimentation and, correlated with it, strong thixotropy, but which are

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[6] Litharge (in water and in sodium hydroxide solution) and rutile (in all four liquids) have probably to be added to this group. They both show certain anomalies. With litharge the volume of sedimentation is rather large (5.6 and 6.4, respectively), but as the latter increases in course of time, its behavior is anomalous and would need further investigation. Rutile in water is partly peptized, the sediment consisting of a brown layer. This is most likely an iron compound, and this impurity may be the reason why rutile pastes show no dilatancy, though this ought to be expected on the ground of their behavior as to the other properties. Titanium dioxide, as it is used for technical purposes and consisting of anatase, gives pastes which are very loosely packed (cf. table 5).

nevertheless passively dilatant and not plastic. In several cases the behavior of the sedimentation volume was anomalous; it increased markedly on repeating the experiment, but this was most likely due to some chemical reaction. This is obvious with the oven-dried gypsum. But this fact does not weaken the force of the argument that a large sedimentation volume favors thixotropy. (In table 7 the values given for the sedimentation volumes are the maximum values obtained.)

(*3*). Pastes which were markedly plastic were invariably thixotropic; they were also not dilatant. Table 8 contains pastes of this kind, but they do not fit into table 5 because the sedimentation volumes were medium or small.

TABLE 7

Sedimentation volumes in cubic centimeters of loosely packed pastes which are strongly thixotropic, passively dilatant, and not plastic

SUBSTANCE	LIQUID PHASE			
	Water	*N* HCl	*N* NaOH	*N* NaCl
Mica	8.45	8.5	8.25	8.0
Gypsum (oven-dried)	7.5	6.9		
Pure $CaCO_3$			7.05	
Iceland spar	6.7		8.4	7.1
Galena			10.9	

The extent of the thixotropic range for the suspensions cited in tables 7 and 8 was hardly less than that for the pastes in table 5, except that for mica it was decidedly smaller. Some examples are:

Substance	*Per cent solid in thixotropic pastes*
Mica	37-43
Gypsum (oven-dried)	41-60
Iceland spar	50-67
Pyrolusite	60-71
Chalk	48-63

The liquid in all cases was water.

Here again, assertions 2 and 3 may not be reversed, as already follows from tables 7 and 8. Many pastes were thixotropic, although they had a small volume of sedimentation, as appears from table 8, and further examples are again aragonite and marble, mentioned above and in table 9; many pastes were also thixotropic but not plastic (table 7).

Pastes of the latter kind were numerous and rather characteristic; in table 9 are given pastes which unite these properties. The sedimentation volume was medium or small, that is, between 3.4 and 6.5 cc.; the pastes showed passive dilatancy, distinct thixotropy, and no plasticity, clear liquid being pressed out of them.

Of these suspensions, gypsum (air-dried sample) has a fairly wide thixotropic range in water, 46 to 67 per cent solid, but the rest showed quite a limited range, for instance, mosaic gold in water, 52 to 60 per cent solid, and aragonite in water, 60 to 67 per cent solid.

The rule under discussion obviously simplifies matters too strongly. The following points have still to be considered.

TABLE 8

Sedimentation volumes in cubic centimeters of strongly plastic pastes which are also strongly thixotropic[6]

SUBSTANCE	LIQUID PHASE			
	Water	*N* HCl	*N* NaOH	*N* NaCl
Pyrolusite	4.6	4.4	4.4	4.6
Barytes	3.1	2.8	3.4	3.1
Selenite	5.5	4.75	3.5	4.3
Chalk	4.45			

TABLE 9

Sedimentation volume in cubic centimeters of thixotropic pastes which have a medium or small volume of sedimentation, and which are passively dilatant and not plastic

SUBSTANCE	LIQUID PHASE			
	Water	*N* HCl	*N* NaOH	*N* NaCl
Mosaic gold	6.0	5.2	4.8	5.8
Gypsum (air-dried)	5.3	5.9	4.7	4.8
Gypsum (oven-dried)			5.5	6.35
Pure $CaCO_3$	5.3			5.4
Limestone	5.3		6.4	5.6
Aragonite	3.65		5.75	3.4
Marble	3.4		4.55	4.2

In order that the pastes should show normal dilatancy, the particles should be quite independent of each other; then they are able to return spontaneously to the state of closest packing after they have been displaced. Particles of pastes with normal dilatancy (tables 4 and 6) are

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[6] Steatite must probably be added to this group. Its sedimentation volume could not be determined with certainty, owing to the very stiff foam which was formed and could not be broken. The plasticity measurements were also not well defined, obviously owing to the poor wettability of the powder. Pastes of selenite also gave only with high pressures well-defined threads when plasticity was measured

indeed very independent of each other. This can be seen in their behavior in the liquid medium under the microscope. They move about independently, and there is no attraction between them; if they come to rest by collision with each other, a slight disturbance can separate them and set them in motion again.

The independent nature of the particles belonging to this group of *pastes* is also shown by their *velocity of sedimentation*. The particles settle quite independently, according to Stokes' law:

$$U = \frac{2}{9} g a^2 \cdot \frac{(\rho - \sigma)}{\eta}$$

U = velocity of fall, g = acceleration due to gravity, a = radius of particles, ρ = density of particles, σ = density of liquid, and η = viscosity of liquid. If the suspension is sufficiently homodisperse, a, and thus U, is constant.

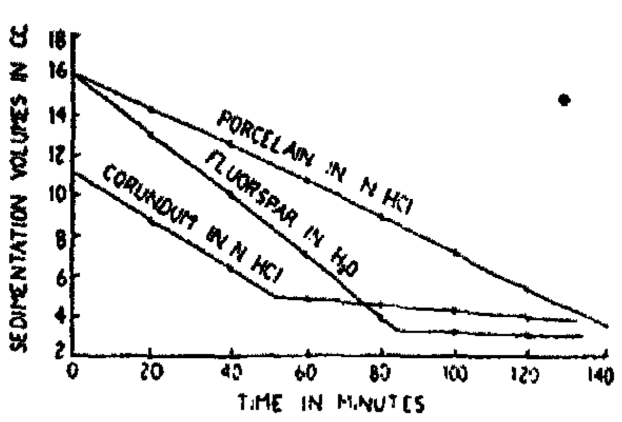

FIG. 2

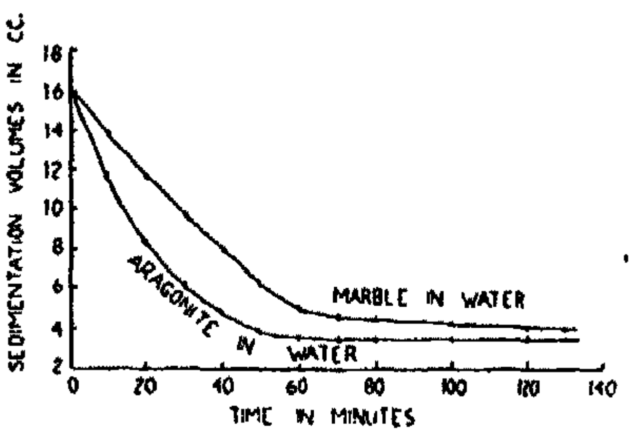

FIG. 3

FIG. 2. Sedimentation curves of porcelain, corundum, and fluorspar
FIG. 3. Sedimentation curves of marble and aragonite

In figure 2 the abscissa is the time in minutes, and the ordinate the volume of sedimentation in cubic centimeters, which is proportional to the space through which the particles have fallen. In the figure there are three curves for substances belonging to this group, porcelain and corundum in N hydrochloric acid solution and fluorspar in water. They are all straight lines approaching the abscissa; i.e., the tangent of the angle between the line and the abscissa, which is proportional to the velocity of sedimentation, is constant.

But the fact that a suspension has a small volume of sedimentation, that is, less than 4.0 cc., is not always an absolute proof that the particles are fully independent of each other, and that the packing is very close. Particles of aragonite and marble showed an anomalous behavior, in so far as they have a small volume of sedimentation in water and sodium chloride solution, but no normal dilatancy and a distinct thixotropy. It was found that their particles were not absolutely independent of each other when they were observed under the microscope. They formed clusters, generally with a large particle in the center, and smaller particles stuck round it. These clusters appeared fairly independent of any neighboring clusters. Their curves of sedimentation were also not so simple as in the first case mentioned (cf. figure 3).

This tendency to form clusters was found with the particles of all pastes mentioned in tables 7 and 9. It is readily understood why these pastes showed passive dilatancy. The liquid in the system is probably associated in part with the clusters, and the rest is free; evidence for this is obtained from experiments with the plastometer, when in all cases with the pastes under consideration clear liquid was pressed out; that is, the free liquid was expressed, and this amounted to about 50 per cent of the original amount. In the passively dilatant pastes, the clusters are buoyed up by the liquid associated with them to such an extent that when determining dilatancy the clusters do not assume a very close packing, and no liquid appears when the paste is left to itself. But when the vessel containing the paste is tapped, the solid phase is encouraged to separate from the liquid, and the free liquid appears on the surface. The clusters do not break up, and the phenomenon is reversible and may be repeated.

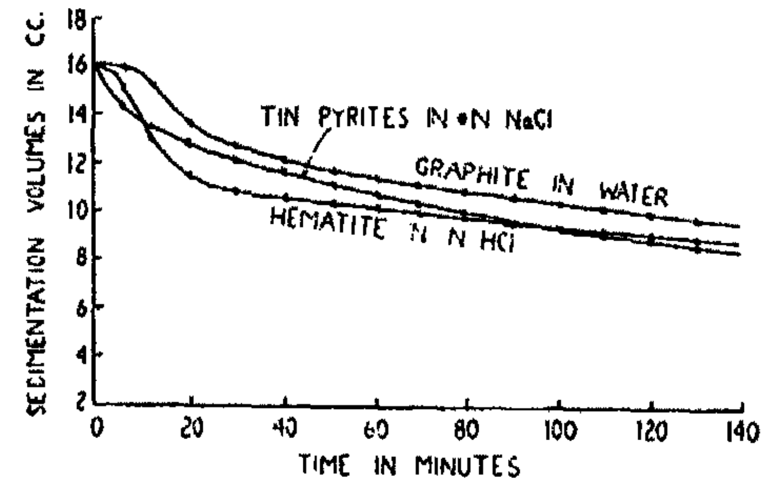

FIG. 4. Sedimentation curves of pastes which are not dilatant but strongly thixotropic and plastic

In pastes which are not dilatant but strongly thixotropic and plastic (tables 5 and 8), the particles aggregate to a much higher degree, as is shown in the microscope. They form a network through the system, and are all stuck together; there is no separation into clusters, and no motion.[7] With systems of this kind there are very irregular curves of sedimentation velocity (cf. figure 4). These are the cases in which the particles cannot

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[7] This difference in behavior—coherent network of clusters and separate clusters, respectively—is also shown by "short" and "long" suspensions of carbon black in hydrocarbons (cf. R. O. Neal and G. St. Perrott, "Carbon Black, its Manufacture, Properties and Uses," Bulletin 192 of the Bureau of Mines, p. 77 et seq., Washington (1922)).

be separated by fractionation. It is obvious that this strong aggregation favors the enclosure of large amounts of liquid, and thus causes a large volume of sedimentation, and thixotropy. There is indeed no exception to the rule that pastes with a large volume of sedimentation are always strongly thixotropic.

But the sedimentation volume need not be very large to cause a certain degree of thixotropy. If the sedimentation volume of the suspension is only a small amount greater than that of the most closely packed sediment, there appears a certain degree of thixotropy. Corundum, for instance, was not thixotropic in *N* hydrochloric acid solution, and its sedimentation volume was 3.75 cc.; but in water it was thixotropic and had a sedimentation volume of 4.45 cc. This small numerical increase of 0.60 cc. goes parallel with an increase in thixotropy.

The following observation on the variation of behavior of quartz particles in different liquid media assists this assertion. Quartz in water was not thixotropic. Quartz particles in water suspension on a microscope slide and viewed under a microscope were quite independent; they moved about, and gradually came to rest, and the smaller particles kept on moving long after the larger ones had ceased. By gently moving the cover glass, the system was disturbed and broken up, and it had to settle down all over again.

Quartz in *N* sodium hydroxide solution was thixotropic; quartz particles in this medium under the microscope moved about, but came to rest in a very much shorter time than in water, and there were no small particles left floating about. The system manifested attracting forces between the particles, and they seemed to cluster together. After the system had been disturbed by gently moving the cover glass, small particles rapidly made their way to the larger particles, and some could be seen to move with an acceleration, and attach themselves with a click.

This small change in behavior is sufficient to produce thixotropy; according to tables 4 and 6, the corresponding change in sedimentation volume for quartz is from 2.0 cc. in water to 3.4 cc. in *N* sodium hydroxide solution.

Here is then a further point, not expressed in the rule as originally specified, that although a large volume of sedimentation is always correlated with strong thixotropy, a large excess of liquid is not necessary to cause the latter phenomenon. Distinct thixotropic behavior may appear if the amount of liquid between the particles is not much larger than when the packing is very close. The volume of sedimentation need not be large. That is why a certain degree of thixotropy is so extremely frequent.

The dilatancy of these pastes and the manner in which they behave in the plastometer show that the liquid may be bound to the particles in a way varying strongly from paste to paste. If the liquid exudes spontaneously as in strongly dilatant pastes, it is bound very loosely, or only to a rather small amount of the particles. The fact that, in the experiments on plasticity, the liquid is pressed out of the paste more or less easily proves that the liquid is readily separated from the particles. If the pastes show passive dilatancy, the liquid is part free, and part bound on to the clusters, and only the free liquid is squeezed out. Here the particles have a marked affinity for each other, they allow clear liquid to be expressed (tables 7 and 9), and the residue is a hard, rather dry cake. In the case of the pastes mentioned in tables 4 and 6, the affinity between the particles is small, with the result that the particles pass out with the liquid without keeping up a coherent structure, and the nature of the extrusion is pasty drops. In the plastic pastes (tables 5 and 8), the coherence is probably due to a mutual affinity both between the particles themselves and between the particles and the liquid.

It is a drawback in the discussion of this problem that the behavior of sedimentation volume is so very complex and not sufficiently known. Some points on this theme have been already mentioned; a further one should not be neglected. There is perhaps a certain tendency to assume that, at least in aqueous pastes, the electrical charge on the particles outweighs all other influences in determining the sedimentation volume.[8] If the particles repel each other because they are markedly electrically charged or have a high ζ-potential, they remain independent and are able to glide over each other until they reach the closest packing. If the particles do not repel each other strongly, they stick to each other, that is, they are coagulated; in consequence they enclose large amounts of liquid, and this causes loose packing. The ζ-potential generally has a maximum in pure water, or in a small excess of OH^- ions, if the particles are naturally negatively charged, or of H^+ ions, if the particles are naturally positively charged; it decreases more or less strongly in solutions of neutral electrolytes, or in more concentrated solutions of acids and alkalis.

We actually frequently find a minimum of sedimentation volume in pure water, for instance, with the following substances,—jet, quartz, rutile, vanadium pentoxide, Monax glass, porcelain, pure calcium carbonate, limestone, Iceland spar, marble, mica, kaolin, steatite, chalk, and Solnhofen slate.

But there are also marked deviations from this normal behavior. A maximum of sedimentation volume in pure water was found in the case of the following substances,—corundum, mosaic gold, gypsum, selenite, and pyrolusite. A smaller volume in *N* acid solution was found with diamond and fluorspar, and a smaller volume in *N* sodium chloride solu-

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[8] The following reasoning is especially due to Ehrenberg (*Bodenkolloide*, p. 83 et seq., Dresden (1918)) and von Buzágh (Kolloidchem. Beihefte **32**, 114 (1930)), but they also take into account the influence of hydration.

tion was found for aragonite. This behavior needs thorough investigation. It is known that the volume of sedimentation may vary strongly with quartz in organic liquids where the electrical charge is of small importance (7, 5). Probably the question of solvation can also not be neglected in the case of aqueous solutions.

There appears to be no correlation between the ζ-potential of particles of different chemical nature, and their behavior concerning sedimentation volume, etc. For a number of particles, the ζ-potential was determined by measuring the electrophoretic velocity, using the well-known microscopic method.[9] Particles whose volume of sedimentation was small and whose pastes were dilatant and not thixotropic had large values of ζ, e.g., quartz, -54 millivolts; diamond, -50; corundum, -58; but also in the case of particles which had a large volume of sedimentation, and which formed strongly thixotropic and plastic pastes, large ζ values were obtained, e.g., graphite, -52 millivolts; hematite, -35.

Most of the particles when observed under the microscope were isometric, i.e., roughly spherical or cubical in general outline. A number of substances were definitely anisometric. The particles were plates in mosaic gold, mica, graphite, kaolin, selenite, and steatite, and were needles in hematite; the particles of gypsum which had been dried in the oven recrystallized from the water in a few minutes into long needles also. The special shape of these particles was also shown by other properties. As was mentioned above, mosaic gold, mica, graphite, and to a certain extent, kaolin also, changed their sedimentation volumes strongly when the particles were oriented. In a number of dilute suspensions of mica, selenite, steatite, graphite, and mosaic gold, beautiful streaks were observed on stirring, a phenomenon which is known to be characteristic of suspensions of non-spherical particles (1). All pastes with anisometric particles were thixotropic. None showed normal dilatancy, but some (mosaic gold and mica) showed passive dilatancy, and were not plastic.

The hardness[10] of the particles proved to be undoubtedly important in the determination of their behavior. Nearly all the substances having a strong tendency to be closely packed (tables 4 and 6) were hard; for example, diamond, 10; corundum, 9; quartz, 7; porcelain, 7; glass, 6, or were fairly hard, litharge, 5–5.5; and fluorspar, 4. Most of the substances whose pastes were loosely packed, and which, therefore, were thixotropic and plastic (tables 5 and 8) were soft, such as graphite 0.5–1; selenite 1.5–2; and steatite 1; or not very hard, galena 2–3; pyrolusite 2–2.5;

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[9] These experiments are perhaps not quite conclusive, as dilute suspensions are used, whereas all the properties we are investigating are determined with very concentrated suspensions.

[10] Hardness is given in the scale of Mohs.

kaolin 2-2.5; and barytes 3-3.5. An exception was hematite, which was fairly hard (5.5-6.5), but whose pastes were loosely packed, thixotropic, and plastic.

A number of substances containing chiefly calcium carbonate but of different crystalline structure and of different degrees of purity were compared: pure calcium carbonate (hexagonal), aragonite (rhombic), limestone, Iceland spar, marble (all three hexagonal), chalk, and Solnhofen slate. The last two contained a certain percentage of impurities insoluble in hydrochloric acid, mainly of a clayey nature; they amounted to 1.23 per cent in chalk (average of two analyses), and to 5.89 per cent in Solnhofen slate (also two analyses). The fairly pure substances behaved very similarly; all showed passive dilatancy, distinct thixotropy, and no plasticity, pure water being extruded. The presence of clay in chalk and Solnhofen slate made the pastes of these two strongly thixotropic and plastic. The volume of sedimentation varied to a certain extent; it was of medium value with pure calcium carbonate, limestone, chalk, and Solnhofen slate, smaller with aragonite and marble, and rather larger with Iceland spar.

Pastes of gypsum are known to be strongly rheopectic (4). This was confirmed. We found further, that a number of other pastes closely related to gypsum were also rheopectic; for instance, pastes of selenite, all sorts of calcium carbonate (pure calcium carbonate, limestone, Iceland spar, marble, Solnhofen slate), and steatite. It is obvious that rheopexy can only be observed if the time of thixotropic solidification is sufficiently long, at least several minutes; rheopexy cannot be distinguished from thixotropy when the time of solidification is too short. In the way the range of thixotropy was determined, the range of rheopexy extends almost right up to the lower limit of thixotropy; for instance, the range of thixotropy in water for air-dried gypsum was from 46 to 67 per cent solid, and the range of rheopexy was from 40 to 46 per cent solid; for pure calcium carbonate in water, the range of thixotropy was from 54.5 to 67 per cent solid, and that of rheopexy from 50 to 52 per cent solid; for Solnhofen slate in water, the range of thixotropy was from 40 to 60 per cent solid, and that of rheopexy from 37.5 to 39 per cent solid. The lower limit of the thixotropic range was chosen so that the paste solidified spontaneously in a short time, one minute or so. Some of the more dilute pastes which fell into the rheopectic range also solidified spontaneously if left for a sufficiently long while, whereas in other pastes the two phases separated before the system solidified.

SUMMARY

In order to test the rule that close packing is joined to a small volume of sedimentation and to dilatancy, but not to thixotropy and plasticity,

whilst loose packing is joined to a large volume of sedimentation, to thixotropy and plasticity, but not to dilatancy, a large number of pastes, made of finely powdered solid substances (thirty different substances, mostly minerals) mixed with water or a few aqueous solutions, were investigated. Sedimentation volume, dilatancy, and thixotropy were determined by the methods generally applied: plasticity by a device similar to the one used in measuring flow pressure. Pastes were considered to be plastic if they were pressed out of a fine hole in coherent threads; in non-plastic pastes the liquid was pressed out in drops. The following results were obtained:

1. The rule holds in a large number of cases, but there are a number of exceptions in so far as thixotropy may be observed when the volume of sedimentation has medium values or is even rather small, and further when there is no marked plasticity.

2. There appears to be a strict correlation in so far as normal dilatancy is observed only when the volume of sedimentation is small and as plastic pastes are always thixotropic.

3. It was not sufficient to distinguish dilatant pastes from non-dilatant pastes. Some pastes showed the following behavior: they did not become distinctly harder when mechanically treated with a spatula and they did not let liquid exude when left to themselves. In so far they appear to be non-dilatant. But liquid did exude when the basin which contained the mechanically treated paste was gently tapped. This kind of dilatancy was called passive dilatancy.

4. There is a group of pastes uniting the following properties: generally a medium volume of sedimentation, passive dilatancy, distinct thixotropy, no plasticity.

5. The degree of independence of the particles is the best criterion for judging the probable behavior of their pastes. Independent particles have no tendency to unite into clusters when seen under the microscope; such particles always form systems according to the closely packed systems of our rule. If the particles are not independent, they are seen under the microscope to unite in clusters. These clusters may unite into continuous groups. Particles which are not independent always give pastes which are to a certain extent thixotropic, but they need not be plastic and their volume of sedimentation may even be fairly small.

6. The degree of independence makes itself felt also in the velocity of sedimentation. Fairly concentrated suspensions of independent particles of uniform size follow Stokes law for a long time of settling. If the particles have a tendency to cluster, a strong anomaly of the velocity of sedimentation is shown during the process of settling.

7. Markedly anisometric, especially plate-like, particles (mosaic gold, mica, graphite, etc.) always give thixotropic pastes.

8. Particles of very hard substances (diamond, quartz, corundum, etc.)

are always strongly independent, and therefore give systems with closely packed particles.

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