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THE CONSTITUTION OF HYDROUS OXIDE SOLS FROM X-RAY DIFFRACTION STUDIES[1]

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Received June 20, 1935

Sols of the hydrophobic type which includes most of the hydrous oxides, can be prepared fairly free from electrolytes, but it was demonstrated first by Thomas Graham and confirmed repeatedly thereafter, that in the absence of protecting colloids some electrolyte must be present in the sols to ensure their stability. Thus ferric oxide sol formed by hydrolysis of ferric chloride or by peptization of the hydrous oxide by ferric chloride always contains traces of chloride however long the dialysis is continued.[2]

The presence of chloride in the dialyzed sols led Wyrouboff and Verneuil (13) to suggest that the various preparations contain basic salts or chlorides of "condensed" hydroxides. This idea was further extended and developed by several investigators especially by Duclaux (3), Malfitano (7), Hantzsch and Desch (4), and Linder and Picton (6). Thus, the constitution of the sols was represented by formulas such as:

$$[20\mathrm{Fe(OH)_3}\cdot\mathrm{FeCl_3}]_n \quad \text{and} \quad [45\mathrm{Fe(OH)_3}\cdot\mathrm{FeCl_3}]_n$$

Pauli (8) considers the colloidal particles to be complex ions resulting from ionization of complex electrolytes allied to the Werner compounds. Since the constitution of a given sol varies with the conditions of preparation he represents it by a general formula. In the case of ferric oxide sol this is

$$[x\mathrm{Fe(OH)_3}\cdot y\mathrm{FeOCl}\cdot\mathrm{FeO}]^+,\ (\mathrm{Cl}^-)$$

in which $x = 32$ to 350 and $y = 4$ to 5.7 in sols formed by hydrolysis. It is difficult to justify this formulation, since no one has established the existence of $Fe(OH)_3$, and FeOCl is obtained only under special conditions in a bomb tube at elevated temperatures.

Thomas and coworkers (9, 10) suggest that the dispersed phase in

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

[2] Sorum sols (J. Am. Chem. Soc. 50, 1264 (1928)) containing no detectable chloride either contain a trace of some other electrolyte or are protected by some material derived from the dialyzing membrane during the prolonged dialysis.

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hydrous oxide sols, such as alumina sol formed by peptization of the gel with hydrochloric acid, consists of olated and possibly oxolated aluminum oxychloride complexes of the Werner type resembling the poly-ol basic chromic salts formulated by Bjerrum (2). Thomas formulates one such hypothetical complex as given in figure 1. The assumption that such hypothetical compounds exist in the sol was made to account for the observation that the pH value of the sol is raised by the stepwise addition of neutral electrolytes, the anion order being: oxalate > acetate > sulfate > halides > nitrate. The increased pH value was attributed to replacement of the OH groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen to form water.

Since hydrous oxide sols formed in the presence of chloride, say, always contain more or less chloride, Thomas believes that such sols should be designated as metallic oxychloride sols rather than as hydrous oxide sols. He recognizes that the term ferric oxychloride hydrosol is objectionable, since it connotes a definite chemical compound when no such meaning is intended. Nevertheless he prefers to regard the hydrous oxide sols as oxysalt sols, since the colloidal particles are not pure hydrous oxides. To be consistent, one should rename the metallic sols and the salt sols, which, like the oxide sols, are not pure insoluble metal or salt. It is difficult to see what would be gained by introducing such a change in our terminology. The ratio of iron to chlorine in a ferric oxide sol has been variously reported as 6, 42, 84, 396, 2700, and higher. To designate a sol with a low chloride content as an oxychloride sol is like calling precipitated barium sulfate a chlorosulfate because it contains some adsorbed barium chloride.

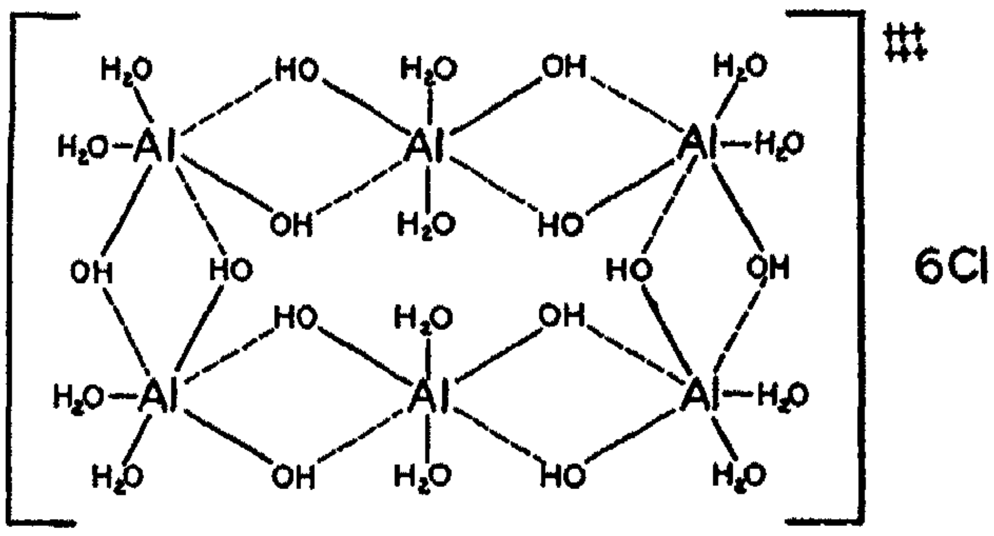

Fig. 1. Formula of a hypothetical alumina complex (after Thomas)

It is now quite generally recognized that the stability of a positive silver halide sol is due to the preferential adsorption of silver ion by unsaturated secondary valence forces on the surface of the crystals. The crystals will also contain some adsorbed silver nitrate. Similarly a hydrous oxide sol formed in the presence of metallic chloride, hydrochloric acid, and their corresponding ions will contain varying amounts of the several components, depending on the precise method of formation and the purification of the sol. The positive charge on a given sol is due to the preferential adsorption of hydrogen and metallic ion on the surface of the hydrous oxide just as the positive charge on a silver halide sol is due to preferential adsorption of silver ion. It is unnecessary to attribute the charge to the presence of an "ionogenic complex attached to the surface" (Pauli) unless the presence of such a complex has been rendered highly probable. Thus to assume the presence of even a simple salt like FeOCl in a ferric oxide sol goes well beyond the established facts.

In recent years investigations (11) have been made of the various phenomena which take place on adding electrolytes stepwise to sols of the hydrous oxides of iron and aluminum. To account for the several phenomena, including the form of the chloride displacement curves and of curves showing the change in pH value, the constitution of the particles may be represented by the general formulas:

$$[(x\mathrm{Fe_2O_3}\cdot y\mathrm{HCl}\,.\,z\mathrm{H_2O})\mathrm{Fe}_m^{+++}\mathrm{H}_n^{+}] \quad (m + n - q)\mathrm{Cl}^-,\ q\mathrm{Cl}^-$$

Solid phase	Inner layer	Diffuse outer layer

and,

$$[(x\mathrm{Al_2O_3}\cdot \mathrm{H_2O}\cdot y\mathrm{HCl}\cdot z\mathrm{H_2O})\mathrm{Al}_m^{+++}\mathrm{H}_n^{+}] \quad (m + n - q)\mathrm{Cl}^-,\ q\mathrm{Cl}^-$$

Solid phase	Inner layer	Diffuse outer layer

Iver (5) accepts this formulation of the constitution of certain oxide sols, but suggests that the outer portion of the double layer contains hydroxyl ions as well as chloride ions. The displacement of the former on titrating with neutral salts would account for the increase in the pH value of the mixture. It seems rather questionable, however, whether hydroxyl ions will be present in the outer portion of the double layer in sols having a pH value of 4 to 5. The increase in the pH value on the addition to the sols of neutral salts, especially those with multivalent anions, is doubtless due to the increase in adsorption of hydrogen ion in the presence of a strongly adsorbed anion. This increased adsorption of cations in the presence of strongly adsorbed anions is a general phenomenon that has been observed with various types of adsorbents such as carbon and fibers as well as with the hydrous oxides. With salts such as citrate, oxalate, and acetate, buffer action increases the pH value of the sol–electrolyte mixture above that of the sol alone.

From the evidence obtained by potentiometric titration of the sols, there would appear to be no necessary reason for assuming that the sols are colloidal electrolytes consisting of basic salts or Werner complexes. On the contrary the indirect evidence suggests that the solid phase consists essentially of the hydrous oxide (or simple hydrate).

Since x-ray diffraction studies have proven helpful in determining the composition of gels, it was believed that similar studies on sols might give direct evidence of the constitution of the colloidal particles in the sols. The chief complication in the examination of the systems is the relatively low concentrations of the solid phase and the scattering of the x-rays by the water in the samples. Böhm and Niclassen (1) showed that the gels from certain oxide sols were not amorphous; but in most cases it was not stated whether the air-dried or moist gel was examined. Since Thomas believes that the elements of water in certain oxide sols are combined in the form of poly-ol basic Werner salts, it is not permissible to air-dry the samples before examination. On the contrary, the sols must be studied directly, or the undried gel, obtained preferably by ultrafiltration of the sols, must be examined. Preliminary experiments were carried out with sols of the hydrous oxides of aluminum, tin, and indium.

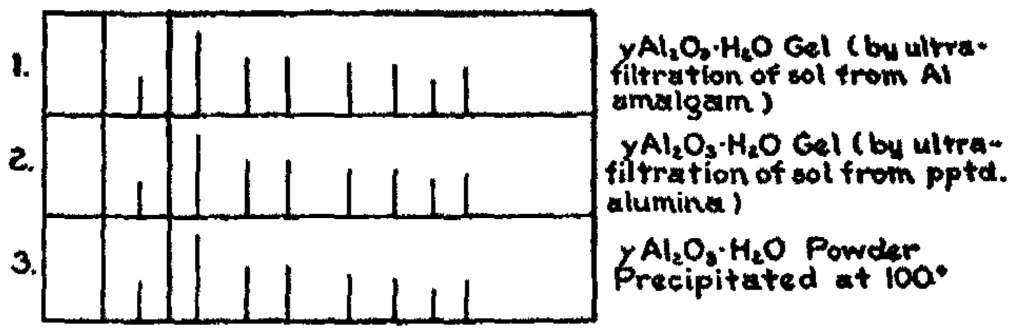

FIG. 2. X-ray diffraction patterns

ALUMINUM OXIDE SOLS

Two sols of aluminum oxide were employed. The first was prepared by peptization, with hot 0.01 *N* hydrochloric acid, of the gel formed by the action of amalgamated aluminum on water. The method of Thomas (10) was used except that the gel was not dried. The second sol was obtained by peptization, with hot 0.05 *N* hydrochloric acid, of the gel thrown down from hot aluminum chloride solution with ammonia and washed by decantation until almost free from chloride. In both cases a large excess of the gel remained unpeptized, from which the sol was decanted. After standing quietly for several days to allow further traces of unpeptized gel to settle, the slightly cloudy sols were examined

Portions of the sols were ultrafiltered through a cellophane membrane, and the resulting moist gels were analyzed by the x-ray diffraction method, using a camera of the Seemann–Bohlin type. Copper radiation filtered through nickel foil, at 60 milliamperes and 50,000 volts, was employed. Under these conditions but five to ten minutes exposure was necessary, so that little or no drying of the gel took place. The results of the observations are shown in diagram form in figure 2 (1 and 2). For the purpose of comparison the diagram of γ-$Al_2O_3 \cdot H_2O$ powder is included in the figure. Reproductions of the negatives are shown in figure 3. From these observations, it would appear that the particles in the alumina sol consist essentially of hydrous γ-$Al_2O_3 \cdot H_2O$. There is no reason to believe that they are made up of simple basic salts or basic salts of the Werner type.

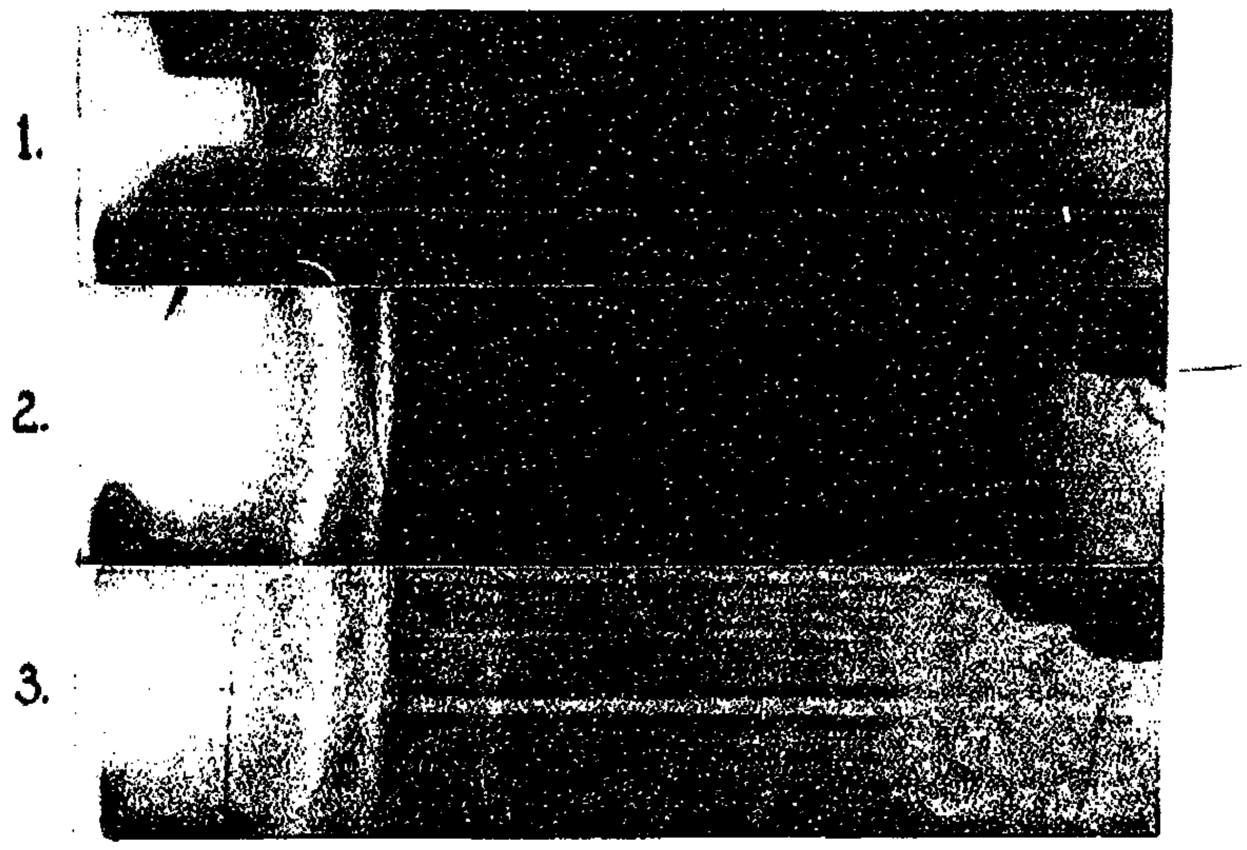

FIG. 3. X-ray diffraction patterns

1. γ-$Al_2O_3 \cdot H_2O$ gel (ultrafiltration of sol from aluminum amalgam)
2. γ-$Al_2O_3 \cdot H_2O$ gel (ultrafiltration of sol from precipitated alumina)
3. γ-$Al_2O_3 \cdot H_2O$ powder (precipitated at 100°C.)

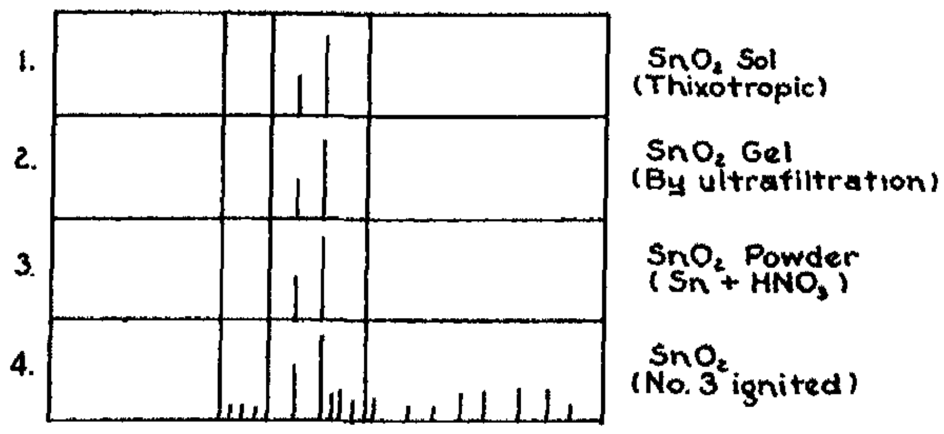

FIG. 4. X-ray diffraction patterns

STANNIC OXIDE

Stannic oxide sol was prepared by the method of Zsigmondy (14). Twenty-five grams of hydrated stannic chloride was dissolved in 20 liters of water and allowed to hydrolyze. The resulting gel was washed until the wash-water was free from chloride. After suspending in 250 cc. of water, it was peptized with three drops of concentrated ammonia and the resulting sol was boiled to remove excess ammonia. The moist gel obtained by ultrafiltration of the clear sol gave the x-ray diffraction pattern of anhydrous stannic oxide or cassiterite, as shown diagrammatically in figure 4 (2). For the purpose of comparison the patterns of the so-called "β"-stannic oxide and of anhydrous stannic oxide are included in the diagram.

The sol concentrated to 100 cc. became thixotropic. This sol gave the pattern shown in figure 4 (1).

INDIUM OXIDE SOL

A solution of indium nitrate was precipitated in the cold with ammonia, the precipitate thoroughly washed, and peptized in the cold with dilute hydrochloric acid. The gel obtained by ultrafiltration of the sol gave the x-ray diffraction pattern shown in figure 5. This is the pattern for $In_2O_3 \cdot 3H_2O$ or $In(OH)_3$ (12).

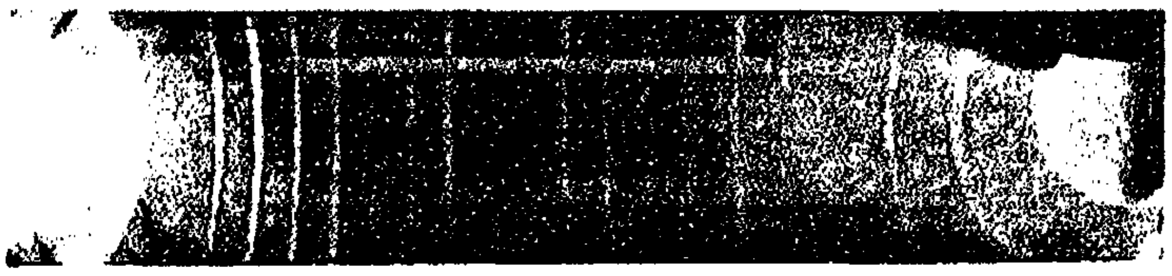

FIG. 5. X-ray diffraction patterns for $In_2O_3 \cdot 3H_2O$ gel (from ultrafiltration of sol)

From the above x-ray studies, it would appear that the particles in typical oxide sols consist essentially of aggregates of minute crystals of hydrous oxides or of simple oxide hydrates. In the sols containing chloride, the latter is not bound in the form of a basic salt in most cases, but is adsorbed in an amount depending on the size and physical character of the particles. Such sol systems are properly referred to as hydrous oxide sols.

In the light of the above, if one prefers to regard the hydrous oxide sols as electrolytes with colloidal ions it must be emphasized that there is a fundamental difference between sols and non-colloidal complex electrolytes such as potassium ferrocyanide, the cobalt amines, the complex platinic salts, etc., formulated by Werner. There is also a distinct difference between a hydrous oxide sol and such colloidal electrolytes as the soaps and Congo red, in that the latter contain ionic micelles made up of groups of ions which have a definite composition and which carry one charge for each equivalent of the ion, whereas the micelles of the former have no definite composition and may carry hundreds or thousands of equivalents for each free charge.

SUMMARY

X-ray diffraction examination of the moist gels from typical hydrous oxide sols indicates that the particles of the solid phase in such sols consist essentially of aggregates of minute crystals of hydrous oxides or of simple oxide hydrates. In the sols containing chloride, the latter is not bound in the form of a basic salt in most cases, but is adsorbed in an amount depending on the size and physical character of the particles.

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ELECTROKINETICS. XVI

STREAMING POTENTIAL IN SMALL CAPILLARIES[1]

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Received June 20, 1935

The applicability of the conventional equation of streaming potential to small capillaries is an important subject. It involves the whole question of streaming potential through membranes, and accordingly should be of particular interest to the biologist. Smoluchowski (13) showed that membranes were subject to the same mathematical treatment he employed for single capillaries and, within the limits of the restrictions, the equations held for capillaries of any size or shape. His equation for streaming potential is

$$\zeta = \frac{4\pi\eta KH}{DP} \tag{1}$$

where ζ is the electrical potential across the double layer, η is the coefficient of viscosity, K is the specific conductance of the streaming liquid, H is the streaming potential, D is the dielectric constant, and P is the pressure forcing the liquid through the capillary.

A marked decrease in the streaming potential has been demonstrated by Bull and Gortner (5) with diaphragms made of fine quartz particles. The effect became apparent with particles slightly below 200 μ in diameter and rapidly became more important, until at 5 μ the streaming potential was only 25 per cent of that for the 200 μ particles. The decrease in potential with the smaller particles is no doubt due to the smaller capillaries. Their data, however, offer no easy way of determining the capillary size. White, Urban, and Krick (16) also found a diminishing streaming potential with decreasing capillary size. The question arises as to the critical size of a capillary below which the simple theory of Smoluchowski is no longer adequate. There are several factors to be considered.

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20–22, 1935.

Published as Paper No. 1353, Journal Series, Minnesota Agricultural Experiment Station.

[2] National Research Fellow in the Biological Sciences.

It was first realized by Stock (14) that surface conductance must be considered and that the specific conductance used in equation 1 was that of the liquid in the membrane or small capillary. An involved mathematical treatment has been given by Cole, Bikerman, Komagata, and others (1). As shown by Briggs (3), the difficulty is easily taken care of experimentally by determining the cell constant of the membrane with $N/10$ potassium chloride; then by determining the resistance of the membrane containing the various solutions, the specific conductivity of the liquid in the membrane (K_s) is easily calculated, and this K_s then replaces the K of equation 1. This, then, presents no serious difficulty for the streaming potential technique in small capillaries.

In the derivation of the streaming potential equation (13), Poisson's equation is integrated for the case of two parallel plates, and the resulting equation applies only when the thickness of the double layer is small in comparison with the radius of the capillary. We are really dealing, however, with two coaxial cylinders whose edges are the thickness of the double layer apart. The electrical potential between these cylinders is

$$\zeta_1 = \frac{4\pi\sigma}{D} r \ln\left(1 + \frac{\lambda_c}{r}\right) \qquad (2)$$

where r is the radius of the inside cylinder, D is the dielectric constant, λ_c is the distance between the cylinders, and σ[3] is the charge per cm.^{2} When $r > > \lambda_c$, this equation reduces to that for two parallel plates.[4]

$$\zeta_2 = \frac{4\eta\sigma}{D} \lambda_p \qquad (3)$$

The ratio of these two potentials is

$$\frac{\zeta_1}{\zeta_2} = \frac{r}{\lambda_p} \ln\left(1 + \frac{\lambda_c}{r}\right) \qquad (4)$$

Except where there is overlapping of the double layers, $\lambda_p = \lambda_c$. Estimation of the critical radius from values of r/λ_p must be done by an approximation (11). If $z_i\zeta < 25$ millivolts (where z_i is the valence of an ion of the i^{th} type),

$$\lambda_p = \frac{1}{\kappa} = a \qquad (5)$$

---

[3] Throughout this portion of the discussion, σ is considered constant.

[4] Since $\ln\left(1 + \frac{\lambda}{r}\right) = \frac{\lambda}{r} - \frac{\lambda^2}{2r^2} + \frac{\lambda^3}{3r^3} - \cdots$

where λ_p is the mean thickness of the double layer when equation 3 holds,

$$\kappa = \sqrt{\frac{4\pi N^2 \epsilon^2}{DRT}} \sqrt{\sum c_i z_i^2} \quad \text{(Debye-Hückel)} \tag{6}$$

and

$$a = \sqrt{\frac{DRT}{4\pi N^2 \epsilon^2 (z_i + z_j) c_i z_i \text{ (or } c_j z_j)}} \quad \text{(Gouy)} \tag{7}$$

N = Avogadro's number, R = the gas constant, $c_i(c_j)$ = ionic concentration in moles per cubic centimeter (1, 9, 11).

The ratio, ζ_1/ζ_2, may be considered as a measure of the deviation from the conventional streaming potential equation. In figure 1 (curve A) this ratio is shown plotted against the capillary radius divided by the thickness of the double layer. It will be noted that a 10 per cent deviation is encountered at a ratio of pore radius to double layer thickness of about 4.

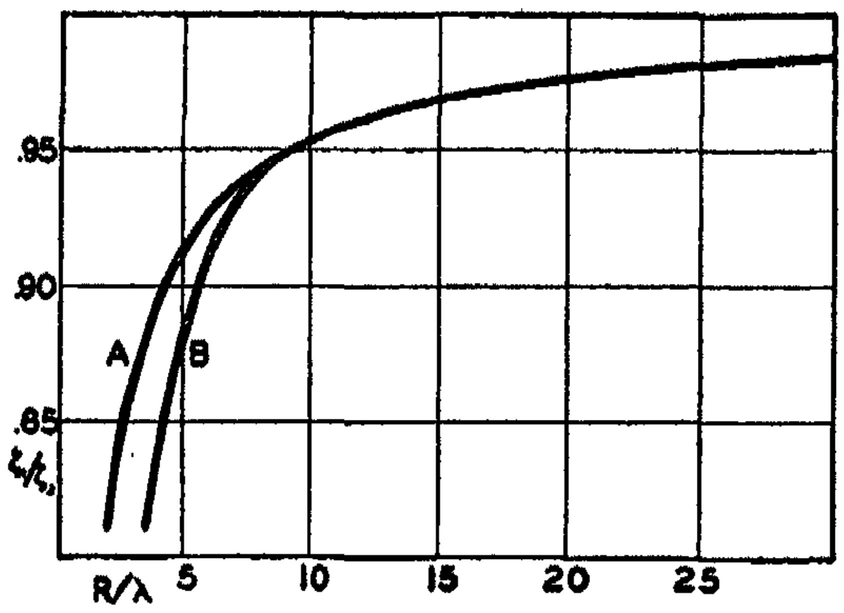

FIG. 1. Diminution in ζ produced by small values of r/λ from equations 4 and 9

Recently Lens (9) investigated the thickness of the double layers between two parallel plates by the use of the Gouy theory. He calculated that in thin slits an interference of the two double layers exists, causing the centers of gravity of the charges in the double layers to be pushed in toward the walls of the slit. He derived the following equation expressing the relation between the thickness of the layer and the half-width of the slit:

$$\lambda_e = a - \frac{r}{e^{r/a} - 1} \tag{8}$$

Calling the half-width of the slit r, we have substituted this value of λ_e in equation 2 and divided by equation 3, thus obtaining the following equation:

$$\frac{\zeta_1}{\zeta_2} = \frac{r}{\lambda_p} \ln\left[1 + \frac{a}{r} - \frac{1}{(e^{r/a} - 1)}\right] \tag{9}$$

Again ζ_1/ζ_2 is plotted against r/λ_p as shown in curve B, figure 1.[5] The values of ζ_1/ζ_2 represent the deviation from the ideal case of a plane surface with no interference. A 10 per cent deviation is encountered in this case at $r/\lambda_p = 6$. While it is perhaps forcing the point to substitute the equation of Lens, which was derived for two parallel planes, into that involving cylinders, we believe the result serves as a first approximation. Table 1, column 2, shows the capillary size which would give rise to a 10 per cent deviation in ζ for various concentrations of a uni-univalent salt (assuming $z_i\zeta < 25$ millivolts (11)).

Komagata (8) has derived expressions showing the influence of capillary size on the streaming potential. By making the Debye–Hückel approximation (1) ($\sin h\,\psi\,F/RT \cong \psi\,F/RT$), he has integrated the fundamental equation of electrokinetics (1),

$$\nabla \cdot \nabla\psi = \frac{\partial^2\psi}{\partial x^2} = \frac{1}{x}\frac{\partial\psi}{\partial x} = \kappa^2\psi \tag{10}$$

for the case of a cylindrical capillary. He arrives at an expression involving J_0 and J_1, Bessel functions of the zero-th and first order and of the first kind,

$$\psi = -\Psi\frac{J_0(i\kappa x)}{J_1(i\kappa r)} \tag{11}$$

where Ψ is the true ζ-potential, x is the coördinate (in the cylindrical system) coinciding with the radius, r, and ψ is the potential at any point on x.

From this, the equation for σ,

$$\sigma = \frac{D\Psi\kappa i J_1(i\kappa r)}{4\pi J_0(i\kappa r)} \tag{12}$$

is developed. This reduces to equation 3 for large values of κr.[6, 7]

Komagata then develops the streaming potential equation after the conventional method (13) and substitutes these values to attain the following equation for streaming potential:

$$H = \frac{PD\,(-\Psi)}{4\pi\eta K_s}\left(1 - \frac{2[-iJ_1(i\kappa r)]}{\kappa r J_0(i\kappa r)}\right) \tag{13}$$

---

[5] In plotting, the assumption was made that $a = \lambda_p = \frac{1}{\kappa}$.

[6] Since $\lim_{r \doteq \infty} J_0(i\kappa r) = \frac{e^{i\kappa r}}{\sqrt{2\pi i\kappa r}} = \lim_{r \doteq \infty} -iJ_1(i\kappa r)$

[7] We are indebted to Dr. Komagata for a personal communication with regard to this point.

By comparing equation 1 with this,

$$|\pm\Psi| = f\zeta \tag{14}$$

where

$$\frac{1}{f} = 1 - \frac{2[-iJ_1(i\kappa r)]}{\kappa r J_0(i\kappa r)} \tag{15}$$

Komagata has calculated limiting values for r, at different concentrations of electrolyte, at which a deviation of 10 per cent between Ψ and ζ should be observed (ref. 8, p. 36). Unfortunately, the decimal point has been misplaced in this table, so that these values are ten times what they should be. Correct values are listed in table 1, column 3. The critical point for a deviation of this magnitude lies at $\kappa r = 20$.

TABLE 1

Limiting values of radii, corresponding to concentrations of uni-univalent electrolyte, at which a 10 per cent diminution in ζ should be observed

CONCENTRATION IN MOLES PER LITER	LIMITING RADIUS IN μ FROM EQUATION 9 ($\kappa r = 0$)	LIMITING RADIUS IN μ FROM EQUATION 14 ($\kappa r = 20$)
10^{-7}	5.78	19.5
10^{-6}	1.83	6.2
10^{-5}	0.578	1.95
10^{-4}	0.183	0.62
10^{-3}	0.0578	0.195

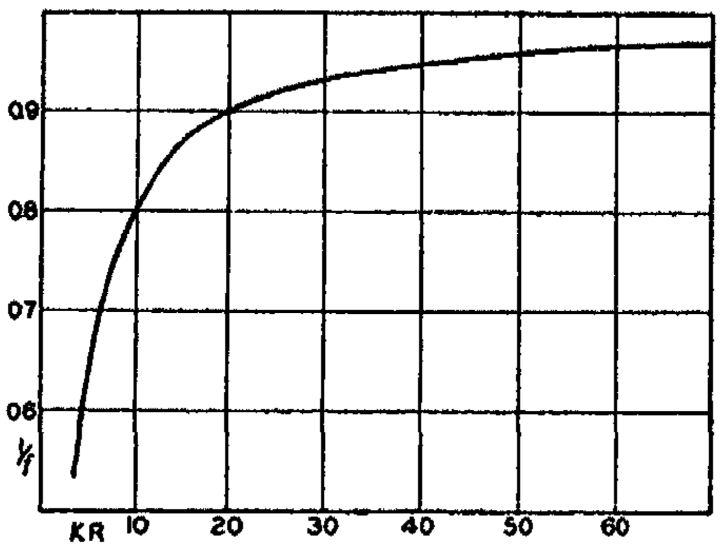

FIG. 2. Equation 15 from the theory of Komagata

The reciprocal of the factor f (equation 15) has been plotted against κr in figure 2 (after Komagata). On comparing figure 1 with figure 2, it will be seen that the factor f, which represents $\zeta_{\text{cylinder}} \div \zeta_{\text{plane}}$, and the ratios of equations 4 and 9 change in an inverse direction as κr varies. When κr is large, ζ_1/ζ_2 in equations 4 and 9 reduces to unity and so does f (in equation 14). But at small values of κr, equation 12 does not reduce to equation 2. In the case of the ratios calculated from the cylindrical and plate condensers (equations 4 and 9), the factor by which the observed ζ (from equation 1) is multiplied is always < 1; in Komagata's equations, it is always > 1. This fundamental difference may reside in the fact that in the first treatment σ was assumed to be constant with changing r and the influence of thickness of the double layer predominant. In Komagata's treatment σ changes with r. The effect of equations 4 and 9 is to reduce ζ; Komagata's equation 13 tends to eliminate the observed lowering in streaming potential with decreasing r.

In the above connection, Bikerman (2) has derived an expression for the current produced by the streaming potential in slits and takes the ionic atmosphere into consideration. He finds that the width of the slit plays a rôle only when it is comparable in size to the thickness of the double layer.

Another factor which must be considered in the treatment of small capillaries is that of viscosity. Terzaghi (15) gives empirical equations expressing the viscosity of water as a function of the width of narrow slits. He found that

$$\frac{\eta}{\eta_0} = 1 + \frac{6.02 \times 10^{-42}}{S^8} \qquad (16)$$

to

$$\frac{\eta}{\eta_0} = 1 + \frac{2.42 \times 10^{-43}}{S^8} \qquad (17)$$

where η_0 is the viscosity of water at 25°C. and η is the viscosity of water in a slit of width $2S$ at the same temperature. Terzaghi worked with membranes of clay. Figure 3 shows the change of viscosity with the half-width of the slit. Equations 16 and 17 are plotted as curve 2 and curve 1 (figure 3), respectively. It is clear that an appreciable change in viscosity is found at a radius of about 9×10^{-6} cm., and thereafter it increases very rapidly. Deriagin (6), likewise, reports that water exhibits rigidity when placed between glass surfaces less than 150 mμ apart. The one surface formed the bottom of a vessel; the other was a convex glass lens which was forced to oscillate about a vertical axis. The distance between the two was measured by observing Newton's fringes. It was found that the rigidity vanished above 150 mμ, which is, as he remarks, in the same order of magnitude as reported by Terzaghi. The viscosity effect would invalidate streaming potential measurements made much below a capillary radius of 10^{-5} cm. In membranes of mixed pore sizes, pores below this value would be virtually inoperative in contributing to the streaming potential.

Electrosmotic effects resulting from the streaming potential must also be considered. This so-called back pressure has been discussed by Bull (4) and Reichardt (12). There is as yet no unanimity of opinion in this respect. It is possible to regard this problem in another way than has yet been done. We can, for example, compare in a very simple and direct fashion the maximum electrical work obtained with the total mechanical work done on a liquid streaming through a diaphragm.

The electrical work per unit time = H^2/R_T joules per second, where H is the streaming potential across the diaphragm in volts, and R_T is the total resistance in the system in ohms. The mechanical work per unit time = $1 \times 10^{-7}\ VP$ joules per second, where V is the volume in cubic centimeters per second and P is the pressure in dynes per unit area.

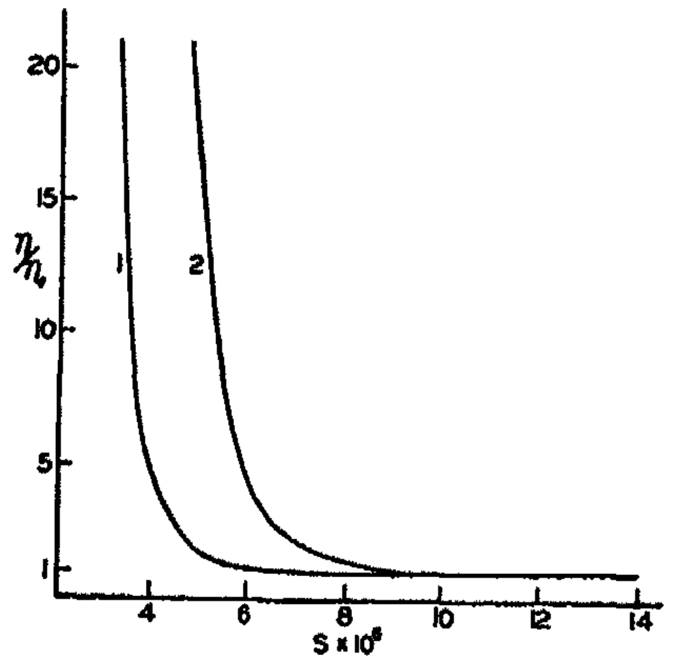

FIG. 3. Changes in the viscosity of water produced by small pore diameters

Dividing the electrical work by the mechanical work, we obtain,

$$\frac{\text{Electrical work}}{\text{Mechanical work}} = 1 \times 10^7 \frac{H^2}{VPR_T} \tag{18}$$

Now if we assume that we are dealing with cylindrical capillaries, we may substitute from Poiseuille's law the value for V,

$$V = \frac{\pi P r^4 n}{8\eta l} \tag{19}$$

where r is the average radius of the capillaries, n is the number of capillaries of radius r, and l is the average length of the capillaries.

Also, we have the electrical resistance,

$$R_T = \frac{l}{\pi K_s r^2 n} \tag{20}$$

Substituting these expressions for V and R_T we have

$$\frac{\text{Electrical work}}{\text{Mechanical work}} = \frac{8H^2\eta K_s}{P^2 r^2} \times 10^7 \tag{21}$$

Since both the electrical work and mechanical work are done over the same distance and area, we may write

$$\frac{\text{Electrical pressure}}{\text{Mechanical pressure}} = \frac{8H^2\eta K_s}{P^2r^3} \times 10^7 \tag{22}$$

This confirms in a satisfactory manner the previous equation of Bull (4), since we obtain

$$\frac{P_1}{P} = \frac{8H^2\eta K_s}{P^2r^3} \times 10^7 \tag{23}$$

by dividing the electrical "Gegendruck," P_1,

$$P_1 = \frac{8\eta K_s H^2}{Pr^2}$$

by the applied (mechanical) pressure and converting from electrostatic to practical units.

If we are dealing with a given solution, η is a constant and, as a first approximation, K_s and H/P are constants. The ratio of the "Gegendruck" to the mechanical pressure varies as the reciprocal of the radius squared. In general, K_s, due to the surface conductivity, increases as the radius decreases, while H/P decreases with decreasing radius in accord with earlier sections of this paper. We hope to investigate equation 22 experimentally in the near future.

The following calculations illustrate the use of equation 18. The diaphragm was of finely powdered quartz about 5 μ in diameter. A 2×10^{-4} N sodium chloride solution was streamed through the diaphragm. The following data were obtained: (1) resistance across diaphragm = 7.05×10^{-4} ohms; (2) pressure forcing liquid through diaphragm = 10.5 cm. Hg = 1.40×10^6 dynes cm.$^{-2}$; (3) E.M.F. across diaphragm = 8.10×10^{-2} volts; (4) rate of flow of solution through diaphragm = 7.20×10^{-3} cc. per second.

Substituting in equation 18,

$$\frac{\text{Electrical work}}{\text{Mechanical work}} = \frac{(8.10 \times 10^{-2})^2 \times 10^7}{7.20 \times 10^{-3} \times 1.40 \times 10^5 \times 7.05 \times 10^4} = 9.24 \times 10^{-4}$$

This shows that in this case back-pressure effects could not interfere with the flowing of the liquid. Results of this same type were obtained from calculations based on measurements made with cellulose diaphragms.

The peculiar results obtained by Bull and Gortner (5) with diaphragms made of heterogeneous-sized quartz particles, where a break in the straight-line relationship between the streaming potential and the pressure was observed at about 25 cm. of mercury pressure, are still unexplained and are apparently inexplicable on the basis of any of the above calculations. This indicates that there are other factors to be considered. These broken lines are, however, only obtained with very close packing, so that this unknown factor or factors need only be considered with capillaries where such broken lines are observed.

During the course of these investigations we were disturbed by the lack of a suitable method for determining the pore radius; although the method of Erbe (7) was tried, it was found not wholly satisfactory for our purposes. We finally solved our difficulties in the following fashion.

By substituting equation 20 in Poiseuille's law (equation 19) and replacing K_sR_T by C, the cell constant of the diaphragm (3), we have

$$r = \sqrt{\frac{8\eta CV}{P}} \tag{24}$$

This equation rests on the assumption (as, in general, with all methods for determining radii) of cylindrical capillaries; results obtained from it are therefore subject to error but serve to characterize any particular membrane and represent, essentially, the rate of flow through that membrane. It is believed that the correct order of magnitude, at least, can be obtained by this method.

TABLE 2

Average pore radii of various diaphragms measured in electrolyte solutions at concentrations not affecting rate of flow

MATERIAL	SALT	NORMALITY	RADIUS IN μ	CHARACTERISTICS
Quartz.......	KCl	10^{-3}	29.9	163 μ particle diameter
Quartz.......	KCl	10^{-2}	20.6	128 μ particle diameter
Quartz.......	NaCl	$> 4 \times 10^{-4}$	1.38	ca. 5 μ particle diameter (mixed)
Cellulose.....	$MgCl_2$	10^{-4}	0.98	Gave normal ζ-concentration curve
Cellulose.....	NaCl	0 to 2×10^{-3}	0.86	Cf. figure 4
Cellulose.....	$BaCl_2$	0 to 2×10^{-3}	0.86	Cf. figure 4 (same membrane)

We applied equation 24 to the calculation of pore radii in several diaphragms and obtained the results shown in table 2. Comparing table 2 with table 1, it will be seen that the mean pore radii of the cellulose diaphragms are above the critical radius for concentrations of 10^{-4} N or greater.

Cellulose prepared from Schleicher and Schüll filter paper after the method of Briggs (3) was packed into a diaphragm. This was the same cellulose preparation as used by Bull and Gortner. As shown in figure 4, no variation in rate of flow (i.e., average radius) was noted in any of the electrolyte solutions (sodium chloride and barium chloride) used, in the range 0 to 2×10^{-3} N. Values for ζ in sodium chloride solutions are also plotted in figure 4 from the data of Bull and Gortner and of Briggs. As may be seen, no significant difference between the two sets of data can be noted, although each is based on a different cellulose preparation and a different membrane. The whole problem of the critical radius for cellulose diaphragms will be discussed in a later paper (10).

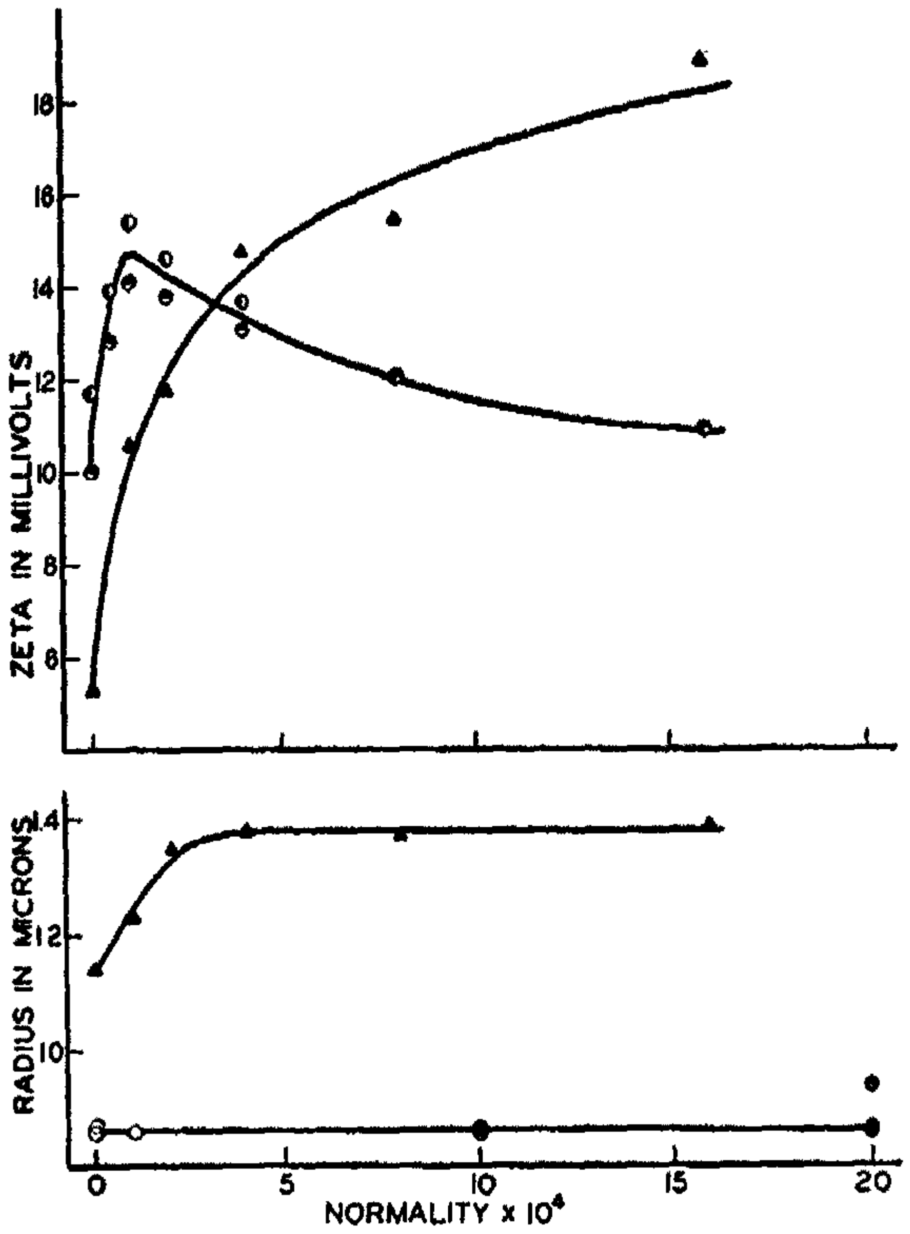

FIG. 4. Comparison of ζ-concentration and radius-concentration curves of a cellulose diaphragm and a diaphragm of quartz below the critical pore size. Triangles, quartz; circles, cellulose. ●, barium chloride solutions; O, sodium chloride solutions; ⊖, data of Bull and Gortner; ◐, data of Briggs. The ζ values for quartz are plotted at half-scale.

It is interesting to note that the pore radius for quartz of 163 μ diameter was 31.8 μ (table 2) and for those particles 128 μ in diameter the average radius was 22.2 μ. Bull and Gortner (5) found the critical radius for 2×10^{-4} N sodium chloride to lie between these two radii. This is surprising, as it is much above that predicted by Komagata (0.43 μ). The explanation possibly lies in the fact that Komagata's equations are derived on the assumption that $z_i\zeta < 25$ millivolts, while actually the potential in this case is about 82 millivolts. White, Urban, and Krick (16) found the critical radius to be about 10 μ for 5×10^{-4} N potassium chloride streaming through glass capillaries. This high critical radius may, no doubt, be traced to the same cause as discussed above, for glass likewise has a high ζ-potential.

Values for the mean pore radii observed with a diaphragm of small quartz particles below the size found critical by Bull and Gortner are plotted as a function of the sodium chloride concentration in figure 4. Constancy is reached at a concentration of 4×10^{-4} N. Incidentally, the rate of flow is independent of time and shows no blocking effects such as those noted with cellophane membranes. This constant value persists at least up to a concentration of $N/10$. It probably represents the true mean pore radius. In all cases, the rate of flow was a linear function of the applied pressure.

The ζ–concentration curve for this quartz diaphragm in sodium chloride (calculated by equation 1) is also shown in figure 4. It will be noted that the usual maximum observed by Briggs (3), Bull and Gortner, and others (see especially Abramson, ref. 1, p. 207) at 10^{-4} N, in the case of uni-univalent electrolytes, is absent here; the curve progresses steadily upward. Values of ζ were approximately 30 per cent of those observed above the critical limit (1, 5). This suggests that membranes which exhibit a maximum at the usual concentration (10^{-4} N) are not in the critical range.

SUMMARY

Conditions in a membrane have been considered in relation to the measurement of the streaming potential and the following subjects are discussed:

1. The equation for the potential between two coaxial cylinders has been substituted for the conventional plate condenser equation in the case of small pore radii.
2. Lens' modification of the thickness of the double layer in thin slits has been introduced into this equation, and the critical value of the radius has been estimated by this method.
3. These equations have been compared with the critical radius calculated from Komagata's equations. It is found that the two sets of equations do not yield concordant results except when the radius is large.
4. The change in the viscosity of water with capillary size has been considered.
5. The electrical "Gegendruck" has been compared with the mechanical pressure, and an equation expressing this relationship has been derived.
6. A method for obtaining the average pore radius has been developed

and tested. The theoretical critical pore radius has been compared with those actually found in diaphragms; the two values do not agree in the case of quartz and glass.

7. Anomalies are noted in the ζ–concentration and flow–concentration curves of quartz diaphragms with pores below the critical point; these curves are compared with cellulose, which behaves in a normal manner.

We wish to take this opportunity to thank Professor R. A. Gortner for his encouragement and helpful suggestions throughout the course of these investigations.

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STUDIES ON SILICIC ACID GELS. VI

INFLUENCE OF TEMPERATURE AND ACID UPON THE TIME OF SET[1]

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INTRODUCTION

In a study of the setting of silicic acid gels in this laboratory, Hurd and Letteron (1) have noted an interesting relation between the "time of set" of the gel mixture and the temperature. They found that the logarithm of the time of set could be represented as a linear function of the reciprocal of the absolute temperature. By making certain rather simple assumptions and treating the process as a chemical reaction, they were able to calculate the value of an energy term analogous to the "heat of activation." The values for several series of different mixtures of solutions of sodium silicate and acetic acid gave the average value 16,940 calories. This was, of course, within the range for chemical reactions.

This result was so interesting that it was decided to run a careful check upon the constancy of this value. In the study reported by Hurd and Miller (2) using several different brands of sodium silicate, with soda-silica ratios ranging from 1:3.86 to 1:2.00, a close agreement in the values for this heat of activation was discovered. With six different series, each of five different silicates, variations of not over 2 per cent in this heat of activation were found. The average value was found to be 16,640 calories. We considered at that time that a sufficiently exhaustive study had been made of the effect of temperature upon time of set of these mixtures involving acetic acid.

The constancy of this quantity for these gels of sodium silicate–acetic acid mixtures has suggested an investigation involving other acids. It would be very interesting to check the constancy of the same quantity for other acids and to compare the values for the different acids. In this way an idea could be obtained as to whether this quantity is the same for any acid–sodium silicate mixture, or varies according to the acid employed. In this paper will be found the results of a study involving comparisons of four possible acids.

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

EXPERIMENTAL

In any study of the setting of silicic acid gels, the factors of temperature and hydrogen-ion concentration play a very important part. The latter has been discussed, among others, by Prasad and Hattiangadi (4) and Hurd, Raymond, and Miller (3). As the latter have pointed out, the time of set is proportional to the concentration of hydrogen ions for concentrations of the latter from 10^{-4} to 10^{-6}. It is possible to duplicate the hydrogen-ion concentration in an acid mixture of solutions of sodium silicate and acetic acid, owing to buffering effect of the sodium acetate formed, and with sufficiently close agreement merely by mixing measured volumes of the solutions of sodium silicate and acetic acid. Such a thing is, of course, completely impossible with any strong acid. In that case a more complicated technique must be employed.

TABLE 1

Time of set of gel mixtures using different acids

Concentration of NaOH = 0.380 gram-mole per liter. Concentration of SiO_2 = 0.636 gram-mole per liter

NO.	CONCENTRATION OF ACID IN GRAM-MOLES PER LITER	pH	TIME OF SET IN MINUTES AT		
			25.1°C.	38.4°C.	53.0°C.
Series I. Acetic acid					
1	0.496		54.5	15.0	4.4
2	0.621		109.5	31.0	9.0
3	0.844		194.5	57.0	15.8
4	1.041		266.5	84.0	23.3
5	1.240		322.0	97.5	28.8
Series II. Tartaric acid					
1	0.414	4.62	75.5	19.0	5.5
2	0.440	4.45	146.0	42.5	10.8
3	0.466	4.25	228.0	70.5	19.5
4	0.518	4.01	415.0	118.0	34.5
Series III. Citric acid					
1	0.500	5.16	27.0	7.4	2.2
2	0.625	4.57	90.5	25.5	8.0
3	0.750	4.21	195.5	56.0	17.3
4	0.875	3.92	341.0	96.5	31.0
Series IV. Succinic acid					
1	0.502	5.31	25.0	7.5	2.1
2	0.564	5.04	43.0	13.0	3.5
3	0.627	4.87	65.5	18.0	5.6
4	0.690	4.74	87.5	24.4	7.5

The work to be described includes a study of all the weak acids found suitable. The acid must be sufficiently weak so that the hydrogen-ion control is satisfactory. It must be sufficiently soluble at 25°C. The acids found suitable were acetic, tartaric, citric, and succinic. The ionization constants are 1.8×10^{-5}, 1.1×10^{-3}, 8×10^{-4}, and 6.6×10^{-5} for the first hydrogen at 25°C. Monobasic and polybasic acids are represented.

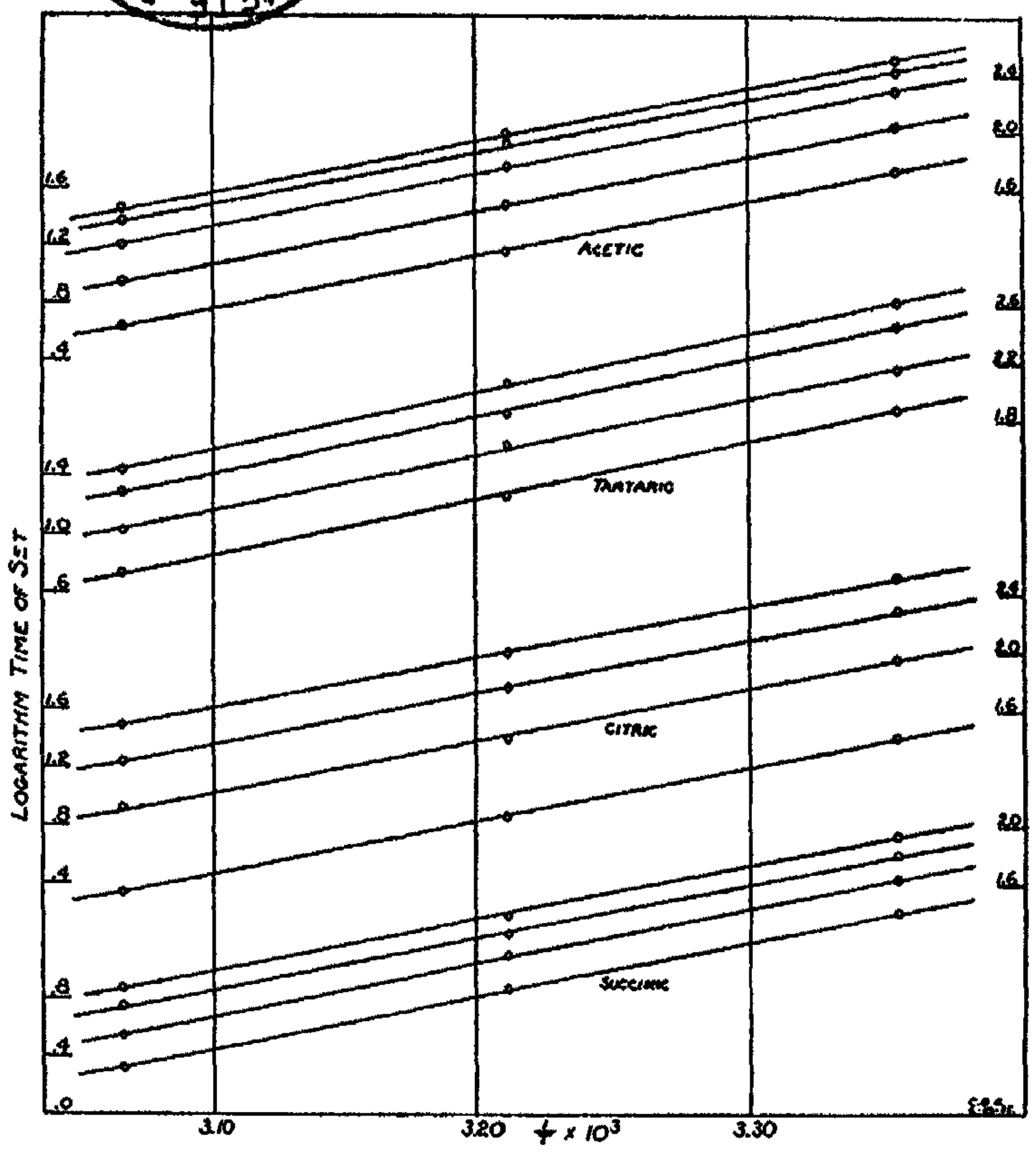

Fig. 1. Effect of temperature on time of set of silicic acid gels with different acids

It is to be regretted that boric acid was not available because of its low solubility.

Mixtures were made as previously described in this series of papers. The silicate used was E brand[3] with a soda–silica weight ratio of 1:3.19.

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[3] The authors wish to thank the Philadelphia Quartz Company for its kindness in supplying all the silicate used in this and other research.

All distilled water was freshly boiled to eliminate carbon dioxide. Standard chemically pure reagents were used.

Mixtures were run at three different temperatures in carefully controlled water thermostats. The mixtures of 80 cc. were thermostated in covered 100-cc. Griffin form Pyrex beakers. The time of set was determined by the "tilted rod" method. Check determinations were always run, agreement in time to 2 per cent or less being obtained. It should be noted that in these containers at the highest temperature, the temperature of the gel mixtures remained a fraction of a degree below the temperature of the bath. The gel mixture temperature was recorded. The data are given in table 1, the times of set being the average of several determinations.

TABLE 2

Values for the slope of the curves for log time of set against reciprocal absolute temperature

MIXTURE	ACID			
	Acetic	Tartaric	Citric	Succinic
1	3820	3920	3720	3700
2	3780	3890	3700	3780
3	3790	3750	3680	3780
4	3680	3760	3700	3740
5	3650			

TABLE 3

Values for the heat of activation for the setting of silicic acid gels with certain weak acids

MIXTURE	ACID			
	Acetic	Tartaric	Citric	Succinic
1	17500	17950	17020	16950
2	17300	17800	16950	17300
3	17350	17170	16850	17300
4	16850	17220	16950	17230
5	16720			
Average.......	17140	17530	16940	17190

These data were plotted, using the logarithm of the time of set as ordinate with the reciprocal of the absolute temperature as abscissa. The curves obtained are apparently linear. Figure 1 shows the type of graph obtained. It should be noted that the ordinates have been adjusted to permit the four curves to be plotted on the same drawing. In obtaining the slopes, of course, each set of curves was plotted separately, obtaining steeper lines and better accuracy.

The slope was determined from the curves obtained. The values of the slopes are given in table 2. By multiplying the slope of the curves by 2.303R, the heat of activation should be obtained. Those values are included in table 3.

DISCUSSION

The data presented here and in the previous work of Hurd and Miller show certain characteristics which are worthy of discussion. The calculated heats of activation are essentially constant for a given acid. It must be remembered that the best results which we have been able to secure for the time of set, after six years of work, show differences up to 2 per cent. At higher temperatures evaporation causes an error which we are unable to avoid with our method of determining the time of set. The heat of activation is determined from the slope of a curve. To secure better results would require a very long series of determinations, such as were reported by Hurd and Miller for acetic acid mixtures. A complete series of runs should be performed at 0°C. We have carried out enough of these for the acids discussed in this paper to convince us that our reported results are correct.

A comparison of the values for a given acid will show an appreciable decrease in the heat of activation as one goes down the series for each acid. This was apparent in the more accurate data on acetic acid reported by Hurd and Miller, and is apparent in the data reported here for acetic and tartaric acids. A comparison of the average results shows an appreciable difference in the value for the different acids.

In the study of the reaction of iodine and acetone, catalyzed by various acids, Rice and his coworkers (5, 6) and Rice and Urey (7) have reported that the heat of activation is decreased somewhat by the addition of a salt of the acid catalyst, when a weak acid is used. Our results do not show this effect, but do show a somewhat lower heat of activation in the case of acetic and tartaric acids as more acid is used.

They have also reported that their reaction showed a lower temperature coefficient for weak acids than for strong acids. The same general effect is shown here, tartaric acid having the highest heat of activation and also the highest dissociation constant, although the differences are not particularly marked.

A striking difference between the effect of the acid should be noted between the reaction studied by Rice and his coworkers and the setting of the silicic acid gels. In the iodine–acetone reaction, the acid serves as a catalyst. In the setting of gels of silicic acid in the acid range, the presence of more acid retards the setting of the gel.

We can give no explanation at present for the similarity and differences of these results.

SUMMARY

The effect of temperature upon the time of set of gels of silicic acid, made by mixing solutions of sodium silicate with solutions of acetic, tartaric, citric, or succinic acids, has been studied.

The heats of activation are essentially constant.

The heat of activation is slightly higher for the strongest acid, tartaric acid.

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X-RAY SPECTROGRAPHY OF ALKALI CELLULOSES[1]

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Bancroft and Calkin (1) have determined previously the true amounts of sodium hydroxide and water taken up by cotton. They suggested a correlation between these data and the x-ray data on ramie of other investigators. In another paper (2) it was shown that the caustic soda might be taken up in three ways, i.e., by formation of a solid solution, by adsorption, or by the formation of a sodium cellulosate which would be adsorbed by the cellulose.

In order to clarify this situation, it is important to have the adsorption data and x-ray data on the same sample. The present investigation deals with the correlation of x-ray data with the previous work.

From an x-ray point of view, ramie is the best material to work with as it gives the best diffraction patterns. However it is difficult to purify, so that adsorption studies have been made on cotton. For this reason, the x-ray data presented here have been obtained on cotton. It is hoped at a later time to purify ramie, determine the amounts of caustic soda and water taken up, and relate the x-ray data to this. The work on cotton and ramie will then present the background for attacking the problem from the organic viewpoint, in order to write the formulas.

Hess and coworkers have been investigating the alkali cellulose problem by means of x-rays. They have recently obtained data on the total amounts of caustic soda and water taken up by ramie (6) by an indirect neutral salt method worked out previously (9, 10). It has been shown (2) that this type of indirect method presents difficulties, and the centrifuge method is therefore considered more reliable (1).

Before describing the experimental results, it appears best to acquaint the reader with certain experimental evidence arrived at by Susich and Wolff (11) and Hess and Trogus (5). The former have investigated the changes occurring when ramie is treated with caustic soda, and the subsequent difference after washing out the caustic soda. The latter have discussed the different x-ray diagrams resulting when caustic soda (and other

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

alkalis) are left in the ramie. The following scheme shows what occurs:

$$\begin{tikzcd}
 & & \text{Caustic pretreated ("hydrate") ramie} \\
\text{Native ramie} \arrow[r, "\text{12.5 per cent NaOH}"] & \text{Na-Cell I} \arrow[ur, "H_2O"] \arrow[r, shift left, "\text{21 per cent NaOH}"] \arrow[d, shift right, "-H_2O"'] & \text{Na-Cell II} \arrow[l, shift left, "H_2O"] \\
 & \text{Na-Cell III} \arrow[u, shift right, "+H_2O"'] &
\end{tikzcd}$$

Hess and Trogus found that when ramie fibers were treated with 16 per cent sodium hydroxide and the solution allowed to remain in the fibers a new diagram resulted, which they ascribed to the formation of Na-Cell I. By desiccating Na-Cell I, they obtained another diagram, that of Na-Cell III, which, in the presence of water, reversed to Na-Cell I. With about 21 per cent caustic soda in the sample they obtained the diagram of Na-Cell II, which did not change on dehydration and reversed to Na-Cell I on the addition of sufficient water. In approaching any modification, the transition did not occur sharply at a given concentration but gradually, that is to say, in the case of the change of native ramie to Na-Cell I, the native diagram was present in a mixed diagram (native and Na-Cell I) approximately over a 3 per cent range. Susich and Wolff have found that the washed-out product yields still another diagram, the "hydrate" or "mercerized" diagram. When cellulose with this latter diagram is treated with caustic soda it gives the same diagram with the caustic in the sample as native fiber treated with caustic soda of the same concentration. When the caustic is subsequently washed out and the fiber dried, the diagrams are the same.

CHANGES IN THE X-RAY PATTERN

Figure 1, reproduced from another paper (1), gives the amounts of caustic and water taken up. It was desired to determine whether or not the x-ray pattern was changed completely at the point of maximum water. In order to determine at what point the x-ray pattern of cotton changed, samples of cotton were treated in caustic soda solution for twenty-four hours at 25°C. The samples were then washed caustic-free, after which they were air-dried. X-ray patterns of the fibers were taken, and it was found, as shown by the data in table 1, that the native pattern begins to change at about 12.8 per cent and is changed completely between 14.3 and 14.4 per cent sodium hydroxide. As will be seen by consulting figure 1, this practically coincides with the place where maximum water is taken up and where the horizontal portion of the change-in-titer (Vieweg) curve comes.

When the caustic soda solution is allowed to remain in the fibers and the x-ray diagram obtained,[3] it is found that a new diagram, that of the product known as Na-Cell I, is obtained. Using cotton the limit for the formation of Na-Cell I is between 13.4 and 14.1 per cent sodium hydroxide, as shown in table 2.

It has been shown previously that the up and down curves with cotton are not the same (see figure 2). For this reason it was believed that the change to Na-Cell I, using mercerized cotton, should occur at a lower concentration than with native cotton. This is the case for, as the data in table 3 show, the limit with cotton pretreated with 14.4 per cent sodium hydroxide is between 10.8 and 11.85 per cent.

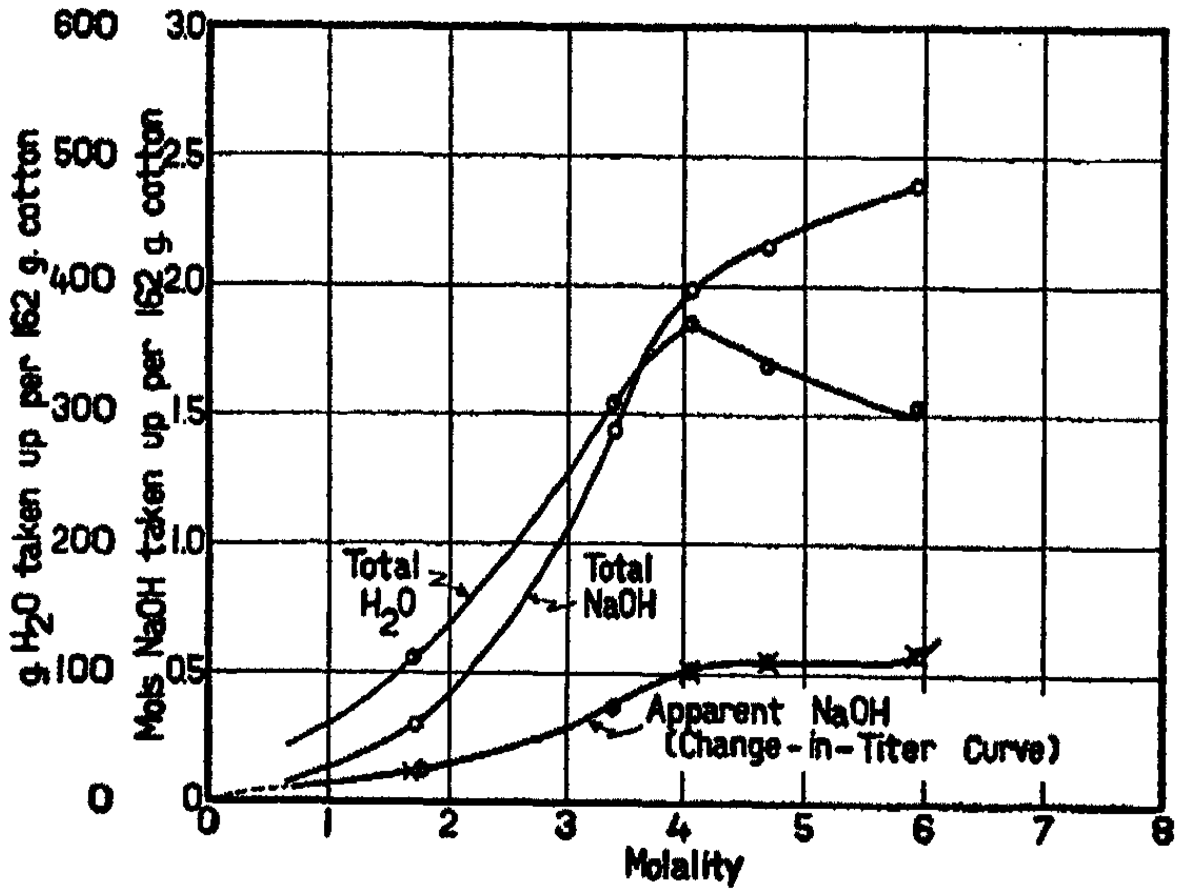

FIG. 1. Sodium hydroxide and water taken up by cotton

Trogus has shown (12) that a greater amount of hydrazine is taken up by cellulose fibers in dilution series than in concentration series, and that the

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[3] Diagrams were obtained in the usual Keesom tubes. A variation from the usual procedure was our method of putting the sample in the tube. A sample of cotton was centrifuged for a given length of time, then the sample for the Keesom tube was pulled out in the usual way. The sample was held by one person and then another person tied one end with fine thread which had been previously threaded through a tube. The ends held by the fingers were then cut off, and the sample was pulled into the tube. The tube was then sealed with wax. Heat was not used because of the danger of drying or scorching the sample. The above method for placing the sample in the tube worked very well after some practice, and the writer is indebted to Dr. Russel for his assistance.

change in x-ray pattern occurs at a lower concentration. From these results of Trogus, our sorption results with various up (concentration) and down (dilution) series shown in figure 2, and our present x-ray results, it is evident that a dilution series from, say, 14 to 15 per cent would lower the limit given in table 3 still further.

Trogus also claims the formation of Na-Cell III′ at low concentration by dilution series from Na-Cell I and by concentration series from pretreated (hydrate) cellulose at 2.65 per cent sodium hydroxide. As shown in table 3, this was not checked with cotton. As Trogus worked with ramie, it was decided to use ramie, but Na-Cell III′ was not checked, as shown in table 4.

TABLE 1

X-ray pattern of native cotton, pretreated for twenty-four hours at 25°C. and washed

CONCENTRATION OF PRETREATMENT	RESULTING X-RAY PATTERN
per cent	
10.3	Native cellulose
12.8	Mostly native, but slight mercerized
13.32	Native and mercerized about equal
14.3	Mostly mercerized, but slight native
14.38	Mercerized

TABLE 2

Effect of caustic solution upon native cotton

CONCENTRATION OF NaOH	RESULTING X-RAY PATTERN
per cent	
6.9	Native cotton
11.09	Native cotton
13.4	Almost pure Na-Cell I; some native
14.1	Na-Cell I

Trogus does not give the concentration of pretreatment but this should not explain the difficulty, as he started with mercerized cellulose. At present, the reason for the discrepancy is not clear.

Cellophane takes up little if any alcohol, and hence should not be appreciably plasticized in alcoholic caustic solution (2). On this basis one should be able to obtain the effect of sodium hydroxide alone on the x-ray pattern. Standard cotton was placed in a concentrated solution of alcoholic caustic soda at room temperature (ca. 23°C.) for twenty-four hours. The change-in-titer amount of caustic taken up was found to be 0.92 mole of sodium hydroxide per mole of cellulose at an outside concentration of 2.35 moles of sodium hydroxide per 1000 grams of ethyl alcohol. The cotton was then neutralized in water-free acidulated (hydrochloric acid) alcohol, and then washed chloride-free with distilled water. The sample was air-dried, and an x-ray pattern of a bundle of parallel fibers obtained. The spacings obtained were those for native cellulose, showing that the taking up of caustic soda from alcohol in caustic soda solution does not change the diagram.

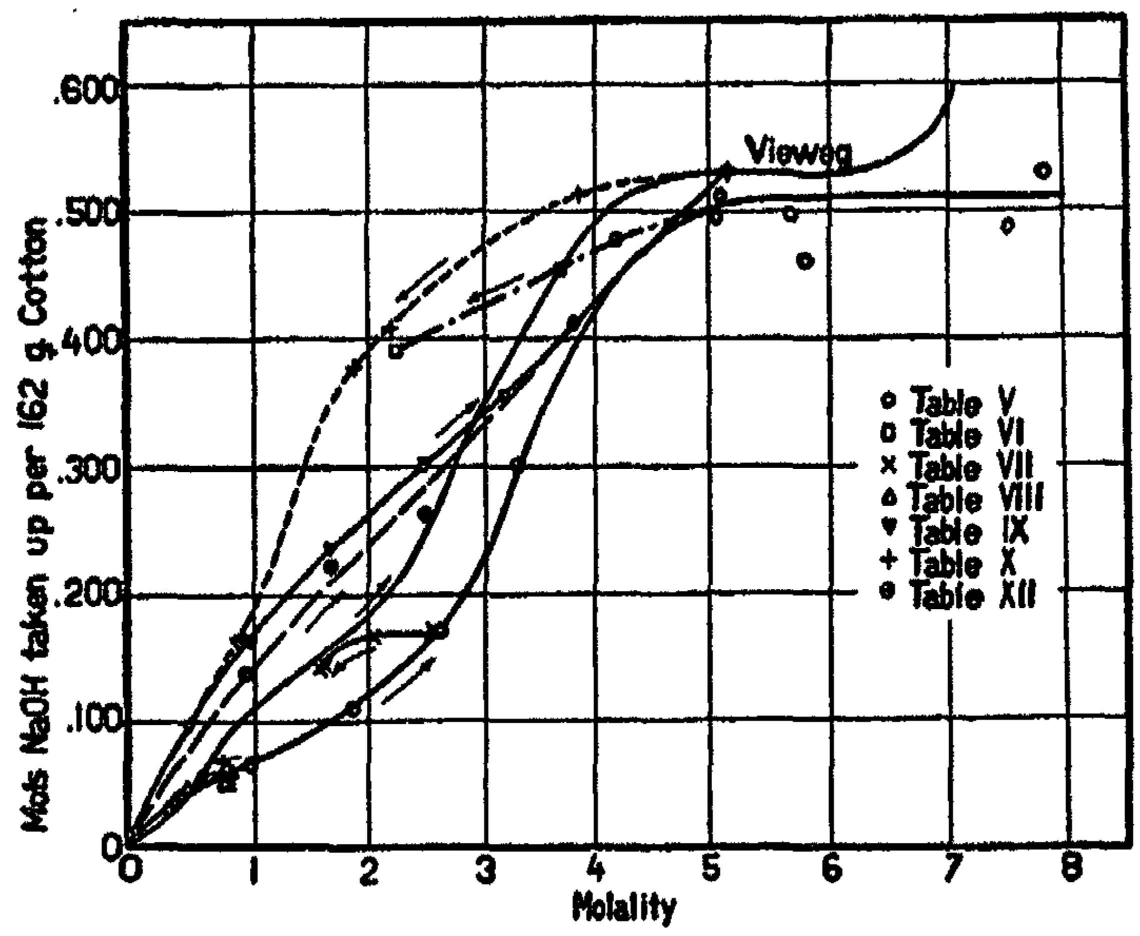

Fig. 2. Sodium hydroxide taken up by change-in-titer method

TABLE 3

Effect of caustic solution upon cotton pretreated with 14.4 per cent sodium hydroxide

CONCENTRATION OF NaOH	RESULTING X-RAY PATTERN
per cent	
2.68	Mercerized
5.99	Mercerized
8.38	Mercerized
10.8	Mercerized and Na-Cell I
11.85	Na-Cell I

Heuser has considered (7) that because the change-in-titer method gives higher values for the sodium hydroxide taken up the alkali cellulose compound should be formed at lower concentrations; he has predicted that the change in the x-ray pattern should result at a lower concentration in aqueous-alcoholic sodium hydroxide solution than in pure water. We have already shown that the true sorption values are many per cent higher than the change-in-titer values (1), and are nearer those from alcoholic solution given above than the change-in-titer values. Furthermore, as shown above, the x-ray pattern of the cellulose does not change when placed in alcoholic caustic soda where the amount taken up is in excess of that of the compound which Heuser holds exists.

Hess and Trogus (5) have obtained some very interesting results with methanol solutions of sodium hydroxide. They found that when ramie fibers are treated with water-free 20 per cent sodium hydroxide–methanol solution for one day there is no change in the x-ray pattern. However, if the fibers are steeped in this liquor for more than a week, the cellulose interferences disappear gradually and the fiber diagram of Na-Cell III or Na-Cell II is obtained. While the experimental data are not at hand, we would expect some swelling of the fibers in sodium hydroxide–methanol solutions, but not as much as in water. Kress and Bialkowsky (8) have shown that water is a better swelling agent for cellulose than alcohol, so that the rôle of the solvent appears to be an "opening wedge" for the penetration of the caustic, although water must be part of the compound Na-Cell I, as the drying of Na-Cell I causes the formation of Na-Cell III (5). However, it certainly appears that the greater the swelling the greater and quicker will be the penetration of the caustic into the lattice. In support of this position Hess and Trogus (5) have shown that unstretched ramie when treated with about 12.5 per cent caustic soda and then washed gives the caustic pretreated ("hydrate") diagram whereas, under unspecified tension, 30 to 35 per cent solution was necessary to obtain the new interferences. They have shown also (4) that ramie fibers under sufficient tension in 45 per cent caustic solution for more than a week gave the interferences of native cellulose when washed out under tension.

TABLE 4

Effect of sodium hydroxide solution upon ramie pretreated in 15.48 per cent sodium hydroxide

CONCENTRATION OF NaOH	RESULTING X-RAY PATTERN
per cent	
0.9	Mercerized diagram; no Na-Cell III′
1.45	Mercerized diagram; no Na-Cell III′
2.38	Mercerized diagram; no Na-Cell III′
3.0	Mercerized diagram; no Na-Cell III′

Hess and Trogus (5) emphasize that water is necessary for the formation of Na-Cell I and for rearrangement of Na-Cell II to Na-Cell I. If by adding water Na-Cell II changes to Na-Cell I, and the latter to "hydrate" cellulose, then one wonders what pattern would be obtained if native cellulose were treated for, say, two weeks with water-free 20 per cent sodium hydroxide–methanol, the caustic neutralized with dry hydrogen chloride, and the sample then washed chloride-free with water. This would tell whether or not Na-Cell I is a necessary stage in the formation of "hydrate" cellulose.

HOW CAUSTIC SODA IS TAKEN UP BY CELLULOSE

If we apply the Phase Rule, using only temperature and concentration as independent variables, we have three explanations for the mechanism, i.e., formation of solid solution, adsorption of caustic soda, or the formation of sodium cellulosate. The first is ruled out as the diagram does not change continuously; the second possibility does not account for the change in diagram as the diffractions are not those of sodium hydroxide; the third does take care of the change in diagram.

Bancroft and Calkin pointed out previously (1) that data should be obtained on the taking up of caustic soda by precipitated cellulose. This would eliminate the possibility of the fibrous or "grown structure" being a variable. Some purified cotton was dissolved in cuprammonium solution, precipitated by extruding into sulfuric acid, and then given the usual 17.5 per cent α-cellulose treatment. Change-in-titer amount of caustic was then determined, the data being given in table 5 and in figure 3. It is evident in figure 3 that the curve is smooth up to 8 molal sodium hydroxide, beyond which the caustic is probably attacking the cellulose. The curve does not necessarily coincide with the previous curves, because the cellulose is modified as one precipitates it.

TABLE 5

Change-in-titer amount of caustic soda taken up by precipitated cellulose

MOLALITY OF FINAL SOLUTION	MILLIGRAMS OF SODIUM HYDROXIDE TAKEN UP PER GRAM OF CELLULOSE
0.399	25.7
0.775	37.3
1.660	61.1
2.600	78.7
3.590	110.9
5.030	118.0
8.470	121.7
12.30	169.0
6.250	118.5
9.690	161.0

The main point to bear in mind is that the fibrous form or "grown structure" of cotton is not a variable so far as the Phase Rule is concerned.

Eisenschitz (3) has shown that with the introduction of a membrane, the concentration and temperature may be varied without violating the Phase Rule. This is simply adding another independent variable, so that

$$F = C - P + 3$$

On this basis Hess (6) has considered that two solid phases (cellulose and sodium cellulosate) are present. We prefer to consider that there is only one solid phase consisting of sodium cellulosate adsorbed on cellulose.

Referring to figure 1, it will be seen that Na-Cell I is formed where two moles of sodium hydroxide are taken up per mole of cellulose. The compound contains water, but progressive dehydrations have not been made, so that it is not possible to say whether the maximum water is necessary.

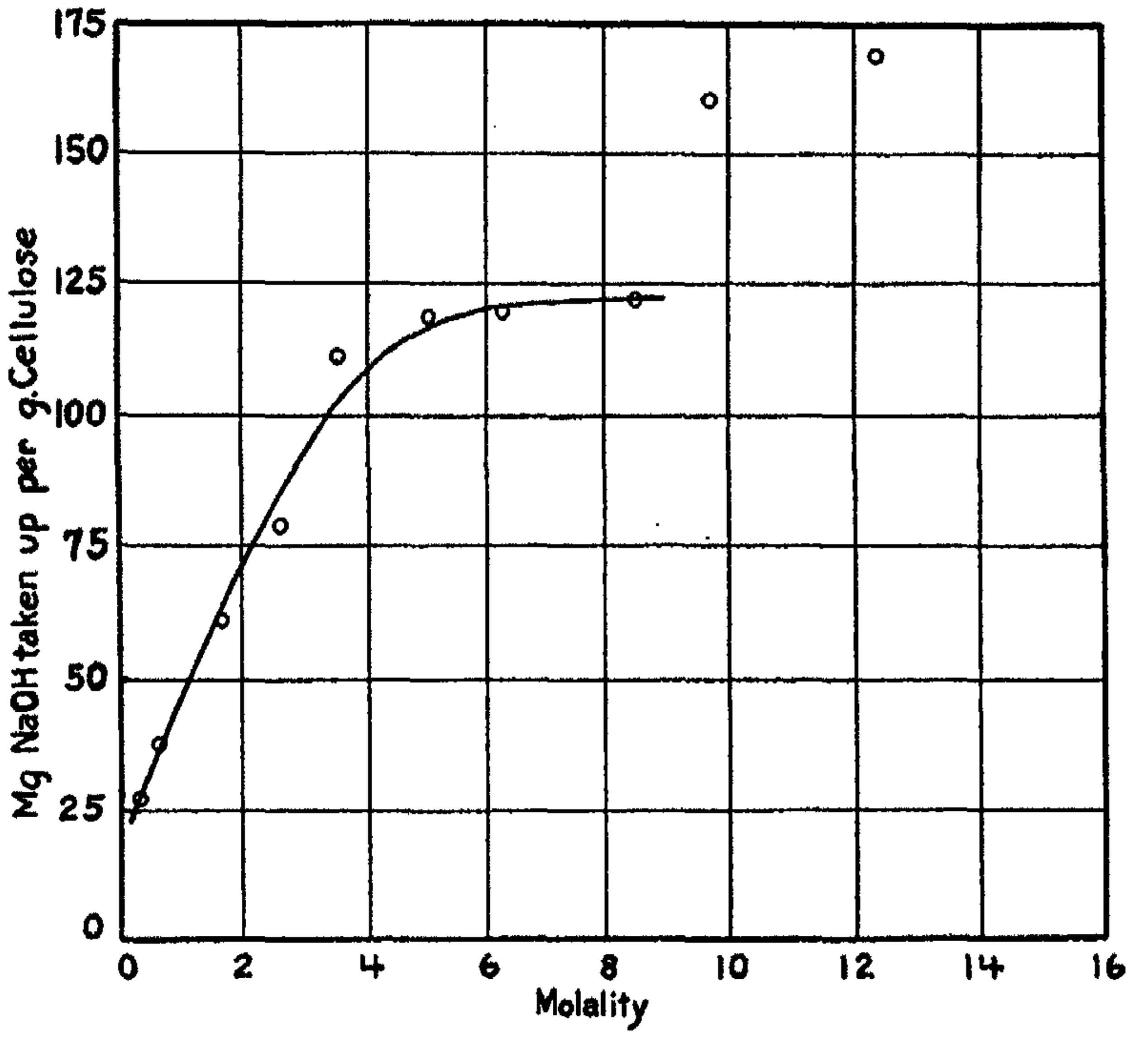

FIG. 3. Sodium hydroxide taken up by regenerated cellulose (change-in-titer method)

Scherer has shown (8a) that when cellulose is placed in liquid ammonia and sodium is added hydrogen is given off. An x-ray analysis of this system may shed light on the composition of the compound.

SUMMARY

1. The x-ray data have been correlated with our previous adsorption values for cotton.
2. It has been shown that cotton treated with sodium hydroxide in ethyl alcohol solution does not form mercerized cotton.
3. Pretreated cotton forms Na-Cell I at a lower concentration than native cotton.

4. It has not been possible to obtain Na-Cell III′ under our experimental conditions.
5. A sodium cellulosate is formed which is adsorbed by the cellulose.
6. The use of the x-ray method to supplement adsorption curves is very important and could be used very profitably.

The writer wishes to acknowledge his indebtedness to Professor Bancroft, under whose direction this work was carried out, to the Textile Foundation for financial assistance, and to Professor Katz for his suggestions and the use of his x-ray equipment.

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rSA-295

THE OXIDE FILM ON PASSIVE IRON[1]

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Nowadays nearly everyone admits that there is an oxide film on the surface of passive iron, but there is still quite a difference of opinion as to the composition of the oxide. In England they incline to the belief that the film is ferric oxide, Fe_2O_3. Evans (3) dissolved the iron from a piece of passive iron and obtained a residual film of ferric oxide. This proves nothing as to the initial composition of the oxide if one admits the possibility, suggested by Bennett and Burnham (2) in the Cornell laboratory, that the film is an instable oxide, stabilized by adsorption on iron. On removal of the iron, the hypothetically-instable, higher oxide would revert at once to the stable ferric oxide.

Hedges (8) heated iron slowly in concentrated nitric acid, and found that at first the iron was passive and the solution almost colorless. At about 65°C. a faint yellow color appeared in the liquid, and at 75°C. a slow evolution of small bubbles of gas occurred at the surface of the metal. At higher temperatures the iron dissolved suddenly and with explosive violence. Powdered ferric oxide was ignited in a silica crucible, cooled in a desiccator, and then placed in a test-tube containing 10 cc. of nitric acid (sp. gr. 1.42). At the ordinary temperature no coloration was produced in the acid and only the faintest yellow was formed when the ferric oxide was left for twenty-four hours at 30°C. The rate of solution of ferric oxide in nitric acid under these conditions is therefore roughly comparable with that of passive iron.

"When the temperature was raised slowly, as in the experiments on the transition of passive iron, the first faint yellow color was produced at 68°; at 75° the solution rapidly became deep yellow, and the thin deposits on the sides of the bottom of the tube vanished between 75° and 77°. The heating was continued up to 90° without further change other than a general deepening of the yellow color. The total amount of ferric oxide dissolved was small. In an experiment carried out in 90 per cent nitric acid, the first faint yellow color appeared at 64°, and the solution became deep yellow over the range of 72° to 77°. It appears, therefore, that *the tempera-*

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

ture at which passive iron becomes active in nitric acid coincides with that at which the rate of solution of ferric oxide becomes appreciable."

This seems quite impressive, but really proves nothing, because the agreement is purely arbitrary and has no theoretical significance. We repeated Hedges' experiment, using ferric oxide which had been sintered at 1000°C. for half an hour. It did not dissolve even in boiling concentrated nitric acid. When the oxide was merely dried at 150°C., it dissolved at room temperature. Hedges happened to give his oxide just the right heat treatment to make the experiment a misleading one.

Bennett and Burnham (2) showed that iron could be made passive by dipping it into a potassium ferrate solution. This proved that the adsorbed oxide film could not be a higher oxide than FeO_3, but did not exclude the possibility of the film being Fe_2O_5 or Fe_2O_4. Actually there were data in the literature by Haber (4) and by Haber and Pick (6) which permit the fixing of a lower limit.

They say that "when wrought iron (sheet, polished with emery) and file-steel are made anodes (at 29° or 22°, respectively) in a caustic potash solution of specific gravity 1.36 (measured at 26°) with a current density of several amperes per square decimeter, red streaks are formed during the first few moments after the circuit has been closed. After several seconds the only anode reaction observed is the evolution of oxygen. This transient formation of ferrate can, however, be produced as often as desired, merely by reversing the current, making the original anode cathode for a moment, and then making it anode again."

We found this experiment easy to repeat, using a strip of Armco ingot iron and an anode current density of about ten amperes per square decimeter. With this current density red streamers of ferrate solution are at first carried away from the anode by the rising bubbles of oxygen. After a few seconds the formation of ferrate ceases, the anode having become completely passive. If we use a much lower current density, ferrate and oxygen continue indefinitely to be formed simultaneously, though in varying relative proportions. When the current density is increased, the formation of ferrate decreases and finally stops altogether, at least so far as visual tests are concerned.

Since the formation of ferrate occurs at a lower current density than the going passive, the oxide film on passive iron in these solutions cannot be a lower oxide than FeO_3. The situation is, therefore, that Haber and Pick (6) have proved that the film producing passivity is not a lower oxide than FeO_3, while Bennett and Burnham (2) have proved that it is not a higher oxide than FeO_3. Consequently the oxide film in these solutions has the composition FeO_3, is an instable oxide, and is stabilized by adsorption on iron, just as the free color-base of rosaniline is stabilized by adsorption on silk (Bancroft (1)).

These experiments prove nothing as to the composition of the oxide film in acid solution. As a matter of fact, we rather hoped that the oxide film would be FeO_3 in nitric acid and FeO_2 or Fe_3O_4 in hydrogen peroxide, but we had no such luck as that. We were able, however, to identify the oxide films obtained in other ways by making electromotive force measurements.

Heathcote (7) showed that nitric acid of sp. gr. 1.20 will not make iron passive, but will keep passivated iron passive for a considerable time. Hence we can passivate iron with any desired passivating agent, dip it into nitric acid (sp. gr. 1.20), and then measure the electrical potential against a normal calomel electrode. The calomel electrode is always anode to passive iron.

The intrinsic instability of the passive film and the fact that adsorption is involved make passive iron potentials difficult to reproduce. The observed potential is a function of time, and of the area, previous history, and conditions of immersion of the sample. If we make a piece of iron passive, measure its potential, make it active again, and repeat, we do not always obtain the same potential. When we try to compare different samples of iron and different passivating agents, annoyingly large variations in potential occur, but valid comparisons are possible if a large number of trials is made.

We are justified in taking the most noble of a series of potential readings as the nearest to the true value for the oxide film. The occurrence of weak spots or "active centers" in the film tends to lower the potential, as pointed out by Haber and Goldschmidt (5), while no conceivable circumstances can cause too high a potential. For these measurements we used lengths of Baker's No. 30 iron wire "for analysis" (Fe = 99.8 per cent) sealed into glass with 1 cm. projecting, giving an exposed area of about 0.08 cm.^{2} When the potential of such an electrode was being measured, the exposed iron surface was immersed completely in the nitric acid (sp. gr. 1.20) in order to avoid an air–liquid–iron junction, at which activation is known to be rapid. Potentials were measured against a normal calomel electrode, using a Leeds and Northrup potentiometer, student type. Table 1 gives typical values of the potential of iron made passive by various means.

Electrode No. 1 was first made passive in nitric acid of specific gravity 1.42, then transferred to nitric acid of specific gravity 1.20 and its potential measured with reference to the normal calomel electrode. The highest value obtained was +0.752 volt with the iron electrode as cathode. After activation in hydrochloric acid, the electrode was made anode in a potassium hydroxide solution of specific gravity 1.36 and polarized with a current of 10 to 15 milliamperes. After this treatment the potential in nitric acid of specific gravity 1.20 was +0.746 volt. The iron wire was reactivated and then made passive by dipping for several minutes in a potassium ferrate solution prepared from iron and potassium nitrate as described by Bennett and Burnham (2). The highest potential this time was +0.741 volt. As a check, the wire was again made passive in concentrated nitric acid, after which it gave a potential of +0.741 volt. The difference between this and the initial value of +0.752 volt is probably due to changes in the surface during the several activations and deactivations.

These potentials lie so near together that iron, made passive by potassium ferrate, by anodic polarization in alkali, and by concentrated nitric acid, must be protected by the same oxide. Since this oxide cannot be either higher or lower than FeO_3, it must be FeO_3.

TABLE 1

Potentials of passive iron in nitric acid (sp. gr. 1.20)

The normal calomel electrode is always anode

ELECTRODE	PASSIVATING AGENT	MAXIMUM E_c
		volts
No. 1	HNO_3, sp. gr. 1.42	+0.752
	Anodic polarization in KOH, sp. gr. 1.36	0.746
	K_2FeO_4 solution	0.741
	HNO_3, sp. gr. 1.42	0.741
No. 2	30 per cent H_2O_2 (superoxol)	0.754
	HNO_3, sp. gr. 1.42	0.753
	8 per cent CrO_3 in water	0.754
	2 per cent CrO_3 in water	0.749
No. 3	HNO_3, sp. gr. 1.42	0.740
	$KMnO_4$ solution, 1.7 *N* (0.3 *N* in H_2SO_4)	0.734
No. 4	HNO_3, sp. gr. 1.42	0.743
	15 cc. HNO_3 + 0.5 cc. H_2O	0.751
	15 cc. HNO_3 + 1.0 cc. H_2O	0.752
	15 cc. HNO_3 + 1.5 cc. H_2O	0.753
	15 cc. HNO_3 + 2.0 cc. H_2O	0.753
	15 cc. HNO_3 + 2.5 cc. H_2O	0.754
	15 cc. HNO_3 + 4.0 cc. H_2O	0.755
	15 cc. HNO_3 + 5.0 cc. H_2O (= sp. gr. 1.35)	0.742
	HNO_3, sp. gr. 1.42	0.739

Electrode No. 2 was made passive successively in 30 per cent hydrogen peroxide, in concentrated nitric acid, and in an 8 per cent and a 2 per cent solution of chromium trioxide in water. The maximum potential attained in each of these cases, measured as before in nitric acid of specific gravity 1.20, lay between +0.749 volt and +0.754 volt with the iron electrode as cathode. This confirms the belief that the passivity produced by all these reagents is due to the formation of the same oxide, FeO_3.

A third electrode was made passive in concentrated nitric acid and then in an acidified potassium permanganate solution. Maximum potentials of +0.740 volt and +0.734 volt were obtained, which are sufficiently close to prove that the passivity produced by acid permanganate is due to the formation of FeO_3.

Electrode No. 4 was made passive successively in six concentrations of nitric acid lying between specific gravities 1.42 and 1.35. In each case the maximum potential lay between +0.742 volt and +0.755 volt, thus proving that the same oxide, FeO_3, is formed by all nitric acid solutions concentrated enough to produce passivity.

Bennett and Burnham (2) emphasized the part played by adsorption in stabilizing the oxide film. If the higher oxide is really adsorbed on the iron, the potential should vary continuously between certain limits. Lest this conclusion would seem to be belied by the relatively consistent potentials given in table 1, we mention again that only the highest, relatively stable values of the potentials have been included in the table. Since these correspond to a practically complete covering of the surface by a maximum thickness of oxide, the data agree fairly well among themselves. Dozens of values between +0.4 volt and 0.7 volt were obtained, especially when the attempt was made to use strips of iron instead of wires. Although these potentials are of no use for comparative purposes, they do indicate that adsorption is playing a part. Since a film of FeO_3 which covers only part of the surface tends either to repair itself or to break down completely, a determination of an adsorption isotherm is out of the question.

While Murphy was studying the oxidizing and reducing action of hydrogen peroxide, he came across a beautiful instance of the misleading experiment. As everybody knows, dilute hydrogen peroxide makes passive iron active. Murphy found that concentrated hydrogen peroxide makes passive iron active. This looked as though concentrated hydrogen peroxide was acting as a reducing agent, but it proved not to be true. Hydrogen peroxide is decomposed catalytically at the surface of passive iron. With concentrated hydrogen peroxide the amount decomposed per unit time is so great that the heat evolved raises the temperature to a point at which FeO_3 breaks down. It is as simple as that, but it had us guessing for a while.

In this paper we have shown that:

1. The evidence brought forward by Evans and by Hedges to show that the film on passive iron is Fe_2O_3 does not prove anything in regard to this.
2. The film making iron passive and produced by adsorption from a ferrate solution, $K_2O \cdot FeO_3$, is an oxide no higher than FeO_3 (Bennett and Burnham).
3. The film making iron passive and produced by anodic polarization of iron in a concentrated solution of potassium hydroxide is an oxide no lower than FeO_3 (Haber).

4. Since the two films are the same, the composition must be FeO_3 (Bancroft and Porter).

5. Electromotive force measurements in nitric acid of specific gravity 1.20 prove that the same film of FeO_3 is formed when iron is made passive by adsorption from an alkaline ferrate solution, by anodic polarization in alkali, or by treatment with hydrogen peroxide, chromic acid, acid potassium permanganate, or nitric acid of specific gravities between 1.35 and 1.42.

6. The activation of passive iron by concentrated hydrogen peroxide is the result of heating and not of reduction.

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THE PHASE RULE IN COLLOID CHEMISTRY[1]

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Gibbs pointed out that the phase rule does not apply, in the form in which he deduced it, to systems involving surface forces, in other words to colloids. On the other hand we make use of the phase rule, consciously or unconsciously, every time that we determine an adsorption isotherm. We have made use of the theorem consciously when studying the action of acids and bases on proteins and on cellulose. What postulates must we make in order to justify our application of the phase rule?

In the first place we must be dealing with reversible equilibrium because the phase rule applies only to reversible equilibrium. In the early days of colloid chemistry, people were interested chiefly in irreversible reactions and metastable states; but that is no longer true.

When dealing with reversible equilibrium in systems containing colloids, it will be profitable to consider separately the adsorbent and the adsorbed substance. Since adsorption depends on the shape and structure of the adsorbing material as well as on its chemical nature, one gram of charcoal may contain a hundred, a thousand, ten thousand, or more solid phases. That seems like a hopeless situation, but it is not really bad. Two different 1-g. lots of charcoal will not necessarily behave alike, but each lot will act like a single phase so long as the individual grains do not change. When we study the adsorption of hydrogen by platinum black, and get an entirely different result after evacuating the hydrogen once or twice, we recognize that the platinum black has sintered and changed its structure. Consequently we put the platinum on an asbestos substrate and get approximately reproducible results because the platinum does not sinter. We see, therefore, that each separate lot of an adsorbent will act as a single solid phase so long as the individual particles are unchanged, but that two separate lots of the same adsorbent will not necessarily act like the same solid phase. With this limitation the phase rule holds for all adsorbents.

When we come to the substance that is to be adsorbed or peptized, we make the explicit assumption that, from the viewpoint of the phase rule, an adsorbed film or a peptized substance shall not be considered as a sepa-

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20–22, 1935.

rate phase even though we know that it is. On this basis, charcoal and a gas which is adsorbed by it constitute a two-component, two-phase system. At constant temperature there is only one amount of adsorption for each pressure and the adsorption isotherm is perfectly definite, so long as the solid phase does not change. The adsorption of caustic soda from aqueous solution by cellulose comes under the phase rule so long as the cellulose does not change.

If we consider a substance peptized by water as not constituting another phase from the viewpoint of the phase rule, the liquid with the suspended particles becomes a phase of varying composition and can be treated as a solution so long as the degree of dispersion remains constant. This enables us to account for the mordanting of cotton with tannin or for the dyeing of cotton by substantive dyes.

We bear up bravely over light being considered either as particles or as waves, depending on the nature of the experiment. If, however, there are any people who do not like to consider a peptized particle or an adsorbed film as being simultaneously both a separate phase and not a separate phase, it is always possible to avoid this by saying that you have a new phase of such a nature that it introduces an extra degree of freedom. Everything can be accounted for on that basis without postulating a dualistic behavior of an adsorbed film or a peptized substance. That has been suggested by a number of people, but it has never proved satisfactory and is therefore objectionable from a pragmatic point of view.

When we study the action of aqueous caustic soda on cellulose from the phase-rule point of view, we get apparently one set of results, and when we study the same system from the x-ray point of view, we get apparently a different set of results. The x-ray people say that their method is the best and that consequently their results are the only ones worth considering. That is foolish, and the two sets of results must somehow be made to agree. There is no question but that the x-ray pattern of cellulose changes irreversibly when treated with a caustic soda solution containing 13 per cent or more of caustic soda. This shows on the adsorption isotherm in a change of direction and in a new set of values at lower concentrations. There is, however, no evidence of two solid phases, although mixed x-ray diagrams can be obtained. The discrepancy disappears if we postulate that each modification of cellulose adsorbs the other and that an adsorbed substance can give an x-ray diagram. The x-ray people have always assumed that a mixed diagram necessarily means two solid phases, but there is no experimental evidence in favor of this contention. The assumption rests on two other explicit assumptions, that the adsorption layer is only one molecule thick and that a layer one molecule thick cannot give an x-ray pattern.

If we eliminate the change in the x-ray pattern of cellulose by starting with mercerized cotton, we find a smooth adsorption curve with no sign of two solid phases. On the other hand an x-ray study of cellulose with caustic soda in it shows clearly the existence of at least two sodium cellulosates which are definite chemical compounds. We must remember that the phase rule does not show in what form caustic soda is taken up by cellulose. It merely shows the number of solid phases present at any moment. In the absence of any other evidence we adopt the simplest form of statement and say that caustic soda is adsorbed by cellulose.

The discrepancy between the two methods of study disappears if we recognize that the phase-rule method shows the number of solid phases and does not show the form in which the dissolved or peptized substance is adsorbed, whereas the x-ray method shows the form in which the adsorbed substance is taken up but does not at present give any evidence as to the number of solid phases. The two methods are complementary and not contradictory.

From the combination of the two methods we can say absolutely that mercerized cotton adsorbs caustic soda as such from dilute solutions, one definite sodium cellulosate from stronger solutions, and another definite sodium cellulosate from still stronger solutions without there being at any time two solid phases present.

The general results of this paper are as follows:—

1. The phase rule can be applied in its ordinary form to reversible equilibrium in colloidal systems provided we remember that a solid adsorbent can be treated as a single solid phase only so long as the number and structure of the individual grains remain unchanged, and provided we treat an adsorbed substance or film and a peptized substance as not constituting new phases in the application of the phase rule, though they do constitute new phases in fact.

2. There are other ways of getting around the difficulty of treating a peptized substance as being simultaneously another phase and not another phase, but the other methods have not recommended themselves to chemists and are therefore unsatisfactory pragmatically.

3. The two modifications of cellulose adsorb each other and do not at any time occur as two solid phases.

4. If one admits that a mixed x-ray diagram does not necessarily connote two solid phases, the apparent discrepancies between the phase-rule method of study and the x-ray method of study disappear.

5. The phase-rule method of study shows the number of solid phases, but does not show the form in which an adsorbed substance is taken up.

6. The x-ray method of study shows, or may show, the form in which an adsorbed substance is taken up, but it does not necessarily show at present how many solid phases coexist.

7. The phase-rule and the x-ray methods of study of the system cellulose, caustic soda, and water are complementary and not contradictory.

8. From a dilute caustic soda solution, mercerized cellulose adsorbs caustic soda as such; from a more concentrated solution one sodium cellulosate is adsorbed; from a still more concentrated solution another sodium cellulosate is adsorbed In none of these cases do two solid phases coexist.

BÖHMITE AND BAYERITE

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An article by Weiser and Milligan (31), entitled "X-ray Studies on the Hydrous Oxides. I. Alumina," appeared in this Journal in December, 1932; from the x-ray photographs of preparations made in various ways the authors arrived at the following conclusions: "... there are two alumina hydrates: (1) gibbsite, $Al_2O_3 \cdot 3H_2O$, both natural and artificial, and (2) diaspore, $Al_2O_3 \cdot H_2O$. Precipitated alumina aged at 100° has been found by x-ray diffraction methods to be a new form of alumina which has been termed δ-Al_2O_3, with adsorbed water." In reply to this article Edwards and Tosterud (8) refer to the existence of an α-$Al_2O_3 \cdot H_2O$ which differed from diaspore (to which they gave the designation β-$Al_2O_3 \cdot H_2O$; cf. in what follows the designation of Haber (18)). Furthermore there was described a β-$Al_2O_3 \cdot 3H_2O$, which differed from gibbsite (hydrargillite, or α-$Al_2O_3 \cdot 3H_2O$, according to Edwards and Tosterud).

The object of this communication is to draw attention to some publications which, although not mentioned by Weiser and Milligan or by Edwards and Tosterud, nevertheless bear on the matter. Proof will, moreover, be brought to show that the preparation which Weiser and Milligan termed "a mixture of δ-Al_2O_3 and gibbsite" has likewise given a distinctive x-ray photograph, according to the radiograms by these authors, which belongs to a definite trihydrate, namely, bayerite, or β-trihydrate, according to Edwards and Tosterud (8).

BÖHMITE

Böhm and Niclassen (4), as well as Fricke and Wever (16), had already shown in 1924 that at higher temperatures (as, for instance, approximately 100°C.) aluminum hydroxide precipitated from a solution of aluminum sulfate with aqueous ammonia gave a hitherto unknown x-ray diagram. A year later Böhm published the reproduction of an x-ray photograph which showed the lattice of a very pure aluminum hydroxide having the composition $Al_2O_3 \cdot H_2O$ from Les Baux. This lattice of very definite form was different from those of diaspore, the trihydrate, and the oxide of aluminum, although the film shows the same lines as those which Böhm and Fricke had obtained from the preparations precipitated at a higher temperature.

The very pure bauxite mineral of Böhm was shown by a series of careful quantitative analyses to have the composition $Al_2O_3 \cdot H_2O$. A preparation absolutely identical with this, both analytically and according to the radiogram, was made up by Böhm (3) from various aluminum hydroxide preparations in an autoclave with superheated steam at 200°C.; he then regarded it as pure bauxite and an "isomer of diaspore." Later, however, it was shown that it is not by any means invariably the case that the bauxite mineral found in nature contains this monohydrate as the predominating aluminum compound, as it may often contain diaspore, gibbsite, and others as well. (In this connection compare F. Rinne with Fricke and Wever (ref. 16, p. 322); see also de Lapparent (25) and the photographs of Weiser and Milligan (ref. 31, p. 3026)). Consequently, at the suggestion of de Lapparent, this isomer of diaspore discovered by Böhm was given the name of "bohmite;" this name has come to be widely adopted in European literature.

In order to avoid confusion, the nomenclature adopted in Europe has been made use of in connection with the subdivision of alumina into α-, β-, etc. forms. According to Haber (18) the aluminum hydroxides which, by elimination of water, give the cubic γ-oxide (2, 5) stable below 1000°C., are termed γ-oxides; to this group belong böhmite, gibbsite, and bayerite, which will be described later (Tosterud designates these as $\alpha\text{-}Al_2O_3 \cdot H_2O$, $\alpha\text{-}Al_2O_3 \cdot 3H_2O$, and $\beta\text{-}Al_2O_3 \cdot 3H_2O$). In contrast diaspore, which, when heated, gives hexagonal-rhombohedral α-corundum (19, 28) belongs, according to Haber, to the α-series (according to Tosterud, $\beta\text{-}Al_2O_3 \cdot H_2O$).

The radiogram for "böhmite" given by Böhm is identical with the diagram of "$\delta\text{-}Al_2O_3 \cdot xH_2O$" published by Weiser and Milligan. According to its artificial representation it is, furthermore, identical with the preparations made and designated $\alpha\text{-}Al_2O_3 \cdot H_2O$ by Tosterud (30).

As has since been definitely ascertained by various observers, böhmite is the first product of aging aluminum hydroxide gel precipitated from solutions of aluminum salts with alkali. This is shown with great clearness by the work of Fricke and Meyring (14), who investigated the aging of aluminum hydroxide in alkaline media by determinations of solubility, pH measurements, and x-ray photographs, as also by the experiments, combined with x-ray photographs etc., conducted by Havestadt and Fricke (20) in regard to the dielectric constants of hydrous hydroxide suspensions depending on the state of aging. Kohlschütter and his collaborators (24) also found in the course of their extensive investigations into the aging of fresh gels that the formation of a crystallized trihydrate can never overtake the formation of the "β-gel" (a term used (24, 32) for a very slightly reactive gel which sometimes shows the x-ray lines of böhmite).

In all these investigations into the course of the aging of amorphous hydroxide, the x-ray diagram of böhmite was always obtained first, even though it did not show (especially at the larger angles of deflection) the lines so clearly and sharply as those obtained from well-crystallized böhmite, which can be obtained from other aluminum hydroxide preparations of the Haber γ-series at 200–350°C. with undersaturated steam in an autoclave (3, 15, 22, 29, 30). Böhmite is also formed by slow thermal disintegration of the (γ)-trihydrate of aluminum oxide (1, 15). Well-crystallized böhmite is very stable and does not exhibit any noticeable signs of aging. At 405°C. böhmite remains undecomposed under a steam pressure of about 500 atmospheres, whereas diaspore under the same conditions breaks up into corundum and water (see ref. 15; this paper also includes some carefully obtained isobaric decomposition curves of böhmite and diaspore).

The density of a pure böhmite produced in an autoclave has been found by Fricke and Severin (15) to be $d_{4°}^{20°} = 3.014$. For a preparation likewise produced in an autoclave von Nieuwenburg and Pieters (27) found a figure of 3.06.

Coblentz (6) deduced from measurements of absorption in the infra-red that bauxite (as in the case of diaspore and gibbsite) is a true hydroxide (in this connection cf. Fricke and Severin, ref. 15, p. 298). The bauxite investigated by him, which had a composition of $Al_2O \cdot OH$, did not show any water bands. At 3μ, however, a band appeared which, from comparisons with other definite hydroxides, must be ascribed to the OH group. The formulation AlOOH is therefore to be preferred here, rather than $Al_2O_3 \cdot H_2O$. (In regard to this, as well as other true hydroxides, cf. Fricke and Ackermann, ref. 12, p. 639.) According to Achenbach (1) böhmite is rhombic.

Weiser and Milligan also find the x-ray interference of böhmite in a series of their preparations. They ascribe these interferences, however, to a new oxide, "δ-Al_2O_3," which had adsorbed varying quantities of water. In proof of this, they state that the preparations having a water content of only 0.65 H_2O per 1 Al_2O_3 show the same radiogram as with a water content of more than 1 H_2O per 1 Al_2O_3. This result is, however, not surprising; neither does it offer anything new in comparison with the findings of other authors, since the preparation with 0.65 H_2O per 1 Al_2O_3 must still contain up to 65 per cent of böhmite, and consequently must show its x-ray diagram. The diagram interference of the 35 per cent γ-Al_2O_3 need be only slightly visible, or even invisible altogether, as the γ-oxide obtained by careful extraction of water from böhmite either reveals only a few, weak and widely-spaced, lines at a small angle of deflection, or even appears quite amorphous from a röntgenographic point of view (ref. 23, p. 328; also ref. 15, p. 301). The assumption of a "δ-Al_2O_3" cannot therefore be deduced from the results of Weiser and Milligan.

BAYERITE

Weiser and Milligan (31) made further preparations according to the directions of Hüttig and Kostelitz (21), and from the x-ray photographs obtained from these preparations they arrived at the conclusion that, in the case of the preparations K_1', K_1'', K_2, K_3, and L_3, according to Hüttig, there was no definite compound, but a mixture of δ-$Al_2O_3 \cdot xH_2O$ and gibbsite. In contrast, Hüttig and his collaborators (21, 23) ascribe these preparations to the "isomers of hydrargillite" first discovered by Böhm (3) and later carefully investigated by Fricke (9, 10, 11), which, in accordance with a proposal made by Fricke (9), because of the precipitation of the substance when alumina is prepared by K. J. Bayer's process, is now termed bayerite in European literature. This bayerite ($Al_2O_3 \cdot 3H_2O$), to the properties of which we shall refer later, also belongs to the γ-series of Haber, since it produces cubic γ-oxide on complete extraction of water. It is metastable at room temperature in contrast to gibbsite (hydrargillite) (9, 10, 11, 17), but stable in comparison with böhmite (3, 20, 24). It is probably identical with the substance designated as β-$Al_2O_3 \cdot 3H_2O$ by Edwards and Tosterud.

It is quite evident from the photographs of Weiser and Milligan that their preparations, made "according to Hüttig," cannot be mixtures of böhmite and gibbsite; this may also be seen from a comparison of the positions of the lines of the alleged "δ-$Al_2O_3 \cdot xH_2O$" (böhmite) and of gibbsite with the positions of the lines of the preparations according to Hüttig. To illustrate this fact table 1 has been compiled from data given by Weiser and Milligan (31).

Some of the special features which show that the preparations made according to Hüttig's method cannot be mixtures of böhmite ("δ-$Al_2O_3 \cdot xH_2O$") and gibbsite, are the following: (1) The strongest böhmite line ($D = 1.85, I = 10$) is exactly the one missing in the case of preparation K_3, and therefore weaker lines could not be expected to appear. (2) The strongest gibbsite line ($D = 4.85, I = 10$) is likewise missing in K_3. (3) Two of the three strongest lines of K_3 ($D = 4.79, I = 10$ and $D = 2.22, I = 10$) are not found in either böhmite or gibbsite.

The intervals between the lines just mentioned and adjacent lines in the different photographs are so great (at least 0.04 A. U.) that the findings given under sections (1) to (3) cannot be due to experimental errors. An arbitrary parallel displacement of the original film also does not permit of any position being found which would justify the interpretation of the preparations "according to Hüttig" as mixtures of böhmite and gibbsite. The preparations of Weiser and Milligan (31) are therefore, from a röntgenographic point of view, also bayerite, or the β-trihydrate of Edwards and Tosterud (8), which they have already indicated. The decomposition curves of Hüttig and Kostelitz (21) show, nevertheless, that their preparations consisted for the greater part of the "γ-gel" identified by Kohlschütter and his collaborators (24) as mixtures of "β-gel" and bayerite. ("β-gel" and "γ-gel" are used in the meaning given by Willstätter, Kraut, and collaborators (32).) Most of the β-gels exhibit, however, either no interferences, or else very weak and diffuse böhmite interferences.

TABLE 1

Comparison of positions of lines

$D = d_{hkl}/n$ in A.U.; I = relative intensity

δ-$Al_2O_3 \cdot xH_2O$ PHOTO D_{II} (BÖHMITE)		GIBBSITE MINERAL		PREPARATION ACCORDING TO HÜTTIG, PHOTO K_3 (BAYERITE)	
D	*I*	*D*	*I*	*D*	*I*
		4.85	10		
				4.79	10
		4.34	9	4.34	10
		3.31	1		
				3.19	4
3.16	5				
		3.12	1		
		2.45	7	2.47	2
		2.38	7	2.37	3
		2.66	1		
2.33	7				
				2.26	1
				2.22	10
		2.17	3		
		2.04	3		
		1.990	2	2.00	2
		1.907	2		
				1.89	1
1.85	10				
		1.798	3		
				1.77	1
		1.741	4	1.72	7
		1.681	5		
		1.642	0.1	1.65	1
		1.580	1	1.60	1
				1.55	2
1.43	8	1.448	4	1.44	3
		1.404	6		
				1.39	3
		1.352	2		
1.32	5	1.312	1	1.33	4
				1.21	2
1.13	1				

With regard to bayerite, reference may be made to the following literature. Böhm (3) discovered a trihydrate of Al_2O_3 which exhibited a very beautiful and characteristic radiogram totally different from that of gibbsite. A reproduction of the picture obtained with iron radiation of this crystal, known generally now as bayerite, may be found in Böhm's article. The angles for a pure bayerite for copper radiation are given by Fricke (10).

Bayerite is produced from böhmite gel ("β-gel" and fresh böhmite) by aging, production being slow under cold water (3, 20, 24), but rapid under dilute alkali (10, 14). In an intermediate stage of the aging, according to Kohlschütter and collaborators (24), "somatoids" form from minute needles of bayerite, which are either wholly or partly surrounded by β-gel (böhmite gel). (Microphotographs of these somatoids may be seen in the paper of Kohlschütter and collaborators (24). Willstätter, Kraut, and Erbacher (32) term these somatoids "γ-gels." Under certain conditions these "γ-gels" can have such a composition that various authors were thereby led to believe that they had found a dihydrate of Al_2O_3.)

Long and extensive shaking with not too dilute alkali, best at a rather high temperature (50–60°C.), causes bayerite to change into gibbsite (hydrargillite) (9). The series order of stability is therefore böhmite > bayerite > gibbsite.

According to the procedure followed, various forms of aluminum hydroxide can be obtained from an alkali-aluminate solution. The rapid introduction of carbon dioxide into a dilute aluminate solution gives röntgenographically amorphous aluminum hydroxide (ref. 20, p. 379; ref. 9). On the contrary, if carbon dioxide be allowed to pass in slowly at ordinary temperatures, so that some days are required for complete precipitation, one obtains bayerite. The aluminate solution may also be more concentrated, for example, with a specific gravity of 1.15 (17). If the carbon dioxide be allowed to act very slowly at ordinary temperature, as, for instance, by allowing the container to stand exposed to the air, then gibbsite is obtained (9). Gibbsite of larger crystalline structure may be obtained more rapidly by allowing carbon dioxide to pass slowly over a solution of aluminate *heated* to 96–100°C. (1).

The same holds good for the spontaneous (hydrolytic) precipitation of the alumina hydrate from a solution of aluminate, which also takes place when air is excluded. Provided the temperature is the same, a slow precipitation is then favorable for the formation of gibbsite, and rapid precipitation for bayerite (9). More accurate details for the production of the two alumina hydrates in this manner, which is important from a technical point of view, may be found in other articles (11, 13, 17).

Apart from x-ray photographs which, in the case of good and well-crystallized preparations, reveal sharp lines up to the highest angles of deflection, the bayerite preparations of Fricke and his collaborators were also investigated, in part for physical uniformity, experiments being made to discover whether the solubility in alkali remained constant with the quantity of excess undissolved solid, where the quantity of alkali was kept the same. If it were a case of a mixture of constituents of different solubilities, the solubility should increase. The results, however, showed a good degree of constancy in a number of cases (ref. 13 and unpublished work).

In the case of these tests care must be taken to see that the alkali used is not too concentrated, so that the sediment does not change into aluminate (see the solution equilibria in the article by Fricke and Jucaitis (13)).

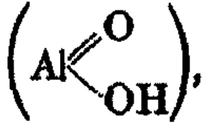
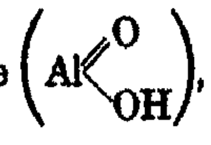
Fricke and Wullhorst determined the heat of solution of bayerite and gibbsite in 12 per cent hydrofluoric acid. They found 37.8_4 and 36.5_9 kg-cal. per mole, respectively, that is, for bayerite an excess of heat content amounting to 1.2 kg-cal., which is quite in accord with the order of stability ascertained by conversion experiments.

Fricke and Severin (15) examined the isobaric thermal decomposition of bayerite, together with that of gibbsite, for vapor pressures of 100 mm. of mercury. In contrast to other earlier work, it was found in these experiments that the reaction spaces amounted in all to only 0.3 to 0.8 cc., of which two-thirds to four-fifths was filled with the hydroxide in a very fine powder. The time for pressure attainment amounted, nevertheless, to as much as sixty days. In this careful method a decomposition temperature of 120°C. was found for bayerite, and for gibbsite 165°C., both for equilibrium with böhmite (badly crystallized) produced by the decomposition. From Nernst's approximate equation it is possible to calculate from these results the heat of formation of bayerite from böhmite and $2H_2O$ (vapor) as 32.4 kg-cal., and for the corresponding heat of formation of gibbsite, 36.3 kg-cal. The figures are again in conformity with the order of stability, but are not capable of rigorous comparison on account of the certainly different energy content of the böhmite formed at the two vapor pressure equilibria as the second phase (12).

In the article by Fricke and Severin (15) there is also to be found an exhaustive discussion of the results of the thermal decomposition experiments of Hüttig and von Wittgenstein (23), of Hüttig and Kostelitz (21), and of other authors.

Finally, it should be pointed out that by investigations of structure conducted by Megaw (26) and Deflandre (7), gibbsite, bayerite, and diaspore are shown to be true hydroxides, in which the water is present not as such, but in the form of OH ions. (Note, also, what has been said previously in regard to absorption measurements in the infra-red.)

SUMMARY

Four definite crystallized forms of aluminum hydroxide are known, namely: diaspore  $\left(\mathrm{Al}\begin{smallmatrix}\mathrm{O}\\\mathrm{OH}\end{smallmatrix}\right)$, which, by extraction of the water, gives hexagonal-rhombohedral α-corundums, and three other forms, which, when water is extracted, give cubic γ-Al_2O_3. These are, in order of increasing stability, böhmite  $\left(Al\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}\right)$, bayerite ($Al(OH)_3$), and gibbsite ($Al(OH)_3$).

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THE DIFFUSION COEFFICIENT AND APPARENT RADIUS OF THE CUPRIC ION IN SILICA GELS

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In a recent paper (1) a mathematical basis has been presented for the calculation of diffusion coefficients from measurements of the rate of penetration of any constant concentration of a diffusing substance into a diffusion medium. The method requires simultaneous measurements of the distance of penetration and the time, and a constant concentration of diffusing substance at zero distance.

The purpose of the present paper is to report the results of measurements of the diffusion of cupric chloride into gels. The photometric method which was used permits making the measurements without disturbing the diffusion process in any way.

APPARATUS

The diffusion apparatus (figure 1) consisted essentially of a light source, a collimating device made up of a series of slits, a cell used as a container for the diffusion system, and a photoelectric cell which was connected to a suitable indicating device.

For a light source of constant intensity a 500-watt projection lamp was operated from a 100-volt storage battery. The bulb was surrounded by a cooling coil to prevent excessive heating, and a red gelatin light filter was placed between the light source and the first slit. The slit nearest the photoelectric cell consisted of two parallel plates 2.2 x 5 cm. The width of the slit system was adjusted to approximately 0.015 cm.

The diffusion cell was formed by clamping rectangular pieces of plate glass (7.5 x 25 cm.) on either side of a glass rod which had been bent into a U-shape and covered with rubber tubing. The cell was fitted into an upright stand so arranged that it could be moved up or down at will by means of a screw adjustment. Readings of the height of the cell were taken to 0.01 cm. by means of a cathetometer.

The photoelectric cell was connected to a vacuum tube amplifier (figure 2). By means of the potentiometer and variable resistance shown in the diagram, it was possible to adjust the plate current of the vacuum tube to any suitable value for normal light intensity on the photoelectric cell. Any change in light intensity was then indicated by a corresponding change in the plate current. The plate current was measured in arbitrary units by a millivoltmeter which gave full scale deflection with a current of approximately 20 microamperes.

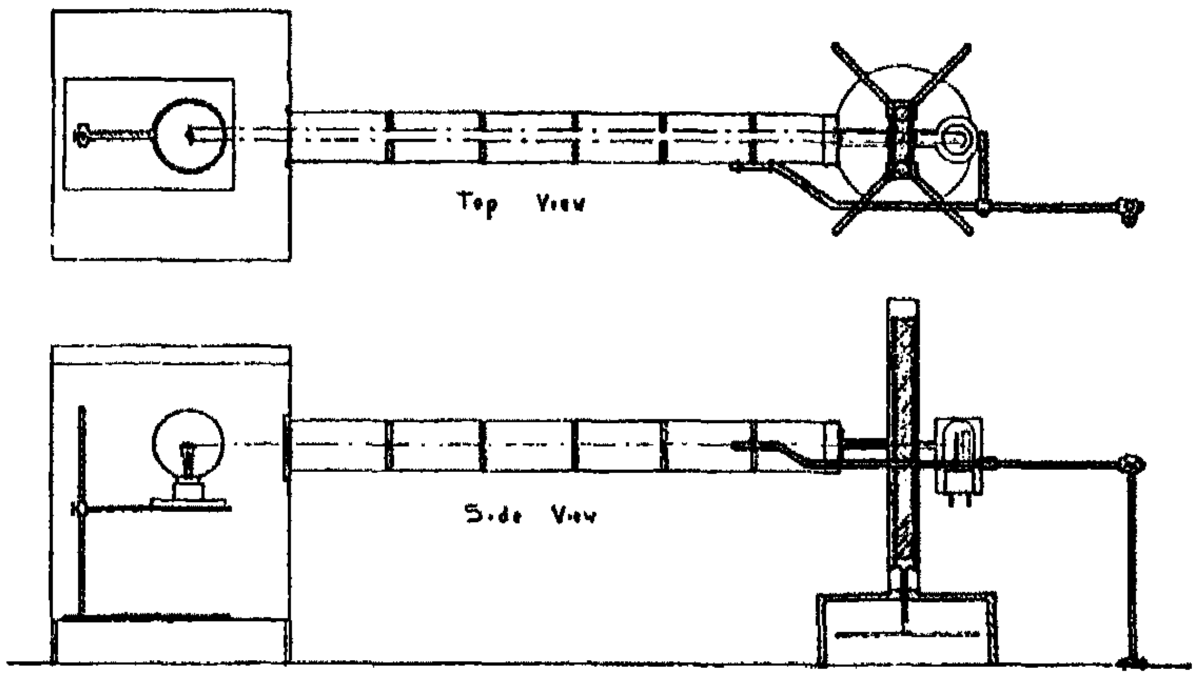

FIG. 1. Diagram of the diffusion apparatus

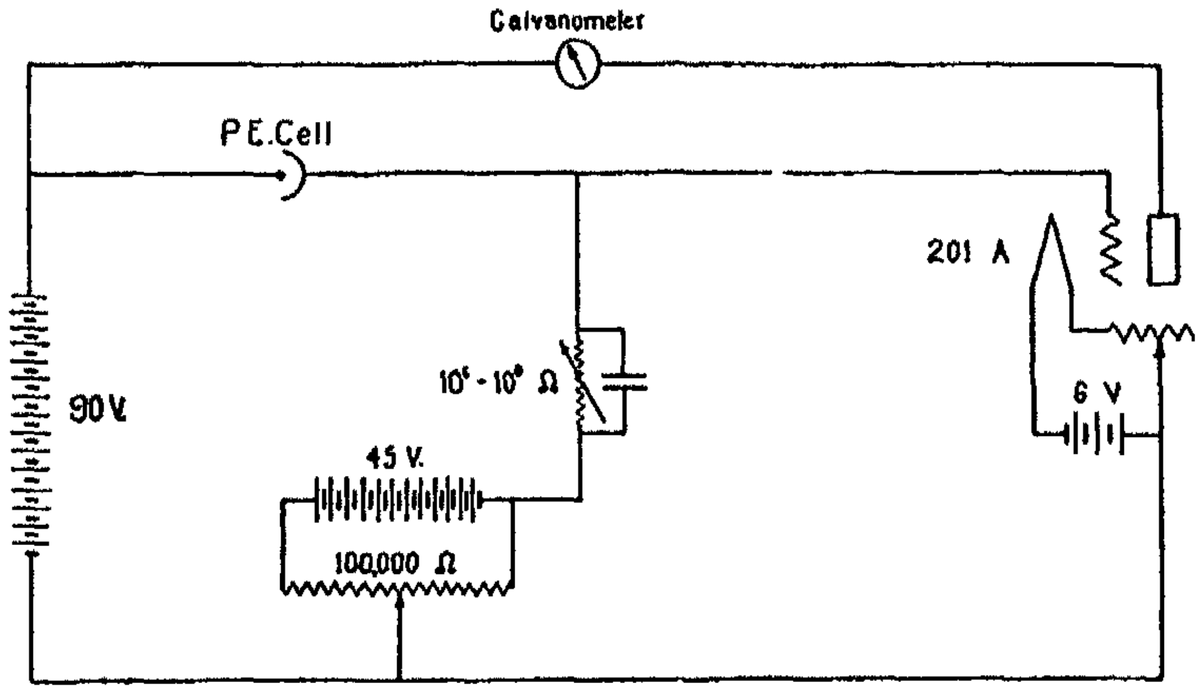

FIG. 2. Wiring diagram of amplifier

Except for narrow slits to permit passage of the light beam, both the light source and the photoelectric cell were enclosed in light-tight metal housings. The experimental work was carried out in a darkened room at 25±2°C.

EXPERIMENTAL METHOD

The sodium silicate (sp. gr. 1.160) which was used in making the gels was 1.59 *N*, as determined by titration with standard acid using methyl orange as indicator. The gels were made by addition of the sodium silicate solution to an equal volume of 4.752 *N* hydrochloric acid. The formation of clear gels required vigorous stirring of the mixture as the silicate was added. When more dilute gels were desired, water was added to the acid before the addition of the sodium silicate.

After the diffusion cell had been placed in the apparatus and a zero reading had been taken corresponding to the position of the cell when the light beam was coincident with the surface of the gel, the diffusing solution was poured on top of the gel. The concentration of the diffusing solution was kept constant throughout the measurement by continuous addition of fresh solution as the less dense solution was drawn off at the top by suction. In making the measurements, the cell was moved upward until further motion resulted in no further increase in the plate current of the amplifier. From this position the cell was moved slowly downward until the light beam passed through a portion of the gel containing cupric ions in the amount necessary to cause a 1 per cent decrease in the plate current. When this point was reached, a reading of the height of the cell was again taken. The distance (X_α) which that particular concentration ($m' = 6.65 \times 10^{-5}$ moles per liter) had moved downward at that time (t) was determined by the difference between this reading and the zero reading.

The most satisfactory results were obtained from one to twenty-four hours after the beginning of the diffusion process. During most of the first hour, the diffusion was too rapid for accurate measurement, and after a day or more there was evidence in some cases of a slight cracking (2) of the gel structure.

The value of the diffusion potential was estimated by measuring the potential difference between a saturated calomel electrode placed in the diffusing solution and a silver-silver chloride electrode placed in the gel. The difference between the voltage obtained using a saturated potassium chloride bridge and that obtained when the diffusing solution and the gel were in direct contact was taken as the diffusion potential. These values are small, as would be expected for systems of uniformly high electrical conductivity throughout.

CALCULATIONS AND RESULTS

Table 1 gives a summary of the values obtained from the diffusion measurements. The values of X_α^2/t were determined from the slope of the straight line obtained by plotting the values of X_α^2 against the values of t. In general the results of duplicate experiments agreed to within 0.1 per cent.

The values of the diffusion coefficient of the cupric ion were calculated by means of the equation

$$D = \frac{X_a^2}{4t}\left(1 - \frac{2UE}{X_a^2/t}\right)^2 \frac{1}{\ln m_0 - \ln m'} \tag{1}$$

In this equation m_0 is the concentration of diffusing substance at zero distance, m' is some constant concentration much lower than m_0, and X_a is the distance of the concentration m' from the surface of the gel at time t. U is the mobility of the diffusing ion and is given the sign of the charge on the ion. E is the potential of the solution referred to that of the gel. U for the cupric ion was given a value of 4×10^{-4} cm. per second, which is approximately 0.7 of the value at infinite dilution. While this is an arbitrary value, the error thus introduced into the final results is small on account of the fact that the value of $\frac{2UE}{X_a^2/t}$ is small compared to 1.

TABLE 1

The diffusion coefficient and apparent radius of the cupric ion in silica gels

SiO_2 PER LITER OF GEL	DIFFUSING SOLUTION		$X_a^2/t \times 10^4$	E	$D \times 10^6$	$r \times 10^8$
	$CuCl_2$ (m_0)	Added electrolyte				
grams	*moles per liter*	*moles per liter*	*cm². per second*	*mv.*	*cm². per second*	*cm.*
104.6	0.5	0.795 NaCl 1.58 HCl	1.233	−3.0	3.59	6.75
104.6	1.0	1.58 HCl	1.293	−2.6	3.47	6.98
69.7	1.0	0.594 HCl	1.796	+0.6	4.64	5.22
69.7	1.0	None	1.659	+9.5	3.93	6.17
52.3	1.0	0.594 HCl	1.791	+1.3	4.60	5.27
52.3	1.0	None	1.671	+8.4	4.00	6.06
5 per cent gelatin	1.0	None	1.153		(3.00)	

In deriving equation 1, it was assumed that the mobility of the diffusing ion is constant throughout the system. This is probably a satisfactory approximation in the case of the silica gels, where the ionic strengths of the diffusing solution and of the gel are uniformly high. It probably is not satisfactory for diffusion into gelatin gels or into pure water, where U is some function of X_a and t. In these systems, a calculation of D (taking $E = 0$) should give a value of the "mean" diffusion coefficient of the two ions of the diffusing electrolyte in the medium used. The results in the 5 per cent gelatin gel have been calculated in this way.

The last column of table 1 gives the values of the apparent radius of the cupric ion as calculated by means of the Stokes-Einstein equation;

$$r = \frac{RT}{N} \frac{1}{6\pi\eta D} \qquad (2)$$

In these calculations, η was taken as the viscosity of water (0.00895). While the usefulness of this equation for calculating the radius of an ion has not been established, it has been shown (3) recently that the similar Einstein-Sutherland equation may be used for the calculation of molecular diameters under certain conditions. An excellent discussion of the validity of equation 2 has been given by Williams and Cady (5).

DISCUSSION

In systems which contain cupric chloride in the presence of other soluble chlorides, an appreciable fraction of the cupric ions may be present in the form of complex ions. Thus an error may have been introduced into the calculated values, owing to the fact that the concentration of the cupric ions was assumed to be equal to that of the cupric chloride. However, since the chloride-ion concentration was uniformly high throughout the system, it is probable that the extent of such complex ion formation was relatively constant, and that the value of the concentration ratio which was used in the calculations was practically unchanged. Furthermore, an error of even 10 per cent in the ratio, m_0/m', would cause an error of only 1 per cent in the value of the diffusion coefficient.

A comparison of the results in the second, third, and fifth lines of table 1, where hydrochloric acid was added to the diffusing solutions in approximately the amounts present in the gels, shows that the highest gel concentration had an appreciable retarding effect on the diffusion process. However, the small difference between the diffusion coefficients in the two more dilute gels indicates that the retarding effect was relatively slight for these gel concentrations, and that the values are practically those which would be obtained in the absence of the gel structure.

The pronounced increase in the diffusion coefficient for a given gel concentration caused by the addition of hydrochloric acid to the diffusing solution seems to illustrate the phenomenon of "accelerated" diffusion discussed by McBain and his coworkers (4). This acceleration was caused by other diffusion processes taking place in the systems. In these silicic acid systems, the diffusion of water was probably negligible. The concentration of the chloride ion was high and relatively uniform throughout the system, and the effect of any spontaneous diffusion of this ion seems to be taken into account in the calculations. However, when no hydrochloric acid was added to the diffusing solution, there was a rapid diffusion of hydrogen and sodium ions from the gel into the solution. Thus the cupric ions diffusing into the gel were retarded by "collision with the molecules of a diffusing column" (4) of positive ions diffusing spontaneously in the opposite direction. Addition of a suitable amount of hydrochloric acid to the diffusing solution practically eliminated this counter diffusion of hydrogen ions, and enabled the cupric ions to diffuse more nearly at their normal rate. The slight difference caused by the addition of sodium chloride to the diffusing solution at the highest gel concentration indicates that similar compensation for the more slowly diffusing sodium ion is relatively unimportant.

It seems probable, therefore, that the values of the diffusion coefficient obtained in the more dilute gels with hydrochloric acid added to the diffusing solution are very nearly equal to the value for undisturbed diffusion of the cupric ion in water. Likewise, the corresponding values of r probably are accurate approximations of the effective radius of the hydrated cupric ion in so far as the use of the Stokes-Einstein equation is justified for this calculation.

SUMMARY

1. A photometric method has been used to study the diffusion of cupric chloride into gels.

2. The most probable value of the diffusion coefficient of the cupric ion in water is 4.6×10^{-6} cm.^{2} per second.

3. A value of approximately 5.2×10^{-8} cm. is suggested for the effective radius of the hydrated cupric ion in solution.

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THE SOLUBILITIES AND FREE ENERGIES OF SOME METALLIC SULFIDES

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In a recent paper, Kolthoff (18) made a critical survey of the literature regarding the solubilities of metallic sulfides, and pointed out the surprising disparity to be found in the various values reported. He showed that the determinations for each sulfide fall more or less distinctly into two groups, in one of which, represented principally by the results of Weigel (33) and of Biltz (3), the solubilities are of the order of 10^{-6} moles per liter, while in the other, represented principally by the results of Bruner and Zawadzki (6), they are very much less. Kolthoff showed that the values in the first group cannot possibly be correct, and suggested that they might really represent the solubilities of oxidation products present at the surfaces of sulfides. This idea is supported by the well-known fact that oxidation products are usually present at the surfaces of sulfide minerals (27), and by the data in table 1, in which the solubilities of some possible oxidation products of a few of the sulfides (4, 7, 8, 19, 28) are compared with the solubilities of the corresponding sulfides as reported by Weigel.

Kolthoff gave an improved list of solubilities and solubility products, but made no attempt to correct for activities, which, in many cases, cause appreciable changes in the values. Since accurate solubility and free energy data of the more important sulfides are required for research work in pyrometallurgy and in flotation, it was considered advisable to make a careful study of the results of previous investigators, and to recalculate their results with the aid of recent activity data.[1]

In order to determine ion-activity coefficients, it has been assumed that the activity coefficients of potassium and chloride ions are equal in potassium chloride solutions, and that the activity coefficient of any ion depends only on the ionic strength (20).

ZINC SULFIDE

Maier (21), using entropy data and the value 43,000 calories (2) for the heat of formation, obtained $\Delta F^\circ_{298} = -41{,}600$ for zinc sulfide. From this,

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[1] Unless otherwise specified, free energies, activity data, electrode potentials, and ionization constants are from Lewis and Randall (20).

the solubility product of zinc sulfide is calculated to be 6.4×10^{-23}. These results are rather uncertain, however, owing to considerable uncertainty concerning the heat of formation.

Glixelli (9) has measured the solubility of zinc sulfide in sulfuric acid solutions of various concentrations at 25°C. He found that the zinc sulfide precipitated from alkaline solution (β-ZnS) is several times as soluble as that precipitated from acid solution (α-ZnS); the β-ZnS, however, slowly changes into the α-ZnS, which Glixelli found to be stable, so evidently only the latter should be considered in calculating the solubility product.

TABLE 1

Comparison of solubilities of possible oxidation products of sulfides with Weigel's data for the solubilities of the sulfides

POSSIBLE OXIDATION PRODUCT	SOLUBILITY	SULFIDES	SOLUBILITY (WEIGEL'S DATA)
	moles per liter		*moles per liter*
Hydrated zinc oxide........	1×10^{-6}	ZnS (ppt.).........	0.71×10^{-6}
Zinc oxide.................	36×10^{-6}	Sphalerite..........	6.6×10^{-6}
Lead carbonate...........	4.0×10^{-6}	PbS (ppt.).........	3.6×10^{-6}
	6.3×10^{-6}	Galena.............	1.2×10^{-6}
Lead oxide.................	55×10^{-6}		
Copper carbonate		CuS...............	3.5×10^{-6}
($CuO \cdot 0.515CO_2 \cdot 0.61H_2O$).	13×10^{-6}	Cu_2S...............	3.1×10^{-6}

TABLE 2

Equilibrium constants for solubility of zinc sulfide in sulfuric acid

H_2SO_4 CONCENTRATION	$(H_2S) \times 10^3$	μ	(H^+)	α_{Zn}	$K_1 \times 10^4$
formal	*moles per liter*				
0.001	0.024	0.00275	0.00178	0.72	1.31
0.01	0.207	0.0205	0.01393	0.52	1.15
0.05	0.927	0.0844	0.05672	0.36	0.96
0.25	4.376	0.35	0.25	0.24	0.74
Mean............					1.04

For the solubility equilibrium

$$ZnS(s) + 2H^+ = Zn^{++} + H_2S(aq)$$

the equilibrium constant is

$$K_1 = (Zn^{++})\,(H_2S)/(H^+)^2$$

In table 2 are shown the results of the recalculations of Glixelli's data. The ionic strengths (μ) and the hydrogen-ion activities (H^+) were calculated from the data of Sherrill and Noyes (30) for acid concentrations of 0.05 molal and less; the activity of hydrogen ion in 0.25 molal sulfuric acid was estimated to be 0.25. The activity coefficients of zinc ion (α_{Zn}) were calculated from the data of Lewis and Randall on potassium chloride and of Scatchard and Tefft (29) on zinc chloride.

In a similar way, the value of $K_1 = 0.91 \times 10^{-4}$ was calculated from the results of Moser and Behr (24), who found the solubility of zinc sulfide (precipitated by hydrogen sulfide from zinc sulfate solution) to be 6.34×10^{-3} moles per liter in 1 molal sulfuric acid saturated with hydrogen sulfide at atmospheric pressure and 20°C. It has been assumed that the decrease in solubility of hydrogen sulfide from 20°C. to 25°C. was approximately compensated by the increase in solubility of the zinc sulfide.

Although the sulfuric acid concentration varies 1000-fold in the two sets of data, the extreme variation of the equilibrium constant is only 1.8-fold. The value $K_1 = 1.0 \times 10^{-4}$ is therefore probably quite reliable. From this value it is found that the solubility product of zinc sulfide is 1.5×10^{-26} and $\Delta F^\circ_{298} = -46{,}960$; with the aid of Maier's entropy data, the value of ΔH is found to be $-48{,}355$.

LEAD SULFIDE

Unfortunately, there are few data available from which an accurate value for the solubility product of lead sulfide can be calculated. Bruner and Zawadzki (6) measured the solubility of lead sulfide in hydrochloric acid solutions and obtained $K_1 = 3.1 \times 10^{-6}$, which corresponds to a solubility product of 3.6×10^{-28}. They give no experimental data, however, but merely state that their result was obtained from several experiments which agreed well with each other; it is impossible, therefore, to recalculate their value.

Jellinek and Czerwinski (14), from measurements of the potentials of a lead electrode in sodium sulfide solutions, obtained values from 6.4×10^{-15} to 13.0×10^{-15} for the solubility product of lead sulfide, and from similar measurements in sodium hydrosulfide solutions, obtained values from 1.4×10^{-13} to 5.0×10^{-13}. Trumpler (31), however, has shown that lead electrodes in sulfide solutions do not exhibit their true potentials, and by making the proper corrections he obtained the value 15×10^{-30} from measurements of the potential of a lead electrode in 2 N sodium sulfide solution.

Trumpler also found that the highest concentration of hydrochloric acid saturated with lead chloride from which lead sulfide can be precipitated by hydrogen sulfide at atmospheric pressure is 2 normal; from this he calculated the solubility product to be 4.9×10^{-29}. A much more accurate value can be calculated with the aid of activity data. From the data of Lewis and Randall on the solubility of lead chloride and on the activity coefficients of hydrochloric acid, and of Harned on the activity coefficients of potassium chloride (10), the value $K_1 = 7.87 \times 10^{-8}$ is obtained for the equilibrium

$$PbS(s) + 2H^+ = Pb^{++} + H_2S\ (aq)$$

which corresponds to the value 9.05×10^{-30} for the solubility product of lead sulfide.

Maier (23) has recently calculated from the thermal data of Jellinek and Zakowski (16) and of Jellinek and Deubel (15) the value $\Delta F^\circ_{298} = -21{,}977$ for the free energy of formation of lead sulfide. From this the solubility product of lead sulfide is found to be 7.00×10^{-30}, which agrees excellently with the value calculated above.

COPPER SULFIDES

Except for the values of Weigel and of Biltz, the only determinations of the solubility of cupric sulfide seem to have been made by measuring the potentials of copper electrodes in sulfide solutions against a normal calomel electrode. From such electromotive force measurements by Immerwahr (11) and by Knox (17), Bruner and Zawadzki (6) calculated the values 5.9×10^{-42} and 1.2×10^{-42}, respectively; Jellinek and Czerwinski (14) from similar measurements obtained values from 1.0×10^{-42} to 5.0×10^{-42}. In spite of the agreement among these results, they very probably are incorrect, since Trumpler (31) has shown that in strong sulfide solutions the only stable copper sulfide is Cu_2S.

Cupric sulfide

Randall, Nielson, and West (26) have calculated the free energy of formation of cupric sulfide to be $-11{,}755$. This corresponds to 3.48×10^{-38} for the solubility product. If the other values given above for the solubility product were correct, the free energy value of Randall, Nielson, and West would be in error by more than 5000 calories, whereas it very probably is correct to within less than 1000 calories.

Cuprous sulfide

It was pointed out above that the measurements of Jellinek and Czerwinski are inapplicable to cupric sulfide. Their measurements can be used, however, to calculate the solubility product of cuprous sulfide, and seem to be the best available for this purpose. They give quite complete data, but unfortunately their experiments were performed at 10°C. Since there are no data from which the electrode potential of cuprous ion at 10°C. can be obtained, it appears that the best procedure is to use the 25°C.

values for the electrode potentials of cuprous ion[2] and of the normal calomel electrode (against which Jellinek and Czerwinski made their measurements). This is equivalent to assuming that the potentials of these two electrodes change approximately the same amount in passing from 25°C. to 10°C., which is not improbable.

The sulfide-ion concentrations in sodium sulfide and in sodium hydrosulfide solutions as given by Jellinek and Czerwinski are undoubtedly incorrect. Much more accurate values can be determined from the ionization constants of hydrogen sulfide and of water at 10°C., which can readily be calculated from the data of Lewis and Randall.

In evaluating the sulfide-ion concentrations, the ionic strength of sodium sulfide has been taken as twice its molality (since it is almost completely hydrolyzed to sodium hydroxide and sodium hydrosulfide), and that of sodium hydrosulfide as equal to its molality; the activity coefficients of hydrosulfide ion and of hydroxyl ion have been assumed to be equal, and have been calculated from data given by Lewis and Randall for potassium hydroxide.

TABLE 3

Solubility product of cuprous sulfide at 10°C.

MOLAL CONCENTRATION	E_c IN VOLTS	$(Cu^+) \times 10^{21}$	$(S^{--}) \times 10^4$	$K_{Cu_2S} \times 10^{44}$
		(a) Na_2S		
0.5	1.131	0.395	656.0	1.02
0.1	1.100	1.41	56.2	1.13
0.05	1.079	3.33	15.6	1.73
0.01	1.060	7.25	0.792	0.417
0.005	1.041	15.8	0.212	0.529
Mean..........				0.963
		(b) NaHS		
0.5	0.990	128.0	0.436	71.3
0.1	0.982	177.0	0.0559	17.5
0.05	0.980	193.0	0.0212	7.91

In table 3 are shown the results of the calculations. The column headed E_c gives the potentials against the normal calomel electrode as determined by Jellinek and Czerwinski. The constants obtained from the measurements in sodium hydrosulfide solutions are rather inconsistent, and differ considerably from those obtained from the measurements in sodium sulfide solutions. Jellinek and Czerwinski prepared their sodium

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[2] $E^0 = -0.522$. Fenwick: J. Am. Chem. Soc. 48, 860 (1926).

hydrosulfide solutions by saturating a sodium hydroxide solution of definite concentration with hydrogen sulfide, sweeping out the excess hydrogen sulfide with a stream of hydrogen, and diluting to the desired concentration. It is possible, however, that the removal of hydrogen sulfide was incomplete, for it is very interesting to note that if it is assumed that an excess of 1 per cent of hydrogen sulfide is present, the following values for the solubility product of cuprous sulfide are obtained from the three sodium hydrosulfide solutions, respectively: 1.88×10^{-51}, 1.21×10^{-51}, and 0.774×10^{-51}. These figures agree well not only with each other, but also with those obtained from the sodium sulfide solutions.

Randall, Nielson, and West (26) have calculated the free energy of formation of cuprous sulfide as −19,955 at 25°C., which corresponds to 36×10^{-51} for the solubility product. The agreement between this value and the value 1.0×10^{-51} obtained above for 10°C. may be considered quite satisfactory, since an increase of 3.3-fold in the solubility of cuprous sulfide in passing from 10°C. to 25°C. would account for the difference.

THALLOUS SULFIDE

The solubility product of thallous sulfide can be recalculated from the complete data given by Bruner and Zawadzki (6) for the equilibrium

$$Tl_2S + 2H^+ = 2Tl^+ + H_2S(aq)$$

They obtained $K_1 = 0.637$. They reached equilibrium by four methods: by precipitating the sulfide with hydrogen sulfide at a pressure of one atmosphere from neutral or slightly acidified solutions of (a) thallous sulfate and (b) thallous nitrate; (c) by dissolving thallous sulfide in sulfuric acid solutions in the presence of hydrogen sulfide at atmospheric pressure; and (d) by dissolving thallous sulfide in sulfuric acid in sealed tubes, in which case thallous ion and hydrogen sulfide are present in equivalent amounts.

In making the calculations, only solutions in which the ionic strength was less than 0.1 have been considered. The hydrogen-ion activities were determined from the data of Sherrill and Noyes (30) for sulfuric acid solutions; activity coefficients for thallous ion were obtained from Lewis and Randall.

In their experiments with sealed tubes (method d), Bruner and Zawadzki measured both the thallous-ion and hydrogen sulfide concentrations at equilibrium, and used both in their calculations. The values for the two should be exactly equivalent, but the values they obtained for hydrogen sulfide are consistently low. The recalculations are based on the thallium determinations, which are probably the more reliable.

The results of the calculations are summarized in table 4. The solutions considered cover a sixfold range of thallous-ion concentrations, and a sevenfold range of hydrogen-ion concentrations. The values of K_1 all agree quite well, although those obtained from method b are somewhat high. If the latter are discarded, the composite mean becomes 0.520 with an average deviation of 5.70 per cent and a maximum deviation of 11.92 per cent; there seems to be no valid reason to discard them, however. The mean, 0.556, corresponds to 6.39×10^{-23} for the solubility product and $-22{,}365$ for the free energy of formation of thallous sulfide.

Moser and Behr (24) have obtained 0.00329 mole per liter as the mean of several measurements of the solubility of thallous sulfide in 0.005 *M* sulfuric acid saturated with hydrogen sulfide at atmospheric pressure and 20°C. Assuming, as in the case of zinc sulfide, that the decrease in solubility of hydrogen sulfide at 25°C. is balanced by an increase in the solubility of thallous sulfide, the value of K_1 is calculated to be 0.42, which agrees reasonably well with the more reliable value found above.

TABLE 4

Equilibrium constants for solubility of thallous sulfide in acid solutions

EQUILIBRIUM METHOD	NUMBER OF EXPERIMENTS	MEAN VALUE OF K_1	AVERAGE DEVIATION FROM MEAN	MAXIMUM DEVIATION FROM MEAN
			per cent	*per cent*
a	10	0.510	4.82	9.22
b	4	0.712	5.13	7.30
c	3	0.560	4.11	6.07
d	4	0.510	6.42	10.20
Composite	21	0.5556	11.53	37.51

SILVER SULFIDE

From data given by Jellinek and Czerwinski (14) on the potentials of a silver electrode in sodium sulfide solutions at 10°C., the solubility product of silver sulfide can be calculated in the same manner as for cuprous sulfide. In this case, however, information is available from which the electrode potential of silver at 10°C. can be determined. For silver ion, $\Delta H_{298} = 24{,}870$ (12). Assuming this to be constant between 25°C. and 10°C., the electrode potential of silver at 10°C. is calculated to be -0.8206 volt. For the half-cell Hg, HgCl, Cl^-, $\Delta H_{298} = 8291$ (Lewis and Randall (20)), and from this, the potential of the normal calomel electrode at 10°C. is calculated to be -0.2862 volt. Using these values, the silver-ion concentrations in table 5 were obtained; the sulfide-ion concentrations were determined in the consideration of cuprous sulfide.

From the mean value, 1.04×10^{-54}, of the solubility product at 10°C, its value at 25°C. can be calculated with the aid of the values of ΔH for silver sulfide, silver ion, and sulfide ion. These are -5022, 24,870, and 10,043, respectively (13). Assuming these to be constant between 10°C.

and 25°C., the solubility product is calculated to be 3.28×10^{-52}, which corresponds to −9930 for the free energy of formation of silver sulfides.

The equilibrium

$$Ag_2S(s) + H_2(g) = 2Ag(s) + H_2S(g)$$

has been investigated at temperatures from about 450°C. to 700°C. by Watanabe (32), who found $\Delta F^{\circ}_{298} = -9098$ for the formation of silver sulfide. This determination, however, probably involved a long extrapolation with the aid of somewhat uncertain heat capacity data. Noyes and Freed (25) have made a careful study of the same equilibrium at 25°C. and obtained values from −1350 to −2116 for the standard free energy change of the reaction. The free energy of formation of hydrogen sulfide is −7840, hence the corresponding values of the free energy of formation of silver sulfide are from −9190 to −9956. The value −9930, calculated from the solubility product, thus falls between these two values.

TABLE 5

Solubility product of silver sulfide at 10°C.

CONCENTRATION OF Na_2S	E_0	$(Ag^+) \times 10^{23}$	$(S^{--}) \times 10^{8}$	$K_{Ag_2S} \times 10^{51}$
molal	*volts*			
0.5	0.928	0.922	656.0	0.558
0.1	0.8895	4.47	56.2	1.12
0.05	0.869	10.35	15.6	1.67
0.01	0.842	31.3	0.792	0.776
0.005	0.822	71.1	0.212	1.07
Mean				1.04

CADMIUM SULFIDE

There seem to be no very reliable data from which the free energy or solubility product of cadmium sulfide can be accurately determined. Bruner and Zawadzki (6) studied the equilibrium

$$CdS(s) + 2H^+ = Cd^{++} + H_2S(aq)$$

under several different conditions and obtained $K_1 = 4.6 \times 10^{-7}$ for cadmium sulfide formed from cadmium sulfate, and $K_1 = 6.6 \times 10^{-6}$ for cadmium sulfide formed from the chloride; these values correspond to solubility products of 5.3×10^{-29} and 7.6×10^{-28}, and free energies of formation of −34,106 and −31,915, respectively. They state that their constants varied rather widely, and that the solid phase did not appear to be well-defined, varying from red to yellow according to the precipitation conditions and the duration of the experiments. Since they give no experimental data, their results cannot be recalculated.

Aumeras (1) recently obtained the value $K_1 = 1.06 \times 10^{-6}$ for the above equilibrium by measuring the solubility of cadmium sulfide (precipitated from the chloride) in hydrochloric acid solutions (0.24 N to 0.885 N) in the presence of varying concentrations of hydrogen sulfide; the cadmium concentration varied from 0.00025 M to 0.003 M. These measurements, however, seem to be quite unsuitable for the determination of K_1, since Lewis and Randall (20) have shown that the activity coefficient of cadmium chloride becomes decidedly abnormal at concentrations greater than about 0.0005 M, and this effect would undoubtedly be greatly enhanced in the presence of relatively strong hydrochloric acid.

Maier (22), from entropy data and Thomsen's value, $\Delta H = -34{,}350$, for cadmium sulfide has calculated the free energy of formation to be $-33{,}038$.

TABLE 6

Free energy and solubility data for sulfides

SULFIDE	TEMPERATURE	$\Delta F°$	SOLUBILITY PRODUCT	SOLUBILITY IN WATER
	°C.			*moles per liter*
ZnS	25	−46,960	1.15×10^{-26}	1.47×10^{-9}
PbS	25	−21,977	7.00×10^{-30}	3.62×10^{-11}
CuS	25	−11,755	3.48×10^{-38}	2.55×10^{-16}
Cu_2S	25	−19,995	3.00×10^{-50}	1.19×10^{-14}
Tl_2S	25	−22,365	6.39×10^{-23}	3.55×10^{-8}
Ag_2S	25	−9,930	3.28×10^{-52}	2.48×10^{-16}
CdS	25	−33,038	1.14×10^{-28}	1.46×10^{-10}
Cu_2S	10		1.0×10^{-51}	4.24×10^{-16}
Ag_2S	10		1.04×10^{-54}	4.29×10^{-16}

Britzke and Kapustinsky (5), from equilibrium measurements of the reduction of cadmium sulfide by hydrogen at high temperatures, obtained $\Delta H_{298} = -19{,}800$, and they suggest the possibility that cadmium sulfide precipitated from solution may have the composition $Cd(CdS_2)$ at room temperature, dissociating into CdS at higher temperatures. In view of the agreement between Maier's free energy value and those calculated from the results of Bruner and Zawadzki, it appears that the former ($-33{,}038$) is the most reliable value available at the present time for precipitated cadmium sulfide.

RÉSUMÉ

In table 6 are listed the values recommended for the standard free energies of formation, the solubility products, and the solubilities in water of the sulfides which have been considered.

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VISCOSITY RELATIONSHIPS IN EMULSIONS CONTAINING MILK FAT

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On the basis of theoretical hydrodynamics, the viscosity of a dilute emulsion is a linear function of the volume percentage of the dispersed phase, and is independent of particle size. The equation derived by Taylor (4) expressing this relationship is:

$$\frac{\eta}{\eta_0} = 1 + 2.5\,\frac{\eta' + \frac{2}{5}\,\eta_0}{\eta' + \eta_0}\,V$$

where η = viscosity of emulsion,
η_0 = viscosity of continuous medium,
η' = viscosity of dispersed phase, and
V = ratio of volume of dispersed phase to total volume.

When η' is infinite, i.e., when the suspended phase is solid, the equation becomes identical with the Einstein formula governing the viscosity relationships in a suspension of solid spheres.

The applicability of equation 1, as well as the Einstein equation, is limited by the assumptions underlying the theoretical development of these equations.

Smoluchowski (3) has pointed out that the range of concentration over which the Einstein equation is applicable is so narrow that the accuracy with which viscosity may be measured is insufficient to establish the validity of the equation, and that consequently an investigation of a suspension over a wide range of concentration, leading to the development of an empirical relationship, is desirable. Such a relationship, according to Smoluchowski, should be reducible for very small concentrations to the relationship expressed in the Einstein equation, and should be generally applicable to suspensions of spherical particles.

For various reasons, and under certain experimental conditions which will be discussed in other parts of this paper, viscosity data obtained in the investigation of milk and related emulsions should be susceptible to treatment on the basis of the conclusions drawn from investigations in theoretical hydrodynamics, provided that in the emulsions under investigation the medium containing the ingredients other than fat may properly be regarded as the continuous medium. An empirical equation developed for these emulsions should be generally applicable to suspensions of spherical particles.

In view of the foregoing considerations, an investigation was undertaken of the viscosity of emulsions containing milk fat suspended in skim milk, in diluted skim milk, in concentrated skim milk, and in a very viscous solution of sucrose in skim milk; first, in order to establish empirically the relationship existing between the following: (1) the viscosity of an emulsion and the concentration of the dispersed phase, (2) the viscosity of an emulsion and the composition of the continuous medium, and (3) the viscosity of an emulsion and the degree of dispersion of the dispersed phase; and, finally, in order to discuss the significance of these empirical relationships.

EXPERIMENTAL

Smoluchowski (3) has pointed out that, in order to test the validity of the Einstein equation, it is necessary to work with suspensions in which the hydrodynamical volume of the suspended material does not differ measurably from the actual volume because of the association of part of the continuous medium with the suspended material. Inasmuch as the clumping of the fat globules is a phenomenon usually encountered in milk and related emulsions, which would contribute towards an increase in the apparent volume of the suspended material, it is necessary to work under conditions such that the clumping is minimized to the extent where its effect on viscosity is entirely negligible. For this reason viscosity measurements by means of a capillary pipet were made at 64°C. on samples stirred uniformly and continuously prior to measurement. The stirring, carried out in such a manner as to avoid the incorporation of air, permitted of uniformity in the distribution of the fat phase, and minimized the probability of the formation of stable clumps.

The temperature of the measurement was selected as one at which, according to the results of Troy and Sharp (5), fat clusters do not form at all in unhomogenized milk, and at which those that are present tend to disintegrate. It may be observed, by means of a microscope, that when milk at approximately this temperature flows through a capillary under the application of a very slight pressure head, the fat globules, as they move past the field under observation, are dispersed as single globules. Although rigid proof of the complete absence of clumps in the more concentrated emulsions is extremely difficult, if not impossible, to obtain, yet, if the empirical equation developed from the viscosity data obtained in the investigation of these emulsions is reducible to the Taylor equation, then it may safely be inferred that the extent of clumping, if clumps are present at all, is small enough to be entirely negligible.

A part of the mix under investigation was forced up under a known pressure into the viscosimeter, the capillary tubing of which was for the most part immersed in the sample, although partly surrounded by a hot-air jacket. Precautions were taken that the temperature of the capillary should be the same as that of the mix prior to the application of pressure.

The pressure at which the determination was made was corrected to compensate for the back head created as the fluid rose in the pipet. The corrected mean pressure was obtained by means of the following formula:

$$P_m = \frac{(h_2 - h_1)d}{2.303 \log \dfrac{P_0 - h_1 d}{P_0 - h_2 d}}$$

where P_m = the mean pressure,
d = the density,
P_0 = the recorded pressure,
h_1 = the distance between the top of the capillary and the top mark of the pipet, and
h_2 = the distance between the level of the fluid in the container and the top mark of the pipet.

The formula may be easily derived and shown to be applicable to the viscosity data reported in this paper.

Viscosity values were calculated by means of the following fundamental equation for flow through a capillary tube as determined by Poiseuille, and amplified by Couette:

$$\eta = K_1 P t - \frac{K_2}{t}$$

where η = the viscosity,
P = the pressure difference causing flow,
t = the time required for a definite volume of fluid to enter the viscosimeter, and
K_1 and K_2 = constants, the values of which depend on the dimensions of the viscosimeter.

In one experiment the pressure was halved in order to note whether the mixes were truly viscous. No indication was found of the existence of any significant plastic effects.

The pressures used in the various measurements ranged from 78.1 to 183.9 g. per square centimeter, depending on the viscosity of the mixes investigated. Both too rapid, as well as too slow, rates of flow were avoided, since these were conditions conducive to turbulent flow on one hand and to creaming on the other.

Composition of emulsions

In order to ascertain the relationship existing between the viscosity of an emulsion and its fat percentage when the composition of the continuous medium is varied, the following series of emulsions were investigated:

I. (a) Cream containing 36.5 per cent fat; (b) skim milk containing 0.02 per cent fat; (c) emulsions containing (a) and (b) in the following proportions: 3:1, 2:1, 1:3, 1:5.

II. (a) Emulsion containing 20 per cent fat, 30 per cent skim milk, and 50 per cent water; (b) suspension containing 50 parts water to 30 parts skim milk; (c) emulsions containing (a) and (b) in the following proportions: 4:1, 3:2, 2:3, 1:4.

III. (a) Emulsion containing 20 per cent fat, 30 per cent skim milk, and 50 per cent condensed skim of a 28.6 per cent milk-solids-not-fat content; (b) suspension containing 50 parts condensed skim milk of a 28.6 per cent solids content to 30 parts skim milk; (c) emulsions containing (a) and (b) in the following proportions: 4:1, 3:2, 2:3, 1:4.

IV. (a) Emulsion containing 28 per cent fat, 42 per cent skim milk, 30 per cent cane sugar; (b) suspension containing 30 parts cane sugar to 42 parts skim milk; (c) emulsions containing (a) and (b) in the following proportions: 4:1, 3:2, 2:3, 1:4.

All emulsions in each of the series were derived from skim milk and cream obtained from the same batch of fresh whole milk. Fat determinations (Babcock) in triplicate on samples taken from the cream used in the preparation of the various mixes served as a basis for the calculation of the fat percentage of the various mixes. The densities of the various suspensions containing no fat, that is, of the continuous media, were determined at 64°C. From these values and that of the density of milk fat at 64°C., as recorded in the literature, the densities of the various emulsions were calculated.

In each of the series of emulsions I, II, III, and IV, only the fat percentage was varied. In the emulsions of series I, II, and III, the continuous medium consisted of skim milk, diluted skim milk, and concentrated skim milk, respectively. In the emulsions of series IV, the continuous medium contained, in addition to the skim milk, sufficient cane sugar to give a rather viscous suspension. The variations in the composition of the continuous medium were such that a very wide range of viscosity values belonging to the continuous medium was obtained. These variations were necessary to the development of an empirical relationship of wide applicability and of theoretical significance. The results of viscosity measurements on the various emulsions are given in table 1.

TABLE I

Relationship between viscosity and fat content of various emulsions

EMULSION SERIES NO. (SEE P. 74)	FAT CONCENTRATION	DENSITY* OF MILK FAT AT 64°C.	DENSITY OF EMULSION	VOLUME OF FAT PER CC. OF EMULSION	η', APPROXIMATE VISCOSITY OF FAT†	P_m, MEAN PRESSURE USED IN VISCOSITY MEASUREMENT	η, VISCOSITY OF EMULSIONS	$\frac{2.5\left(\eta' + \frac{2}{5}\eta_0\right)}{\eta' + \eta_0}$	$\frac{\eta}{\eta_0}$ (MEASURED)	$\frac{\eta}{\eta_0}$ CALCULATED BY MEANS OF EQUATION 2
	per cent			*cc.*	*centipoises*	*grams per cm².*	*centipoises*			
I	36.5	0.8887	0.9652	0.397	14.0	147.5	3.117	2.44	4.84	4.82
	27.4	0.8887	0.9766	0.302	14.0		1.952		3.03	3.00
	18.3	0.8887	0.9889	0.204	14.0		1.281		1.99	1.97
	9.1	0.8887	1.002	0.103	14.0		0.872		1.35	1.35
	6.1	0.8887	1.008	0.069	14.0		0.777		1.21	1.21
	0.0	0.8887	1.015	0.000	14.0		0.644 (η_0)			
II	20.0	0.8887	0.970	0.218	14.0	78.1	0.986	2.45	2.07	2.09
	16.0	0.8887	0.975	0.177	14.0		0.857		1.80	1.78
	12.0	0.8887	0.979	0.132	14.0		0.697		1.49	1.49
	8.0	0.8887	0.983	0.0889	14.0		0.612		1.29	1.29
	4.0	0.8887	0.988	0.0447	14.0		0.532		1.12	1.13
	0.0	0.8887	0.993	0.000	14.0		0.476 (η_0)			
III	20.0	0.8887	1.021	0.230	14.0	137.5	2.506	2.39	2.21	2.19
	16.0	0.8887	1.029	0.185	14.0		2.047		1.81	1.81
	12.0	0.8887	1.037	0.140	14.0		1.739		1.54	1.53
	8.0	0.8887	1.045	0.0941	14.0		1.490		1.31	1.32
	4.0	0.8887	1.053	0.0474	14.0		1.270		1.12	1.14
	0.0	0.8887	1.061	0.000	14.0		1.134 (η_0)			
IV	28.0	0.8887	1.090	0.343	14.0	182.9	8.427	2.27	3.35	3.34
	22.4	0.8887	1.111	0.280	14.0		6.409		2.55	2.53
	16.8	0.8887	1.130	0.214	14.0		4.800		1.91	1.94
	11.2	0.8887	1.150	0.145	14.0		3.818		1.52	1.52
	5.6	0.8887	1.172	0.0739	14.0		3.064		1.22	1.22
	0.0	0.8887	1.195	0.000	14.0		2.512 (η_0)			

* Value obtained from work of Rahn: Milchwirtschaft. Forsch. 3, 512 (1926).

† Value obtained from work of White and Twining: J. Ind. Eng. Chem. 5, 568 (1913).

In order to ascertain the relationship existing between the viscosity of an emulsion and the degree of dispersion of the fat phase the following emulsions were investigated: (I) cream containing 10 per cent fat and 1 part of sodium citrate per 100 parts of mix; (II) emulsion containing 10 per cent fat, 23⅓ per cent skim milk, 66⅔ per cent water, and 100 grams of sodium citrate per 30 pounds of mix.

These emulsions were heated to 60°C. and divided into two portions; one portion was homogenized at 2500 pounds, and rehomogenized at 500 pounds pressure. Viscosity measurements were then made on the homogenized and unhomogenized portions of emulsion I. The mixes obtained from emulsion II were condensed under vacuum to contain approximately 40 per cent fat, after which they were standardized to contain exactly 30 per cent fat. Viscosity measurements were then made on these emulsions.

TABLE 2

Showing effect of an increase in dispersion of fat globules on viscosity

FAT CONCENTRATION	DIAMETER OF FAT GLOBULES	PRESSURE USED IN VISCOSITY MEASUREMENT	TIME OF FLOW			η VISCOSITY AT 64°C.
per cent	μ	*grams per cm.*^{2}	*sec.*	*sec.*	*sec.*	*centipoises*
30	3	145.0	59.6	59.6	59.4	2.476
30	0.7	145.0	59.8	59.5	59.4	2.476
10	3	152.0	24.6	24.7	24.7	0.924*
10	0.7	152.0	24.6	24.7	24.7	0.924

* Viscosimeters used for 10 per cent mixes and 30 per cent mixes differed.

Microscopic observations under a magnification of 800 to determine the average size of the fat-globules were made on samples diluted 1:200 and mounted as hanging drops. These results, together with the results of viscosity measurements, are tabulated in table 2.

The addition of sodium citrate to the emulsions, and subsequent rehomogenization, serve to render decidedly unfavorable the chances for the formation and the existence of clumps. Thus, Hening and Dahlberg (2) report that the addition of sodium citrate to an ice cream mix prior to homogenization serves to reduce the size and the number of clumps in the homogenized mix, while rehomogenization is well known as a means to disintegrate the clusters formed during homogenization.

DISCUSSION

That the suspensions containing no fat may be considered identical in composition with the continuous media of the corresponding emulsions containing fat presupposes that the extent to which protein is adsorbed by the fat is negligible. Evidence exists to support such an assumption. The ratio of water to milk-solids-not-fat in cream, according to information contained in *Fundamentals of Dairy Science* (1) has repeatedly been demonstrated to be the same as the ratio in the milk from which the cream was produced. Proof of a more decisive character to justify the assumption, however, may be obtained from the investigation of Troy and Sharp (5), who report that the variation of the rate of rise of individual fat globules in milk with variations in the radius of the globules obeys quite exactly Stokes' law. This conformation to Stokes' law should have its counterpart in the conformation to Taylor's equation, in the case of dilute emulsions, of the viscosity data reported in this manuscript.

Table 1, which gives the results of the viscosity measurements on emulsions varying in their fat content and in the composition of the continuous medium, also gives the values calculated from the following relationship deducible from these results:

$$\ln \frac{\eta}{\eta_0} = 2.5 \left(\frac{\eta' + \frac{2}{5} \eta_0}{\eta' + \eta_0} \right) (V + V^{\frac{5}{3}} + V^{\frac{11}{3}}) \tag{2}$$

where the significance of the terms may be obtained by reference to equation 1. It is readily seen that for small values of V the equation may be reduced to:

$$\frac{\eta}{\eta_0} = 1 + 2.5 \, \frac{\eta' + \frac{2}{5} \eta_0}{\eta' + \eta_0} V$$

which is identical with the equation derived by Taylor on the basis of theoretical hydrodynamics.

In connection with the power series involving V, and occurring in the exponent of equation 2, it may be explained that $V^{\frac{5}{3}}$ is included as the next term in the series in conformity with the suggestion of Smoluchowski (3) that, if the development of the Einstein equation is extended to apply not only to very dilute suspensions but also to more concentrated ones, the series development involving V should include, in addition to V, $V^{\frac{5}{3}}$ as a very close approximation to the next term. The third term, $V^{\frac{11}{3}}$, in the series has no theoretical significance, and is included in order to effect an agreement between the measured and calculated values of η, for the emulsions containing comparatively high concentrations of fat.

The form of the equation and the constant occurring in it are independent of the milk-solids-not-fat content of the continuous medium. The equation may be reduced for dilute emulsions to that derived by Taylor, regardless of the composition or the viscosity of the continuous medium. Consequently, the designation of the suspension, containing particles small in size relative to the fat globules, as the continuous medium is justified, and the validity of the application of Taylor's equation to the emulsions under investigation may be considered to be established. The multiplication of the constant 2.5 in the Einstein equation by the term

$$\frac{\eta' + \frac{2}{5}\eta_0}{\eta' + \eta_0}$$

to compensate for the currents set up within the particle, when the dispersed phase is fluid, is supported experimentally by the results given in table 1. Thus, η_0 may be varied by the addition of water, condensed skim milk, or cane sugar to skim milk, so that the expression

$$\frac{\eta' + \frac{2}{5}\eta_0}{\eta' + \eta_0}$$

is varied from 2.27 to 2.45, and yet the calculated values of the ratio between the viscosity of the emulsion and that of the continuous medium agree within experimental error with the measured values.

Considered together with the evidence already offered in the experimental part, the fact that empirical equation 2 is reducible to the theoretical equation may be taken as proof that the extent of clumping is insignificant, not only in the dilute emulsions under investigation but also in the more concentrated ones.

The results contained in table 2, concerning the effects of subdivision of the fat globules on the viscosity of the emulsions containing 10 per cent and 30 per cent fat, indicate that, within the limits of experimental error, no measurable increase in viscosity attends a fourfold reduction in the diameter of the fat globules, in agreement with the theoretical demands implicit in equation 1. This independence of viscosity with respect to the size of the fat globules indicates that the viscosity relationships obtained for the unhomogenized emulsions may be applied without change to the corresponding homogenized emulsions, provided of course that the homogenized emulsions are free of fat clusters.

Although adsorption of protein undoubtedly occurs as a result of the increase in area of the fat phase, there is correspondingly no measurable increase in the viscosity of the emulsion. This may signify perhaps that only an insignificant quantity of protein has been adsorbed. However, it is extremely doubtful whether an increase in viscosity should attend an increase in the quantity of adsorbed protein, primarily because adsorption may be considered to result only in a change in the distribution of suspended material in a suspension in which water is the suspending medium, rather than in a change in the hydrodynamical volume of the suspended material. This conclusion, of course, follows as a result of a change in viewpoint from the consideration of the medium containing the ingredients other than fat as the continuous medium to the consideration of water as such. It would also follow if the increase in viscosity associated with the increase in the hydrodynamical volume of the fat phase is considered to be exactly compensated by the decrease in viscosity of the continuous medium due to the removal of protein from this medium.

An increase in the viscosity of an emulsion may attend an increase in the specific area of the dispersed phase because of a quasi-viscous effect due to electrokinetic influences. The modified Einstein equation in which the contribution to the viscosity of the quasi-viscous effect appears, is given by Smoluchowski (3):

$$\frac{\eta}{\eta_0} = \left[1 + 2.5\,V\left(1 + \frac{10^{-4}\,RD^2\,\zeta^2}{36\pi^2a^2\eta_0}\right)\right]$$

where D = the dielectric constant,
R = the specific resistance in c.g.s. units,
ζ = the zeta potential in volts,
a = the radius of globule in centimeters, and
η and η_0 = the viscosities in poises of the suspension and of the continuous medium, respectively.

In suspensions containing very small quantities of salt, the specific resistance is sufficiently low to render the quasi-viscous effect negligible. Thus, in the case of milk, the factor 2.5 appearing in equation 3 is multiplied by $1 + 0.0005\zeta^2$ when the approximate values 60 for D, 2×10^{-10} c.g.s. units for R, 2×10^{-4} cm. for a, and 0.01 poises for η_0 are inserted in the equation. Consequently, unless the zeta potential of the fat globules is inordinately high, the quasi-viscous effect and the influence on viscosity of the factors contributing to the effect, particularly the degree of dispersion of the suspended material, may be neglected.

It is reasonable to conclude from the results presented in table 2 and from the discussion pertaining to these results, that the viscosity of a suspension is independent of particle size, and that any deviation from this relationship may be attributed to the amplification of the volume of the suspended material by means of the suspending medium.

In view of the general applicability of equation 2 to emulsions varying both in the degree of dispersion of the fat phase, and in the composition of the continuous medium, and in view of its reducibility for low concentrations of fat to Taylor's theoretical equation, it seems reasonable to assume its applicability not only at the temperature employed in the measurements herein recorded, but at all temperatures, and not only to the suspensions under consideration but to all suspensions of spherical particles.

Obviously, however, these conclusions cannot be construed to apply without further investigation to emulsions exhibiting marked plastic or elastic properties.

In view of the results obtained, the increase in viscosity usually attending the homogenization of cream and ice cream mixes may now be attributed solely to clustering and, consequently, this increase may serve as a basis for the evaluation of an appropriate index of the extent of clumping. Sharp and Troy (5) have shown that the variation of the rate of rise of fat clusters of indefinite shape in milk, with variations in the mean diameter of the cross-section of these clusters, obeys reasonably well Stokes' law governing the relationship existing between the rate of rise of spherical particles and their diameters. If, accordingly, the fat clusters in cream and ice cream mixes may be considered to behave as aggregates spherical in shape, then equation 2 may be applied to such mixes provided that the significance of V, the volume of fat per unit volume of mix, is extended to include, in addition to the fat volume, the apparent volume of the continuous medium included in the interstices of the fat clusters per unit volume of mix. The evaluation of this volume of continuous medium with the aid of equation 2 necessitates two viscosity measurements—one on the mix under consideration and the other on the continuous medium. The difference between the measured and calculated values of V, divided by the measured value of V, gives the apparent volume of continuous medium associated with the fat clusters per unit volume of dispersed fat; and this quantity may appropriately be designated as a clumping index.

SUMMARY

The viscosity of emulsions containing milk fat does not vary within the limits of experimental error with variations in the degree of dispersion of the fat phase, provided that in these emulsions the actual volume of the fat phase is not measurably amplified by the association with the fat phase of a portion of the continuous medium.

An empirical equation expressing the relationship between the viscosity and the fat content of these emulsions has been obtained. For low concentrations of fat, this equation reduces to that derived by Taylor on the basis of theoretical hydrodynamics, regardless of the composition of the continuous medium, that is, of the medium in which the fat is suspended.

The difference between the hydrodynamical volume of fat, calculated from viscosity data, and the actual volume provides a basis for the calculations of a clumping index applicable to cream and ice cream mixes.

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ADSORPTION AT CRYSTAL-SOLUTION INTERFACES. VIII

INFLUENCE OF DYES AND OTHER ORGANIC COMPOUNDS ON THE CRYSTAL HABIT OF BARIUM AND LEAD NITRATES[1]

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Barium and lead nitrates were selected for study because they are isomorphous and because x-ray evidence indicates the possibility that the three sets of most commonly appearing faces are populated by alternating planes of M^{++} ions in one plane and $(NO_3)^-$ ions in the next. Thus the effect of various dyes on two crystals differing only in the size of their unit cells can be compared. Furthermore, if three different sets of faces exist populated by planes of ions of like charge, one would predict, on the basis of the theory of adsorption and habit modification developed in the previous investigations of this series (1), that certain faces would adsorb given dyes and other faces different dyes, depending in part on the distribution of polar groups in the dye molecule and on the ionic spacing of the faces. It was also thought that the data obtained from these adsorption studies might be of value in determining which of the two forms, pyrite or distorted calcium fluoride, is the more closely approximated in these salts.

EXPERIMENTAL

The lead nitrate and barium nitrate salts were purified by recrystallizing the C.P. material twice from water solution. The solutions in which the crystals were grown were prepared by adding the required volumes of solutions of the foreign materials to the warm saturated salt solutions. The solutions were cooled to room temperature, and the small amount of salt which often crystallized out on cooling was filtered off. Small regular seed crystals were mounted on copper or nichrome wires by means of a tiny spot of sealing wax. The wires were suspended from notched corks fitted into vials containing the various saturated solutions, and the crystals allowed to grow undisturbed for periods ranging from two or three days

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TABLE 1

Influence of organic compounds on the crystal habit of barium and lead nitrates

FOREIGN SUBSTANCE	CONCENTRATION IN GRAMS PER CC.	DESCRIPTION OF CRYSTAL	
		$Ba(NO_3)_2$	$Pb(NO_3)_2$
Picric acid	0.0005		_111_, traces 210—pale yellow
Picric acid	0.001	_111_,† traces 100—yellow	_210_*—yellow
_p_-Nitrophenol	0.001	_111_, traces 100 and 210	_111_, two 100 faces
_p_-Aminophenol	0.001	Insoluble	_111_
_p_-Nitroaniline	0.001	_111_, also 100, traces 210	_111_, also 100, traces 210
Benzamide	0.001	_111_, also 100, traces 210	_111_, also 100, traces 210
Acetanilide	0.001	_111_, also 100	_111_, traces 100
Hydroquinone	0.001	_111_, also 100	_111_, also 100 and 210
Dye No. 4	0.00025	_210_,—violet	_210_,* also 100
Dye No. 4	0.001	210,—violet	210,* _chocolate_
Dye No. 5	0.00025	111 and 210	
Dye No. 5	0.001		111* and 100—pale pink
Dye No. 6	0.00025	210,—pale pink	
Dye No. 6	0.001		111* and 210—pale pink
Dye No. 7	0.001	_111_,—traces 100	_111_*—pink
Dye No. 8	0.001	_111_,— traces 100—yellowish	_111_*—tinted
Dye No. 9	0.001	_111_,—also 100	Insoluble*
Dyes No. 10–No. 15	0.001	_111_,—traces 100	_111_,* tinted in some cases
Dye No. 16	0.001	_111_, and 210, pale green	_111_,* bluish
Dyes No. 17–No. 18	0.001	_111_, traces 100	_111_,* tinted
Anthraquinone green	0.001	_111_, traces 100—green	Insoluble*
Bismarck brown	0.0005		_111_, also 100—tan
Bismarck brown	0.001	_111_, traces 100, tan	_111_,—brown
Methylene blue	0.001	111 and 100—blue on 100	_100_—blue
Congo red	Insoluble		
Diamine sky blue	0.0005	Irregular 111, 100, 210—bluish	
Diamine sky blue	0.002		_111_*—light blue
Oxamine blue	0.002	210, traces 100, 111—green	_111_*—blue
Methylene blue Dye No. 4	0.00002 0.001		_210_—violet
Methylene blue Dye No. 4	0.0001 0.0005	210 and 111	_111_, also 100 111 edges and 100 faces blue
Methylene blue Dye No. 4	0.0005 0.0005		_100_—purplish blue clump

* Results of Starr: Master's thesis, Ohio State University, 1933.

† Italicized faces are predominant ones.

TABLE 1—*Concluded*

FOREIGN SUBSTANCE	CONCENTRATION IN GRAMS PER CC.	DESCRIPTION OF CRYSTAL	
		$Ba(NO_3)_2$	$Pb(NO_3)_2$
Methylene blue	0.00002	*210*, light green	
Dye No. 5	0.0005		
Methylene blue	0.00002	*111* also 100—tan	
Dye No. 6	0.0005		
Methylene blue	0.0001	*100*—small, muddy brown	
Dye No. 6	0.0005		
Methylene blue	0.0005		*100*—deep blue, slightly irregular
Dye No. 6	0.0005		
Methylene blue	0.00002	111 and 100, pale brown	111—slightly more predominant than 100—111 mottle gray, 100 mottled blue
Bismarck brown	0.0005		
Methylene blue	0.00002		*111*—mottled brown
Bismarck brown	0.0005		
Methylene blue	0.0001	*111*—traces 100—black	
Bismarck brown	0.0005		
Methylene blue	0.0005		Little growth; slight darkening of 100 faces
Bismarck brown	0.0005		

in the case of the lead nitrate to nearly a week in the case of the less soluble barium nitrate.

Table 1 gives the substance present as impurity, its concentration, and the type of crystal formed by both lead nitrate and barium nitrate. The formulas for the series of dyes designated by number have previously been published (1d).

DISCUSSION OF RESULTS

Crystal structure

Considerable doubt still exists concerning the crystal structure of the isomorphous nitrates of barium and lead. Certain crystallographic evidence (2) leads to the assignment of an isometric tetrahedral (T^4) symmetry. On the other hand certain other facts, including evidence from x-ray studies (4, 5), indicate a pyritohedral (T_h^6) symmetry. Assuming T_h^6 as correct, an early estimation of the parameters of barium nitrate led to the conclusion that the structure is a distorted calcium fluoride grouping, while a later determination of parameters based on powder photographs indicates a pyrite (FeS_2) arrangement. Wyckoff (5) states that, "Since the positions developed from powder data do not give planar nitrate groups or interatomic distances that agree with those in $NaNO_3$, additional experiments are to be desired."

If the structure is a pyrite arrangement (which may be most simply considered as a sodium chloride grouping of iron and pairs of sulfur atoms), it is easily seen that the 111 faces have alternating planes of M^{++} in one plane and $(NO_3)^-$ in the next, and that the 110 and 210 faces both possess a checkerboard arrangement of the above ions but have different interionic distances. If, on the other hand, the structure is a distorted calcium fluoride grouping, the 110 face has alternating rows of positive and negative ions, while the 111, 100, and 210 faces all consist of alternating planes of M^{++} and $(NO_3)^-$ with varying interionic distances.

While neither structure can explain perfectly the habit assumed by crystals of lead and of barium nitrates grown either from pure solution or from solutions containing foreign material, the evidence obtained in this study shows that the distorted calcium fluoride grouping comes much nearer to fitting the experimental results.

Pure crystals of both lead nitrate and barium nitrate show 111 planes predominating, usually accompanied by very small 100 planes and sometimes by other forms, especially the 210. The results of this study show that foreign substances may be adsorbed on the 111, 100, and 210 faces of these salts.

If Spangenberg's (3) theory is correct, that those faces which are populated by like ions grow most rapidly and hence tend to disappear the soonest, while faces populated by unlike ions grow more slowly and hence become the principal forms, it is seen that a pyrite grouping is immediately ruled out. If this structure were the correct one, the 111 faces, populated by like ions, would grow most rapidly and tend to disappear, while the 100 and 210 faces would grow more slowly and become the predominant forms. Also, according to the theory of modification of crystal habit by foreign substances developed in the earlier investigations of this series (1), impurities should be adsorbed at those faces having the stronger fields of force, in this case the 111. Actually, however, dyes have been observed to be adsorbed at the 210 and 100 faces as well as at the 111 face.

If, on the other hand, the distorted calcium fluoride grouping is taken as the unit cell, the 100, 111, and 210 faces, all populated by alternate planes of like ions, would have strong electrical fields and hence rapid growth rates. But, owing to the different interionic spacings, these faces would all have different rates of perpendicular displacement, and therefore varying degrees of prominence on the crystal. Also, it is to be expected that dye would be adsorbed, if at all, on one or more of these three faces, which is what actually occurs. One discrepancy, however, exists, namely, the fact that the 110 face, with alternate rows of positive and negative ions and hence with a relatively slow growth rate, does not appear on the pure crystal. This difficulty is no doubt less serious than it at first appears to be, since the slight distortion from the true calcium fluoride grouping which is known to exist may be sufficient to account for the failure of the 110 face to appear. Likewise the apparent lack of agreement between the external and internal forms based on crystallographic and x-ray evidence (2) may also be due to this distortion of the calcium fluoride grouping.

Habit modification

An examination of table 1 shows that in general the influence of the simple organic compounds and also of the dyes used is similar for both lead and barium nitrates. This similarity, however, does not hold in all cases. For example, dyes No. 5 and No. 16 and oxamine blue favor the 210 faces of barium nitrate but not of lead nitrate with the concentrations used; again, while methylene blue produces similar modifications with both salts, a given concentration produces a much greater effect on lead nitrate than on barium nitrate. This general but not complete similarity in behavior is in accord with the theory of habit modification suggested previously (1). It is to be expected from this theory that adsorption would occur on corresponding faces of salts having similar structures (since these faces would have similar force fields), but that the actual foreign substances adsorbed at a given face might not be the same in the two crystals, owing to their different interionic distances. This is borne out by the experimental data.

It is also interesting to note that in some instances only one set of faces adsorbs dye, while in others more than one set is colored. If the distorted calcium fluoride structure is accepted as correct, the 111, 100, and 210 faces are all populated by planes of like ions, so that it might be expected that a given dye would be adsorbed on one, two, or even three of these faces, depending on whether the nature and position of its polar groups were such as to fit the interionic spacings on one, two, or three of the faces. Thus if the structure of the foreign molecule were such that it could be adsorbed on both the 111 and 210 faces, but slightly more on the 210, then, as in the case of picric acid and lead nitrate, a greater retardation of the growth rate of the 210 than of the 111 faces would be expected, with the resulting appearance of both faces colored yellow at low picric acid concentrations and the disappearance of the 111 faces at higher concentrations. In the case of methylene blue, which is adsorbed only on the 100 faces of lead nitrate, or of Bismarck brown, which colors only the 111 faces, it follows that a kind and distribution of polar groups probably exists in these dyes such that the former fits only into the ionic spacing of the 100 face, and the latter only into that of the 111.

Mixed dyes

The influence of a mixture of two dyes on crystal habit provides an interesting problem which is worthy of considerably more study. For the most part, the mixed dyes used in this study exerted an approximately additive effect. In all cases methylene blue was one of the dyes used; the second dye was one which favored either the 111 or the 210 faces. Where the concentration of methylene blue was very low (0.00002 g. per cubic centimeter), the effect of the second dye usually predominated; with a higher concentration of methylene blue the effect of this dye masked any influence the second dye might have had, or the sets of faces favored by each dye appeared. When fairly high concentrations of both dyes were used, growth was greatly inhibited.

In two cases where mixed dyes were used, once with Bismarck brown and once with dye No. 4, the effect was not additive. The absence of the expected additive results in this case indicates the need for further study.

Powder photographs

X-ray powder photographs of the opaque crystals of lead nitrate obtained from water solution, of the clear crystals formed in a solution containing a little nitric acid, and of the deep blue crystals colored by methylene blue, all indicated that the lattice constants are the same for each of the three types of crystals.

SUMMARY

1. The habit assumed by crystals of lead nitrate and of barium nitrate grown both from pure solutions and from solutions containing foreign materials indicates that of the two possible structures—pyrite and distorted calcium fluoride—suggested by x-ray and crystallographic evidence for these crystals, the latter is most closely approximated.
2. The results obtained on the adsorption of foreign material by growing crystals of lead and barium nitrates furnishes further evidence in favor of the theory previously suggested, in the earlier papers of this series of investigations, to account for adsorption and habit modification.
3. The effect on the crystal habit of barium and of lead nitrates of a mixture of two dyes, both of which produce a modification when present alone, is generally, but not always, approximately an additive one.

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OBSERVATIONS ON POLYMORPHISM[1]

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I. THE DETERMINATION OF TRANSITION POINTS BY MEANS OF THE DIPPING REFRACTOMETER

The determination of enantiotropic transition points is generally based on one of two methods: first, the study of properties which are different for each crystalline form, as specific heat, specific volume, specific resistance, etc.; second, the study of properties which become identical at the transition point, such as solubility, electrode potential, properties of saturated solutions, etc. Tammann (26) barely mentions the second method because of the difficulties involved in determinations of this nature. However, when the differences in the physical properties of the two forms are very small and the change from one form to the other occurs slowly, the second group of methods is the more accurate, provided chemically and physically pure enantiomorphs can be prepared. The specific properties can be determined over definite ranges of temperature on both sides of the transition point, so that little or no extrapolation is necessary. The solubility method is an excellent one in such cases, but it is time-consuming and difficult. Dunstan and Langton (7) tried to avoid these difficulties by plotting the viscosities of saturated solutions against temperatures. However, there are many possibilities for error in the procedure and their results were not highly accurate. Cohen (5) has determined the conductivities of saturated solutions on both sides of the transition point. This method is very accurate, but it involves the transfer of a saturated solution to a conductivity cell, or else the use of a cell in which the solution can be stirred.

We propose the following method, which is free from the difficulties found in other procedures. The refractive indices of the saturated solutions of the two enantiomorphs are determined over the required tempera-

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[1] This article is based upon part of a thesis submitted by H. E. Phipps to the Faculty of the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1931, and was presented at the Eighty-first Meeting of the American Chemical Society, held in Indianapolis, April, 1931.

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ture range by means of a dipping refractometer. The data are then plotted or treated mathematically, and the point of intersection of the two curves determined. This method is superior to the ordinary solubility method because (1) the readings may be taken at any temperature within the range of the instrument in less than one minute, (2) any slight change in concentration is easily and quickly detected, (3) readings are taken while the liquid is in intimate contact with the suspended solid, and (4) after the apparatus is set up and the determination started, no experimental manipulations are necessary other than reading the scale of the refractometer and the temperature-recording device. The method is limited to the temperature range of the instrument and to solutions which transmit the sodium line. Other types of refractometers might be used to overcome these difficulties.

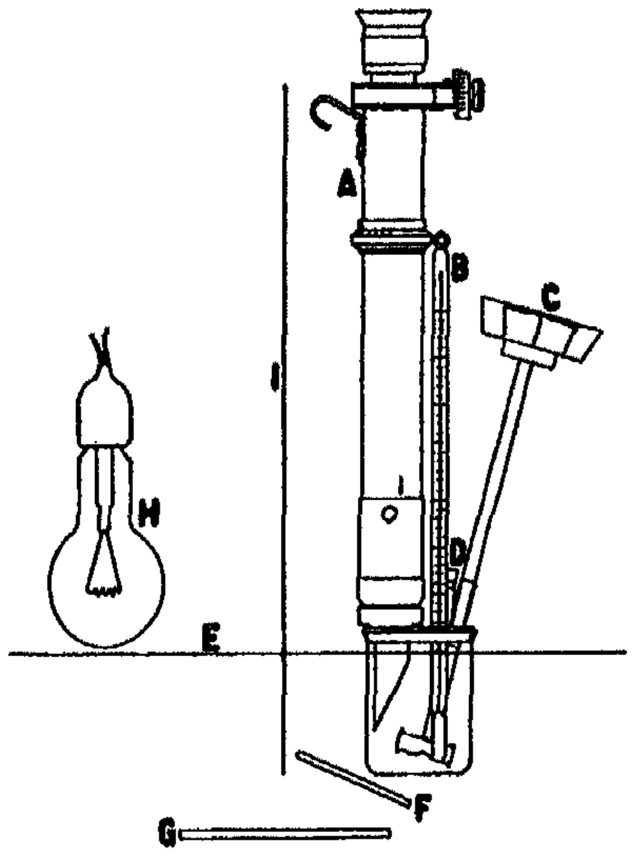

FIG. 1. The apparatus

APPARATUS AND PROCEDURE

The apparatus is shown diagrammatically in figure 1. A is a Bausch and Lomb dipping refractometer equipped with interchangeable prisms. The dipping prism is inserted through a cork which is fitted into the top of a 125-cc. beaker. The thermometer B was graduated to 0.05°C. and had been calibrated by the United States Bureau of Standards. C is a small centrifugal stirrer operated by means of a jet of air. The tube D is added to the apparatus to simplify addition of the solid or removal of solution from the beaker while a determination is in progress. The beaker and contents were placed in a thermostat which could be regulated to 0.01°C. of the desired temperature. The water level in the thermostat is shown by the line E. The light was supplied by a Mazda bulb H and was reflected by the mirror G. The ground glass F was placed so as to give the maximum sharpness to the division line in the refractometer eye-piece. I was a shield to stop extraneous light from reaching the eye of the observer.

Temperature and refractive index measurements were made simultaneously, and in order to be certain that the solution was saturated and that the material was not changing from one physical modification to another, repeated readings were taken at the same temperature. Any change taking place in the solution could be followed easily by the refractive index measurements. When the readings of temperature and refractive index remained constant for an interval of 30 minutes, it was assumed that equilibrium had been established. In some cases as much as twenty-four hours were necessary for constant readings to be obtained. In order to be doubly certain that the solution was saturated, the final temperature was approached from both directions.

Determination of the transition temperatures of sodium sulfate and sodium carbonate as a check on the method

The method was checked experimentally by determining the transition temperature of the hydrates of sodium sulfate. Richards and his coworkers (24), and Dickinson and Mueller (6) had previously determined the temperature of the transition $Na_2SO_4 \cdot 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$ to be 32.383°C. and 32.384°C., respectively, the latter value being more generally accepted.

The starting material was C.P. sodium sulfate. It was recrystallized four times, completely dissolved, filtered, and recrystallized again. The mother liquor was drained off and the crystals placed on a suction filter and washed with a little cold water. When nearly dry, they were crushed in a mortar and stored in a tightly stoppered bottle until wanted. During the actual determination, enough crystals were always present to cause a slight turbidity in the solution. Four series of determinations were made with sodium sulfate, representative results of which are graphically shown in figure 2. Each scale reading recorded is the average of three or more separate readings. The readings very rarely differed from the mean by more than 0.01 scale division. The thermometer readings were corrected for emergent stem and calibration errors.

The transition point was found to be 32.36°C. in every case. Using the hydrated salt, the saturation point was quickly reached with either rising or falling temperatures, and the results were easily reproduced. This was not the case with the anhydrous material. It was necessary to stir the solution for a considerable period of time in order to obtain equilibrium conditions with falling temperature.

Since the transition point was found to be 0.02°C. lower than the accepted value, the transition temperature was determined by the method recommended by Dickinson and Mueller (6), in which the crushed decahydrate was placed in a tube in cold water until recrystallization commenced. The tube was then jacketed and placed in a thermostat. The value obtained by this method was identical with the first, viz., 32.36°C. This probably means that the thermometer reads 0.02°C. low at this temperature. Since it was calibrated to 0.05°C., this difference is not outside the limits of experimental error, especially since there was no ice point marked upon it.

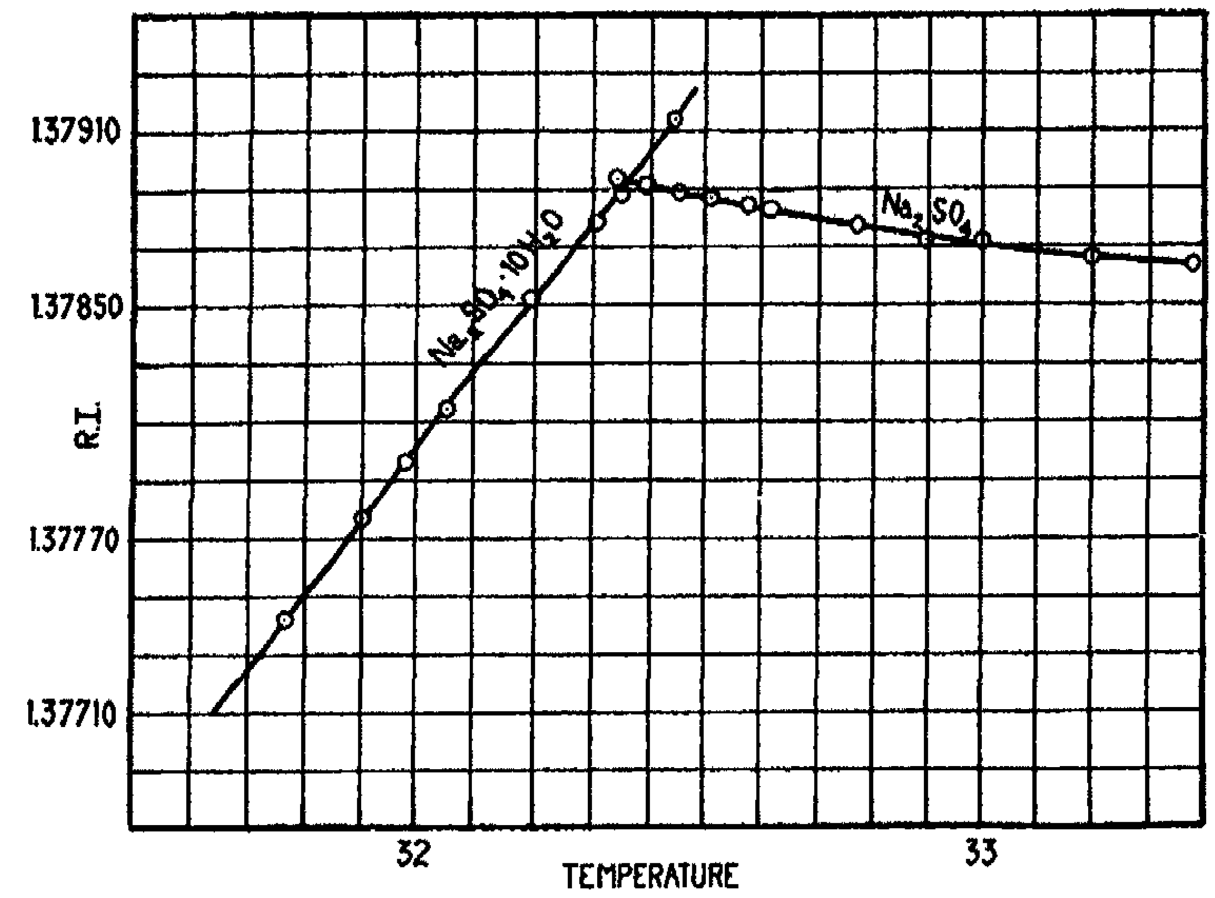

Fig. 2. Transition point of sodium sulfate

A second check on the dipping refractometer method for determining transition points was made by checking the two following well-known points: $Na_2CO_3 \cdot 10H_2O \rightleftarrows Na_2CO_3 \cdot 7H_2O + 3H_2O$, and $Na_2CO_3 \cdot 7H_2O \rightleftarrows Na_2CO_3 \cdot H_2O + 6H_2O$. Using highly purified material, Richards and Fiske (23) found the transition temperature of the first to be 32.017°C. Other determinations were as follows: 31.8°C. by Epple (8), 31.85°C. by Ketner (17), 32.00°C. by Wells and McAdam (29), and 31.85°C. by Ussanovich (27). Wells and McAdam seem to be the only ones who have determined the heptahydrate–monohydrate transition with great care, obtaining 35.37°C. as the best value. Epple gave the temperature as 35.1°C., while Richards and Churchill recorded it as 35.2°C. Wells and McAdam also determined the temperature of the metastable decahydrate–monohydrate transition and found it to be 32.96°C.

The starting material used in this investigation was a high grade of C.P. sodium carbonate. It was purified in the same manner as the sodium sulfate, except that it was recrystallized ten times instead of five, the final recrystallization being carried out just before the material was used. Richards and Fiske found that if the crystals stood for some time before they were used, they took up carbon dioxide from the air and were partially converted to the bicarbonate. They carried out their final recrystallization in platinum dishes, in order to avoid contamination by silica from the glassware. Since this raised the transition point only a few thousandths of a degree, and since Pyrex dishes were used throughout the present work, this was thought unnecessary.

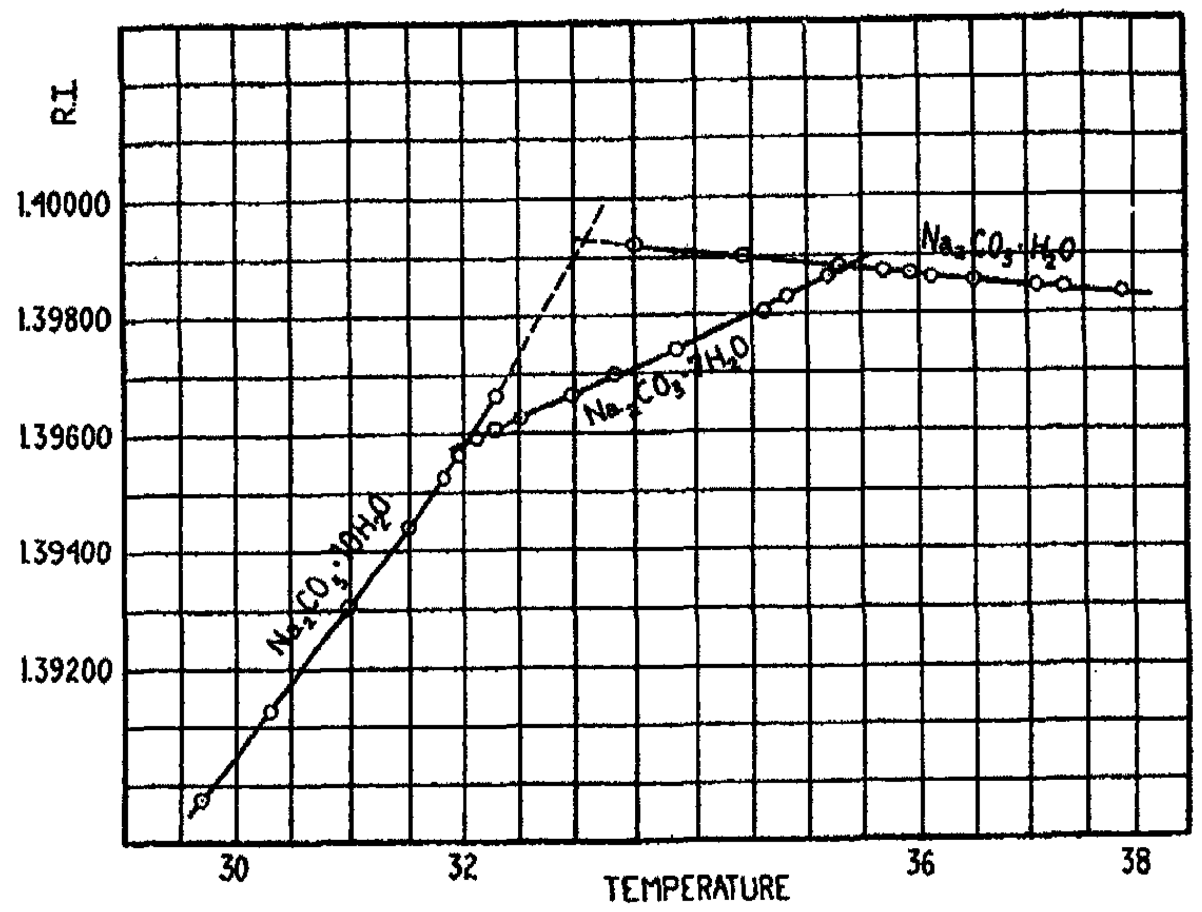

FIG. 3. Transition point of sodium carbonate

Two determinations of the transition points of sodium carbonate were made. No difficulty was found in obtaining perfect checks at the various temperatures, as in the case of the anhydrous sodium sulfate. Equilibrium was quickly established with either rising or falling temperatures. The results are shown in figure 3. From these data, the decahydrate–heptahydrate transition temperature was found to be 32.02°C., the heptahydrate–monohydrate temperature was 35.34°C., and, by extrapolation, the metastable decahydrate–monohydrate temperature was 33.1°C. The limits of error were of the order of 0.02°, 0.02°, and 0.1°C., respectively. These results show that this method can be used to determine transition points with considerable accuracy.

II. THE CRYSTALLINE FORM OF AMMONIUM NITRATE III

During the course of some unpublished work on the transition temperature of ammonium nitrate III ⇄ ammonium nitrate IV (also designated as γ and β), it was found that there was no general agreement in the various references in chemical literature as to whether ammonium nitrate III is orthorhombic or monoclinic.

Ammonium nitrate was first reported to be dimorphic by Frankenheim (10) in 1854. Later, Lehmann (19) showed that there are five distinct forms stable at atmospheric pressure, and Bridgman (2) has found a sixth form stable only at high pressures. In reporting his work, Frankenheim placed the form stable at room temperature (NH_4NO_3 IV) in the rhombic system, but was undecided as to what system NH_4NO_3 III belonged to. Marignac (20), von Lang (30), and others have studied the crystalline properties of ammonium nitrate, but seem to have worked with form IV exclusively. Lehmann placed both forms in the rhombic system, and reported that IV has a higher birefringence than III. He designated them as α-rhombic and β-rhombic, respectively. In 1905 Wallerant (28) reported the crystals to be "monocliniques quasiquadratiques." He stated that if Lehmann had examined form III with oblique polarized light, he would have found that it belonged to the monoclinic rather than the rhombic system. However, Wallerant worked with the solidified melts of modification III which had been stabilized by the addition of potassium nitrate. Caillart (3) studied the solubility curves for mixtures of ammonium and potassium nitrates, and found that crystals separating from different compositions have different crystal structures, as follows: crystals containing less than 17.2 mole per cent of ammonium nitrate show the regular rhombic structure of potassium nitrate; crystals containing 55 to 94.5 mole per cent of ammonium nitrate are monoclinic (cf. Wallerant's crystals); and crystals containing 98 to 100 mole per cent ammonium nitrate are rhombic (modification IV). As Jänecke (14) has pointed out, Wallerant was probably working with a solid solution of potassium nitrate in ammonium nitrate. It is also possible that equilibrium had not been established in the crystals on the microscope slide. In this way it is easy to explain how he may have assigned the crystals to the wrong system. Flörke (9) referred to both forms as belonging to the rhombic system. Bowen (1) reported that modification III was monoclinic or orthorhombic with a moderately high birefringence, but not as high as that of form IV. Since the completion of our work (1931), Hendricks, Posnjak, and Kracek (12), from an x-ray examination, have come to the conclusion that form III is probably orthorhombic.

Experimental

The ammonium nitrate used in this work was of C.P. grade, recrystallized three times.

The first experiments were made with crystals which had been melted and allowed to cool slowly on the stage of a petrographic microscope. The three transitions were not always observed with this pure material; sometimes only two were found. On the other hand, if crystals which had not been recrystallized were used, three transitions were always found, either on heating or cooling. The failure to find the IV→III transition was at first thought to be due to the supercooling of modification III,—a behavior not uncommon in very pure substances. Very careful examination showed that form III was entirely absent, and that the transition progressed in the order I→II→IV on cooling, and IV→II→I on heating. This is in agreement with the work of Bowen, who found that a metastable region between II and IV often develops upon cooling a melt of pure salt. He also found that, in some ways, the II→IV transition is more easily reversed than with the more stable forms. However, if modification III was formed at any time, the direct transition II→IV could not be observed unless the material was melted or else completely converted to modification I. The difference between forms III and IV is shown in the microphotograph (figure 4). The perfect crystals of form III obtained from melts were always rhombic. However, since this is not the best procedure for determining a crystal system (vide Chamot and Mason (4)), a second series of experiments was undertaken.

An electrically heated hot stage was devised, and adjusted to 37°C. by means of a thermostat. A drop of a hot concentrated solution of ammonium nitrate was placed on the slide, covered with a cover glass, and allowed to crystallize slowly. When equilibrium between the crystals and the mother liquor was reached, a coating of collodion was placed around the edge of the cover glass to prevent creeping and evaporation. This had no detrimental effect, and made a more leisurely and thorough examination possible. At least two hundred crystals were examined in this way. Many were so oriented as to give a good biaxial interference figure with convergent polarized light. All the crystals examined showed parallel extinction, and were long needles or diamond-shaped plates. If the temperature was allowed to fall below 32°C. and remain there for a few hours, these needles and plates changed in appearance, and showed the presence of many smaller crystals which also belonged to the rhombic system, but were more highly birefringent. If the temperature was raised to 37°C., the change took place in the opposite direction. The large crystals again appeared perfectly homogeneous, only occasionally showing cleavage cracks or crystal boundaries where there were none before.

Since it was possible that the crystals examined might have been so oriented that only two crystallographic axes were examined for the extinction angle (vide Johannsen (15)), some large well-formed crystals were grown at 37°C. These were oriented so that the different crystallographic axes were parallel and perpendicular to the optical axis of the microscope. Refractive index measurements indicated that the axes of elasticity coincide with the crystallographic axes. Parallel extinction was found in all

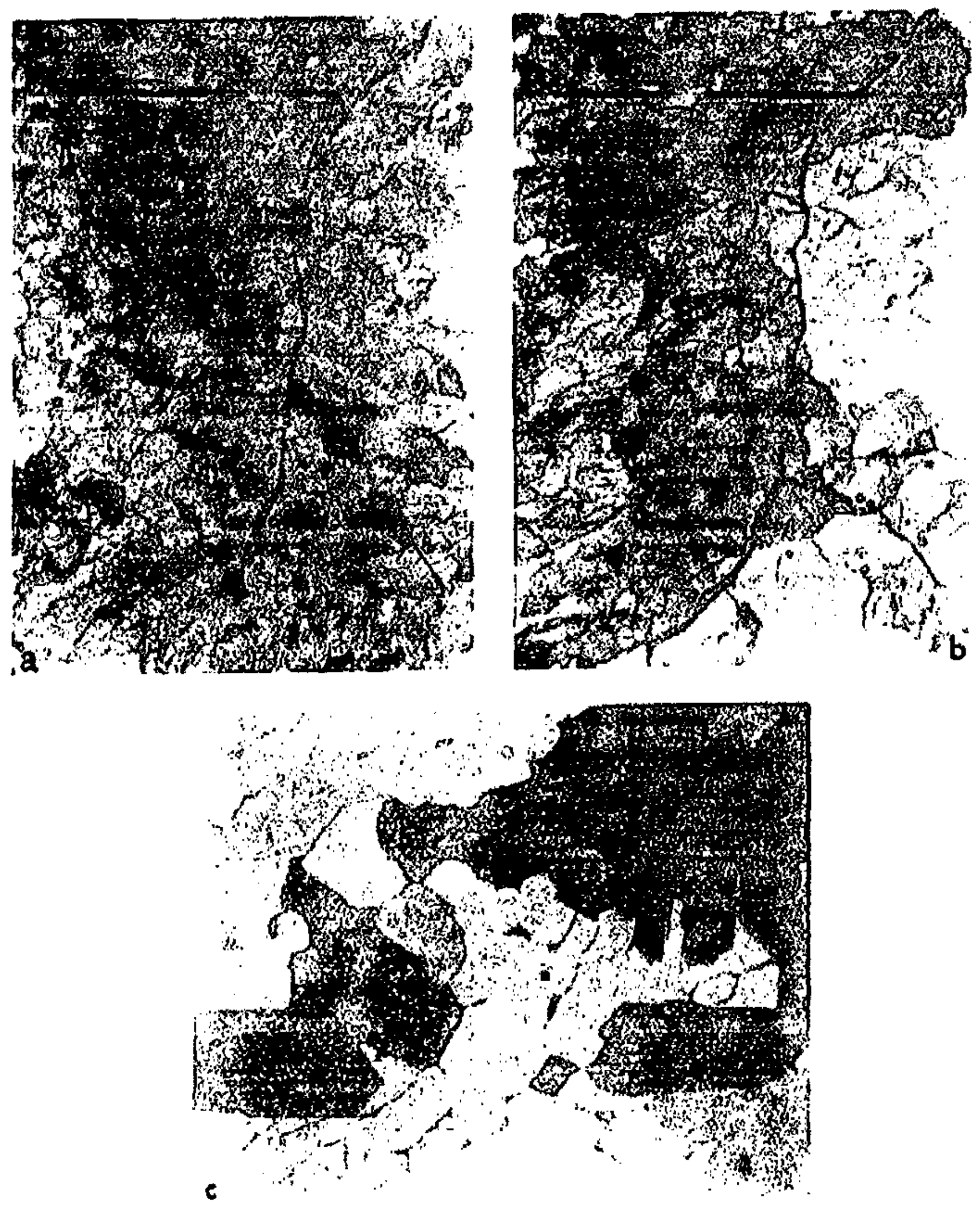

FIG. 4. Microphotographs of ammonium nitrate III and IV. a, ammonium nitrate III; b, ammonium nitrate IV; c, ammonium nitrate IV (black) growing at the expense of ammonium nitrate III (light).

cases, so that there can be no doubt that ammonium nitrate III is orthorhombic.

III. THE TRANSITION POINT OF CARBON TETRACHLORIDE

The transition temperature of carbon tetrachloride has been previously determined by several investigators. Goldschmidt (11) reported it as −45 ± 5°C., Latimer (18) −48.5°C., McCullough and Phipps (21) −48.54 ±0.02°C., and Skau and Meier (25) −47.55 ± 0.12°C. Since the last value is a degree higher than that previously found by the junior author, a redetermination was undertaken to locate the cause of the difference. Since this work was completed (1931), Johnston and Long (16) have reported a value of −47.66 ± 0.05°C., and have proposed that it be used as a fixed point in thermometry.

Experimental

The carbon tetrachloride used in this work was obtained through the United States Bureau of Standards from Dr. Timmermans, who gave its freezing point as −22.85°C. A sample of chlorobenzene with a freezing point of −45.35°C. was obtained from the same source, and served admirably as a check on the thermocouple calibration.

TABLE 1

Transition points

SUBSTANCE	PHENOMENON	HEATING	COOLING	TIMMERMANS' VALUES
		°C.	*°C.*	*°C.*
CCl_4..............	Freezing point	−22.83 ±.01	−22.84 ±.01	−22.85
CCl_4..............	Transition point	−47.46	−47.87	
C_6H_5Cl...........	Freezing point	−45.32 ±.01	−45.35 ±.01	−45.35

The thermocouple used in this work was made of No. 30 constantan and No. 36 copper wire. There were five junctions, each of which was placed in a very thin-walled capillary tube, containing a drop of light oil to improve the thermal contact. The thermocouple was tested for inhomogeneities by interchanging the ends in steam and ice and in ice and liquid air. No differences in the readings were detected under these extreme conditions. The couple was calibrated at the steam point, the ice point, the freezing point of mercury (−38.87°C.) (13), and the sublimation point of carbon dioxide (78.2°C.). Of these points, the last is the least reliable. A carefully calibrated type K potentiometer and type HS galvanometer were used to determine the E.M.F. of the thermocouple.

A 10-g. sample was placed in a specially constructed Dewar tube, so arranged that the air content between the walls could be varied. The tube was placed in a small cryostat, the temperature of which could be changed slowly. Besides the thermocouple, the tube also contained a small stirrer.

The third and fourth columns of table 1 show the values obtained for the freezing points of carbon tetrachloride and chlorobenzene, and for the transition point of carbon tetrachloride. Both the heating and cooling curves were used in obtaining these values. For comparison, Timmermans' values are placed in the last column.

A temperature gradient of 0.1°C. per minute was used. A more rapid change (e.g., 0.3°C. per minute) did not change the freezing points, but the transition point was not sharp. Evidently the velocity of the reaction is not sufficient to maintain a constant temperature.

In a later run, a slight amount of impurity was accidentally introduced into the carbon tetrachloride, resulting in a lowering of the freezing point of 0.1°C. and of the transition point of 0.27°C. Timmermans has stated that the freezing point of carbon tetrachloride is very sensitive to minute traces of impurities. Evidently the transition point is affected to a much greater degree. In the determination made by the junior author in 1928, the material was not as pure as might be desired, as shown by the fact that its freezing point was −22.95°C., and there was no evidence of supercooling at the transition point. With very pure carbon tetrachloride, supercooling of 2 to 3°C. was extremely difficult to prevent. The results in this earlier work were based entirely upon cooling curves, and the rate of temperature change was approximately 0.2–0.3°C. per minute. These facts explain why the first result was 0.9°C. lower than the present value, which is in practical agreement with that of Johnston and Long.

In their paper on the transition point of carbon tetrachloride, Skau and Meier (25) make the following statement: "It was found that the heating curve value was fairly reproducible, but that the value obtained from cooling curves varied from −47.67 to −47.99°, depending on the conditions; that is, on the degree of supercooling and on the rate of cooling. In such cases as this, where one cannot establish equilibrium by stirring, due to the fact that the change takes place in the solid state, it is of course to be expected that the proper degree of supercooling before the transition takes place is very important. Our best curves for this point were obtained with a supercooling of 3 to 4°, the rate of cooling being about 0.3° per minute."

These authors cited Nernst's discussion of the danger of supercooling too little or too much in cryoscopic determinations in dilute solutions (22). On the other hand, the conditions prevailing in dilute solutions may be vastly different from those prevailing in the enantiotropic transition of a pure substance. Tammann (26) states that supercooling and superheating should be avoided as much as possible, because they change the form of the curves at the point of halt. This makes the true equilibrium very difficult to obtain. Consequently excess supercooling should be avoided.

SUMMARY

1. A new method for determining the transition temperature of soluble substances by means of the dipping refractometer has been devised. This method is especially useful in cases where the velocity of transition is so small that ordinary methods are inaccurate. It is much simpler and faster than the solubility method and just as exact.

2. Examination of ammonium nitrate III by means of a petrographic microscope indicates that it is orthorhombic.

3. The transition point of carbon tetrachloride has been redetermined as -47.66 ± 0.2°C. from heating and cooling curve measurements. This temperature is affected by impurities nearly three times as much as the melting point, and is not recommended as a fixed point in thermometry.

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ADSORPTION ON CHROMITE CATALYSTS

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The close relation between the adsorption of gases by solids and contact catalysis is quite generally accepted, and has been much discussed in the literature. In this laboratory the chromites have been thoroughly studied as catalysts for the oxidation of carbon monoxide by Lory (5) and later by Lockwood (4). This suggested that a detailed study of the adsorption by chromite catalysts of carbon monoxide and oxygen, paying particular attention to the so-called "activated adsorption," would not be without interest and value in shedding more light on the question of the relation between adsorption and catalytic activity.

If adsorption does play a major part in contact catalysis, it is certainly this high-temperature variety, with its "energy of activation," which must be considered. For, as Garner pointed out (3), when Taylor (7) described the phenomenon in 1931, he suggested the term "activated adsorption" merely to indicate that the process taking place was one which involved a temperature coefficient, although the fact that it occurs at the temperatures at which the surface under consideration is catalytically active might be construed as indicating that the term might equally well have been used to mean that the adsorbed molecules are in some active state.

Since the surface of the chromite catalyst under consideration is catalytically active for the combination of carbon monoxide and oxygen at temperatures of 100–200°C., its adsorption of both of these gases was studied over this range in temperature, noting particularly the rate at which the adsorption process takes place. The purpose of the investigation was to measure the extent to which the adsorption takes place, and also to obtain sufficient data on its rate to permit the calculation of the energy of activation associated with the process in each case.

APPARATUS

The apparatus used in making these measurements was essentially the same as that described by McKinney (6) and used also by Taylor and

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Strother (8). Like McKinney's apparatus, it was so designed as to permit the measurement of adsorption at constant pressure, with its rate, and also to measure the adsorption at constant volume in order to plot the isothermals.

The gas buret used in these measurements was graduated in hundredths of a cubic centimeter, and the distance between these graduations was over a millimeter,—large enough so that fractions of a division could be estimated with considerable accuracy. The buret was surrounded by a water jacket through which a constant stream of small bubbles of air was kept flowing in order to insure uniformity of temperature along the length of the buret. A thermometer, graduated in fifths of a degree, was suspended in the water jacket, and the temperature was recorded each time a reading was made.

THE CATALYST

The sample of copper chromite used in the adsorption measurements was the Copper Chromite No. 1 prepared and tested for its efficiency by Lockwood (4). At the conclusion of the adsorption measurements, the catalyst was again tested, using the same apparatus used by Lockwood. The results obtained were, within a reasonable experimental error, the same as those of Lockwood, which are summarized in table 1.

TABLE 1

Efficiency of copper chromite No. 1 after the adsorption measurements

TEMPERATURE	CONVERSION
°C.	*per cent*
139	40
166	85
181	100

MATERIALS

The gases used in the adsorption measurements were very carefully purified before being placed in their storage bulbs. Each gas was passed through its purification train for at least an hour, in order to sweep out the air, before being admitted to the system.

EXPERIMENTAL RESULTS

Adsorption of oxygen at constant pressure

The adsorption of oxygen at a pressure of 350 mm. Hg was studied at temperatures covering the range over which the activity of copper chromite as a catalyst for the air oxidation of carbon monoxide varies from practically no activity at all to 100 per cent conversion of carbon monoxide to carbon dioxide.

In order to make the results at different temperatures comparable, the catalyst was heated, before each run, to 300°C. under 400 mm. Hg of carbon monoxide, and then thoroughly evacuated. Lory (5) states that any surface chromate formed is reduced by carbon monoxide at 100°C. The treatment given the catalyst, then, should surely prevent any chromate formed during the previous run from interfering with the results. All of

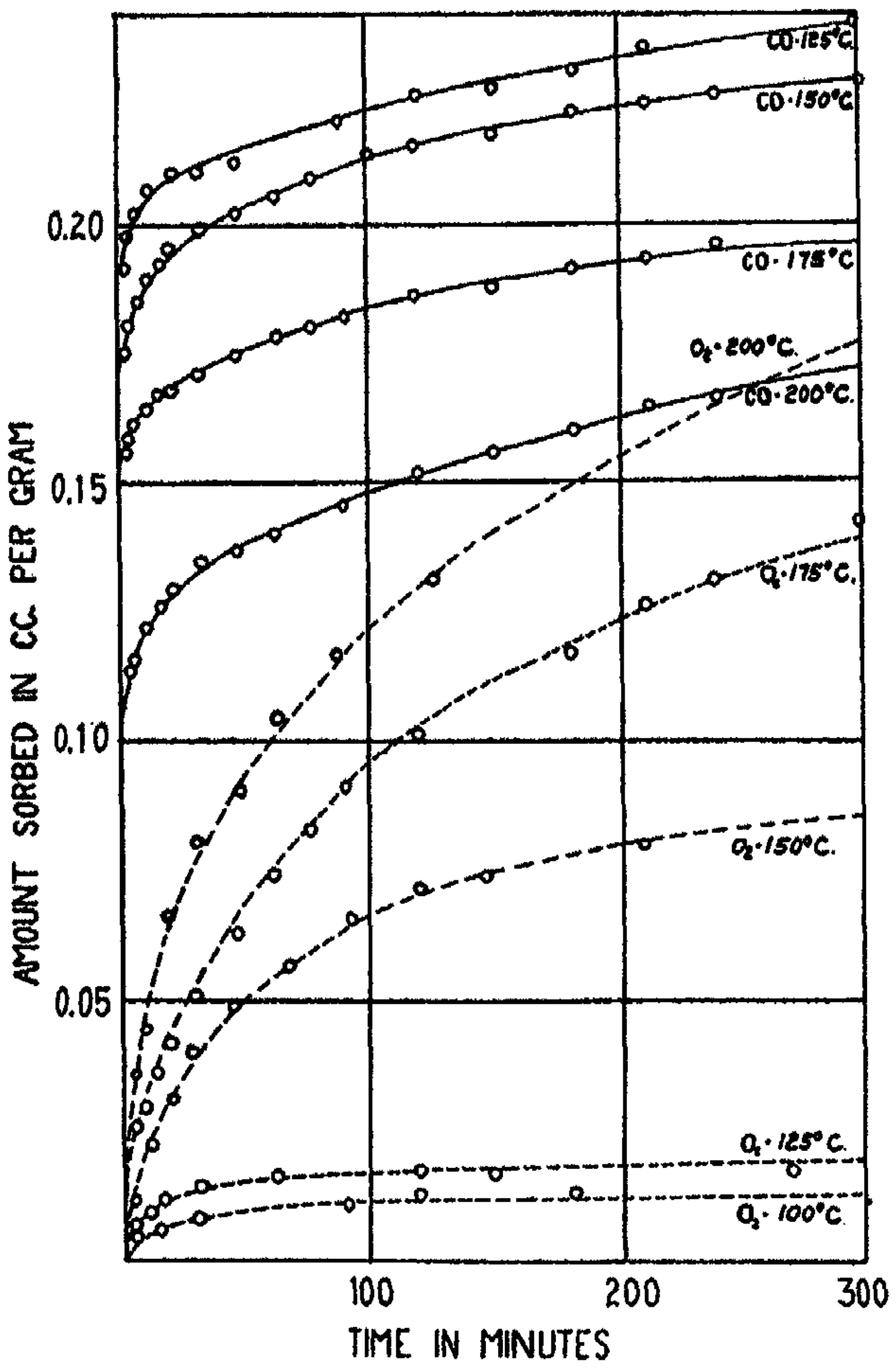

FIG. 1. Adsorption of carbon monoxide and oxygen on copper chromite at 350 mm. of mercury

the runs were checked several times, and the curves obtained could be duplicated within about 2 per cent. The data on the adsorption of oxygen are represented graphically in figure 1.

It is evident from the figure that the adsorption of oxygen at these temperatures exhibits the one chief characteristic of activated adsorption to which Taylor called attention,—a rate which, over the temperature range studied, shows a marked increase with increasing temperature. In this case, not only the rate, but also the extent to which the adsorption occurs, increases greatly with rising temperature.

TABLE 2

Activation energies of adsorption of oxygen on copper chromite

AMOUNT ADSORBED	E (IN KG-CAL.)					
	100-125°C.	100-150°C.	125-150°C.	150-175°C.	150-200°C.	175-200°C.
0.00500	15.43					
0.00625	15.78					
0.00750	17.41	16.19	14.79			
0.00875	17.71					
0.01000	19.11	17.50	15.66			
0.01125	20.51					
0.01250	25.51	22.62	18.66			
0.01500	22.04					
0.03				9.59	9.31	8.99
0.04				9.46	9.54	9.63
0.05				10.19	10.29	10.40
0.06				11.76	11.53	11.28
0.07				13.07	12.29	11.41
0.08				16.50	13.79	10.76
0.09					17.19	10.61
0.10						10.89
0.11						10.96
0.12						11.03
0.13						11.61
0.14						12.72
0.15						15.64

If, at two temperatures T_1 and T_2, adsorption takes place to the same extent in the time intervals t_1 and t_2, the energy of activation to be associated with the adsorption process over that temperature interval may be calculated from the equation

$$\ln \frac{t_2}{t_1} = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Calculating, with this equation, the energy of activation, E, from the data illustrated in figure 1 on the adsorption of oxygen at constant pressure by copper chromite, we obtain the values for E listed in table 2.

The fact that the activation energies for the lower temperature ranges come out considerably higher than those at somewhat higher temperatures is due to the fact that the calculations at the lower temperatures involve a much more nearly saturated surface, since the total amount of adsorption which takes place at these temperatures is so much less. At the higher temperatures, the energy of activation is rising to similar values as more of the gas is adsorbed.

Adsorption of carbon monoxide at constant pressure

The adsorption of carbon monoxide on copper chromite at a constant pressure of 350 mm. Hg was studied at the same temperatures used in the study of the oxygen adsorption.

A great deal has been written, particularly by Burrage (2), about the importance, when comparing the rates of reaction found in different runs, of being certain that the surface of the absorbent was in the same condition at the start of each run. When each carbon monoxide run was made after simply pumping off the gas from the previous run at the temperature at which the run had been made, the results obtained could not be checked and appeared to be without meaning. Evidently the condition of the catalyst surface at the beginning of a run varied considerably, according to whether the previous run had been made at a temperature higher or lower than that at which the succeeding run was to be made.

It was decided to make a set of runs after giving the catalyst a definite treatment, the same treatment being used before each run. The catalyst was first heated to 275–300°C. for an hour under a definite pressure of carbon monoxide. Then the catalyst was thoroughly degassed, and allowed to cool down to the desired temperature. Runs made in this manner could be checked to within 2 to 5 per cent. A set of data from such runs is shown graphically in figure 1.

These runs, in which the condition of the catalyst surface should have been about the same, indicate that the amount of adsorption is less the greater the temperature. Obviously, it is impossible to apply the formula used before to the data of figure 1 and to calculate energies of activation. It is apparent, however, that the order in which the curves fall is determined by the amount of instantaneous adsorption.

This part of the adsorption has the characteristics of van der Waals adsorption. Benton (1) stated that in most cases the van der Waals adsorption disappeared at about 200°C. above the boiling point of the gas. However, he found a type of adsorption which showed the speed characteristic of the van der Waals adsorption with carbon monoxide on copper at 110°C., while the boiling point of carbon monoxide is −192°C. The van der Waals adsorption in the case of carbon monoxide on copper chromite appears to be prominent even at a temperature nearly 400°C. above the boiling point of the carbon monoxide, as is shown by the 0.11 cc. per gram adsorbed instantaneously at 200°C. A brief run was made at 300°C., and the 1-minute reading at this temperature, in cc. per gram, was 0.03, the curve starting out similarly to those for oxygen at the lower temperatures. This would indicate that finally, 500°C. above the boiling point of the carbon monoxide, the van der Waals adsorption is disappearing from the picture.

If we take the 1-minute reading for each of the carbon monoxide runs, whatever it may be, as zero, and plot the amount adsorbed over and above this fixed quantity against time, curves like those in figure 2 are obtained.

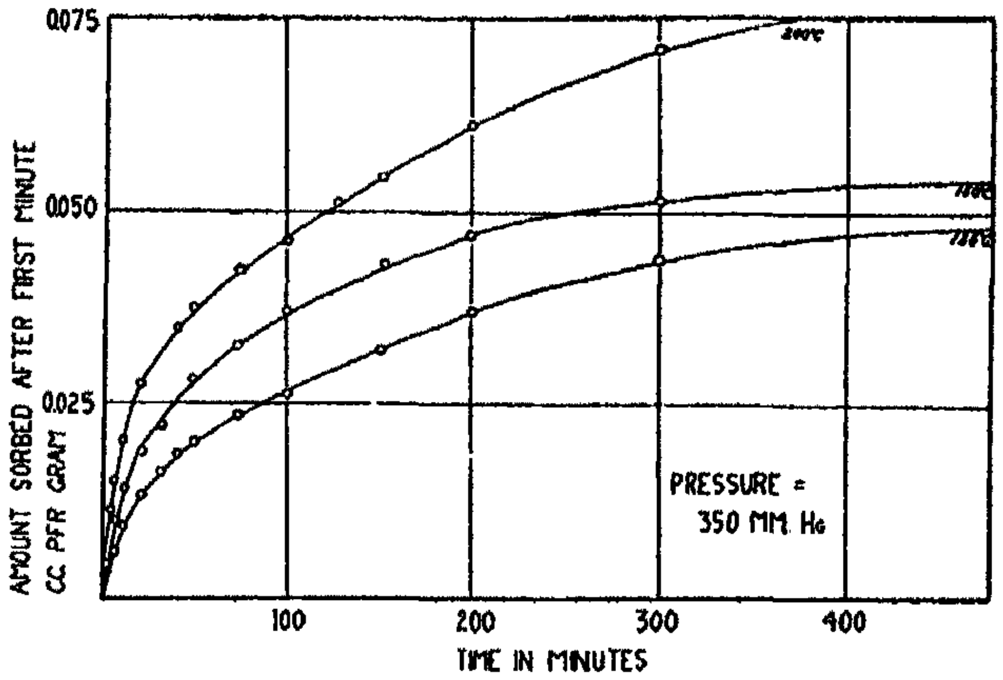

FIG. 2. Activated adsorption of carbon monoxide on copper chromite

These curves are similar to those for oxygen, and are suitable for the calculation of energies of activation.

Since the amounts adsorbed used in plotting the original adsorption versus time curves of figure 1 are obtained by subtracting one experimental value from another nearly the same size, the percentage error in the reading is greatly multiplied by the time the adsorption curves are obtained. The final curves, those of figure 2, are obtained by repeating the process of subtracting one value from another very nearly the same size. Thus the original numbers (the volumes read on the gas buret) have now shrunk to new values numerically only about one-fiftieth of the size of the original ones, and it is to be expected that as a consequence of this the percentage errors will have grown to large proportions.

Nevertheless, it is possible to take these last curves of figure 2 and to calculate from them fairly consistent energies of activation, although the agreement is quite naturally not nearly as good as in the case of the adsorption of oxygen at constant pressure. Some of the calculations of energies of activation are summarized in table 3.

The rapidity with which a considerable amount of carbon monoxide is adsorbed on the chromite suggested that perhaps something approximating a monomolecular layer is formed at once, and that the "activated" adsorption consists of building up a thicker layer.

TABLE 3

Energies of activation: carbon monoxide on copper chromite

AMOUNT ADSORBED	E (IN KG-CAL.)		
	125-150°C.	125-200°C.	150-200°C.
0.0100	8.17		
0.0125	7.92		
0.0150	9.34		
0.0175	10.11		
0.0200	11.06	8.61	7.16
0.0225	11.29	8.64	7.07
0.0250	11.74	8.45	6.49
0.0275	11.38	8.42	6.67
0.0300	10.42	8.28	7.01
0.0325	9.70	7.83	6.71

TABLE 4

Carbon monoxide adsorption in the first minute

TEMPERATURE	ADSORPTION
°C.	*atoms per gram*
100	5.54×10^{18}
125	5.26×10^{18}
150	4.75×10^{18}
175	4.16×10^{18}
200	2.76×10^{18}

Lory (5) studied the amount of chromate that could be leached off samples of various chromites with water, after the chromites had been heated in the air to form a surface layer of the chromate. From the data which he obtained in this manner, he calculated the number of chromium atoms on the surface of the catalyst. For copper chromite he obtained the value 4.11×10^{18} atoms of chromium on the surface for each gram of the catalyst.

The sample of copper chromite used in these measurements was prepared by following Lory's method to the smallest detail, and may be assumed to have approximately the same number of surface chromium atoms. If we assume that the adsorption takes place on the chromium atoms, then a monomolecular layer must be considered as one molecule of carbon monoxide to each surface chromium atom, or about 4.11 × 10^{18} atoms per gram. The observed amounts of carbon monoxide adsorption in the first minute, converted from cubic centimeters per gram to atoms per gram are given in table 4. Obviously, the amount of this rapid adsorption is, at the temperatures studied, of the same order of magnitude as that required to form a monomolecular layer on the surface of the catalyst.

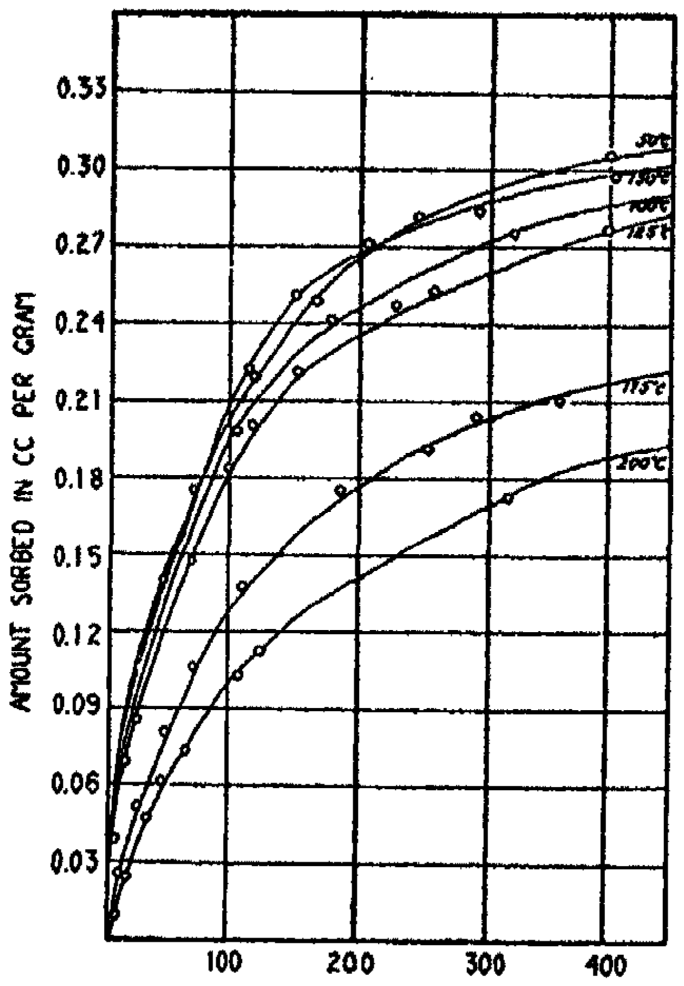

Fig. 3. Adsorption of carbon monoxide on copper chromite at constant volume

Adsorption of carbon monoxide at constant volume

The different character of the adsorption versus time curves for carbon monoxide, as compared with those for oxygen, suggested that the processes taking place were not of the same nature.

In order to obtain a better understanding of the question of the adsorption of carbon monoxide, it was considered worth while to obtain the data necessary to plot the isotherms for the adsorption of carbon monoxide,—the total adsorption of all kinds when equilibrium had been reached. With this in mind, constant volume runs were made at seven temperatures, covering the entire range where the catalyst is active. The data thus obtained are shown graphically in figure 3.

DISCUSSION

The adsorption of oxygen by copper chromite appears to be a straightforward process. It seems probable that it is simply a chemical reaction, that of surface chromate formation. At the temperature range over which the adsorption was studied, which is the important range as regards catalysis, the activated adsorption is the only process taking place, so that there are no complications introduced by concurrent reactions.

The case of the adsorption of carbon monoxide on copper chromite is not so simple. Two adsorption processes combine to give the observed results, and it is only by separating the two and considering each one individually that we can obtain any understanding of either one. The curves of figure 4 represent both the sum of the van der Waals and the activated adsorption, and each one separately. Considering only the one pressure used throughout the rate measurements, 350 mm. Hg, curve 1 is taken from the isotherms in figure 3, and shows the total amount adsorbed at equilibrium at this pressure and at each of the temperatures considered. These amounts diminish regularly with increasing temperature except in the neighborhood of 150°C., where a sharp maximum is observed. It would be expected that this maximum, coming at such a high temperature, would be due to the activated adsorption rather than to the van der Waals variety.

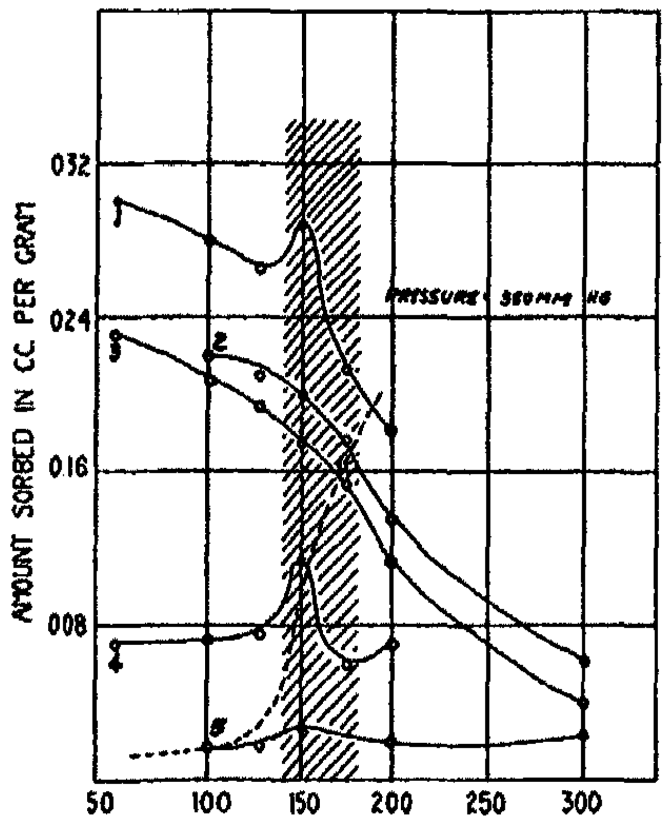

Fig. 4. Summary of carbon monoxide adsorption

Curve 3, which shows the 1-minute readings from the constant pressure runs, bears out this expectation. This curve may be taken as representing the van der Waals adsorption alone at each of the temperatures. Evidently this type of adsorption falls off rapidly with rising temperatures, and exhibits no maxima or minima.

The difference between curves 1 and 3, then, must obviously represent the total *amount* of activated adsorption which takes place. This is represented graphically in curve 4, and the maximum in the region of 150°C. is very pronounced. The temperature range in which the catalytic efficiency of the chromite in assisting the combination of carbon monoxide and oxygen rises from about 40 per cent to 100 per cent is shown by the shaded area. In this range of temperature the amount of activated adsorption is considerably less than the amount of van der Waals adsorption, although it appears likely that this condition will be reversed at a somewhat higher temperature.

Curve 2 is the representation of the 30-minute readings taken from the curves of figure 1. The difference, then, between this curve and curve 3 will be the amount adsorbed at each temperature in the interval from one to thirty minutes, and will be proportional to the *rate* of the activated adsorption. This difference is represented by curve 5. It is evident that there is a maximum in the rate of the activated adsorption at about the same temperature at which we find the maximum in the extent to which it takes place.

These maxima in the amount of activated adsorption and in its rate suggest that perhaps there are two distinctly separate and entirely different processes taking place at the surface in addition to the van der Waals adsorption, which, for the moment, we are neglecting. Both of these processes, of course, would be included in a general definition of adsorption as any way in which a gas is taken up by a solid. But although each takes place at a measurable rate, the amount of one falls off with rising temperatures, whereas on the contrary, the amount of the other becomes greater as the temperature becomes higher.

In figure 5a the solid line curve is a duplicate of curve 4 in figure 4. Similarly, in figure 5b the solid curve is a duplicate of curve 5 in figure 4. In each case the broken-line curves marked a and b are arbitrarily drawn, regular curves which, when added together, give the curves with the maxima.

It does not seem wholly improbable that what we have been considering, then, as the activated adsorption of carbon monoxide on the chromite surface might possibly be really the summation of two distinctly separate processes, which, although in no sense do they work at cross purposes, nevertheless vary in a different way with temperature. These two processes, if such exist, could then be represented by curves of the type of those drawn in broken lines in figures 5a and 5b.

In figure 5a these curves will represent the extent to which these processes take place before equilibrium is reached at a pressure of 350 mm. Hg and the temperatures indicated, while the curves of figure 5b would be proportional to the rates at which the processes take place.

If we may represent the adsorption as the sum of two such hypothetical processes, one of them, that represented by b, diminishes with rising temperature, not only as regards the extent to which it occurs, but also in the rate at which it takes place.

It must be remembered that the differences between the adsorption curves for carbon monoxide are not large in comparison with the values involved. It may be possible that experimental errors are responsible for the maxima obtained in figures 4 and 5. However, the fact that the maxima occur in the same temperature interval in each case and are so similar appears to bring the hypothetical processes suggested into the realm of possibility. If they do exist, perhaps one of the processes is one of solution, or diffusion, or some such phenomenon. At any rate, the exact nature of the two processes is of no importance as regards the relation of the adsorption process to catalytic activity, as we shall see directly.

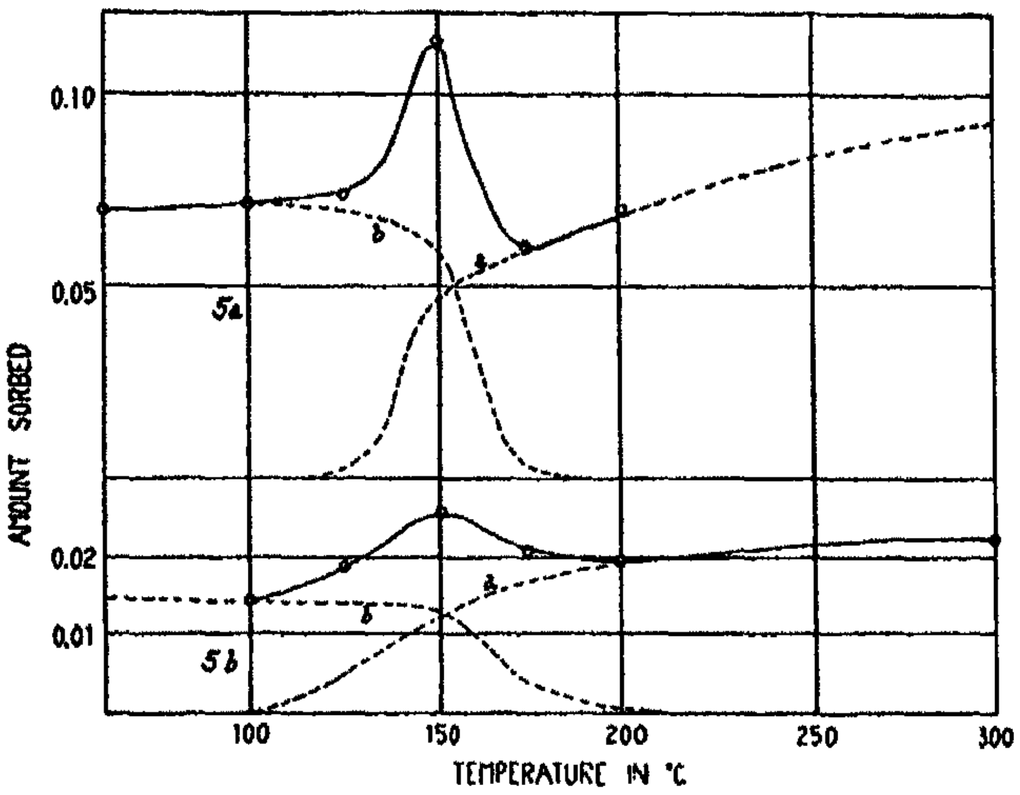

Fig. 5. Activated adsorption of carbon monoxide

In the range over which the efficiency of the chromite as a catalyst for the oxidation of carbon monoxide nears 100 per cent, the adsorption of carbon monoxide is falling off rapidly from its maximum, which makes it seem doubtful that it is of major importance in the mechanism of the catalytic reaction.

As the temperature is increased over this range, however, the adsorption of oxygen rises extremely rapidly. It seems more likely, then, that the determining factor in the activity of the surface is the adsorption of oxygen. A suggested mechanism which seems reasonable is that the oxygen is first adsorbed on the chromite surface with an energy of activation of the order of those calculated. If the temperature is high enough so that the adsorption of the oxygen reaches sufficient proportions, any carbon monoxide passing over the catalyst surface either reacts directly with the adsorbed oxygen, or else is first adsorbed and then reacts, after which the carbon dioxide produced is desorbed.

Lory suggested that the catalytic activity was due to alternate oxidation of the chromite surface by oxygen and its reduction by carbon monoxide. If the term "adsorption" is defined as including *all ways* in which a gas is taken up at a solid surface, without regard to the nature of the binding between the surface and the adsorbed gas, adsorption would of course include the oxidation of the surface chromium atoms by gaseous oxygen. So in the strictest sense there is no real difference between the suggested mechanism and that proposed by Lory.

However, since the oxidation of the chromite is probably a process involving the addition of oxygen to the *surface* chromium atoms only, it seems wise to speak of it as an adsorption process, thus emphasizing the fact that it is a surface phenomenon,—for the surface is all-important in contact catalysis. At least, until it may be shown that the binding of the adsorbed gas to the surface is identical with that between atoms of the surface material and of the gas in their known compounds, it appears more to the point to use the term "adsorption" rather than "oxidation" to describe the process.

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PENETRATION OF SOLAR AND COSMIC RAYS INTO FRESH WATER LAKES

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The purpose of the present article is to show that the equation given in a recent paper (2), expressing the relation between turbulence and depth of the ocean, applies equally well to the decrease in temperature and to the penetration of solar heat and cosmic rays with increase in depth of fresh water lakes. Of the accumulated data given in the literature (3), two examples of each topic will suffice to illustrate these phenomena.

TABLE 1

Relation between temperature and depth

LAKE CAYUGA			LAKE SENECA		
$\theta_\infty = 16.0$; $K = 6.004$; $\log k = -7.90156$			$\theta_\infty = 16.0$; $K = 4.142$; $\log k = -5.31832$		
D	t	θ	D	t	θ
meters	°*C.*		*meters*	°*C.*	
0	20.0	0.0	0	20.0	0.0
10	19.8	0.2	5	19.4	0.6
14	19.6	0.4	10	19.0	1.0
15	19.0	1.0	12	18.8	1.2
16	18.5	1.5	15	18.4	1.6
17	16.1	3.9	16	17.3	2.7
18	13.8	6.2	17	14.9	5.1
19	11.5	8.5	18	12.3	7.7
20	10.1	9.9	19	11.1	8.9
25	7.9	12.1	20	10.2	9.8
30	5.9	14.1	25	6.8	13.2
40	4.8	15.2	30	5.8	14.2
50	4.5	15.5	40	4.8	15.2
60	4.5	15.5	50	4.3	15.7
70	4.4	15.6	70	4.2	15.8
80	4.2	15.8	80	4.2	15.8
100	4.1	15.9	100	4.1	15.9
121	4.1	15.9	120	4.1	15.9

The methods of calculation and of tabulation are fully discussed in the paper referred to (2). The results of the present calculations are presented in three tables and are illustrated graphically in six figures. In

TABLE 2

Relation between heat and depth

LAKE CAYUGA			LAKE SENECA		
$H_\infty = 26900$; $K = 2.483$; $\log k = -2.83347$			$H_\infty = 32900$; $K = 1.850$; $\log k = -2.09603$		
D	$-H$	H	D	$-H$	H
meters	*calories*	*calories*	*meters*	*calories*	*calories*
0	26900	0	0	32900	0
10	18600	8300	10	21000	11900
20	6900	20000	20	10800	22100
30	3100	23800	30	6600	26300
40	1800	25100	40	4500	28400
50	1400	25500	50	3300	29600
60	1100	25800	60	2600	30300
70	860	26040	70	2000	30900
80	590	26310	80	800	32100
100	320	26580	100	800	32100
			150	290	32610

TABLE 3

Relation between depth and cosmic ray ionization

LAKE ARROWHEAD				GEM LAKE			
$I_\infty = 53.00$; $K = 1.043$; $\log k = -0.58787$				$I_\infty = 80.00$; $K = 1.113$; $\log k = -0.47993$			
D	I' (obsd.)	I' (calcd.)	I	D	I' (obsd.)	I' (calcd.)	I
meters				*meters*			
0.82	43.80	43.80	9.20	0.85	64.10	62.70	17.30
1.50	37.50	38.00	15.00	1.00	60.10	60.10	19.90
2.00	33.50	34.49	18.41	2.00	43.80	46.61	33.39
3.00	29.50	29.25	23.75	4.00	30.40	31.38	48.62
4.00	25.50	25.38	27.72	43.00	3.62	3.52	76.48
5.00	23.10	22.17	30.77	50.00	3.30	2.96	77.04
6.00	21.10	19.79	33.19	60.00	2.49	2.48	77.52
6.25	20.60	19.29	33.71	72.55	2.00	2.00	78.00
8.25	17.33	15.90	37.10				
10.64	14.52	13.10	39.90				
15.90	10.23	9.43	43.57				
21.10	7.89	7.37	45.63				
26.25	6.07	6.20	46.80				
30.35	5.21	5.26	47.74				
37.05	4.25	4.35	48.65				
42.78	3.79	3.76	49.24				

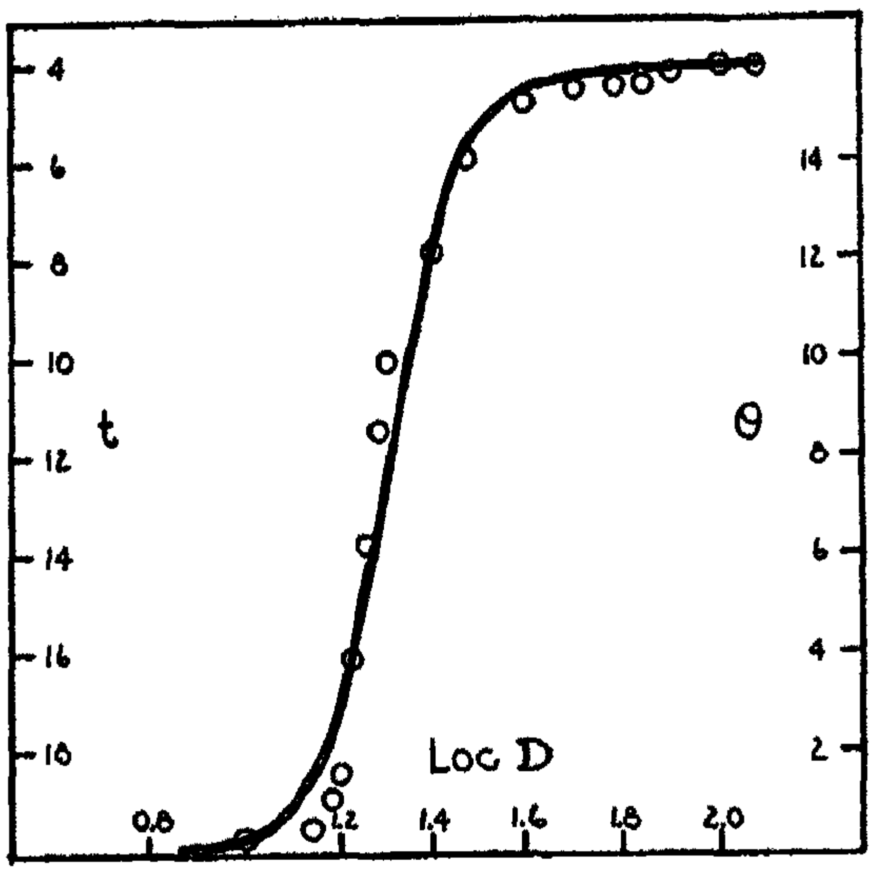

FIG. 1. Relation between temperature and depth—Lake Cayuga

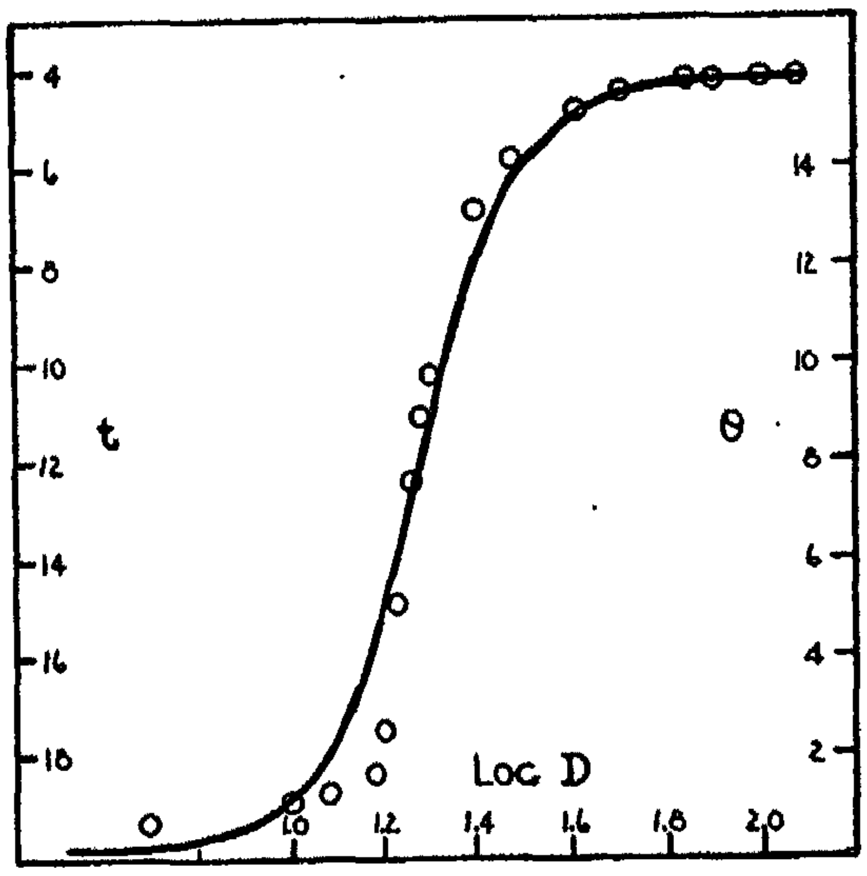

FIG. 2. Relation between temperature and depth—Lake Seneca

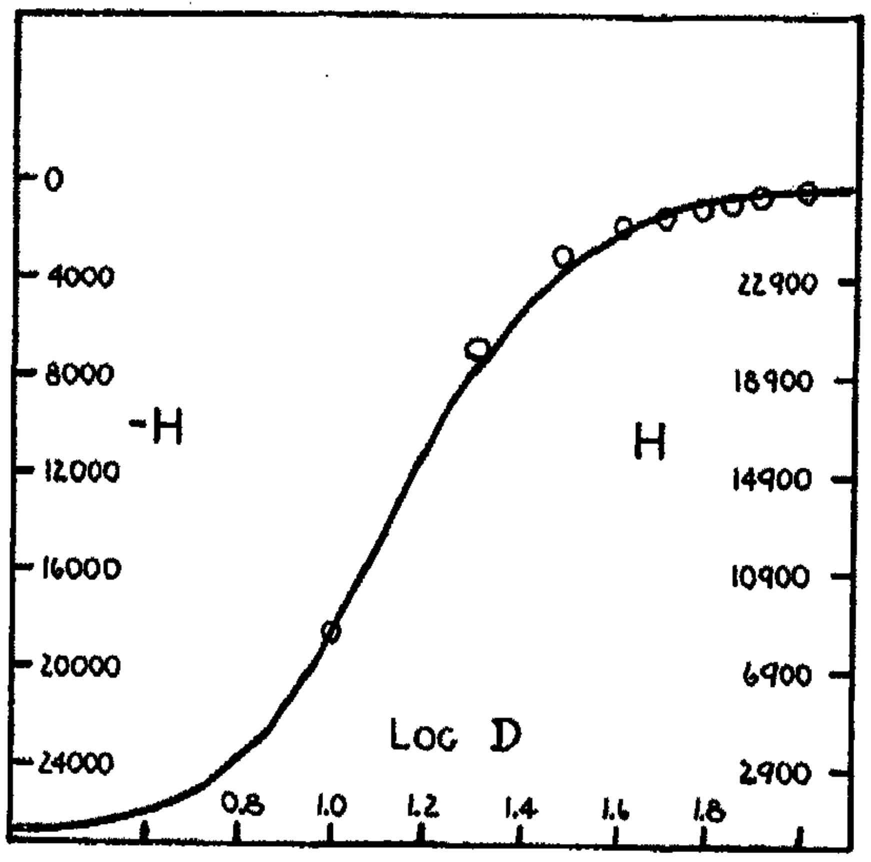

FIG. 3. Relation between heat and depth—Lake Cayuga

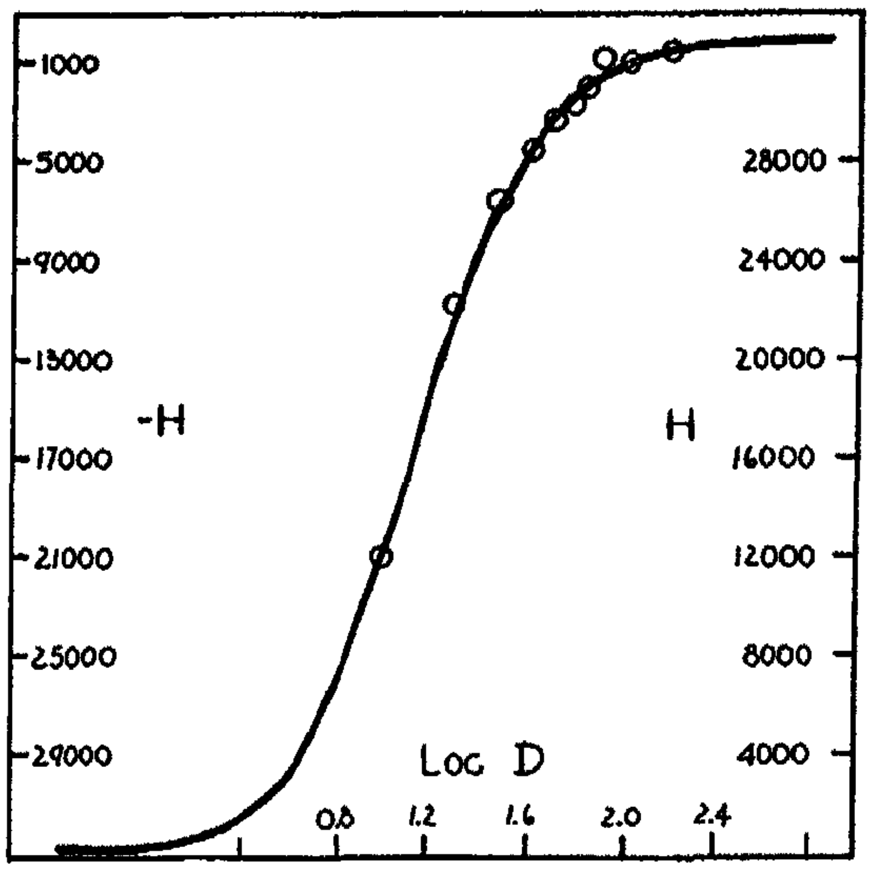

FIG. 4. Relation between heat and depth—Lake Seneca

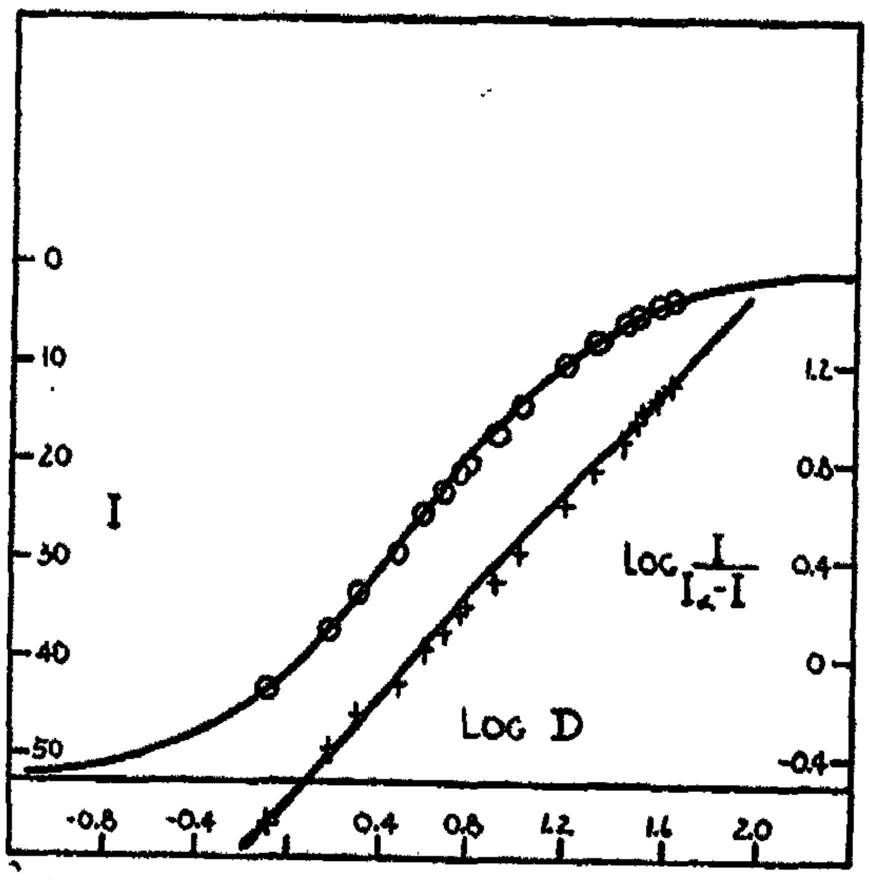

FIG. 5. Relation between depth and cosmic ray ionization—Lake Arrowhead

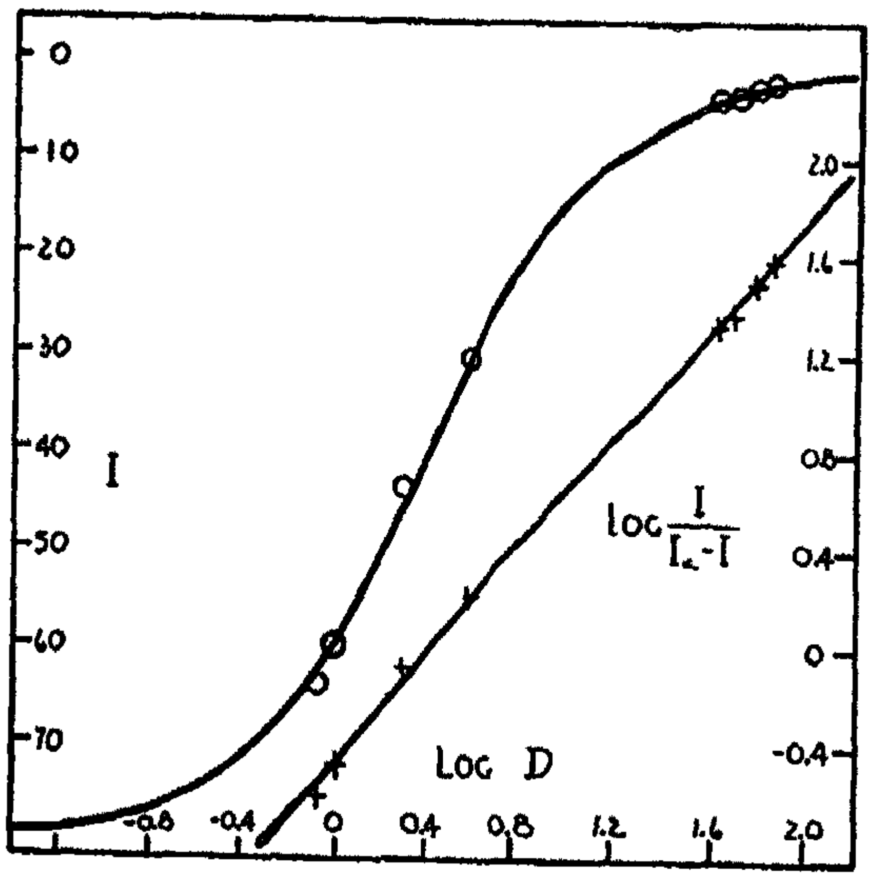

FIG. 6. Relation between depth and cosmic ray ionization—Gem Lake

table 1 are given the depths (D), the temperatures (t), and the total drop in temperature at each point (θ); in table 2, the depths (D), the solar heat ($-H$) in calories per unit of surface, and the total drop in heat at each point (H); and in table 3, the depths (D), the cosmic ray ionizations (I') per unit of surface per second, and the total drop in cosmic ray ionization at each point (I).

CONSTRUCTION OF THE GRAPHS

The constants (K and $\log k$) necessary for the construction of figures 1 and 2 were obtained from the data given in table 1 and the straight line equation

$$\log \theta/(\theta_\infty - \theta) = K \log D + \log k$$

those for the construction of figures 3 and 4, from the data given in table 2 and the equation

$$\log H/\,(H_\infty - H) = K \log D + \log k$$

and those for the construction of figures 5 and 6, from the data given in table 3 and the equation

$$\log I/(I_\infty - I) = K \log D + \log k$$

The quantities with the infinity subscripts (θ_∞, H_∞, and I_∞) were readily found from the graphs of the respective equations, which may be written in the general form

$$y = y_\infty\, ke^{K \log x}/(1 + ke^{K \log x})$$

This is obvious from the symmetry of the curve when y is plotted against $\log x$; for if the second derivative of y with respect to $\log x$ is placed equal to zero, $y = \frac{1}{2}y_\infty$. The values of these quantities, together with those for K and for $\log k$, are given at the head of each table.

DISCUSSION OF THE RESULTS

A glance at the graphs will show that the experimental values distribute themselves closely along the calculated curves, and, considering the uncontrollable experimental conditions, the fit in each case is as good as can be expected. This is especially true of the experimental points in figures 1, 2, 3, and 4. However, the experimental values shown in figures 5 and 6 represent a much higher degree of experimental control, and it seemed worthwhile, therefore, to place in table 3 calculated values alongside the experimental ones for comparison. The agreement is quite satisfactory.

In conclusion it may be noted that the similarity in the behavior of the three processes, presented in the three tables and in the six graphs, is not accidental. A comprehensive treatment of these and of similar processes, including the derivation of the general equation, is reserved for a final paper.

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CARBON DIOXIDE CLEAVAGE FROM DIBROMOMALONIC ACID. II

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The decomposition of dibromomalonic acid into carbon dioxide and dibromoacetic acid

$$\mathrm{Br_2C(COOH)_2 \rightarrow CO_2 + Br_2HCCOOH} \tag{1}$$

was studied in a previous paper (1). It was shown that the univalent ion decomposes spontaneously, the undissociated acid and the divalent ion being stable.

The carbon dioxide cleavage of β-keto- and α-nitro-carboxylic acids has been examined by Pedersen (2). From the fact that α,α-dimethylacetoacetic acid and α,α-dimethylnitroacetic acid take up bromine with the same velocity as they decompose, he concludes that an intermediate unsaturated compound is first formed by the cleavage:

$$\mathrm{CH_3\cdot CO\cdot C(CH_3)_2COOH} \rightarrow$$

$$\begin{tikzcd} \mathrm{CO_2 + CH_3COH{:}C(CH_3)_2} \arrow[r] \arrow[dr, "+\mathrm{Br_2}"] & \mathrm{CH_3\cdot CO\cdot CH(CH_3)_2} \\ & \mathrm{CH_3\cdot CO\cdot CBr_2(CH_3)_2 + HBr} \end{tikzcd} \qquad (2)$$

$$\mathrm{O_2N\cdot C\cdot (CH_3)_2\cdot COOH} \rightarrow$$

$$\begin{tikzcd} \mathrm{CO_2 + HOON{:}C(CH_3)_2} \arrow[r] \arrow[dr, "+\mathrm{Br_2}"] & \mathrm{O_2N\cdot CH(CH_3)_2} \\ & \mathrm{O_2N\cdot CBr(CH_3)_2 + HBr} \end{tikzcd} \qquad (3)$$

The structure of dibromomalonic acid bears some analogy to that of β-keto acids. A mechanism analogous to that of scheme 2 is therefore suggested:

$$\mathrm{HO\cdot CO\cdot CBr_2COO^-} \rightarrow$$

$$\begin{tikzcd} \mathrm{CO_2 + HO\cdot CO^-{:}CBr_2} \arrow[r] \arrow[dr, "+\mathrm{Br_2}"] & \mathrm{{}^-O\cdot CO\cdot CHBr_2} \\ & \mathrm{{}^-O\cdot CO\cdot CBr_3 + HBr} \end{tikzcd} \qquad (4)$$

In order to test this suggestion some bromination experiments were carried out. It was shown that bromine is taken up during the decomposition. Since neither dibromoacetic acid nor dibromomalonic acid reacts with bromine under the experimental conditions, an intermediate product is surely responsible for the disappearance of bromine.

EXPERIMENTAL

In order to compare the results with those of the previous communication (1) the experiments were carried out at 25°C. and in the following solutions of hydrochloric acid and potassium chloride: x M HCl + (1 − x) M KCl; x M HCl + (0.2 − x) M KCl; and x M HCl + (0.1 − x) M KCl.

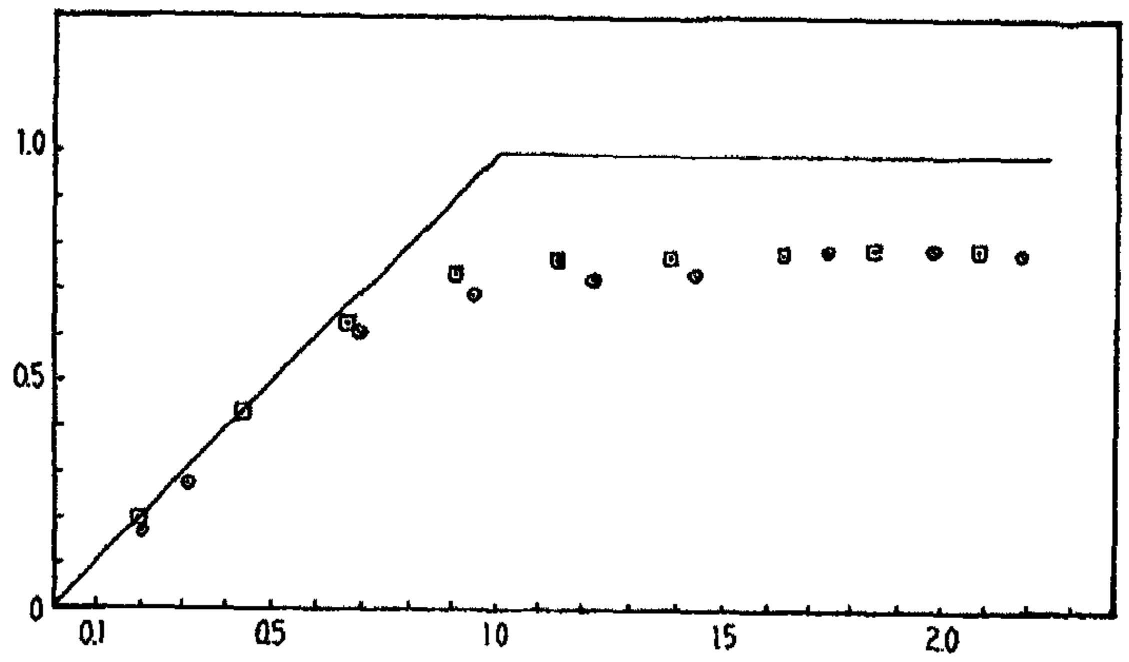


FIG. 1. Abscissa: moles of bromine added per mole of dibromomalonic acid. Ordinate: moles of bromine used per mole of dibromomalonic acid. $C_{Br_2C(COOH)_2} = 7.26 \times 10^{-3}$. —— theoretical value if all the dibromomalonic acid reacts according to scheme 4b. ⊡ ⊡ , experiments in 0.1 N hydrochloric acid; ⊙ ⊙, experiments in 0.1 N hydrochloric acid and 0.9 N potassium chloride.

In addition, known amounts of bromine and dibromomalonic acid were present. A suitable time after the start of the reaction an excess of 0.1 N arsenious acid was added. The arsenious acid reacts instantaneously with bromine.

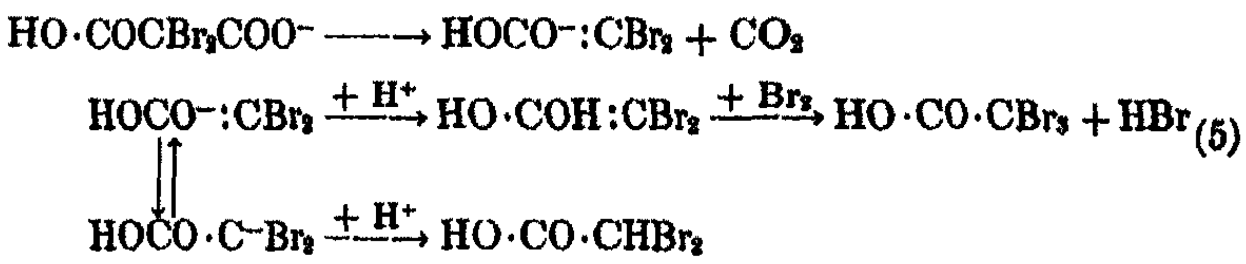
$$As_2O_3 + 2Br_2 + 2H_2O \rightarrow As_2O_5 + 4Br^- + 2H^+$$

but does not react with the other substances present. The excess of arsenious acid was titrated with bromine water.

In most experiments the dibromomalonic acid was about 0.007 M. The amount of bromine taken up during the reaction increases with increasing bromine concentration. However, when the initial concentration of bromine is about 0.012 M, further increase does not increase the amount of bromine taken up (figure 1).

The amount of bromine disappearing when the reaction is allowed to proceed until completion also depends upon the concentration of hydrochloric acid, as shown in table 1.

The fact that only a fraction of dibromomalonic acid reacts with bromine, and that this fraction is independent of the bromine concentration within a large range of concentration, is not in accordance with scheme 4. Part of the dibromomalonic acid must be converted into dibromoacetic acid without forming an intermediate product capable of reacting with bromine. The following mechanism of reaction is suggested.



$$HO{\cdot}COCBr_2COO^- \longrightarrow HOCO^-{:}CBr_2 + CO_2$$

$$\begin{tikzcd} HOCO^-{:}CBr_2 \arrow[r, "+H^+"] \arrow[d, shift right] & HO{\cdot}COH{:}CBr_2 \arrow[r, "+Br_2"] & HO{\cdot}CO{\cdot}CBr_3 + HBr \\ HOCO{\cdot}C^-Br_2 \arrow[u, shift right] \arrow[r, "+H^+"] & HO{\cdot}CO{\cdot}CHBr_2 & \end{tikzcd} \quad (5)$$

TABLE 1

Bromine taken up by dibromomalonic acid

$C_{Br_2C(COOH)_2} = 7 \times 10^{-3}$; $C_{Br_2} = 12 \times 10^{-3}$. n = moles of bromine reacting per mole of dibromomalonic acid

HCl	x *M* HCl (1 − x) *M* KCl	x *M* HCl (0.2 − x) *M* KCl	x *M* HCl (0.1 − x) *M* KCl
	n	*n*	*n*
M			
1.00	0.852		
0.75	0.859		
0.50	0.868		
0.25	0.838		
0.20	0.815	0.820	
0.10	0.792	0.795	0.781
0.08	0.753	0.780	0.770
0.05	0.718		

It fulfills the requirement, and it seems likely that the first step of the reaction is much slower than the following and thus determines the rate of the reaction. But of course other mechanisms may be proposed.

Without stating anything definite about the mechanism of the reaction, it is obvious that two reactions take place simultaneously. The one leads directly to dibromoacetic acid, the other to the formation of a product which reacts with bromine. If the ratio of the velocities of these reactions is $(1 - n)$: n, we see that, at the time t, when c moles per liter of carbon dioxide have been split off, nc moles per liter of bromine have been used. If the initial concentration of dibromomalonic acid is c_0, nc_0 moles per liter of bromine have been used at the end of the reaction. From the expression

$$-kt = \log \frac{c_0 - c}{c_0} = \log \frac{nc_0 - nc}{nc_0}$$

it is readily seen that k, computed by means of the development of carbon dioxide, should be identical with k computed from the disappearance of bromine, when we substitute the amount of bromine actually taken up for the amount which would be taken up if only tribromoacetic acid were formed.

In table 2 k_1 is the velocity constant previously found for the carbon dioxide cleavage. k_2 is the velocity constant of the bromination computed as just explained. k_2 does not differ much from k_1, indicating that the assumption of the formation of an intermediate unsaturated compound is correct.

In order to show that the presence of bromine does not interfere with the first step of reaction 5, the velocity of the carbon dioxide cleavage was determined by the method previously used in 0.1 *M* hydrochloric acid, containing bromine of the same concentration as in the bromination experiments. Without bromine the velocity constant was 4.31×10^{-3}, with bromine 4.30×10^{-3}.

TABLE 2

Velocity constants of the bromination

$C_{Br_2C(COOH)_2} = 7 \times 10^{-3}$; $C_{Br_2} = 12 \times 10^{-3}$; $t = 25°C$.

HCl	x *M* HCl (1 − x) *M* KCl		x *M* HCl (0.2 − x) *M* KCl		x *M* HCl (0.1 − x) *M* KCl	
	$k_1 \times 10^3$	$k_2 \times 10^3$	$k_1 \times 10^3$	$k_2 \times 10^3$	$k_1 \times 10^3$	$k_2 \times 10^3$
M						
1.00	2.83	3.07				
0.75	3.25	3.51				
0.50	3.99	4.30				
0.25	4.41	4.71				
0.20	4.56	4.70	4.07	4.46		
0.10	4.48	4.75	4.26	4.50	4.31	4.64
0.08	4.22	4.87	4.40	4.46	4.25	4.68
0.05	4.10	5.64			4.24	4.73

SUMMARY

The mechanism of the decomposition of dibromomalonic acid has been studied.

It has been found that simultaneously with the carbon dioxide cleavage bromine was taken up. The rate of the reaction of the bromination was approximately the same as that of the carbon dioxide cleavage.

From this result it was concluded that the first step of the reaction was the formation of an unsaturated compound.

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MOLECULAR DIMENSIONS FROM VISCOSITY STUDIES[1]

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THEORETICAL CONSIDERATIONS

The viscosity of a bulk liquid is known to be increased by the presence of a suspended particle. The complete mathematical treatment of this problem for the case of spherical particles has been solved by Einstein (1).

Jeffery (5) has extended the work carried out by Einstein, for the case of ellipsoidal particles. Great difficulties were encountered in the solution of the problem and the results were left in a rather indeterminate form, owing to the fact that a number of motions were possible for a given set of boundary conditions.

Eisenschitz (2), assuming that the ellipsoidal particle so orients itself at the time $t = 0$ (beginning orientation) that its axes coincide with the principal axes of deformation of the fluid, calculated, both for pure motion of deformation and for plane laminar flow, the value of this numerical factor in terms of ratio of length to diameter. His results for plane laminar flow are as follows:

$$\frac{\eta}{\eta_0} = 1 + \frac{1.15\frac{a}{b}}{\pi \log_e 2\frac{a}{b}} \cdot \frac{v}{V}$$

where a = the long axis of the ellipsoid,
b = the short axis of the ellipsoid,
η and η_0 = viscosities of solution and solvent, respectively,
v = volume of particle, and
V = volume of solution.

We applied this equation to stearic acid dissolved in carbon tetrachloride as well as to lecithin in the same solvent.

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[1] Published as Journal Series No. 1363, Minnesota Agricultural Experiment Station.

[2] This paper is taken from a thesis presented by Robert M. Theis to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Master of Science, June, 1935.

VISCOSITY MEASUREMENTS

Measurements were made with the Ostwald type of viscosimeter. For 8 cc. of carbon tetrachloride the time of out-flow was about 90 seconds, while for the same volume of water it was over 120 seconds. The neck of the instrument was drawn out to about half its thickness to facilitate the recording of an accurate starting point. This narrow constriction was etched with hydrogen fluoride, as also was the capillary tube. The instrument was kept filled with cleaning solution when not in use, especially overnight. The densities of the solutions were determined by means of a pycnometer, which was accurately calibrated. As the apparatus must be extremely clean to get reliable measurements, the following procedure was followed: The apparatus was washed twice with waste carbon tetrachloride, once with pure carbon tetrachloride and once with acetone, and dried by evacuating.

The stearic acid used was recrystallized from benzene. It melted at 69°C., which indicated that it was quite pure. The solutions were prepared by dissolving a known weight of stearic acid in carbon tetrachloride and making up to correct volume. The data are given in table 1 and graphed in figure 1.

Fikentscher and Mark (3), taking into account the process of solvation, have proposed the following formula:

$$\frac{\eta}{\eta_0} - 1 = \frac{\text{``}a\text{''}\,\Phi c}{100 - \Phi c}$$

where Φ is the volume occupied by 1 g. of substance in solution (volume of solvated particle), c the concentration in grams per 100 cc. of solution, and "a" equals 2.5.

Φc in the denominator of the above expression is analogous to the b term in van der Waals' equation of gases. The value of the constant "a" will be 2.5 for spherical particles only.

Treating "a" and Φ as general constants and rearranging the above expression in the following form, one obtains:

$$\frac{c}{\eta_{sp}} = \frac{100}{a\Phi} - \frac{1}{a}c$$

where

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1$$

The variables in this equation are $\frac{c}{\eta_{sp}}$ and c. If one plots $\frac{c}{\eta_{sp}}$ as ordinate and c as abscissa, as is done in figure 1, a straight line with intercept equal to $\frac{100}{a\Phi}$ and with a negative slope of $1/a$ is obtained. From the values of the slope of the line and the ordinate intercept, a is 0.885 and Φ is 4.185 cc. per gram.

TABLE 1

Viscosity of solutions of stearic acid in carbon tetrachloride

CONCENTRATION IN GRAMS PER 100 CC. OF SOLUTION	η_r	c/η_{sp}
2.0	1.0809	24.72
1.5	1.059	25.33
1.0	1.0387	25.82
0.5	1.0186	26.87

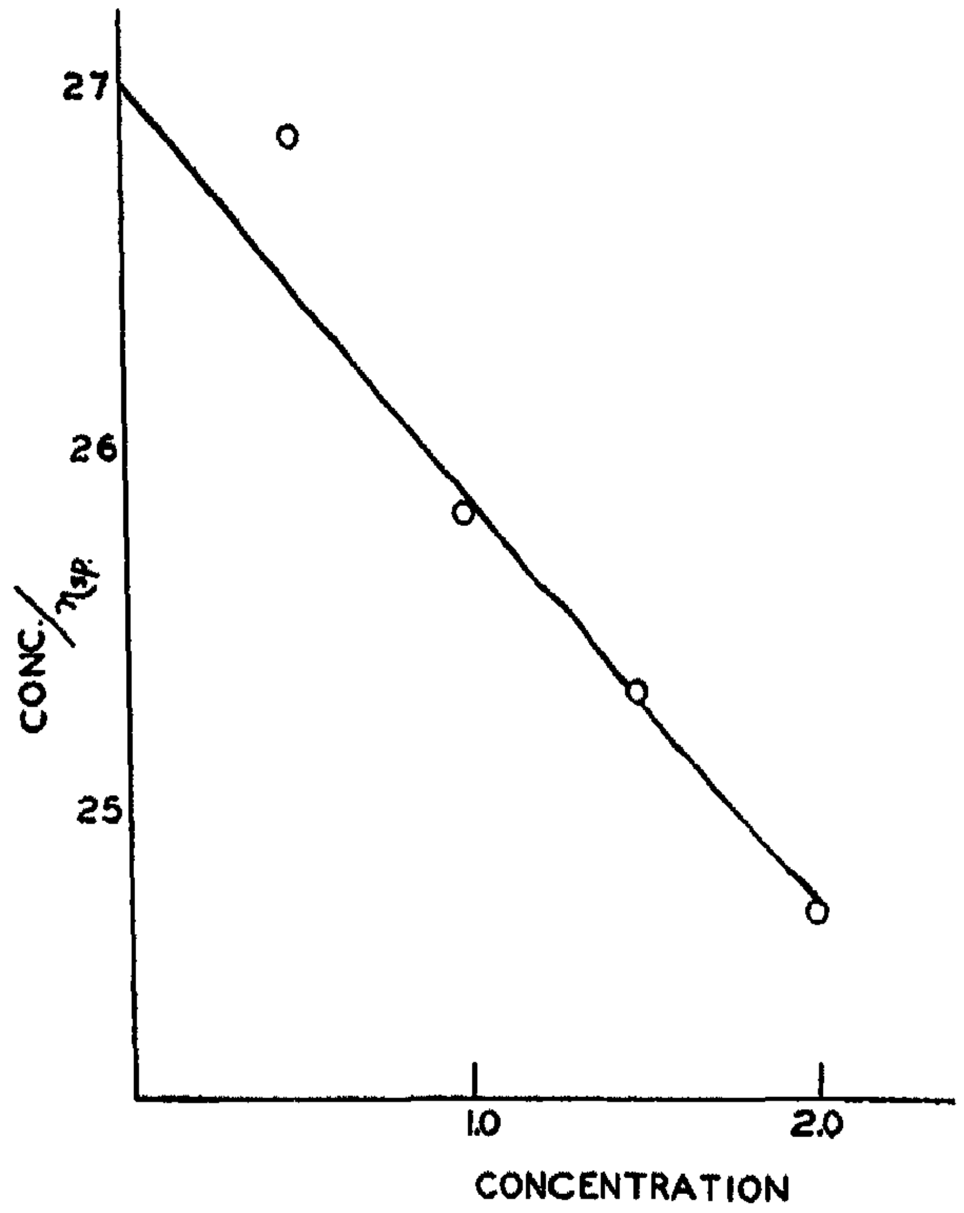

Fig. 1

The specific gravity of stearic acid at room temperature is approximately 0.85. This corresponds to a specific volume of 1.17 cc. On the other hand, the apparent specific volume from viscosity measurements turned out to be 4.185, about 3.5 times the expected value. There is no reason to believe that a gram of substance should occupy the same volume in both the solid state and in solution. However, when solvation takes place, in the case of stearic acid, the carbon tetrachloride becomes part of the stearic acid particle, so that the apparent specific volume now becomes the volume occupied by 1 g. of stearic acid plus an unknown number of grams of carbon tetrachloride, but this total volume is calculated on the basis of 1 g. of stearic acid.

We do not know whether the solvent is included between the particles of solute or a shell of solvent is built around each particle. In either case the particle assumes a definite shape with some deformability, so that the solution still behaves as a homogeneous liquid. The value of the constant "a" (found) indicated that stearic acid does not form spherical particles in solution. Assuming that we are dealing with ellipsoids of revolution instead of spheres, we applied Eisenschitz's equation to determine what ratio of length to diameter corresponds to the value of the constant "a," obtained experimentally. If we assume that the motion of the particle is plane laminar flow and that the ratio of length to diameter is 6 to 1, then the value of "a" by the above equation is:

$$a = \frac{0.159\ (6/1)}{\log_{10} 12} = 0.884$$

which corresponds to the value of "a" (0.885), found experimentally.

From x-ray data of Francis, Piper, and Malkin (4) the diameter of a stearic acid molecule is 3.7 to 4.0 A.U. and the length of a single molecule is 23.4 A.U. (this is calculated on the basis of the above work). This will give us a ratio of length to diameter of approximately 6 to 1.

The lecithin was prepared by a modification of the method of Sueyoshi (7). The reagents were carefully purified and tested for their purity. Analysis of the lecithin gave the following results: total nitrogen, 1.835 weight per cent; phosphorus, 4.094 weight per cent; N:P ratio, 1:1.007; amino nitrogen, 0.39 weight per cent.

Van Slyke analysis shows a high contamination of cephalin (21 per cent), but since the N:P ratio is practically 1, it indicates that the material obtained is free from other lipids. The presence of cephalin would hardly affect viscosity measurements, as there is little difference between the molecular structure of lecithin and of cephalin.

In table 2 are the results of our viscosity measurements of lecithin in carbon tetrachloride at various concentrations. These values are graphed in figure 2.

Treating the data obtained for lecithin in the same way that we did for stearic acid, we found a similar relation between viscosity and concentration. A comparison of figures 1 and 2 will disclose the fact that the points

TABLE 2

Viscosity of solutions of lecithin in carbon tetrachloride

CONCENTRATION IN GRAMS PER 100 CC. OF SOLUTION	η_r	c/η_{sp}
11	1.4920	22.357
8	1.3318	24.111
5.7	1.2209	25.121
3.7	1.1410	26.24
1.8	1.0648	27.77
0.9	1.0259	34.74

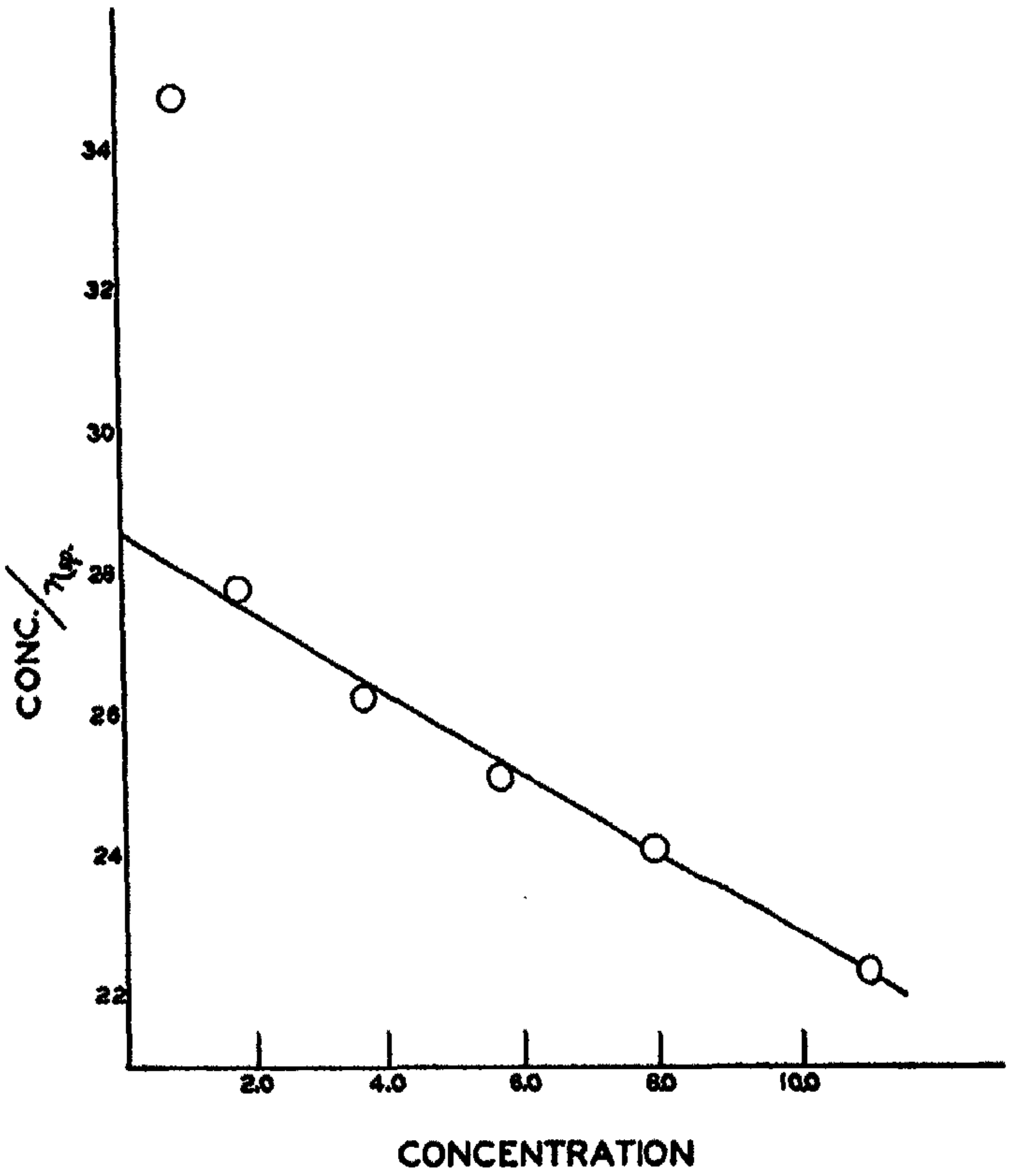

FIG. 2

do not lie on a straight line for small concentrations. If one rewrites the ordinate in the form $\frac{c\eta_0}{\eta - \eta_0}$ it can be seen that small errors in $\eta - \eta_0$ will greatly affect the results. This usually occurs for small concentrations where η is not much different from η_0.

Carrying out the same sort of calculation for lecithin as for stearic acid, we found $\Phi = 1.99$ cc. per gram and $a = 1.76$.

Assuming that lecithin forms ellipsoidal particles and applying Eisenschitz's equation, "a" from experiment corresponds to a 17 to 1 ratio of length to diameter, i.e., if a/b is 17/1 then:

$$a = \frac{0.159\,(17)}{\log_{10} 34} = 1.76$$

According to Leathes (6) the cross section of a lecithin molecule is about 70 (A.U.),[2] which corresponds to a diameter of a little over 8 A.U. For a 17 to 1 ratio of length to diameter the length of lecithin molecules would have to be about 136 A.U. This corresponds to the length of four lecithin molecules in a straight chain.

CONCLUSIONS

The information which we hope to gain by this type of research is not as complete as expected. The discrepancy lies not in the fact that the measurements yield results which are not reliable, or that we are dealing with too complicated a material, but that we are handicapped in the application of equations based on purely theoretical grounds. Thus it can readily be seen that when one tries to apply the Eisenschitz equation to experimental results certain limitations arise, as for example: (1) The equation of Eisenschitz has been derived under the assumption that $a >> b$. As the ellipsoidal particle approaches that of a sphere, the equation can no longer be applied. (2) The question arises as to whether the equation can be applied to cases where there is a formation of long chains.

If the ratio of length to diameter of lecithin is too small to apply the above equation to the results obtained, then lecithin must be approaching the form of an oblate or prolate spheroid. However, if we assume that the equation is applicable, then lecithin forms chains of four molecules on the average.

More experiments must be performed to determine the limitations of Eisenschitz equation, as well as the applicability of the same to associated systems.

SUMMARY

1. Viscosity measurements of stearic acid and lecithin dissolved in carbon tetrachloride were made at various concentrations, and a linear relation found when c/η'_{sp} is plotted against c.

2. The application of the Eisenschitz equation to experimental results is discussed with reference to ratio of length to diameter of both stearic acid and lecithin.

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THE PRODUCTION OF FURFURAL FROM XYLOSE SOLUTIONS BY MEANS OF HYDROCHLORIC ACID-SODIUM CHLORIDE SYSTEMS

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I. INTRODUCTION

One of the outstanding achievements in the utilization of agricultural wastes in the manufacture of industrial chemicals is the development of the furfural industry. The furfural is produced by heating oat hulls at about 60 pounds pressure with about 5 per cent sulfuric acid for five or more hours (14, 16, 5). The yield is about 50 to 60 per cent of the theoretical. The studies reported in the present communication have to do with the production of furfural from strong xylose solutions by various combinations of hydrochloric acid and sodium chloride, in order to establish general principles of procedure which could be applied directly to the agricultural material or to the xylose-containing hydrolysates made therefrom. The presence of the salt decreases the solubility of the furfural, ensuring its more rapid and complete removal by the solvent. The salt likewise increases the activity of the acid. This latter phenomenon has been studied with reference to various hydrolytic actions (2, 3, 4, 6, 7, 8, 9, 10, 11, 20). In general, the hydrolytic action of a strong acid, such as hydrochloric acid, is proportional to the "apparent" hydrogen-ion concentration, which is conveniently expressed in terms of pH. So far as the authors are aware, this principle has not been applied to a dehydration action such as the production of furfural from xylose. Adams and Vorhees (1), Hurd and Isenhour (13, 14), and others have employed salts in this reaction for the purpose of reducing the solubility of the furfural in order to facilitate distillation.

II. GENERAL PROCEDURE AND PRELIMINARY EXPERIMENTS

A. *General procedure*

The aqueous xylose solutions plus the dehydrating agents were refluxed with an immiscible solvent in which furfural is very soluble. These solvents included benzene, toluene, and carbon tetrachloride. Toluene is the solvent employed in the studies here reported in detail. The purpose of the solvent is twofold. It removes the furfural as formed, thus cutting down the opportunity for polymerization of the furfural in the presence of the dehydrating reagents, and it also permits the building up of high concentrations of furfural in the solvent, thus allowing an easy and economical separation by distillation.

The concentration of furfural in the toluene was determined by specific gravity measurement with a Westphal chainomatic balance. Quantitative experiments showed the specific gravity of toluene–furfural systems to be a linear function of the concentration of furfural. Toluene was refluxed with equal volumes of the sodium chloride–hydrochloric acid solutions of the strength employed in subsequent experiments; there was no significant change in specific gravity. The toluene solutions of furfural, obtained by action of the sodium chloride–hydrochloric acid systems upon xylose, were shaken with sodium sulfite. The specific gravity was restored to that of the pure toluene. These toluene–furfural systems were subjected to fractional distillation. The distillation curve corresponded to that obtained for known furfural-toluene systems. The furfural so obtained was identical with pure furfural.

The xylose was analyzed by three different methods, those of Shaffer and Hartmann (18), Slater and Acree (19), and Kline and Acree (15). The purity was found to be 95.5, 96.2, and 95.5 per cent by the respective procedures, with an average value of 95.7 per cent. Since the theoretical yield of furfural from pure xylose is 64 per cent, the maximum yield from the xylose used would be about 61 per cent.

B. The influence of volume ratios upon yields of furfural

In table 1 are given data showing the influence of volume ratios upon the yield of furfural from 20 per cent xylose refluxed for five hours in the presence of 0.50 *N* hydrochloric acid–40 per cent sodium chloride. The concentrations of sodium chloride and of xylose throughout this paper are expressed in grams per 100 cc. of acid used. It is evident that the yield of furfural increased slightly up to a ratio of 67:100 and was practically constant beyond that point. In subsequent experiments the toluene and aqueous systems were employed in equal volumes.

C. Influence of xylose concentrations on yields of furfural

In table 2 are given data on the yield of furfural from various concentrations of xylose refluxed for five hours in the presence of 0.50 *N* hydrochloric acid–40 per cent sodium chloride. The results show a decrease in yield with increase in xylose concentration. In subsequent work a xylose concentration of 20 per cent was employed.

D. The effect of certain salts

Preliminary experiments showed some interesting effects of salts upon strong xylose solutions. For example, 250 cc. of water was added to 75 g.

of xylose and 75 g. of ammonium chloride. The solution was heated on a hot plate; a strong odor of furfural was soon evident. However, the furfural could not be readily extracted from the mixture by means of benzene, toluene, or carbon tetrachloride. On vigorous shaking, the mixture proved to be an excellent emulsifying agent for the solvent. When subjected to distillation the furfural began to distill over at about 110°C. At 120°C. the mixture had a strong tendency to foam and the furfural distilled in such amounts that each drop was diphasic. These results indicate the formation of an intermediate product, which is insoluble in the solvents employed but which at higher temperatures yields furfural readily. Similar results were obtained with ammonium sulfate, ammonium dihydrogen phosphate, and ammonium tartrate.

TABLE 1

Effect of varying volume ratios of toluene with 20 per cent xylose solution with 0.50 N hydrochloric acid and 40 per cent sodium chloride for five hours

TOLUENE	AQUEOUS SOLUTION	TOLUENE PER 100 CC. OF AQUEOUS SOLUTION	YIELD OF FURFURAL PER 100 G. OF XYLOSE
cc.	*cc.*	*cc.*	*grams*
20	103	19.4	29.8
35	93	37.6	30.7
50	93	53.8	30.7
100	159	62.9	31.8
80	119	67.2	33 3
125	184	67.9	33.2
65	93	69.9	34.0
150	188	80.0	34.0
50	50	100.0	33.6

TABLE 2

Effect of varying concentrations of xylose, using 0.50 N hydrochloric acid and 40 per cent sodium chloride for five hours

XYLOSE	YIELD OF FURFURAL PER 100 G. OF XYLOSE	PER CENT OF THEORETICAL YIELD	XYLOSE	YIELD OF FURFURAL PER 100 G. OF XYLOSE	PER CENT OF THEORETICAL YIELD
per cent			*per cent*		
4	42.5	70	30	29.4	48
8	40.0	66	40	28.0	46
10	39.4	65	50	25.5	42
15	36.0	59	60	22.7	37
20	33.6	55			

Strong solutions of aluminum sulfate and of zinc chloride also gave furfural on boiling with concentrated solutions of xylose, but in these instances the furfural was readily extracted with the solvents. Strong solutions of sodium chloride, calcium chloride, or of sodium sulfate did not lead to the formation of furfural.

TABLE 3

Yields of furfural from 20 per cent xylose solution with various combinations of hydrochloric acid–sodium chloride

NORMALITY OF HCl	NaCl	pH	2 HOURS			4 HOURS			6 HOURS			8 HOURS		
			f	f_1	f_2	f	f_1	f_2	f	f_1	f_2	f	f_1	f_2
N	*per cent*													
0.25	0	0.60	0	1.1	1.1	2.8	2.2	2.2	1.8	2.7	2.7	4.7	3.7	3.7
	5	0.46	1.1	1.5	1.5	3.1	3.1	3.1	2.5	3.7	3.7	5.1	5.0	5.0
	10	0.32	1.7	2.0	2.0	4.0	4.2	4.2	4.3	5.0	5.0	6.3	6.8	6.8
	15	0.18	2.5	2.8	2.8	6.0	5.7	5.5	7.2	7.1	6.8	9.4	9.3	8.7
	20	0.04	3.7	3.8	3.8	7.9	7.9	7.4	8.1	9.5	8.9	13.0	12.6	11.5
	25	−0.10	5.1	5.1	5.1	10.5	10.5	10.0	12.6	12.9	12.3	17.3	17 4	15.1
	30	−0.24	7.4	7.1	7.1	13.6		13.2	16.3		16.6	20.1		20.0
	35	−0.38	10.2	10.0	10.0	16.8		17.8	19.6		22.4	24.6		25.7
	40	−0.52	12.4		12.6	19.3		22.9	23.8		26.3	26.4		30.2
	45	−0.66				20.6		26.9	26.4		30.9	30.4		33.1
0.50	0	0.27	1.6	2.2	2.3	5.2	4.5	4.6	3.4	5.9	5.5	8.3	6.5	7.1
	5	0.13	3.9	3.1	3.2	7.1	6.2	6.2	7.3	7.9	7.6	8.7	8.9	9.5
	10	−0.01	4.3	4.3	4.3	8.8	8.5	8.5	11.7	11.2	10.5	13.2	12.3	12.9
	15	−0.15	6.0	5.8	5.8	12.2	11.5	11.0	15.5	13.5	13.5	18.2	16.6	16.6
	20	−0.29	8.4	7.9	7.9	15.9	15.5	15.1	19.8	20.4	18.2	22.8	22.9	22.4
	25	−0.43	10.7	10.7	10.7	19.3	20.9	19.5	24.8		24.0	28.8		28.8
	30	−0.57	14.8	14.8	14.8	23.2		23.4	28.8		28.8	32.9		32.4
	35	−0.71	17.2		19.0	27.5		28.2	32.7		32.4	33.4		33.9
	40	−0.85	19.3		22.4	30.4		30.9	36.1		36.3	34.0		35.5
	45	−0.99	19.3		25.1	30.4		32.4	33.5		37.1	36.9		38.0
0.75	0	0.07	3.7	3.7	3.6	5.6	6.6	6.9	5.0	8.5	8.5	11.5	10.7	10.7
	5	−0.07	5.3	5.1	4.9	9.7	9.1	9.1	12.8	11.8	11.2	15.3	14.8	14.5
	10	−0.21	6.9	7.1	6.6	13.0	12.6	12.6	16.7	16.7	15.1	22.4	20.4	18.6
	15	−0.35	9.6	9.5	9.1	18.3	18.2	17.0	21.8	21.9	20.9	26.4	26.3	24.5
	20	−0.49	13.2	13.2	12.6	22.5	23.4	21.4	25.7		25.7	32.4		31.6
	25	−0.63	18.0	18.2	17.8	26.8		26.9	31.8		30.9	35.8		33.1
	30	−0.77	20.2		21.4	31.6		30.2	33.6		33.9	37.6		34.7
	35	−0.91	24.4		24.5	34.4		33.1	39.0		36.3	39.8		36.3
	40	−1.05	24.6		27.5	34.7		34.7	39.0		38.0	40.4		38.0
	45	−1.19	25.7		29.5	35.6		35.5	40.8		40.7	40.3		39.8
1.00	0	−0.01	2.5	4.2	4.2	9.4	8.9	6.8	10.2	10.0	10.5			
	5	−0.15	5.0	5.6	5.7	12.7	12.0	11.0	16.4	15.5	14.5			
	10	−0.29	7.7	7.8	7.8	17.5	16.6	15.1	20.3	20.9	19.1			
	15	−0.43	10.7	10.7	10.5	21.2	22.4	20.4	25.8		24.5			
	20	−0.57	15.3	14.4	14.5	25.9		25.7	32.0		28.8			
	25	−0.71	19.3	19.5	17.4	31.5		29.5	34.0		33.1			
	30	−0.85	23.0		22.9	34.2		31.6	35.2		33.8			
	35	−0.99	25.5		26.3	34.8		34.7	36.8		34.5			
	40	−1.13	26.8		28.8	38.1		35.5	37.5		35.5			
	45	−1.27	26.2		30.9	37.8		36.3	38.4		36.3			

TABLE 3—*Concluded*

NORMALITY OF HCl	NaCl	pH	2 HOURS			4 HOURS			6 HOURS			8 HOURS		
			f	f_1	f_2	f	f_1	f_2	f	f_1	f_2	f	f_1	f_2
N	*per cent*													
1.50	0	−0.24	4.1	7.2	7.1	13.9	13.5	13.5	19.8	19.1	20.0			
	5	−0.38	9.7	9.8	9.5	18.9	18.6	18.6	25.4	25.7	25.7			
	10	−0.52	14.5	13.5	13.2	24.0	25.1	23.4	30.3		31.6			
	15	−0.66	18.0	18.2	18.2	29.0		28.2	34.4		33.8			
	20	−0.80	22.9		22.4	33.0		30.9	36.0		34.7			
	25	−0.94	26.2		25.1	35.7		33.9	35.1		35.0			
	30	−1.08	31.0		28.8	36.9		35.5	34.0		35.0			
	35	−1.22	31.6		36.8	36.8		36.3	34.2		35.0			
	40	−1.36	32.8		31.6	39.2		36.7	34.9		35.0			
	45	−1.50				38.9		37.1	34.7		35.0			
2.00	0	−0.45	13.4	12.6	11.5	17.4	17.0	20.4						
	5	−0.59	17.6	17.4	15.9	23.4	23.4	24.6						
	10	−0.73	23.5	23.4	21.9	28.6		28.8						
	15	−0.87	28.3		24.6	32.4		31.6						
	20	−1.04	31.5		28.2	33.8		33.9						
	25	−1.18	35.5		30.9	34.0		35.5						
	30	−1.32	36.0		32.4	35.0		35.9						
	35	−1.46	36.4		33.9	34.7		36.3						
	40	−1.60	35.9		35.5	36.0		36.3						
	45	−1.74	36.7		36.0	36.4		36.7						

f = experimental yield of furfural, in grams produced per 100 grams of xylose.
f_1 = yield calculated by the relation $\log f = a + 0.028 \times$ per cent NaCl.
f_2 = yield as read from a diagram of $\log f$ against pH for all values for all combinations of sodium chloride and hydrochloric acid.

III. THE YIELD OF FURFURAL IN THE PRESENCE OF VARIOUS COMBINATIONS OF SODIUM CHLORIDE–HYDROCHLORIC ACID

In table 3 are given data for the yields of furfural from 20 per cent xylose in the presence of 0.25, 0.50, 0.75, 1.00, 1.50, and 2.00 *N* hydrochloric acid with concentrations of sodium chloride from 0 to 45 per cent for various periods of time. The data show the marked effect of the presence of the salt. The highest yield without salt is 20 per cent at 1.50 *N* hydrochloric acid after six hours. This same yield was given in two hours by approximately the following hydrochloric acid–sodium chloride systems: 0.50 *N*–40 per cent; 0.75 *N*–30 per cent; 1.00 *N*–25 per cent; and 1.50 *N*–15 per cent. The highest yields are 35 to 40 per cent, or 57 to 65 per cent of theoretical.

IV. THE RELATION OF YIELD OF FURFURAL TO THE pH OF THE SODIUM CHLORIDE–HYDROCHLORIC ACID SYSTEMS

In table 4 are given data for the pH values of 0.25 *N* hydrochloric acid in the presence of varying concentrations of sodium chloride. These values were determined potentiometrically. No corrections were made for diffusion potential. Data are also presented showing the effect of the sodium chloride upon the solubility of the furfural. While the "apparent" hydrogen-ion concentration increased nearly ninefold, the solubility is decreased only to one-third.

The relation between pH and concentration of sodium chloride for table 4 is

$$\text{pH} = 0.60 - 0.028 \times \text{per cent NaCl} \tag{1}$$

Also, for a given time period, the yield of furfural is a linear function of the "apparent" hydrogen-ion concentration, through a major portion of the curve. The deviation from this linear relationship is associated with decreased yield, due to polymerization of the furfural and other factors which cause a marked darkening of the reaction mixture. During the range for which equation 1 holds,

TABLE 4

Effect of sodium chloride upon the pH of 0.25 N hydrochloric acid and upon the solubility of furfural at 25°C.*

PER CENT NaCl	pH	"APPARENT" C_{H^+}	RELATIVE C_{H^+}	FURFURAL IN TOLUENE	FURFURAL IN WATER	DISTRIBUTION RATIO
0	0.57	0.273	1.00	2.90	0.60	0.207
5	0.46	0.346	1.27	2.98	0.52	0.174
10	0.32	0.476	1.74	3.06	0.44	0.144
15	0.18	0.654	2.39	3.10	0.40	0.129
20	0.07	0.860	3.15	3.14	0.36	0.114
25	−0.09	1.228	4.50	3.19	0.31	0.097
30	−0.25	1.763	6.46	3.20	0.29	0.091
35	−0.37	2.331	8.54	3.25	0.25	0.077

* Seven per cent furfural in toluene used, 50 cc. of 0.25 *N* hydrochloric acid, and 50 cc. of toluene–furfural solution.

$$\log f = a + 0.028 \times \text{per cent NaCl} \tag{2}$$

that is, the logarithm of the yield of furfural is a linear function of the concentration of salt and also of pH.

Equation 2 was applied to all the hydrochloric acid–sodium chloride systems; these values are given as f_1 in table 4. The agreement is entirely satisfactory through ranges in which the yield of furfural is a linear function of the "apparent" hydrogen-ion concentration. In general the relation is linear up to about 22 per cent yield of furfural. This treatment permits the calculation of yields below 10 per cent, which are somewhat erratic owing to the low concentrations in the toluene.

Graphs of pH against furfural yield (f_t) for the 0.25 *N* hydrochloric acid-salt combinations for the 2-, 4-, and 6-hour periods permitted the calculation of the pH of other concentrations of pure acid, on the assumption that the yield of furfural is a function of pH only. Such values are given in table 5. There are also included data for various concentrations of hydrochloric acid calculated from the activity coefficients given by Randall and Young (17). Our value for 0.25 *N* hydrochloric acid is pH = 0.60 as compared to 0.71 calculated from the activity coefficient. Relative values of the activity coefficients, γ', were used to correct our values to the basis of the data of Randall and Young. It is evident that the pH values

TABLE 5

The pH values of 0.50 N, 0.75 N, 1.00 N, 1.50 N, and 2.00 N hydrochloric acid as calculated on basis of yields with 0.25 N hydrochloric acid–sodium chloride systems, compared to pH values as calculated from the activity coefficient of hydrochloric acid

CONCENTRATION OF HCl		pH FROM GRAPH FURFURAL YIELD FOR 0.25 *N* HCl-NaCl				pH FROM VALUES OF γ HCl				
Molar	Molal	2 hrs.	4 hrs.	6 hrs.	Average	γ	Relative value of γ	$\gamma'm$	$pH_1 = \log 1/\gamma'm$	$pH - pH_1$
0.25	0.25					0.761	1	0.25	0.60	0
0.50	0.50	0.29	0.27	0.26	0.27	0.757	0.995	0.50	0.30	−0.03
0.75	0.76	0.04	0.09	0.09	0.07	0.780	1.03	0.78	0.11	−0.04
1.00	1.02	−0.02	−0.02	+0.01	−0.01	0.815	1.07	1.09	−0.04	+0.03
1.50	1.54	−0.24	−0.23		−0.24	0.901	1.18	1.82	−0.26	+0.02
2.00	2.08	−0.50	−0.40		−0.45	1.04	1.37	2.85	−0.45	0

TABLE 6

*Values of pH of various combinations of sodium chloride and hydrochloric acid**

PER CENT NaCl	NORMALITY OF HCl					
	0.25	0.50	0.75	1.00	1.50	2.00
0	0.60	0.27	0.07	−0.01	−0.24	−0.45
5	0.46	0.13	−0.07	−0.15	−0.38	−0.59
10	0.32	−0.01	−0.21	−0.29	−0.52	−0.73
15	0.50	−0.15	−0.35	−0.43	−0.66	−0.87
20	0.04	−0.29	−0.49	−0.57	−0.80	−1.04
25	−0.10	−0.43	−0.63	−0.71	−0.94	−1.18
30	−0.24	−0.57	−0.77	−0.85	−1.08	−1.32
35	−0.38	−0.71	−0.91	−0.99	−1.22	−1.46
40	−0.52	−0.85	−1.05	−1.13	−1.36	−1.60
45	−0.66	−0.99	−1.19	−1.27	−1.50	−1.74

* Data for 0.25 *N* hydrochloric acid based on experimental data from the relation, pH = 0.60 − 0.028 × per cent NaCl. Data for other concentrations calculated from table 5, using the relation pH = *b* − 0.028 × per cent NaCl.

calculated from yields of furfural in the presence of the pure acid agree remarkably well with those calculated from the activity coefficients.

It was noted above that equation 2 applies, within specified limits, to all combinations of hydrochloric acid and sodium chloride. The assumption seems warranted that the pH of other concentrations of acid decreases at the same rate as obtained for 0.25 *N* hydrochloric acid, that is,

$$\text{pH} = b - 0.028 \times \text{per cent NaCl} \qquad (3)$$

Values so calculated are given in table 6.

Graphs were constructed by plotting log *f* against pH for the 2-, 4-, 6-, and 8-hour periods. Each curve included all the data for all combinations of hydrochloric acid and sodium chloride for the given period. From these graphs the furfural yield for each pH value was read. The data so obtained are given as f_t in table 4. It is evident that, within experimental accuracy, the yield of furfural from 20 per cent xylose solution in the presence of hydrochloric acid–sodium chloride combinations is determined by the pH values of the wide variety of combinations employed.

V. SUMMARY

Studies are reported on the production of furfural from strong xylose solutions using hydrochloric acid–sodium chloride solutions as dehydrating agents. The xylose–hydrochloric acid–sodium chloride systems were refluxed, at atmospheric pressure, with toluene. The furfural yield was determined from the specific gravities of the resulting furfural–toluene solutions. The concentrations of hydrochloric acid used were 0.25, 0.50, 0.75, 1.00, 1.50, and 2.00 normal, each in the presence of 0, 5, 10, 15, 20, 25, 30, 35, 40, and 45 per cent sodium chloride. The yield of furfural was twice as great for 4 per cent xylose as for 60 per cent xylose. Detailed experiments were performed for xylose at 20 per cent concentration for which the yield in furfural is about 20 per cent less than for 4 per cent xylose.

The yield of furfural is increased about one-third for each 5 per cent addition of sodium chloride up to a furfural yield of about 22 per cent. From this point the increase in yield is less. For all cases, for a given time period, the yield of furfural is, within reasonable limits, dependent only upon the pH of the hydrochloric acid–sodium chloride combinations. That is, the yield is dependent upon the thermodynamic degree of dissociation of the acid (the activity coefficient).

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A METHOD FOR THE DETERMINATION OF THE WALL CORRECTION FOR THE FALLING SPHERE VISCOMETER[1]

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INTRODUCTION

The use of the simple Stokes' equation in the determination of viscosity rests upon a number of assumptions. According to Arnold (3) these are: (a) there is no slip between the medium and the surface of the sphere; (b) the velocity of fall is small; (c) the sphere is rigid; (d) the discontinuities of the medium are small, compared to the size of the sphere; and (e) the liquid is infinite in extent.

The cylinder containing the liquid is immersed in a constant-temperature bath and fixed in an accurately vertical position. The sphere is introduced axially into the liquid by means of a glass tube passing through a stopper at the top of the cylinder. Ladenburg (8) released the sphere beneath the surface by means of an electromagnet. The velocity of fall is determined over the middle third of the liquid column; the timing lines should extend around the cylinder in order to avoid parallax. The liquid must be free from gas bubbles and convection currents. Lemin (9) found in measuring the viscosity of glycerol, that it was necessary to wait ten minutes between the passage of the spheres in order to obtain consistent results. The requirement of spheres is easily met by the use of ball-bearings, which are made in standard sizes with an accuracy of 0.001 inch. Ladenburg (8) found the velocity of fall of spheres with corroded surfaces to be identical with that for spheres with polished surfaces. Lemin (9) stated that with very small spheres the slippage must be taken into account, but that this factor is not significant with sphere sizes employed in the laboratory viscometer. Gibson and Jacobs (7), Poynting and Thomson (11), and Allen (1) have emphasized the fact that there is a lower limit to the viscosity which can be measured with the falling sphere viscometer and an upper limit of the size of the sphere which can be employed using the simple Stokes' equation.

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[1] This work was supported in part by a grant from the Industrial Science Research funds of the Iowa State College for the study of the granulation of honeys.

The simple Stokes' law may be formulated as

$$\eta = \frac{2(d_1 - d_2)\, g r^2}{9v} \tag{1}$$

in which v = velocity of fall, d_1 = density of sphere, d_2 = density of the medium, η = absolute viscosity of the medium, r = radius of the sphere, and g = the gravity constant.

It is evident that the extent of the liquid and the height of the column of liquid are factors in the rate of fall of the sphere. Ladenburg (8) applied two linear equations to the simple Stokes' law to correct for variations in the extent of the liquid and for the height of the liquid column. His correction for the "wall effect" is

$$v(1 + 2.4r/R) = v_\infty \tag{2}$$

in which v is the observed velocity, v_∞ the velocity in infinite medium, r the radius of the sphere, and R the inside radius of the cylinder. The above relation has been verified, within limits, by Gibson and Jacobs (7), Lemin (9), and others. Lemin found the relation to hold for values of r/R up to 0.06.

The correction for the "end effect" is

$$v(1 + 3.3r/h) = v_\infty \tag{3}$$

in which h is the height of the column of liquid.

Sheppard (13) derived an empirical equation in an endeavor to extend the wall correction to wider ranges of r/R. His relation is

$$T = T_\infty + \frac{C}{(R/r - 1)^2} \tag{4}$$

in which T is the observed time of fall, T_∞ the time of fall in infinite medium, and C a constant. With reference to the above equation Gibson and Jacobs (7) state, "Although the expression may fit the author's data when suitable constants are chosen, this does not prove that the value of T_∞ is the correct one."

Equation 4 may be written,

$$\log (T - T_\infty) = -2 \log (R/r - 1) + \log C \tag{5}$$

The above equation was applied graphically to the data of Lemin (3) (see table 2) for the viscosity of glycerol. The value of T_∞ so obtained gave a viscosity of 20.5 poises. This is higher than the three lowest values given by Lemin and 2 poises higher than the value using Ladenburg's correction.

Gibson and Jacobs (7) suggested that the viscometer should be calibrated by using a liquid of known viscosity; they employ the relation,

$$\frac{\eta_1}{\eta_2} = \frac{(d_1 - d_3)T_1}{(d_1 - d_3)T_2} \tag{6}$$

In regard to the above equation Bingham (4) states: "Workers have felt dependent upon calibrating liquids, and since there is a dearth of calibrating liquids of high viscosity, liquids are often chosen in which the velocity of fall is too great for strict application of Stokes' law and a correction has to be made."

The work here was undertaken during the course of studies on various properties of honeys as correlated with their tendency to granulate (6). Chataway (5) found the water content of honeys to be correlated with viscosity as determined by the falling sphere viscometer and gives tables for this purpose. The value of r/R for his viscometer was 0.317, which involves a large correction factor. He points out in a second communication that his tables apply only for a viscometer of the same dimensions as employed by him.

The determination of the viscosity of honeys is complicated by the fact that some samples have been shown to exhibit an anomalous behavior. For example, deBoer and Kniphorst (2) found the viscosity of heather honey to be decreased by stirring, with subsequent increase in viscosity on standing. They describe the phenomenon as an example of thixotropy. Paine, Gertler, and Lothrop (10) noted that certain honeys show a slight decrease in viscosity with increase in stress. Scott Blair (12) made detailed studies of the thixotropy of heather honey under shearing in both its undisturbed ("gel") and stirred ("sol") forms. In both cases, the viscosity increased at low stresses, but in neither case was there found any sharp elastic limit (yield value). The sol form showed (considering its high viscosity) only a very small deviation from truly fluid behavior." He describes a viscometric test to characterize honeys having thixotropic properties.

EXPERIMENTAL

In tables 1 to 6 are given data for the viscosities of various liquids with various values of r/R and h. The data for castor oil, glycerol, and a system of colophony–turpentine are adapted from the literature, while those for a system of colophony–turpentine and for two honeys were determined in these laboratories. It was found that, within limits, the determined viscosity is an exponential function of r/R such that,

$$\log(\eta_x - b) = mr/R + \log(\eta_\infty - b) \tag{7}$$

TABLE 1

Viscosity of castor oil at 20°C.

Calculated from data of Gibson and Jacobs (7). $h = 25.5$; $r = 0.0794$

R*	r/R	η_x	η_x'	η_∞	η_L
2.270	0.0350	10.66	10.55	9.91	9.73
1.750	0.0454	10.84	10.73	9.89	9.67
1.050	0.0756	11.51	11.39	9.85	9.64
1.000	0.0794	11.88	11.76	10.09	9.88
0.570	0.1395	13.35	13.21	9.79	9.89
0.425	0.1870	15.43	15.27	9.89	10.54

* In this and the following tables r = radius of sphere, R = inside radius of cylinder, η_x = viscosity calculated by simple Stokes' law, η_x' = viscosity corrected for end effect by Ladenburg equation 3, n_∞ = viscosity for infinite liquid calculated by equation 11, η_L = viscosity for infinite liquid calculated by Ladenburg equation 2.

TABLE 2

Viscosity of glycerol at 12°C.

From data of Lemin (9). $h = 30.0$; $r = 0.0794$

R	r/R	η_x	η_x'	η_∞	η_L
4.84	0.0164	19.0	18.8	18.3	18.1
2.90	0.0274	20.3	20.1	19.2	18.9
2.35	0.0338	20.2	20.0	18.9	18.5
1.70	0.0467	20.6	20.4	18.8	18.4
1.43	0.0557	21.1	20.9	18.9	18.5
1.30	0.0610	21.3	21.1	18.9	18.4
0.860	0.0923	22.7	22.6	18.8	18.4
0.435	0.1825	29.8	29.5	19.4	20.5
0.280	0.2835	37.3	37.0	17.3	22.0

TABLE 3

Viscosity of colophony–turpentine

From data of Ladenburg (8)

r/R	r/h	η_x	η_x'	η_∞	η_L
0.0107	0.00312	1396	1382	1357	1347
0.0141	0.00414	1415	1396	1363	1348
0.0189	0.00312	1424	1409	1364	1349
0.0213	0.00625	1438	1409	1358	1338
0.0249	0.00414	1447	1427	1367	1344
0.0283	0.00826	1456	1417	1348	1328
0.0340	0.00312	1490	1475	1389	1362
0.0376	0.00625	1491	1461	1394	1340
0.0450	0.00414	1515	1494	1368	1349
0.0500	0.00826	1515	1475	1347	1318
0.0680	0.00625	1600	1568	1378	1346
0.0901	0.00826	1681	1636	1379	1348

TABLE 4

Viscosity of colophony-turpentine at 25°C.

R	r	r/R	h	η_x	η_x'	η_∞	η_L
2.15	0.1587	0.074	33	75.3	74.1	64.3	62.9
2.15	0.2381	0.111	33	84.0	82.4	65.7	65.1
2.15	0.3170	0.147	33	95.9	92.9	67.5	68.7
2.15	0.3970	0.185	33	102.9	98.9	64.4	68.5
0.55	0.1181	0.215	22	115.7	113.7	67.5	75.0
2.15	0.5000	0.232	33	121.7	115.9	65.0	74.4
0.55	0.1587	0.288	22	150.5	147.0	67.6	86.9
2.15	0.6350	0.295	33	150.9	141.9	63.6	83.1
0.55	0.2381	0.433	22	274.7	265.2	66.6	130.6
0.55	0.3170	0.576	22	645.6	616.3	77.6	258.7

TABLE 5

Viscosity of holly honey at 25°C.

R	r	r/R	h	η_x	η_x'	η_∞	η_L
2.15	0.1181	0.055	33	238.1	235.3	212.6	207.8
2.15	0.1587	0.074	33	249.1	245.2	212.1	208.2
2.15	0.2381	0.111	33	265.1	258.9	206.4	204.4
2.15	0.3170	0.147	33	285.5	276.7	201.1	204.5
2.15	0.3970	0.185	33	306.0	294.3	191.8	203.8
2.15	0.5000	0.232	33	367.2	349.7	196.4	224.6
2.15	0.6350	0.295	33	451.2	424.2	190.1	248.4

TABLE 6

Viscosity of sourwood honey at 25°C.

R	r	r/R	h	η_x	η_x'	η_∞	η_L
2.15	0.1181	0.055	33	73.7	72.7	65.7	64.3
2.15	0.1587	0.074	33	76.8	75.5	65.5	64.1
1.25	0.1181	0.095	30	79.2	78.2	64.8	63.7
2.15	0.2380	0.111	33	85.2	83.2	66.3	65.7
1.25	0.1587	0.127	30	89.0	87.4	66.9	66.9
2.15	0.3170	0.147	33	95.1	92.2	67.0	68.1
2.15	0.3970	0.185	33	104.3	100.2	65.3	69.4
1.25	0.2381	0.191	30	107.0	104.2	66.8	71.6
2.15	0.5000	0.232	33	121.3	116.6	65.4	74.9
1.25	0.3170	0.254	30	126.7	122.4	64.4	76.0
2.15	0.6350	0.295	33	150.1	141.2	63.3	82.6
1.25	0.3970	0.318	30	156.2	149.7	61.3	84.9
1.25	0.5000	0.400	30	216.0	204.8	59.6	104.5
1.25	0.635	0.508	30	372.1	347.8	61.3	156.6

in which η_x is the determined viscosity, η_∞ the viscosity in liquid of infinite extent, and b is a constant.

Equation 7 may be written as,

$$\frac{\eta_x - b}{\eta_\infty - b} = 10^{mr/R} \tag{8}$$

While there was some variation in the value of m, the average value was 2.4, which is identical with the factor in the Ladenburg equation (equation 3) for correction for the wall effect.

It was also found that b is proportional to η_∞, or,

$$b = 0.700\eta_\infty \tag{9}$$

Substituting in equation 8

$$\frac{\eta_x - 0.7\,\eta_\infty}{\eta_\infty - 0.7\,\eta_\infty} = 10^{2.4r/R} \tag{10}$$

and,

$$\frac{\eta_x}{\eta_\infty} = 0.3 \times 10^{2.4r/R} + 0.7 \tag{11}$$

A table of values of $0.3 \times 10^{2.4\,r/R}$ as a function of r/R permitted the calculation of η_∞ for the data in tables 1 to 6. Somewhat more concordant results were obtained by making a correction for end effect, using equation 3 (Ladenburg's). These values are given as η_x'. Values are also given for η_∞ as calculated by equation 11 and by means of Ladenburg's equation (equation 2) for correction for the wall effect. It is at once evident that while the Ladenburg equation is valid up to a value of r/R of about 0.100, equation 11 gives concordant results up to a value of r/R of about 0.500. Through the range of validity of Ladenburg's equation, the two methods of calculation agree within reasonable limits. It should also be noted that the values for η_∞ for the honeys, as calculated by means of equation 11, show some tendency to decrease with increase in r/R. This drift is in harmony with the thixotropic properties of honeys as previously discussed.

SUMMARY

An equation has been derived by means of which the wall correction for the falling sphere viscometer can be made for values of r/R up to about 0.500.

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THE EFFECT OF CERTAIN SUGAR ALCOHOLS AND THEIR ANHYDRIDES ON THE DISSOCIATION OF BORIC ACID

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INTRODUCTION

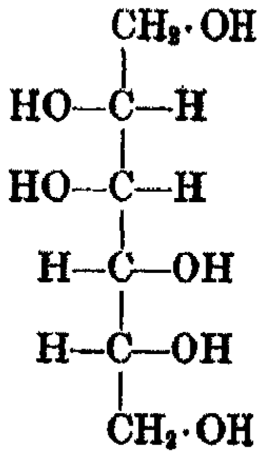
The use of the polyhydric alcohols in the titration of boric acid with alkalies is a well-established analytical procedure. The increase of the dissociation constant of the acid in the presence of various polyhydric alcohols and phenols was studied extensively by Böeseken (1). The subject was studied further and comprehensively reviewed by Mellon and Norris (2). The authors became interested in the fate of certain sugar alcohols and their anhydrides in the animal body (3, 4) and in bacterial culture media (5). The differences in effect were so striking that a comparison of the influences of these substances on the titration curves of boric acid suggested itself. Previously van Romburgh and van der Burg (6) have measured the difference between the electrical conductivity of boric acid in mannitol, mannitan, and isomannide solutions.

MATERIALS

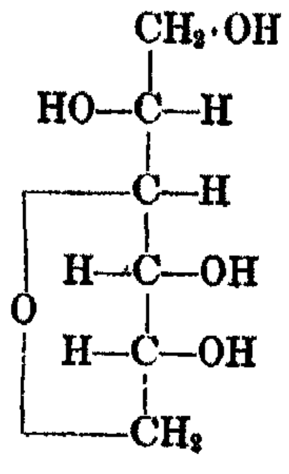
The mannitol used in this investigation was supplied through the courtesy of Merck and Company, Inc., Rahway, N. J. The aqueous solution of the compound (1:10) is neutral to litmus and very slightly dextrorotatory. The mannitan was prepared from mannitol by a slight modification of the method of Vignon (7), in which the dehydration is accomplished by means of sulfuric acid. The compound was acetylated and the resulting ester distilled *in vacuo*. The fraction distilling between 200–210°C. at 10 mm. was saponified. The calculated percentage of acetic acid is 72.31; that found was 71.70. The mannide was prepared by the method devised by Liebermann (8). Analysis gave: C, 48.37 per cent; H, 7.32 per cent. The calculated values are: C, 49.27 per cent; H, 6.90 per cent. The isomannide was prepared by Fauconnier's method (9). The compound melted sharply at 87°C. (uncorrected).

The dulcitol employed was Pfanstiehl's c.p. product, m.p. 188°C., free from galactose. The dulcitan was prepared by Berthelot's method (10). Analysis gave the following composition: C, 43.79 per cent; H, 7.20 per cent. The calculated values are: C, 43.87 per cent; H, 7.37 per cent.

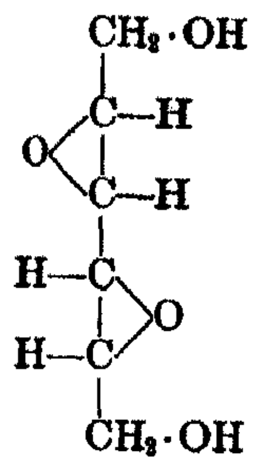
The following formulas indicate the structural relationships existing among the compounds.



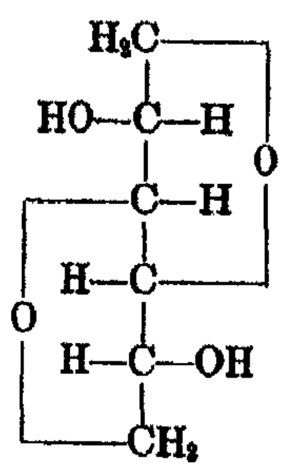
Mannitol



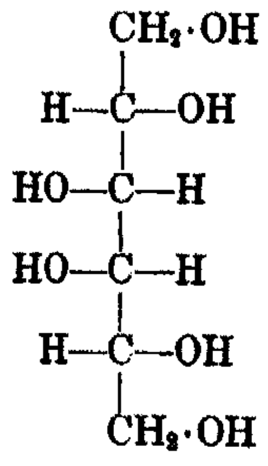
Mannitan



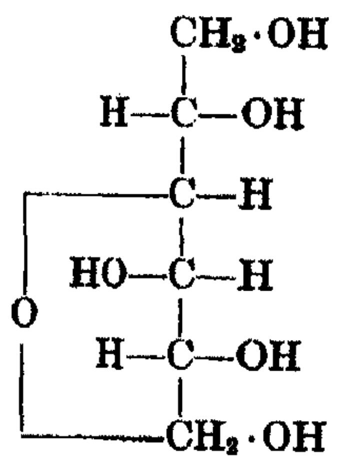
Mannide



Isomannide



Dulcitol



Dulcitan

METHOD

The solutions of the various compounds used 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 11 cc. Immediately after the addition of the alkali the pH of the solution was determined electrometrically at 25 ±0.5°C., using a Wilson (11) type hydrogen electrode. The results are set forth in figure 1.

DISCUSSION

It will be observed that the two hexahydric alcohols have practically the same dissociation-potentiating capacity on solutions of boric acid. The second anhydride of mannitol, namely isomannide, with two ring structures in the molecule, does not possess the capacity to influence the dissociation of boric acid, and the titration curve for the acid containing isomannide is practically identical with that of the acid alone. The curves for the two first anhydrides lie intermediate between the values obtained for the alcohols and those obtained for pure boric acid.

The curve for the double anhydride of mannitol, mannide, shows this substance to have a greater potentiating influence on the dissociation of boric acid than the first anhydrides. A comparison of this fact with the structure assigned to mannide by Liebermann (8) is incompatible with the hypothesis of Böeseken (1), namely, that the strongly dissociating complexes of boric acid are formed when two hydroxyl groups are situated on the same side of adjacent carbon atoms to which they are bound. The authors observed the rather rapid conversion of mannide into mannitol in the presence of alkali. It is possible that the partial conversion of this double anhydride into the polyhydric alcohol is responsible for the observed effect on the titration curve.

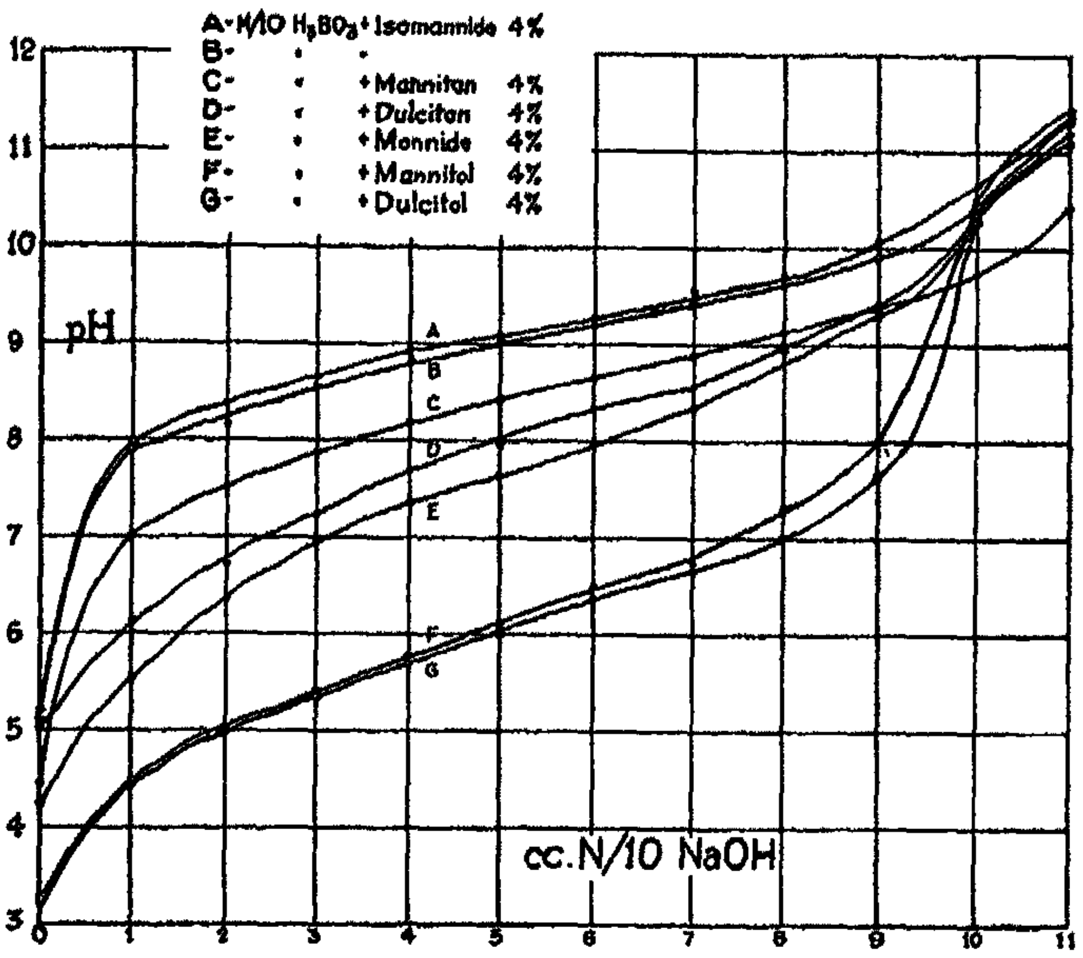


FIG. 1. Titration curves of boric acid in the presence of certain sugar alcohols and their anhydrides

SUMMARY

The influence of two polyhydric alcohols, mannitol and dulcitol, on the titration curve of boric acid has been studied. This effect has been compared with the action of the anhydrides mannitan, mannide, isomannide, and dulcitan.

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THE RADIOCHEMICAL DECOMPOSITION OF DEUTERO-AMMONIA

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INTRODUCTION

The study of the mercury photosensitized decomposition of the ammonias at room temperature (2) showed that under comparable conditions ammonia decomposes eleven times faster than the ammonia-d_3. Part of this ratio can be ascribed to the lower quenching power of deutero-ammonia; this fact taken into account brings the decomposition ratio to 5. This corresponds to a difference in activation energy of 950 calories (1).

It has been shown that the rates of decomposition on a hot tungsten wire yield the ratio 1.6:1, corresponding to a difference in activation energy of 900 calories (3).

It was considered of interest to find out how this difference in activation energy would affect the radiochemical reaction.

EXPERIMENTAL DETAILS

For this study the method of central irradiation was chosen. This allows both numerous runs and comparable conditions. The α-ray bulb was mounted in the center of a 100-cc. sphere in which the gases were submitted to irradiation. The gases produced by decomposition were pumped off, after the undecomposed ammonia had been frozen out, and measured in a Ramsay gauge. The ammonia could then be vaporized and a new run started, the same sample being used throughout the series of runs. The first run was systematically discarded. Because the decrease in pressure due to the removal of the products of decomposition is very small (about 1/1000 of total pressure), the experiments can be considered as carried out at the same pressure.

It was not judged necessary to measure the emanation, because only relative values were wanted. The activity of all the bulbs used was of the order of 50 millicuries.

For the runs at 20°C. the temperature was controlled by keeping the reaction vessel in a large Dewar flask filled with water. For the runs at

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100°C. and 184°C. the vessel was kept in steam and aniline vapor, respectively.

The gases used in these experiments were prepared by passing H_2O and D_2O over magnesium nitride, obtained by interaction of purified nitrogen and magnesium at 700°C. The deuterium content of the hydrogen in the two samples of heavy ammonia submitted to reaction was 68 per cent and 98 per cent. The last sample analyzed spectrographically before and after a long irradiation did not reveal a difference in deuterium concentration.

DATA

Influence of temperature

The data on the decomposition of ammonia and deutero-ammonia are given in table 1. The first column gives the nature and the pressure at 20°C. of the gas submitted to reaction. The temperature at which the experiments were carried out is given in the second column. The emanation E, present at the beginning, and the emanation ΔE decayed during the reaction are given in the third and fourth columns. These data are obtained from Kolowrat's table, the sealing of the bulb being taken as origin. The pressure ΔP of the decomposed gases measured in a volume of 2 cc. is recorded in the fifth column. The sixth column shows the rate of decomposition $\Delta P/\Delta E = R$. The value of R for the decomposition of ammonia at 184°C. is obtained by extrapolation of Wourtzel's curve, with which

TABLE 1

Decomposition of ammonia and of deutero-ammonia

PRESSURE IN MM.	T IN °C.	E	ΔE	ΔP	R
		NH_3			
52.5	20	64558	2446	5.33	218
	20	61648	3373	7.42	222
	20.3	57814	3914	8.76	224
	22	53239	4418	10.12	229
	100	48284	2182	9.11	418
	100	45442	2129	8.85	416
	100	42797	1904	7.91	415
	184				580
		ND_3			
52.6	100	36381	2378	6.67	281
	20.7	33647	2830	4.92	174
	100	30333	1694	4.86	286
	22.1	28437	2810	5.03	179
	100	25337	1810	5.18	281
	20.5	23283	2535	4.49	177
	184	20603	2601	9.21	354

our results at 20°C. and 100°C. are in perfect agreement. These data yield the following values for the ratios of the rates of decomposition.

T in °C.	20	100	184
R_{NH_3}/R_{ND_3}	1.27	1.47	1.64

Influence of the concentration of D_2

A sample of ammonia containing 68 per cent deuterium compared with the ordinary ammonia yielded the data contained in table 2. The columns have the same significance as in table 1. These data in connection with those of table 1 give the variation of the rate of reaction with concentration in D_2.

TABLE 2

Decomposition of ammonia containing 68 per cent deuterium

PRESSURE IN MM	T IN °C.	E	ΔE	ΔP	R
			NH_3		
54.9	20.2	92600	6582	11.98	182
	20.0	84926	4490	8.07	179
	20.4	78782	6574	11.90	187
R					181
			ND_3		
54.75	20	62462	3232	4.92	152
	22	58275	2977	4.52	152
	21	54567	5034	7.86	154
R					153

Concentration in per cent	0	68	98
$R_{NH_3}/R_{N(H_xD_y)_3}$	1	0.84	0.79

These data show a practically linear relationship between the rate and the deuterium concentration.

DISCUSSION

The rate of decomposition $\Delta P/\Delta E$ is a function of the stopping power, the specific ionization, and the ion yield,

$$V = \frac{\Delta P}{\Delta E} C \left[S, K, \frac{M}{I} \right]$$

C is a constant independent of the nature of the gas. All these data are well known for ordinary ammonia. A very careful determination of the ion yield has been made by A. Luyckx (5). In the case of the deutero-ammonias S can be determined by Glasson's law, giving the stopping power as a function of the atomic number: this gives $S_{NH_3} = S_{ND_3}$. No determination of k_{ND_3} has yet been made, but as the specific ionization varies for simple compounds between rather restricted limits one can consider the specific ionization of proto-ammonia and deutero-ammonia as being practically equal. The fact that the rate of polymerization is the same for proto-acetylene and acetylene-d_2 (4) seems to justify this assumption. It is thus safe to admit that the ion yields are very closely in the same ratio as the rate of reaction. The fact that this ratio, close to one at low temperature, rises with increasing temperature is in striking contrast with the reactions where the rate of reaction is determined by the activation energy. It has been shown that the photochemical reaction of ammonia is a component of decomposition and partial recombination. This is most probably also the case in the radiochemical reaction. The lower ion yield, and especially its slower rise with temperature, cannot be ascribed to a more efficient recombination in the case of ammonia-d_3, its activation of formation being higher than for ordinary ammonia. The lower ion yield has thus to be ascribed to the decomposition process itself.

No satisfactory explanation is at hand, but the increase in ion yield with temperature for both ammonias points towards a chain-like mechanism, which is best explained by admitting the clusters formed by the molecules around an ion as reaction center. It is likely that it is the difference in growth in this chain, determined by the activation energy of the decomposition, which controls the ratio of the reaction rates.

SUMMARY

The rate of decomposition of ammonia-d_3 was compared with the rate of decomposition of ordinary ammonia and found to be inferior, to rise more slowly with increasing temperature, and, at constant temperature, to increase with decreasing deuterium content.

I wish to express my heartiest thanks to Professor S. C. Lind, Director of the School of Chemistry of the University of Minnesota, for his advice and for placing his laboratory and the necessary amount of radon at my disposal. My thanks go also to Professor Hugh S. Taylor of Princeton University for kindly supplying me with the necessary quantity of deuterium oxide.

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THE DETERMINATION OF CONTACT ANGLES FROM MEASUREMENTS OF THE DIMENSIONS OF SMALL BUBBLES AND DROPS. I

THE SPHEROIDAL SEGMENT METHOD FOR ACUTE ANGLES[1]

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INTRODUCTION

The present methods of measuring contact angles all require that the solid material be obtainable in some special shape, such as a flat plate or capillary tube. Many surfaces, for example, those of plant materials, occur in irregular forms and must be dealt with *in situ*, because of the inhomogeneity of the body. The chief value of the method herein described is that its applicability is largely independent of the form of the solid surface.

Some of the earliest determinations of contact angles were made from measurements of the dimensions of bubbles and drops. The work has been confined to large drops, but the use of very small drops may be shown to possess several advantages: (1) Small drops may be applied successfully to small plane areas in an irregular surface or even to surfaces with an approximately constant degree of curvature. (2) Small drops show a much greater variation in height for small variations in magnitude of contact angle than do large drops. Accordingly, this dimension does not have to be measured with such extreme accuracy as is necessary with large drops. (3) Small drops assume the advancing angle of contact, while larger drops exhibit a fluctuating angle of contact varying roughly between the advancing and receding angles.

Other generally applicable means of measuring contact angles are the various modifications of the tilting plate method (1), and methods depending upon visual observation of the image of a drop, bubble, or meniscus projected upon a screen or photographic plate (7, 8, 3). It may be noted that in each of these methods the contact angle is measured at a single point on the surface. Such a procedure is somewhat unsatisfactory for

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[1] Approved by the Director of the New York State Agricultural Station for publication as Journal Paper No. 44.

working with naturally occurring objects having variable surface properties. The proposed method has the advantage of yielding a value for the contact angle which is the integral of the sum of all the separate angles along the circumference of the drop.

THEORY OF THE SPHEROIDAL SEGMENT METHOD

The principle of the spheroidal segment method is based upon the fact that the shape of a small drop of liquid having an acute angle of contact is only slightly affected by the influence of gravity. Consequently, the surface will be nearly spherical, and as a first approximation the drop may be considered to be a segment of a sphere.

The angle between the horizontal plane through the base of the drop and the tangent to the spherical surface at the point of contact is

$$\theta = 2 \tan^{-1} (h/x) \qquad (1)$$

where h is the greatest height of the drop and x is the radius of the base of segment. The distance x is easily measured on a scale in the eyepiece of a low power microscope, but the value of h is usually much smaller and more difficult to measure. This is especially true in the case of small angles on a surface which is not perfectly plane. Another difficulty is the fact that small drops evaporate very rapidly if the surrounding vapor is not in equilibrium, a condition which is difficult to accomplish and even more difficult to maintain.

The problem may be solved by substituting the volume for the height as a measurable dimension of the drop. The volume of a number of equally formed drops may be measured in an auxiliary reservoir and such measurements will be entirely independent of the shape of the solid surface. Furthermore, the volume measurement is made at the time the drop is first formed and is unaffected by subsequent changes caused by evaporation. It was observed experimentally that an evaporating drop maintained its original radius long after its other dimensions, such as height, volume, and contact angle, had been considerably reduced.

Thus from an experimental point of view, it appeared highly desirable to determine the contact angle from measurements of the radius and volume of the drop. This may be done by expressing the value of h in equation 1 as a function of the radius and volume of a spherical segment. The equation relating these quantities is

$$h^3 + 3hx^2 = 6(V/\pi) \qquad (2)$$

No simple algebraic expression for h in terms of x and V can be obtained, however. The solution of the cubic equation leads to a result in the form of two slowly convergent infinite series.

A preferable procedure is to transform equation 2 into the dimensionless form

$$(\pi/6)\,(h/x)^3 + (\pi/2)\,(h/x) = V/x^3$$

and tabulate numerical solutions of h/x in terms of V/x^3. Table 1 contains the values of h/x corresponding to values of V/x^3 from 0 to 2.0944, this being the range within which the angle remains acute.

TABLE 1

Related values of V/x^3 and h/x

V/x^3	h/x	V/x^3	h/x
0.0	0.0000	1.1	0.6206
0.1	0.0636	1.2	0.6656
0.2	0.1267	1.3	0.7089
0.3	0.1887	1.4	0.7504
0.4	0.2495	1.5	0.7904
0.5	0.3085	1.6	0.8288
0.6	0.3657	1.7	0.8659
0.7	0.4208	1.8	0.9016
0.8	0.4738	1.9	0.9361
0.9	0.5248	2.0	0.9695
1.0	0.5737	2.1	1.0018

TECHNIQUE

The solid to be investigated was imbedded on a paraffined glass plate. The liquid was placed in a short length of glass tubing, one end of which had been drawn out into a very fine capillary. A spiral in the capillary tube facilitated the manipulation of the tip. Drops of the liquid were formed slowly on the tip by gravitational force. By touching the glass tip to the solid surface at definite time intervals, drops of a constant and reproducible size were detached. Ten or more drops were measured at a time so that each determination yielded a truly average result. To minimize evaporation the solid and supporting plate were enclosed in a low form weighing bottle. The cover of this bottle was fitted with a window of optically plane glass. The diameters of the drops were observed through this window in the ocular scale of a low power microscope. The volume of liquid used for a given number of drops was obtained by measuring the difference in height of the liquid in the upper part of the glass tube before and after the drops were removed. Since the diameter of the tube was known, the cylindrical volume could be calculated.

In this investigation a tilting plate method and a direct observation method were used in order to check the measurements made by the spheroidal segment method. The procedure used in the tilting plate method was that of Adam and Jessop (1). In the visual observation method the apparatus was arranged so that the drop could be viewed directly in a microscope. The eyepiece was fitted with an accurately centered cross-line micrometer disc and a pointer which indicated the angular measure on a scale fastened around the draw tube of the microscope. The glass tip on which the drop formed was allowed to remain on the surface under examination, so that expanding and contracting drops could be produced by changing the air pressure at the other end of the glass tube.

TABLE 2

Effect of drop size upon the contact angle

Distilled water on apple wax

RADIUS OF DROP	VOLUME OF DROP	CONTACT ANGLE CORRECTED
cm.	*cm.*^{3}	
0.1562	0.00365	58°
0.1212	0.00142	50°
0.0773	0.00039	53°
0.0687	0.00038	66°
0.0663	0.00041	74°
0.0601	0.00046	90°20′
0.0560	0.00035	88°30′
0.0418	0.00015	89°30′
0.0390	0.00012	88°50′

TABLE 3

Comparison of contact angles obtained by different methods

SYSTEM	METHOD	ANGLE OF CONTACT	
		Advancing	Receding
Distilled water on azobenzene	Spheroidal segment	89°	
	Tilting plate	90°	62°
	Direct observation	92°	64°
0.05 per cent soap solution on paraffin	Spheroidal segment	48°	
	Tilting plate	48°	27°
	Direct observation	49°	30°
Distilled water on apple wax	Spheroidal segment	89°	
	Tilting plate	87°	62°

DISCUSSION OF RESULTS

Bartell and Hatch (2) found that a series of fairly large drops detached from a capillary tip formed widely different angles of contact on the same surface. This observation is confirmed by the results contained in the upper portion of table 2. But it is apparent that if the drop is made small enough, the angle attains a constant maximum value. In table 3 it is shown that this maximum is the advancing contact angle.

It has been shown (6, 9) that both expanding and contracting drops or bubbles may be caused to assume an equilibrium contact angle by tapping the support. This is true only for large drops, for vibration had no effect upon the advancing angles formed by small drops. Recent work has seemed to indicate that advancing and receding angles are themselves equilibrium angles for the surface under each of two different conditions (4).

From the foregoing it appears that the ease with which a drop may be made to spread further over a solid surface after having formed the advancing contact angle depends largely upon the drop size. The hydrostatic pressure due to the weight of the drop is exerted in the direction of further spreading. The capillary pressure within the drop is opposed to any extension of the liquid air surface. Since this pressure is inversely proportional to the radius of curvature, it will be greater in small drops. Hence with increasing drop size both the hydrostatic and capillary forces favor the probability of irregular extension of the drop.

CORRECTION FOR THE EFFECT OF GRAVITATIONAL FORCE ON THE FORM OF THE DROP

In the past considerable discredit has been cast upon sessile drop methods because unwarranted assumptions were made in the development of the mathematical equations to describe the form of the capillary surface. Therefore, in order that the proposed method may be employed with confidence, it is necessary to examine critically the effect of gravitational force upon the shape of the drop. The formulation of a correction term to compensate for this deviation from the spherical form would serve not only to evaluate the error due to this source, but also to determine the range of conditions within which the error is sufficiently small so that it may be ignored.

Consider a drop of liquid resting upon a solid surface *OP* under the influence of gravity and surface tension. In figure 1 the solid lines *PR* and *PR'* are the actual forms of two drops making contact angles of θ and θ' with *OP*. The dotted lines *PQ* and *PQ'* represent spherical surfaces and are the forms which the drops would assume if the gravitational force were removed. The surfaces *PQ* and *PR* have a common tangent *PM*, and *PQ'* and *PR'* also have a common tangent *PM'*.

The measured quantities are x and V, where V is the volume generated by rotating the area *OPR* about the *OR* axis. The equation for the contact angle requires that the volume be enclosed by a spherical surface. A spherical surface *PQ'* can be constructed such that the volume under *PQ'* is equal to that under *PR* (the true volume of the drop). This volume is used to calculate h, and the value of h/x thus obtained yields a value of $\theta'/2$ or θ' which is somewhat less than the true angle of contact θ.

By evaluating the small distance e, the true contact angle may be found from the equation

$$\tan(\theta/2) = (h + e)/x \tag{4}$$

In order to calculate e we need to have given the approximate angle of contact θ', the radius x of the drop, and the capillary constant a of the liquid. From θ' and x the volume V' of the spherical segment POQ' may be calculated by geometrical methods. For the same angle θ', the volume of the actual drop POR' may be calculated from the tables of Bashforth and Adams (5). Let the difference between the two volumes be $\Delta V' = V_{POQ'} - V_{POR'}$. If $(\theta - \theta')$ is small, $\Delta V'$ will be very nearly equal to $\Delta V = V_{POQ} - V_{POR}$. Since by construction $V_{POR} = V_{POQ'}$,

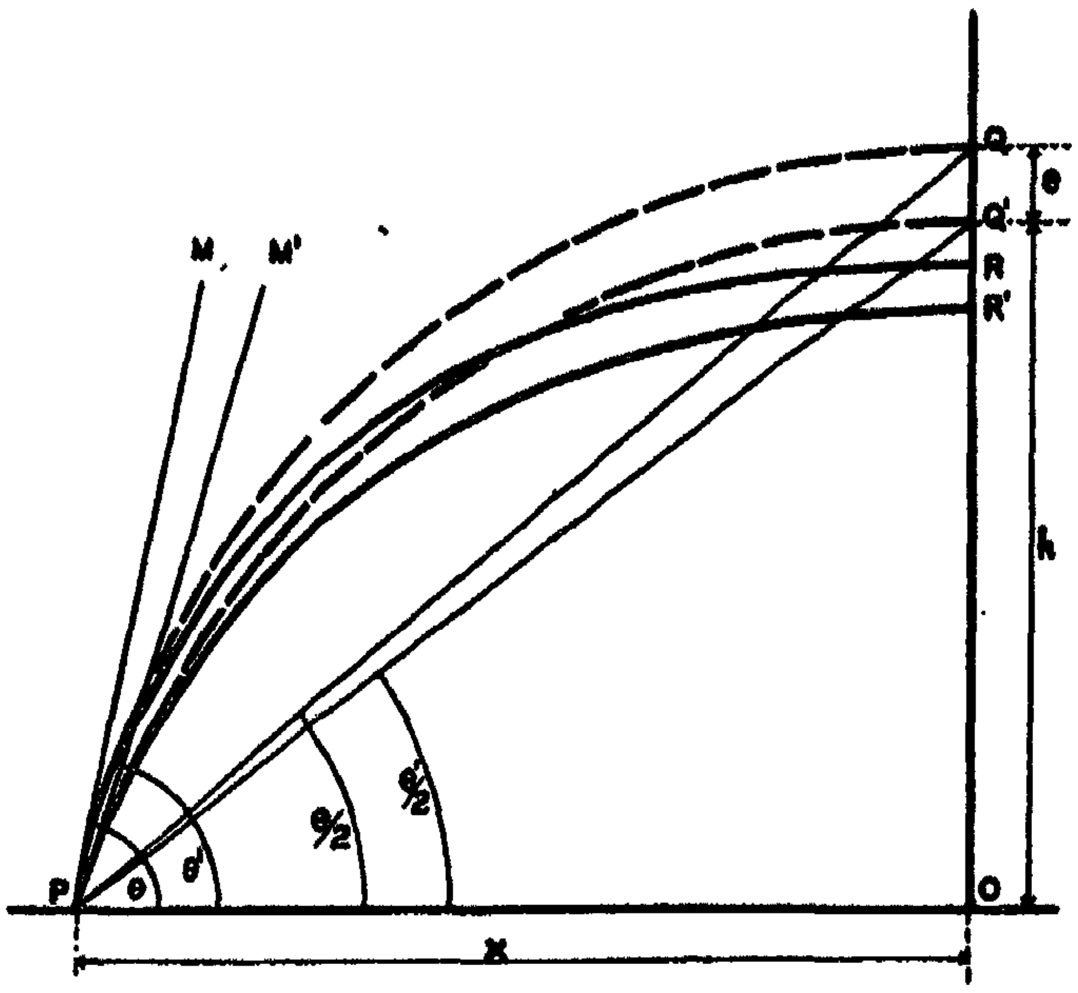

FIG. 1. Outline of a drop of liquid resting upon a solid surface under the influence of surface tension and gravity.

$$\begin{aligned}\Delta V &= V_{POQ} - V_{POQ'}\\ &= (\pi/6)\,[(h + e)^3 + 3x^2(h + e) - (h^3 + 3x^2h)]\end{aligned}$$

Since e is very small, the term e^3 may be ignored and the equation reduces to

$$e^2h + e(x^2 + h^2) - 2\Delta V/\pi = 0 \tag{5}$$

The general solution of the quadratic equation for e may be expressed in the form

$$e = -\left(\frac{x^2 + h^2}{2h}\right) \pm \left(\frac{x^2 + h^2}{2h}\right)\left[1 + \frac{8h\Delta V}{\pi(x^2 + h^2)^2}\right]^{1/2}$$

The terms within the brackets may be expanded in series according to the binomial theorem. After simplifying and expressing in numeric form, the equation becomes

$$\frac{e}{x} = \frac{2\Delta V/\pi x^3}{[1 + (h/x)^2]^{-1}} - \frac{(2\Delta V/\pi x^3)^2(h/x)}{[1 + (h/x)^2]^{-3}} + \frac{2(2\Delta V/\pi x^3)^3(h/x)^2}{[1 + (h/x)^2]^{-5}} - \cdots \quad (6)$$

TABLE 4

Related values of θ', x/a, and $\Delta V/x^3$

Values of $\Delta V/x^3$ are given in the body of the table for the corresponding values of θ' and x/a along the margins

θ'	x/a				
	0.1	0.2	0.3	0.4	0.5
90	0.017	0.041	0.085	0.143	0.208
85	0.011	0.029	0.062	0.105	0.154
80	0.008	0.021	0.046	0.078	0.115
75	0.006	0.016	0.034	0.059	0.088
70	0.004	0.012	0.026	0.045	0.068
65	0.003	0.009	0.020	0.035	0.053
60	0.003	0.007	0.016	0.027	0.041
50	0.002	0.005	0.010	0.017	0.026
40	0.001	0.003	0.006	0.011	0.016
30	0.000	0.002	0.004	0.007	0.011
20	0.000	0.001	0.002	0.004	0.006
10	0.000	0.000	0.001	0.002	0.003

Substituting this value of e/x in equation 4, one obtains

$$\tan(\theta/2) = \tan(\theta'/2) + (2\Delta V/\pi x^3)\cos^2(\theta'/2) - (2\Delta V/\pi x^3)^2 \tan(\theta'/2)\cos^6(\theta'/2) + \ldots\ldots \quad (7)$$

The series is convergent if

$$[(8\Delta V/\pi x^3)\tan(\theta'/2)\cos^4(\theta'/2)]^2 < 1$$

It is apparent that no error need be involved in the previous assumption that $\Delta V' = \Delta V$, since a more exact value of ΔV may be obtained by successive approximations to the value of θ. Practically, the first approximation is well within the experimental error.

The relative magnitude of the correction terms in equation 7 may be shown by means of an example. Suppose a drop of water to have the following characteristics: surface tension, 72.8 dynes per centimeter; radius, 0.1 cm.; contact angle, 90°. Then $V = 6.5 \times 10^{-5}$ cm.^{3}, and the total correction due to the influence of gravity is +1°10′. In equation 7 the error in ignoring all correction terms beyond the first is −0°0′44″. If the angle of contact is reduced to 60°, the radius and surface tension remaining the same, the total correction is only +0°29′. These calculations make it apparent that for the present purpose the gravitational effect is of little practical importance in measuring small contact angles.

CORRECTION FOR THE CURVATURE OF THE SOLID SURFACE

The application of the method can be extended to include solid surfaces with an approximately constant degree of curvature. Two corrections to the determined angle of contact must be made. First the tangent to the solid surface at the point of contact is inclined at an angle to the horizontal plane through the base of the drop. This additive correction is partially counterbalanced by that due to the small solid segment which projects above the base of the drop.

TABLE 5

Corrections for curvature of the solid surface

$R/x = 20$

θ	ANGULAR CORRECTION +2°52′	
	Volume correction	Net correction
90	−0°41′	+2°11′
75	−1°7′	+1°45′
60	−1°35′	+1°17′
45	−2°3′	+0°49′
30	−2°27′	+0°25′
15	−2°45′	+0°7′
0	−2°52′	+0°0′

If x is the radius of the drop, and R is the radius of curvature of the solid surface, the angular correction ϕ is given by the equation

$$\tan \phi/2 = R/x - \sqrt{(R/x)^2 - 1}$$

The change in contact angle caused by subtracting the volume of the solid segment from the volume of the drop may be calculated from ϕ and x according to the methods previously given (equations 1 and 3 and table 1). While the angular correction depends only upon R/x, the volume correction is also a function of the contact angle. Table 5 shows the relative values of these corrections when $R/x = 20$. The angular correction is almost exactly inversely proportional to R/x, and the volume correction deviates only slightly more from the linear relationship. Hence for practical purposes, table 5 may be used for any value of R/x. It is only necessary to multiply any given correction by the appropriate value of $\frac{20}{R/x}$.

SUMMARY

A method has been devised for the determination of acute angles of contact which is largely independent of the form of the solid surface. It was shown that the contact angle is a function of the radius and volume of a small spherical drop of liquid.

An equation has been developed for evaluating the effect of gravitational force upon the form of the drop.

The validity of the method has been checked by repeating the determination of the contact angles upon the same materials by two different methods. Satisfactory agreement was obtained in all cases.

The author wishes to express his appreciation to Professor F. E. Bartell for much helpful advice.

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THE DETERMINATION OF CONTACT ANGLES FROM MEASUREMENTS OF THE DIMENSIONS OF SMALL BUBBLES AND DROPS. II

THE SESSILE DROP METHOD FOR OBTUSE ANGLES[1]

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INTRODUCTION

It has been suggested in a previous communication (3) that widely variant surface energies may exist at closely adjoining points on a surface. Well-substantiated theory as to the surface structure of solid catalytic materials is in accord with this view (7). The "active patches" on the catalytic surfaces are an extreme example of irregularity in the surface energy, but it seems reasonable to suppose that such irregularities may exist to a lesser degree in nearly all ordinary surfaces. Photographic evidence in support of this proposition appears in the work of Wark and Cox (9), who found that the same air bubble under a mineral surface wet with water might have an angle of contact on the right side different from that on the left.

Instead of measuring the contact angle directly, it may be calculated from the dimensions of the drop. The angle so obtained may be regarded as the integral of the sum of all the various contact angles existing along the circumference of the drop. Thus each determination yields an average result not unduly influenced by irregularities at a given point on the surface.

For precise determinations the method should have an especial advantage over the usual procedure of direct measurement, because the error in personal judgment involved in drawing the tangent to the curved drop surface at the point of contact is eliminated. This error becomes increasingly important as the contact angle approaches 180°, while the dimensions of the drop may be measured with the same degree of accuracy as before.

If the image of the drop is recorded on a photographic plate, the capillary

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constant of the liquid may be determined, without any additional experimental data, by the method of Dorsey (2). This serves as a valuable check upon the purity of the liquid-air interface and upon the reliability of the contact angle determination.

THEORETICAL

The tables of Bashforth and Adams (1) give the necessary information for calculating the contact angle from the dimensions of the drop. For the present purpose a considerable rearrangement of their data was necessary, because the units tabulated by them cannot be readily calculated from experimental data. In choosing other units, those have been selected which may be measured precisely or which may be readily calculated from other experimental data.

The most easily measured dimensions of the drop represented by figure 1 are the total height z and the radius r. These two lengths determine the size of the drop. Unfortunately, the contact angle depends not only upon the size of the drop but also upon its shape. In a drop of given size, the shape may be related to the capillary constant a of the liquid, or to the radius of curvature at the apex of the drop (b in figure 1). The contact angle is thus a function of two independent variables. Hence the contact angles contained in the body of table 1 must be related to both the size factor z/r listed in the vertical column at the left and to the shape factor r/b arranged in the horizontal column at the top of the table.

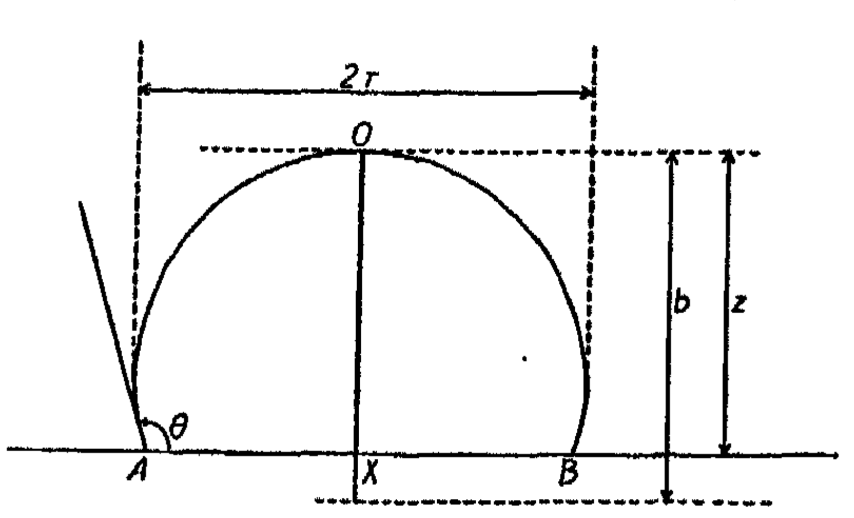

FIG. 1. Outline of a drop *AOB* resting upon the horizontal plate *AB*

The procedure employed in making up table 1 was as follows: The original Bashforth and Adams tables contain, for each 5° interval of θ, values of z/b corresponding to given values of r/b and $\beta = 2b^2/a^2$. The values of z/r were found by dividing z/b by the corresponding value of r/b. Then for each value of θ, the values of z/r corresponding to equal increments of r/b were obtained by numerical interpolation. For each even value of r/b so obtained, the values of θ corresponding to equal increments of z/r were determined. This could be done with sufficient accuracy by means of graphical interpolation. The values of θ are correct to the nearest 0.1°. This error is well within the accuracy of most experimental data.

The calculations for the factor r/b have been extended only to $r/b = 0.90$. This is far enough to include a drop of water nearly 4 mm. in diameter.

TABLE 1

Values of θ corresponding to related values of z/r and r/b

$\frac{z}{r}$	$\frac{r}{b}$										
	1.00	0.99	0.98	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.90
0.90										90.6	91.5
0.95					90.1	90.9	91.8	92.7	93.7	94.6	95.6
1.00	90.0	90.8	91.7	92.5	93.5	94.4	95.4	96.4	97.5	98.7	99.8
1.05	92.9	93.8	94.8	95.7	96.8	97.9	99.1	100.4	101.6	102.9	104.2
1.10	95.7	96.8	97.9	99.1	100.3	101.6	102.9	104.3	105.7	107.3	108.8
1.15	98.6	99.9	101.1	102.4	103.9	105.3	106.8	108.5	110.1	111.9	113.7
1.20	101.5	102.9	104.3	105.9	107.5	109.1	110.9	112.8	114.7	116.8	118.9
1.25	104.5	106.0	107.6	109.4	111.2	113.1	115.1	117.3	119.6	122.0	124.6
1.30	107.5	109.2	111.0	113.0	115.1	117.3	119.7	122.2	124.9	127.8	131.0
1.35	110.5	112.5	114.6	116.8	119.2	121.8	124.6	127.6	130.8	134.3	138.3
1.40	113.6	115.8	118.2	120.8	123.5	126.5	129.9	133.5	137.6	142.0	147.3
1.45	116.7	119.3	122.1	125.1	128.3	131.8	135.8	140.3	145.5	152.1	161.4
1.50	120.0	123.0	126.1	129.8	133.4	137.7	142.8	148.9	157.1	173.3	
1.55	123.4	126.5	130.4	134.6	139.2	144.8	151.2	161.8			
1.60	126.9	130.8	135.1	140.1	146.1	153.8	167.0				
1.65	130.5	135.1	140.3	146.7	155.0	171.6					
1.70	134.4	139.8	146.4	155.1	174.2						
1.75	138.6	145.1	153.9	171.5							
1.80	143.1	151.4	165.9								
1.85	148.2	159.8									
1.90	154.2										
1.95	161.8										
2.00	180.0										

It has been shown (3) that greater precision in contact angle measurements can be attained by the use of small drops. Hence there is nothing to be gained by working with larger drops of correspondingly flatter shape.

The quantity b used in table 1 cannot be experimentally determined except by optical methods unsuited to the attainment of the requisite degree of accuracy. It may be readily calculated, however, from the value of the capillary constant a. The simplest relation between a and b is given by the equation

$$h = \frac{a^2}{b} \tag{1}$$

where h is the height of rise of the liquid in a capillary tube of unit radius. By substituting this value of h in Rayleigh's equation (4) for a in terms of r and h, and transforming, a solution for b is obtained in the form of an infinite series, as follows:

$$b = r + \frac{r^3}{3a^2} - \frac{2r^5}{9a^4}(3 \log 2 - 2) + \frac{r^7}{27a^6}(78 \log 2 - 53) - \cdots \tag{2}$$

Verschaffelt (8) has developed equation 2 in this form as far as the third term on the right-hand side of the equation, and has pointed out its usefulness for calculating the value of b. By taking known values of b from the Bashforth and Adams tables, substituting the corresponding values of r and a in equation 2, and solving for b, the error involved by leaving off successive terms of the infinite series may be calculated. This procedure reveals an interesting fact which no one appears to have noticed heretofore. The last two terms in equation 2 add very little to the accuracy of the approximation even when r/a is small. For larger values of r/a, these latter terms actually increase the error beyond that existing after the calculation of the second term. The simplified equation

$$\frac{b}{r} = 1 + \frac{1}{3}\frac{r^2}{a^2} \tag{3}$$

is amply sufficient for the present purpose. For $r/a = 0.5$, the error in calculating b from equation 3 is 0.06 per cent, from equation 2 it is 0.05 per cent. These amounts are insignificant in comparison with the experimental error in determining the contact angle.

A further advantage in the use of equation 3 is that the value of a need be known only approximately. An error of 1 per cent in the determination of a produces an error of only 0.06 per cent in the value of b when $r/a = 0.3$. The value of r/a must be determined with great precision only when θ approaches 180°. For smaller angles, the values of r/a and r/b have much less effect on the determination of θ.

Sugden (6) has published a table which may also be used for finding r/b when r/a is known.

EXPERIMENTAL

The apparatus necessary to measure the dimensions of the small drops and bubbles consists of the following items. A low-power microscope is equipped with a filar micrometer eyepiece or a camera attachment. The solid surface requires a holder adjustable by rack and pinion movements in three directions. A microburet of the type used by Rehberg (5) is needed to form the very small bubbles and drops. The solid holder and the tip of the microburet project downward through the glass cover into an absorption cell with plane glass sides. The cell holds the liquid into which air bubbles are blown, and, in the case of drops in air, it protects the surface from contamination by dust particles. Rapid evaporation of the very small drops is prevented by previously saturating the air within the cell with the vapor from other drops of the same liquid. A comparator or travelling microscope is convenient for measuring the small distances on the photographic plates, particularly if the capillary constant is to be determined by Dorsey's method (2).

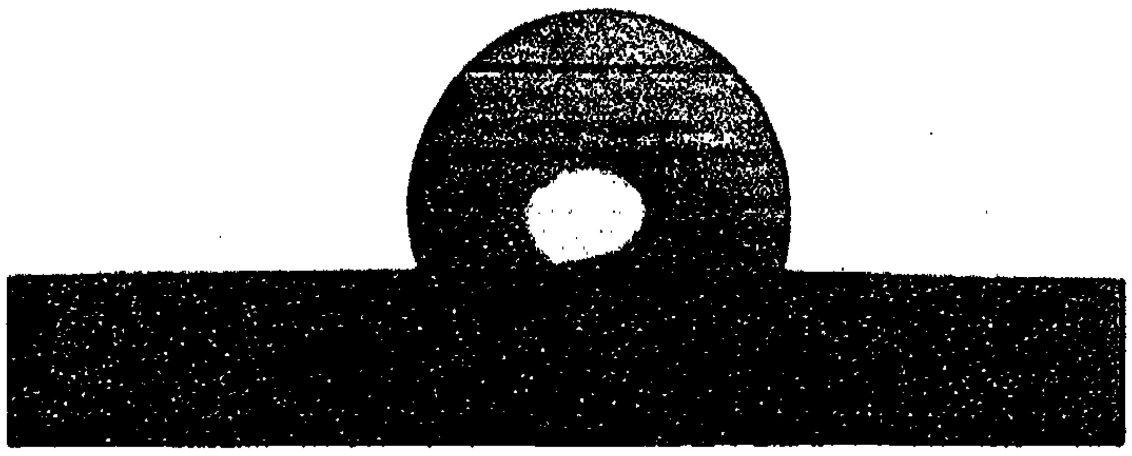

FIG. 2. Water drop on paraffin solidified in moist air. $z/r = 1.281$; $r/b = 0.9919$; θ (calculated) $= 107.7°$; $\theta_l = 107.5°$; $\theta_r = 102.8°$.

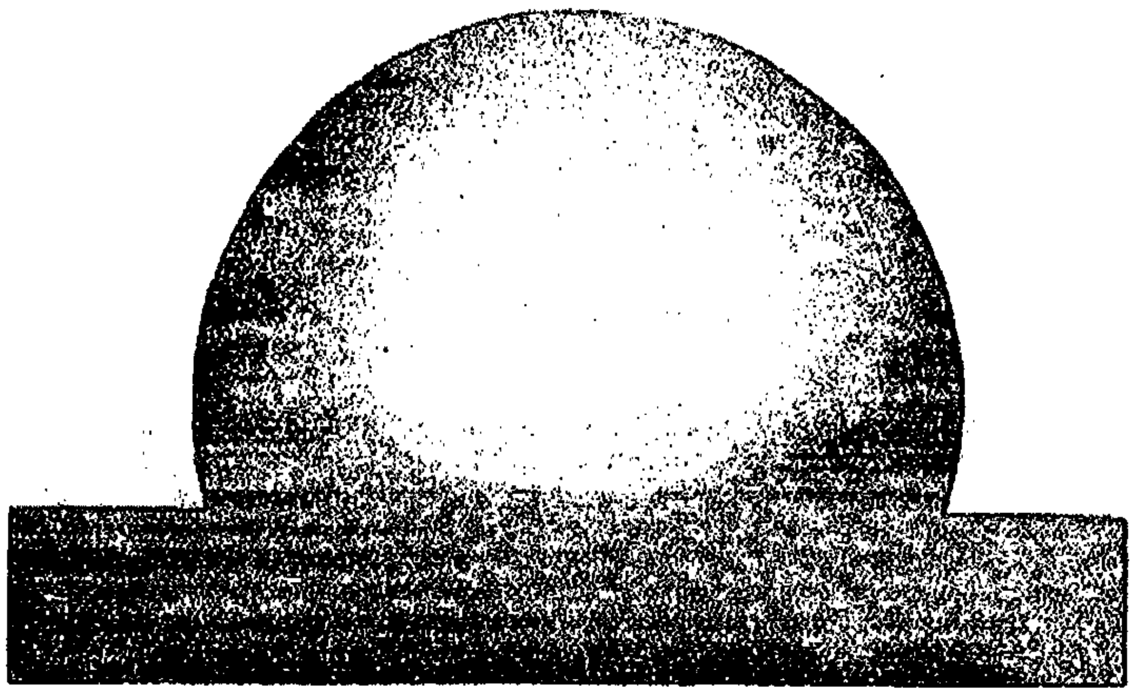

FIG. 3. Water drop on paraffin solidified in moist air. $z/r = 1.239$; $r/b = 0.9768$; θ (calculated) $= 107.4°$; $\theta_l = 107.1°$; $\theta_r = 107.3°$.

The following cases will serve to illustrate the use of the proposed method of determining contact angles. The paraffin surfaces shown in figures 2 and 3 were solidified in air of 60 per cent humidity and then kept for one hour in the cell containing saturated water vapor. The drop in figure 2 was selected as an extreme example of irregularity in a paraffin surface. *It is apparent that the low value of the contact angle on the right side of the drop is not characteristic of the surface as a whole.* The observed angle on the left side agrees well with the calculated value. Figure 3 shows

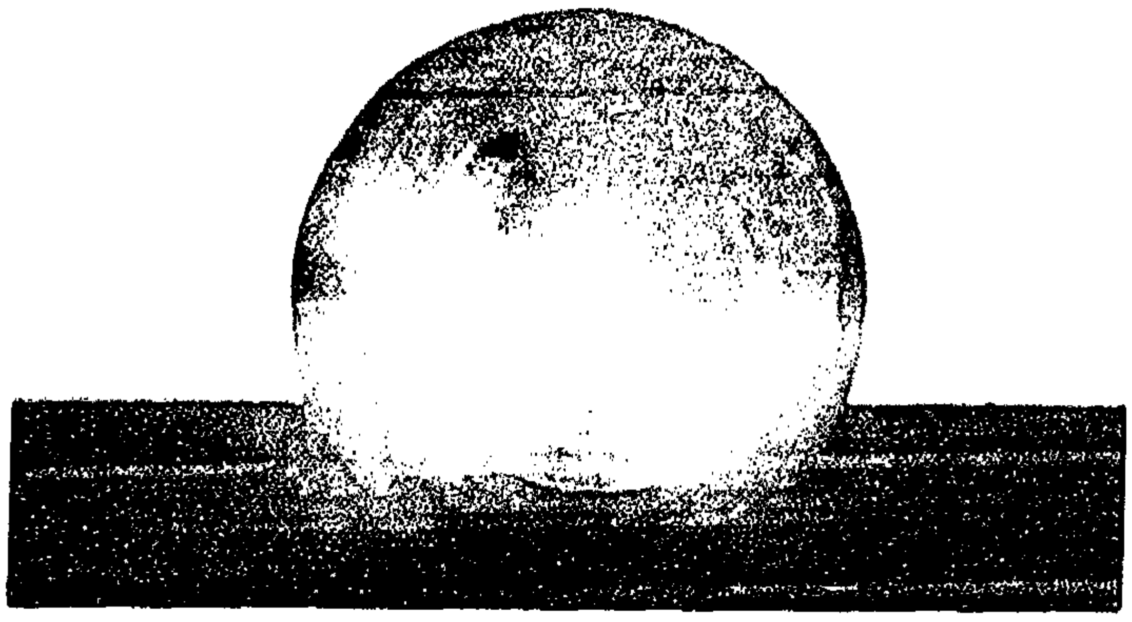

FIG. 4. Water drop on paraffin solidified in dry air. $z/r = 1.310$; $r/b = 0.9955$; θ (calculated) $= 108.9°$; $\theta_l = 109.8°$; $\theta_r = 108.0°$.

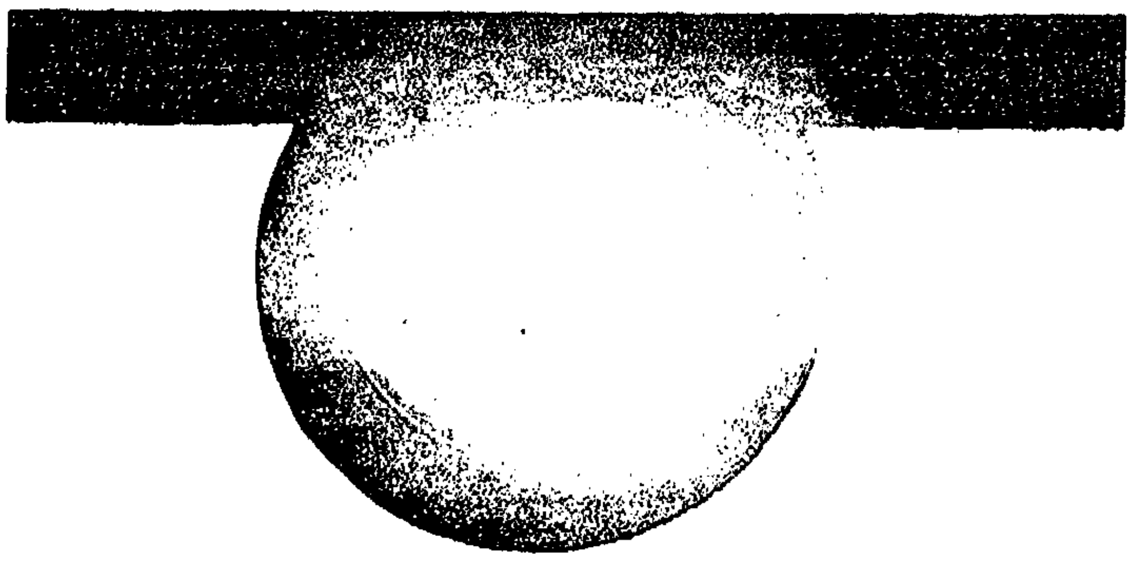

FIG. 5. Air bubble under paraffin immersed in 0.01 per cent soap solution. $z/r = 1.391$; $r/b = 0.9615$; θ (calculated) $= 180 - 122.4 = 57.6°$; $\theta_l = 57.8°$; $\theta_r = 57.0°$.

a much larger drop a little more than 2 mm. in diameter, while in figure 4 a fairly small drop of less than half that size is shown. In the latter case the paraffin was solidified in air dried over phosphorus pentoxide, and the photograph was taken immediately after the surface was placed in the absorption cell.

The method may be applied to bubbles as well as drops (figures 5 and 6). The paraffin surface is immersed in aqueous solutions of a proprietary spreading agent, and air bubbles are formed on the under side of the plate. The disadvantage of direct measurement is evident in figure 6. As the contact angle approaches 180°, it becomes increasingly difficult to draw the tangent to the curved surface at the point of contact. The dimensions z, r, and b may still be determined with the same degree of accuracy, however.

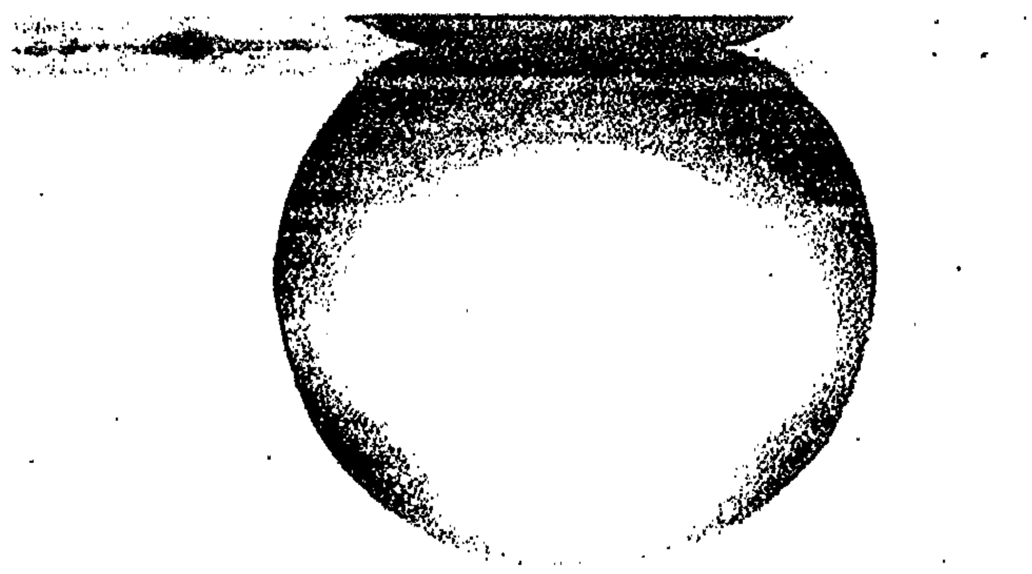

FIG. 6. Air bubble under paraffin immersed in 0.1 per cent soap solution. $z/r = 1.659$; $r/b = 0.3936$; θ (calculated) $= 180 - 180 = 0 \pm 0.5°$.

SUMMARY

A method has been proposed for determining obtuse contact angles from measurements of three dimensions of sessile drops of bubbles under a plate. These dimensions are the vertical height z, the horizontal radius r, and the radius of curvature b at the apex of the curved surface.

A simplified equation is given for calculating the value of b from that of the capillary constant of the liquid.

The proposed method is shown to have several advantages over the direct method of measurement with a protractor.

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ADSORPTION AT CRYSTAL-SOLUTION INTERFACES. IX

The Concentration of Foreign Substances in Solution Relative to the Quantity Adsorbed by the Host Crystal[1]

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A number of explanations have been offered from time to time to account for the adsorption of impurities by crystals, but no satisfactory theory has yet been completely developed to account both for the selective nature of this adsorption and for the modifications of habit engendered in the host crystal by the impurity.

A review of the literature relevant to this problem reveals three general types of papers: (a) those attempting to find relationships between the amount of adsorbed material in the crystal and its concentration in the mother liquor (2, 3, 7, 8, 9, 10, 11, 20, 21, 22, 27, 28, 30, 34); (b) those attempting to account for the modifications of habit produced in crystals that are grown in the presence of impurities (1, 16, 18, 19, 24, 32); and (c) those presenting a general theory of the adsorption of impurities by growing crystals. The explanations offered by Buckley (4) and by France and coworkers (5, 12, 13, 14, 23, 25, 26, 29, 35) have been compared in an earlier paper (35). It has been suggested also that adsorption of impurities leading to habit modification is due to the same cause as oriented overgrowth (17). A close relationship between mixed crystal formation, adsorption of impurities by crystals, and oriented overgrowth has been found by Bunn (6) in the conditions necessary for their occurrence. He points out that mixed crystals and crystals built up by a continuous adsorption of impurity differ only in degree, and that the condition necessary for strong adsorption is similarity of lattice structure and interatomic dimensions in specific planes only of the two substances involved. This condition is the same that is known to be necessary for oriented overgrowth of different crystals on one another. Royer (31) has reached similar conclusions. In addition he finds (a) that the ions of the oriented crystal which replace those of the crystal support must have the same polarity as the latter, and (b) that the mode of linkage must be the same for replaced and replacing ions.

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

The development of a successful general theory has been impeded by two factors,—namely, the failure of workers to base conclusions of a theoretical nature on a sufficiently wide and diversified selection of data, and the absence of quantitative studies. The second of these factors is the more important, for until quantitative data have been assembled the laws governing the adsorption of impurities and the resultant habit modifications cannot be correctly known.

Therefore the chief purpose of this investigation was to determine quantitatively the relation between the concentration of impurity in solution and the amount of impurity adsorbed by a crystal grown spontaneously under equilibrium conditions. The substances selected for study were alkali halide crystals grown in the presence of urea as impurity, urea grown in the presence of alkali halides, and crystals of barium and lead nitrates and of ammonium and potassium alums grown in solutions containing various dyes. The halides ammonium chloride, sodium chloride, potassium chloride, and potassium bromide were chosen because their crystal structure is well known, and because urea greatly modifies the habit of sodium chloride and ammonium chloride and has very little effect on potassium chloride and potassium bromide. The nitrate and alum crystals were grown in the presence of dyes as a continuation of work on habit modification previously carried out in this laboratory.

Alkali halide crystals were grown from saturated salt solutions made up to contain a range of concentrations of urea. Crystallization took place at room temperature (23°C.) in 3-inch crystallizing dishes provided with paper covers to keep out dust and air currents. The crystals were removed for analysis after approximately 5 per cent of the salt had crystallized out. They were washed once with water and dried at room temperature. The same procedure was followed with urea crystals grown in the presence of alkali halides and with nitrate and alum crystals obtained from solutions containing dye. Thirty-one sets of crystals were grown and analyzed, each involving on an average ten concentrations of impurity. In some cases several sets of crystals were grown and analyzed for the same pair of substances.

The number of moles of adsorbed impurity per mole of host crystal were determined in both the solution and solid phases for all crystallizations made. The crystals containing adsorbed dye were analyzed for dye content, using a Duboscq type of colorimeter. Analysis for halide present in urea crystals and in the ammonium chloride crystals contaminated with urea was made by titration with silver nitrate, using a dichromate indicator. The other alkali halide crystals containing urea were analyzed for urea content by a gas analysis method involving the reaction between urea and alkaline sodium hypobromite to produce nitrogen.

An ultramicroscopic examination was made of two solutions containing dyes, to observe any possible relation between the concentration of colloidal particles in the solution and the amount of dye taken up. X-ray powder spectrographs were made in several cases, in order to discover any change in lattice constants produced by the impurity. Optical examinations with a polarizing microscope were made of a number of crystals to observe the presence or absence of dichroism.

The data obtained disclose the following facts about the nature of the adsorption process.

(1) A plot of the number of colloidal particles observed ultramicroscopically against the concentration of dye in the solutions studied shows that a linear relation exists between the two quantities. On the other hand, the amount of dye taken up by the crystals obtained from these solutions plotted against the dye concentration follows a type of exponential curve which starts at a considerable distance from the origin (cf. curve 1, figure 1). It must therefore be concluded that in the crystals studied the amount of dye taken up is not related to the number of colloidal particles present in the dye-salt solutions. These results are in agreement with those obtained by one of us in earlier studies of a somewhat similar nature (14).

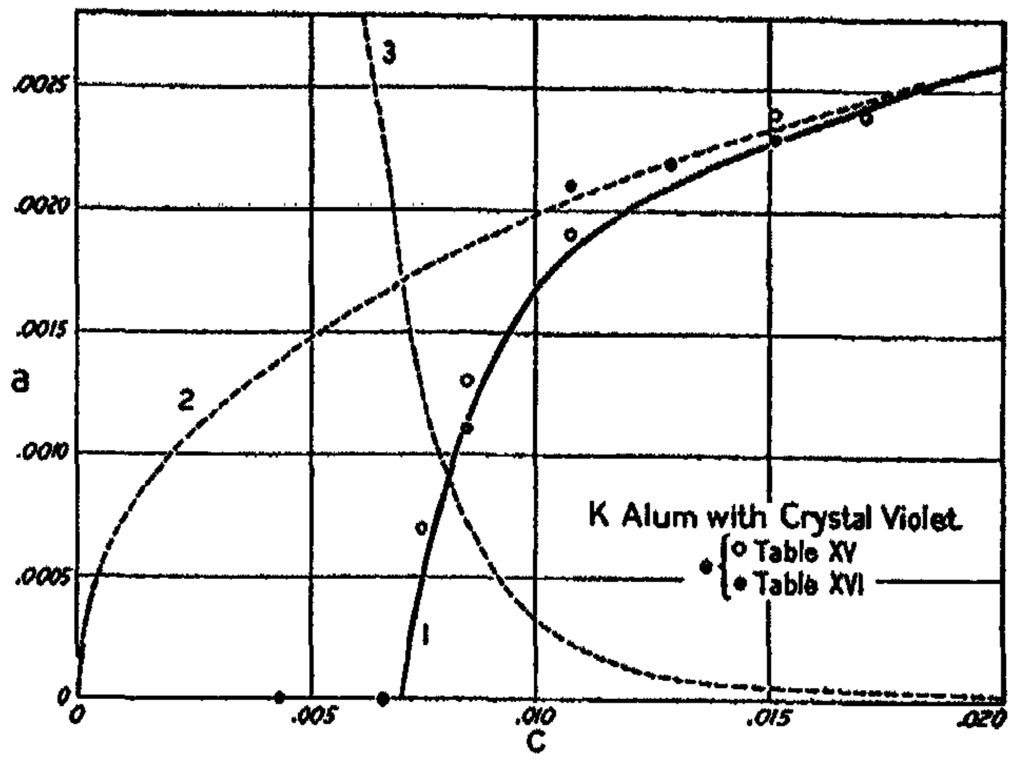

Fig. 1

(2) A careful checking of four x-ray powder spectrographs for the four pairs of substances (1) pure sodium chloride–sodium chloride + urea, (2) pure sodium chloride–sodium chloride + chromic chloride, (3) pure urea–urea + sodium chloride and (4) pure lead nitrate–lead nitrate + methylene blue showed that in all cases there was no displacement of the

lines produced by the contaminated crystals, and therefore no appreciable change in the lattice constant due to the adsorption of impurities. This interesting result is in agreement with work reported by earlier investigators (13, 33). The absence of lattice distortion may be due to (a) the presence of too little impurity to produce a perceptible distortion, (b) some type of interstitial adsorption such that the host crystal envelopes the molecules of impurity without alteration of its space lattice, or (c) similarity of the lattice constants in one plane of the host crystal to those in one plane of the foreign crystal so that deposition occurs in such a way that the similar planes coincide.

(3) Pronounced dichroism was observed in thirty-one out of thirty-two crystals of ammonium alum colored with Pontamine Sky Blue 6B, and a characteristic but less pronounced dichroism was shown by ammonium alum crystals colored with crystal violet. This dichroism may be accounted for by the assumption that the dye molecules are oriented with respect to themselves and to the face on which they are adsorbed. The color effects observed under the polarizing microscope lead to the view that the dye molecules were probably adsorbed with their long axes perpendicular to the cube faces of the alum crystals. Neither potassium nor ammonium alum crystals colored with dye No. 11 showed dichroism; several types of random distribution of dye molecules might lead to this absence of dichroism.

(4) Points shown in figures 1, 2, and 3 show typical results obtained when a, the concentration of foreign material deposited in the crystals expressed as moles of foreign material per mole of host crystal, is plotted against c, the number of moles of impurity per mole of crystal in the solution. The curves obtained in similar plots of thirty-one sets of crystallizations were tested to determine whether or not they were described by the more common adsorption equations, including the adsorption isotherm and Langmuir's equation for monomolecular adsorption of gases.

Figure 4, constructed from the same data as that in figure 1, shows that a curve is obtained instead of a straight line as required by the logarithmic form of the equation of the adsorption isotherm. Likewise a curve results (figure 5) instead of a straight line when the c/a and c values, obtained from a rearrangement of the Langmuir equation in which the concentration c is substituted for the pressure p, are plotted against each other. From figures 4 and 5 it would seem that something more than a simple adsorption process describable by either the adsorption isotherm or the Langmuir equation is involved when a dye is taken up from a solution by a growing salt crystal. Freundlich (15) has shown that the retardation of crystallization by varying quantities of foreign substances is expressed by an exponential of the same form as the adsorption isotherm. This would indicate that an adsorbed layer of impurity expressed by the adsorption isotherm is formed at the surface of a growing crystal. It is evident from the failure of the curves obtained in this study to pass through the origin (cf. figures 1 and 2 as typical examples) that either some condition exists or a process occurs during crystal growth which prevents, at least at low dye concentrations, the incorporation of the expected amount of dye in the growing crystal.

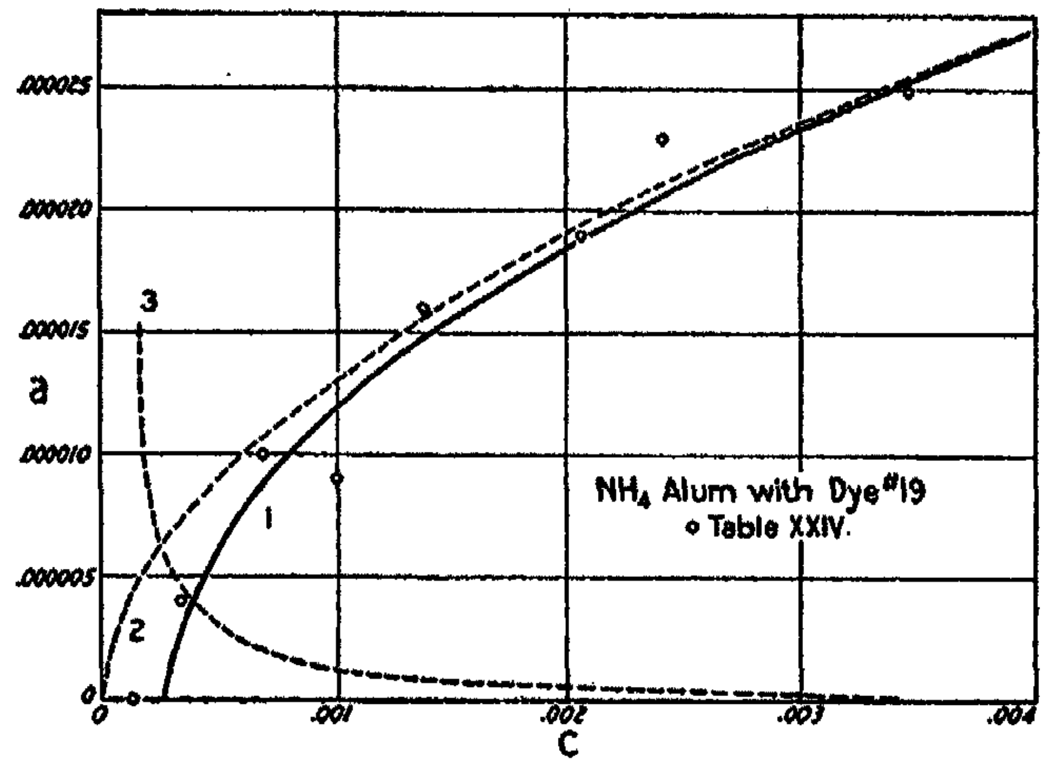

FIG. 2

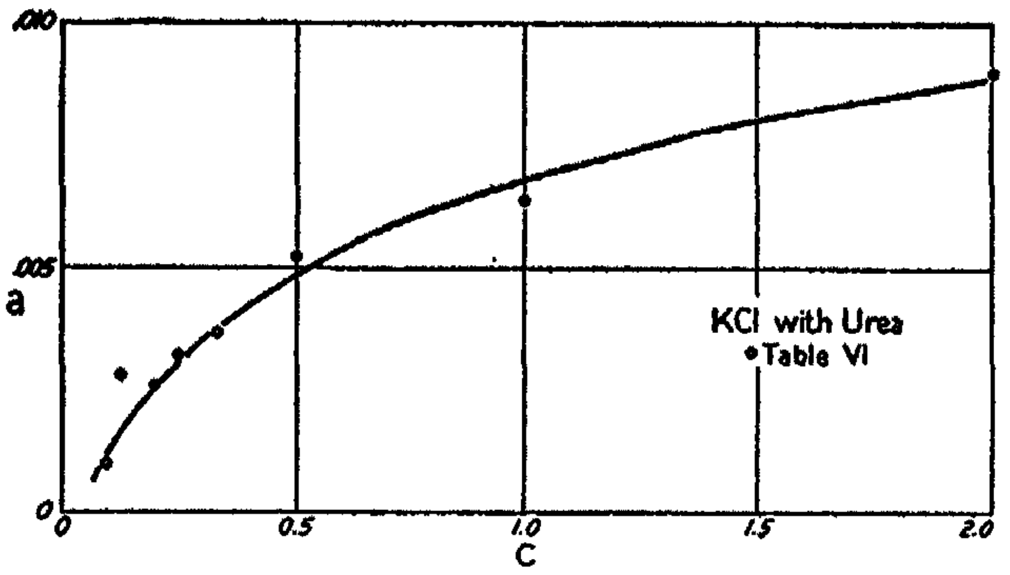

FIG. 3

An attempt was therefore made to find an empirical equation relating a and c, which would take into account this counter-adsorption process. It was assumed, partly from the appearance of the a–c curves (curves No. 1 in figures 1 and 2) and partly from the tendency of the log a–log c curves (figure 4) to become linear at high values of c and a, that the counter-adsorption process is significant only at low values. Values of k and $1/n$ were then found for the adsorption curve which reproduced the best smooth curve through the experimental points at higher concentrations. The lower part of the curve was then found to be obtainable by assuming that

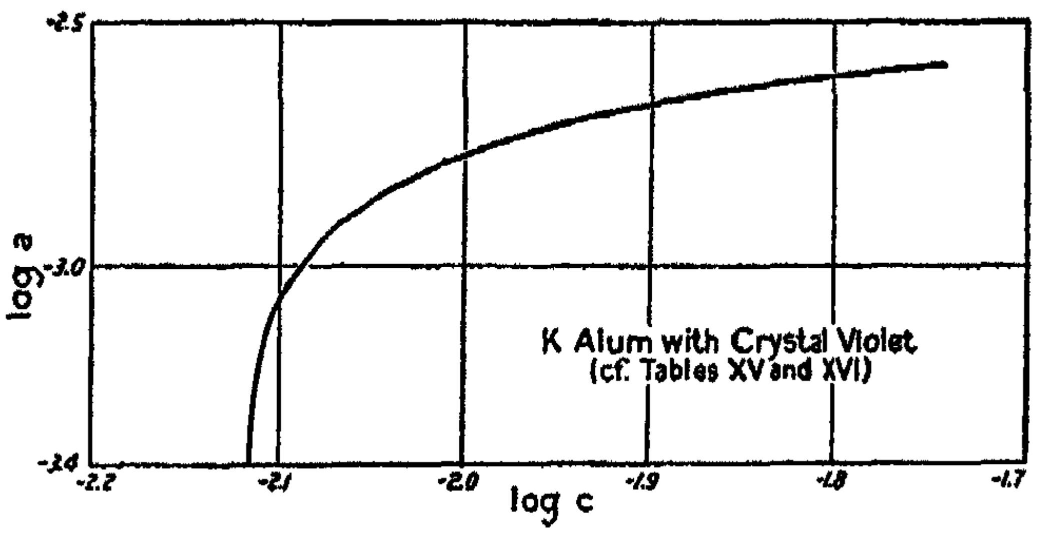

FIG. 4

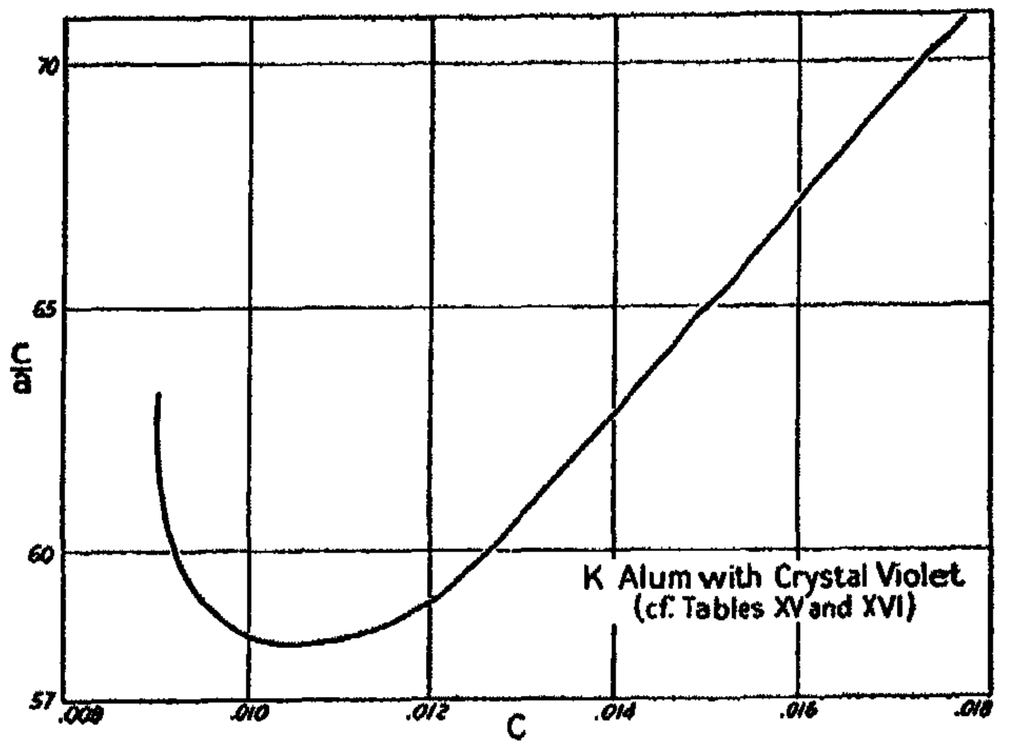

FIG. 5

the counter-adsorption process was represented by an expression of the form

$$a' = k'c^{-1/n'} \tag{1}$$

and that the experimental curve was the difference between an adsorption isotherm and this second exponential. Thus the experimental data are expressed fairly well in all cases by the relation

$$a = kc^{1/n} - k'c^{-1/n'} \tag{2}$$

The significance of the second term in the right-hand member of the equation is not completely evident; but it seems to indicate that whatever the nature of the counter-adsorption process, it is a function, primarily, of the dye concentration, is infinite at zero dye concentration, and rapidly approaches zero even at low concentrations. This conclusion, together with the results obtained in earlier work of the authors on the effect of stirring and growth ratios on the habit and dye adsorption of alum crystals (29), suggests the following explanation for the failure of the curves to pass through the origin. Those faces of a normally growing crystal having the stronger fields of force are the ones that experience the most rapid perpendicular displacement. As a result of this rapid growth there is a tendency to lower the concentration of the crystal ions in the layer of solution adjacent to the rapidly growing faces. Any effect acting to maintain a higher concentration of the crystal ions in this layer should result in an accelerated displacement of these faces. Thus in the case of potassium alum the growth ratio (100)/(111) was increased from 1.61 to 1.75 by rapid stirring. It would seem therefore that in the presence of an adsorbable dye the crystal takes up its own ions in preference to the dye as long as such ions are readily available. However, in the absence of a plentiful supply of its own ions the crystal will satisfy its growth forces by taking up adsorbable dye ions or molecules when the concentration of the dye adjacent to the rapidly growing face becomes sufficiently great relative to that of the crystal ions. The distance from the origin to the point of intersection of the curve with the c axis apparently represents the minimum dye concentration required to establish this condition.

In figures 1 and 2, curve 1 represents the values of a calculated from equation 2, curve 2 values from the equation of the adsorption isotherm, and curve 3 those from equation 1. It should be noted that equation 2 predicts that at high values of c the adsorption isotherm would fit the data; this was not always found to be true because of the precipitation of part of the dye at higher concentrations in some instances.

In the case of the systems alkali halides–urea it was not possible to obtain even approximately accurate values of the amount of foreign material adsorbed at low concentrations, and hence to extend the curve to zero adsorption and also to fit equation 2 unequivocally. Qualitatively, however, it is evident that the adsorption curves are similar to those for dyes adsorbed by salts (cf. figure 3), and it seems quite likely that equation 2 would fit if sufficient data were available at low concentrations of impurity to warrant its application.

One fact of interest with regard to the adsorption of urea by the alkali halides studied should be noted. In spite of the fact that ammonium chloride and sodium chloride crystals are much more modified in habit by the presence of urea, potassium chloride and potassium bromide crystals adsorb a larger quantity of this impurity.

SUMMARY

1. No relation was found between the number of colloidal particles of dye present in solution, and the amount of dye adsorbed by a given host crystal.

2. X-ray powder spectrographs of crystals containing adsorbed impurities showed the same lattice constants for impure as for pure crystals.

3. The dichroism observed in crystals containing adsorbed dye is accounted for by the assumption that the dye molecules are oriented with respect to themselves and to the face on which they are adsorbed. The color effects observed under the polarizing microscope in crystals of ammonium alum and dye No. 13 lead to the view that the dye molecules are adsorbed with their long axes perpendicular to the cube faces of the alum crystal.

4. The data for the adsorption of dye by alum and nitrate crystals failed to fit either the Langmuir or the adsorption isotherm equation, but were reproduced over most of the range by the equation

$$a = kc^{1/n} - k'c^{-1/n'}$$

5. The second term in the right-hand member of equation 2 indicates the occurrence of a counter-adsorption process. Examination of this term shows (a) that adsorption does not commence at $c = 0$ but at a value of c such that

$$kc^{1/n} = k'c^{-1/n'}$$

and (b) that $k'c^{-1/n'}$ possesses the value ∞ at $c = 0$ but falls off rapidly to zero at low values of c.

6. Equation 2 predicts that at high values of c an adsorption isotherm would fit the data within the limits of error, but this was not always found to be true because of the precipitation of part of the dye at higher concentrations.

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SPECTROSCOPIC ESTIMATION OF ADSORBED IONS[1]

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Theories of colloid stability, of the mechanism of coagulation, and of the charge on the colloid particle are all intimately related to the adsorption of ions. A knowledge of the total number and kinds of ions adsorbed by colloidal particles under given conditions would greatly assist in the understanding of colloidal behavior.

Attempts have been made to measure such adsorption by chemical analysis (12, 11, 2), but the concentrations to be measured are so small (usually from $0.0001M$ to $0.00001M$) that ordinary chemical methods are not sufficiently sensitive.

Concentration cells have been used to measure the number of ions remaining free in the intermicellar liquid after adsorption has taken place (4, 10). The field of application of this method is very limited, and furthermore many difficulties, such as the effects due to the activity of the ions and the presence of foreign substances, are encountered in the interpretation of these results.

Quantitative spectrum analysis for the measurement of small quantities of materials has been developed rapidly during the past few years. This paper applies emission spectrum analysis to the estimation of the adsorption of ions in colloidal solutions.

The spectra may be excited in various ways; the methods used with solutions are outlined below: (1) The flame method of Lundgårdh (7, 9, 6) is the most sensitive one for use with the alkali metals. The solution to be investigated is vaporized and mixed with the illuminating gases in a special burner. Using 2 or 3 cc. of solution the probable error is claimed to be as low as 2 to 5 per cent. (2) The uncondensed spark method is the one recommended by Gerlach (5) for general work. A high voltage spark takes place between the surface of the solution and a metal electrode suspended above it. So much heat is produced by the spark that it is necessary to cool the electrode by surrounding it with ice or cold water (see figure 1). (3) Recently Gerlach (5) used an interrupted arc with the same types of electrodes as described in the second method. The arc

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20–22, 1935.

between the surface of the liquid and the metal electrode is opened and closed several times a second by a cam arrangement run by an electric motor. This method is particularly useful in cases where it is desirable to reduce the intensity of unavoidable band spectra. (4) Twyman and Hitchen (8), and Brode and Steed (1) use a spark between two liquid jets in order to avoid contamination at the sparking surfaces.

In this work the uncondensed spark method was used in conjunction with a Hilger medium quartz spectrograph E2. Sensitive plates giving good contrast are required; Ilford's Zenith and Hypersensitive Panchromatic plates were used. By suitably adjusting a spherical condensing lens the intensity of the spectrum due to the metal electrode may be greatly reduced and that due to the substances in solution increased, since the points of maximum emission of the two spectra are some distance apart.

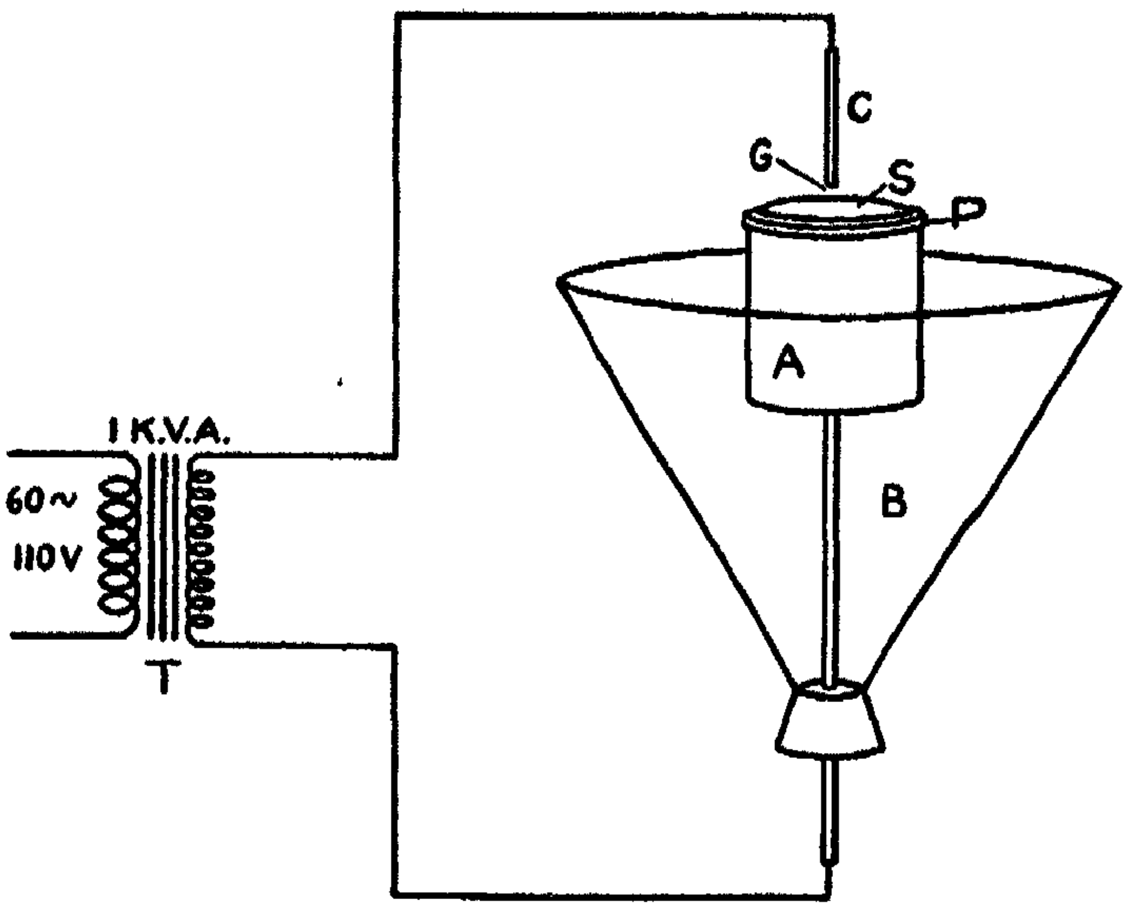


FIG. 1. The apparatus. A, iron block; B, ice; C, copper electrode; G, gap ca. 3/8″; P, platinum cap; S, solution, 5 cc.

The gold colloid used in this investigation was prepared by under-water sparking at a voltage of about 10,000 and a frequency of about 10^6 cycles per second. In the first experiments the usual salts were used,—sodium hydroxide as stabilizer (added to the water before sparking) and aluminum chloride as coagulating electrolyte. As the spectroscopic method of analysis is only suitable for use with metal ions, later experiments were confined to the use of salts containing metals in both ions,—sodium permanganate as stabilizer and magnesium chromate as coagulating electrolyte.

The amount of electrolyte *necessary* to coagulate the sol was taken as the *minimum* quantity which when mixed with an equal volume of the sol caused complete precipitation of the colloidal material in about three days.

For analysis the coagulated solution was first centrifuged to obtain good separation of the precipitated gold and the supernatant liquid. This liquid was poured off and the gold was dissolved in aqua regia and diluted to the same volume as the supernatant liquid. When testing for aluminum it was necessary to concentrate the solutions to one-fiftieth of their original volume to get measurable concentrations; when testing for magnesium it was not necessary to concentrate at all. All solutions were made slightly acid before analysis, as this has been found to increase greatly the spectroscopic sensitivity.

Plates were also taken with gold sols precipitated by freezing in liquid air, i.e., without the addition of any coagulating electrolyte; and with copper sols prepared as the gold sols were but without the addition of any stabilizing electrolyte, and precipitated by magnesium chromate.

The concentrations of metal ions in the unknown solutions were found by comparing the intensities of certain lines in their spectra with the intensities of those lines in the spectra of standard solutions which were taken on the same plate under the same conditions of excitation, exposure, etc. The intensities were compared visually, as it was found that with practice this method was just as satisfactory as using a microphotometer. The uniformity of lines due to some reference material present in all the solutions in equal concentration is usually considered as proof that electrical conditions have remained the same throughout a series of exposures.

In general the probable error was about 10 per cent of the amount measured. (In spectrum analysis the error is a certain percentage of the amount present and not an absolute amount, as in most chemical methods.) When the distribution of an ion between the supernatant liquid and the precipitate is very unequal, say ten to one, the amount of the ion adsorbed may be determined with much greater accuracy—often to within 1 or 2 per cent of the amount added—for the error involved is 10 per cent of the smaller amount analyzed. In all spectrum analysis work the sensitivity varies considerably with the element investigated, with the type of spectrograph, with the type of photographic plate, with the conditions of excitation, the length of exposure, etc. In this investigation the following limits of sensitivity have been found: $M/100,000$ for gold, manganese; $M/50,000$ for magnesium, chromium, sodium; $M/1,000$ for aluminum. Some elements, for example, sodium, are often present in the purest materials obtainable, or in the air, in concentrations sufficient to be visible spectroscopically. Such concentrations can be allowed for by including a suitable blank spectrum on each test plate.

The results up to the present may be summarized as follows:

I. See figure 2A. The sodium lines are clearly visible in the photograph with the supernatant liquid (No. 7), and cannot be seen at all with the precipitated gold (No. 2). The aluminum lines appear with the gold (No. 2) and cannot be seen with the supernatant liquid (No. 7).

FIG. 2. Spectra showing metal lines in the coagulating liquids taken in various strengths as standards and for comparison lines present in spectra of supernatant liquid and coagulated material. Details of individual spectra are given below.

A. Gold sol, 0.8 g. per liter (stabilized by 0.001 M sodium hydroxide)

1. Aluminum chloride solution in concentration just sufficient to produce coagulation—M/10,000.
2. Gold precipitated by 1 and dissolved in acid.
3. Aluminum chloride solution, 80 per cent of the strength of 1.
4. Aluminum chloride solution, 60 per cent of the strength of 1.
5. Aluminum chloride solution, 40 per cent of the strength of 1.
6. Aluminum chloride solution, 20 per cent of the strength of 1.
7. Supernatant liquid corresponding to 2.
8. Acid blank.

B. Gold sol, 0.8 g. per liter (stabilized by 0.001 M sodium permanganate)

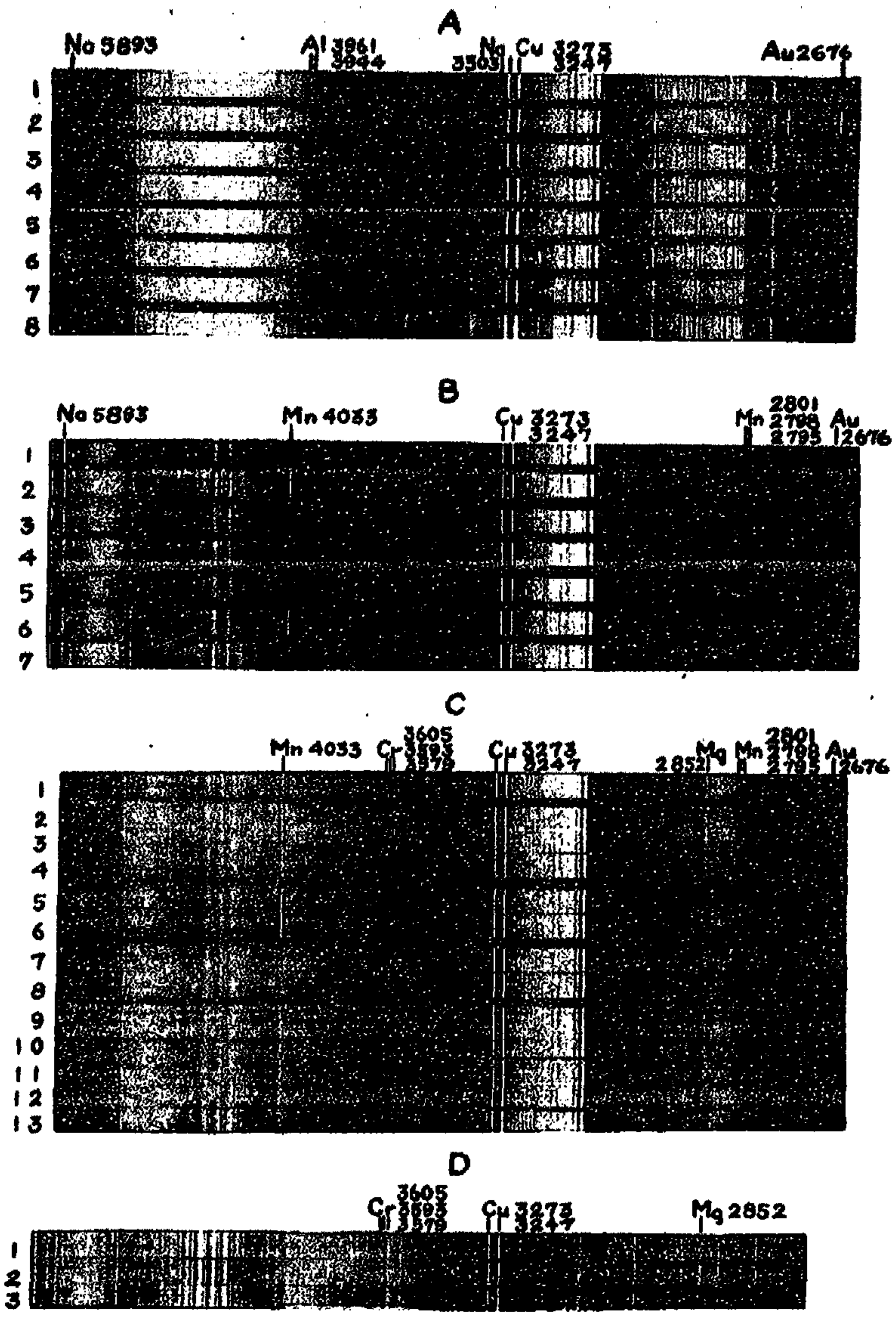
1. Supernatant liquid from gold sol precipitated by freezing in liquid air.
2. M/1000 sodium permanganate solution.
3. M/5000 sodium permanganate solution.
4. M/25,000 sodium permanganate solution.
5. M/125,000 sodium permanganate solution.
6. Precipitated gold corresponding to 1.
7. Acid blank.

C. Gold sol, 0.8 g. per liter (stabilized by 0.001 M sodium permanganate)

1. 0.00040M magnesium chromate and M/10,000 sodium permanganate.
2. 0.00035M magnesium chromate and M/10,000 sodium permanganate.
3. 0.00030M magnesium chromate and M/10,000 sodium permanganate.
4. 0.00025M magnesium chromate and M/10,000 sodium permanganate.
5. Gold precipitated by M/8000 magnesium chromate and dissolved in acid.
6. Gold precipitated by M/12,000 magnesium chromate and dissolved in acid (minimum amount necessary for coagulation).
7. Supernatant liquid corresponding to 5.
8. Supernatant liquid corresponding to 6.
9. 0.00020M magnesium chromate and M/10,000 sodium permanganate.
10. 0.00015M magnesium chromate and M/10,000 sodium permanganate.
11. 0.00010M magnesium chromate and M/10,000 sodium permanganate.
12. 0.000066M magnesium chromate and M/10,000 sodium permanganate.
13. Acid blank.

D. Copper sol, 0.6 g. per liter

1. Copper precipitated by M/25,000 magnesium chromate and dissolved in acid (minimum amount necessary for coagulation).
2. Supernatant liquid corresponding to 1.
3. Acid blank.


A
Na 5893
Al 3961
3944
Na 3303
Cu 3273
3247
Au 2676
1
2
3
4
5
6
7
8
B
Na 5893
Mn 4033
Cu 3273
3247
Mn 2801
2798
2795
Au
2676
1
2
3
4
5
6
7
C
Mn 4033
Cr 3605
3593
3579
Cu 3273
3247
Mg 2852
Mn 2801
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8
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10
11
12
13
D
Cr 3605
3593
3579
Cu 3273
3247
Mg 2852
1
2
3

FIG. 2

Thus when gold sols stabilized by sodium hydroxide are precipitated by aluminum chloride, at least 90 per cent of the aluminum ions are adsorbed by the gold and at least 98 per cent of the sodium ions remain in the supernatant liquid. The gold particles acquire a negative charge in preparation, presumably by the adsorption of hydroxyl ions. Owing to this negative charge the gold attracts the trivalent positive ion of the coagulating electrolyte, but leaves the monovalent positive ion of the stabilizing electrolyte free in the supernatant liquid.

II. See figure 2B. The manganese lines are very prominent in the photograph with the precipitated gold (No. 6), but are not visible at all with the supernatant liquid (No. 1). The sodium line is visible in all the spectra but its concentration in the precipitated gold (No. 6) is no higher than that in the acid blank (No. 7).

When gold sols stabilized by sodium permanganate are precipitated by freezing in liquid air, at least 99 per cent of the manganate ions are precipitated with the gold and 95 to 98 per cent of the sodium ions remain free in the supernatant liquid. This is not in agreement with the theory of those who believe that the non-stabilizing ion of the stabilizing electrolyte (the sodium in this case) appears free in the supernatant liquid only when displaced from the neighborhood of the particles by the coagulating electrolyte.

III. See figure 2C. Chromium lines are visible in No. 7 and No. 8—the supernatant liquid—but not in No. 5 and No. 6—the precipitated gold. The magnesium line is much more intense in No. 7 and No. 8—the supernatant liquid—than in No. 5 and No. 6—the precipitated gold. The manganese lines may be clearly seen with the gold as in figure 2B; not a trace of them appears with the supernatant liquid.

When gold sols stabilized by sodium permanganate are precipitated by magnesium chromate, at least 95 per cent of the chromium ions remain in the supernatant liquid. Chromium cannot be detected with the precipitated gold until about twenty times the minimum coagulating concentration of magnesium chromate is added to the colloid.

When just sufficient magnesium chromate is added to produce coagulation, about one-third of the magnesium ions is adsorbed by the gold. The amount of magnesium adsorbed increases slightly (about three times) when many times (up to eighty times) this amount of magnesium chromate is added. At least part of this increase is due to traces of supernatant liquid remaining with the precipitated gold. The precipitate was not washed, as it was found difficult to be certain that washing the precipitate did not remove some of the adsorbed ions (see also Weiser (10)).

These results are not in agreement with those of Freundlich (4) or of Euler and Zimmerlund (3). Freundlich found that appreciable amounts of both ions of the coagulating electrolyte were adsorbed by the precipitated particles of an "electrolyte-free" gold sol. Euler and Zimmerlund found that equal amounts of both ions of an electrolyte were adsorbed by fine gold powder.

IV. See figure 2D. Here the chromium lines may be clearly seen in No. 1, the precipitated copper, but not at all in the supernatant liquid (No. 2); while the magnesium line appears strongly in No. 2 but not at all in No. 1.

Thus when copper sols, which are positively charged, are precipitated by the minimum necessary quantity of magnesium chromate, at least 90 per cent of the chromate ions are adsorbed by the copper and at least 95 per cent of the magnesium ions remain in the supernatant liquid. This distribution is, of course, just opposite to that obtained in a negatively charged gold sol; there the magnesium ions are adsorbed and the chromium ions left in the supernatant liquid.

Further work is now in progress.[1]

In conclusion, the authors wish to express their sincere appreciation to Professor E. F. Burton, Director of the McLennan Laboratory at the University of Toronto, for his suggestion of the problem and his advice throughout the investigation.

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[1] *Note added in proof:* It is apparent that the spectra reproduced will not show plainly lines which are clearly visible on the original plates; the statements made in paragraphs I, II, III, and IV will have to be considered as true for the original plates.

40-282.

VAPOR PRESSURE-WATER CONTENT RELATIONS FOR CERTAIN TYPICAL SOIL COLLOIDS[1]

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Several attempts have been made to utilize the information obtained by allowing air-dry soil to absorb moisture at various relative humidities. The water absorbed by soil colloids when allowed to come to equilibrium over a sulfuric acid-water mixture containing 3.3 per cent sulfuric acid by weight has been made the basis for a method of estimating the quantity of colloid present in a soil (6). The water held under this condition (99 per cent relative humidity) falls below the hygroscopic coefficient. The British soil workers (8) have also used a determination of the moisture held at 50 per cent relative humidity as a criterion of soil properties. More recently, workers in the Bureau of Chemistry and Soils of the United States Department of Agriculture (5) have made determinations of the amounts of water held over sulfuric acid-water mixtures of various concentrations by different soil colloids. An attempt was made to correlate the ratios between some of the values so obtained with the chemical composition of the soil.

The vapor pressure-water content curves of a number of soils have been studied by Thomas (13, 14) and by Puri, Crowther, and Keen (11). They covered the entire range from oven-dry at 105°C. to saturation. It was found in both investigations that an inflection point in the curves occurred near 50 per cent of the vapor pressure of pure water. No breaks were found; this indicated no sudden change in the nature of the forces holding the water. Puri, Crowther, and Keen reached the conclusion that the curves were all of the same type, but that the general slopes of the curves were decreased with increases of clay and organic matter content. Thomas

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[1] Abstracted from a thesis submitted by Lyle T. Alexander to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1935.

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also reached the conclusion that the slope of the curve is influenced by the quantity of fine material present, but concluded that the organic matter played a minor rôle in water vapor absorption. Brown and Byers (5) and also Anderson and Mattson (3) have called attention to the correlation between the avidity of a soil colloid for water and its chemical constitution. Since it has been shown that the coarser fractions of a soil only serve as a framework or as diluting material for the colloid, it seemed advisable to study the colloid extracted from the soil rather than the soil itself. This would eliminate the variable factor mentioned by Puri, Keen, and Crowther concerning the change in slope of the vapor pressure curve with clay content.

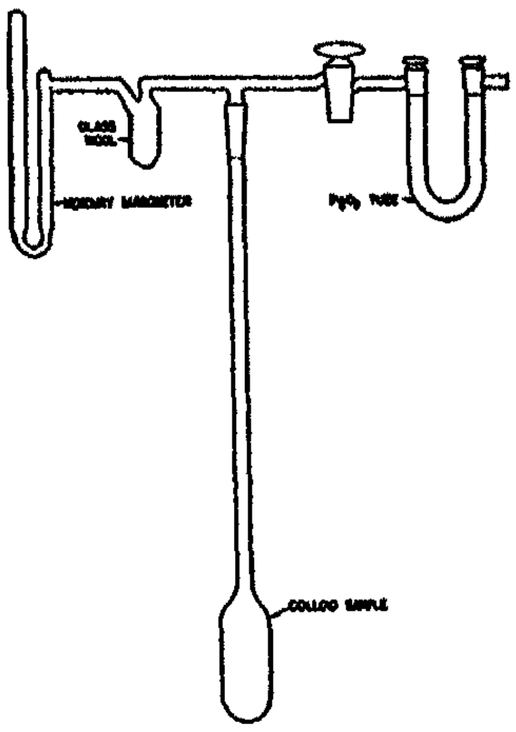

FIG. 1. Vapor pressure apparatus

EXPERIMENTAL

The soils selected for this study represent a wide range of progressive weathering. The Barnes soil is a black dry land grass soil from North Dakota. It has been formed from calcareous glacial till. It has not been subjected to severe hydrolysis because of the low rainfall.

The Carrington soil is a fertile prairie soil of Iowa. Like the Barnes soil, it has been developed from calcareous glacial till, but under conditions of more rainfall, and therefore its degree of hydrolysis is greater.

The Miami, a gray-brown podsolic soil from Indiana, has been developed under somewhat higher rainfall than the Carrington. This is a timber soil and not a grassland one.

The fourth soil selected is the Cecil, a red soil from North Carolina, that has been developed from decomposed granites and gneisses under condi-

TABLE 1

Relation between the vapor pressure and water content of the Barnes colloid at 25°C.
Sample No. 10307. Dry weight of sample = 9.101 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
mm. Hg	*grams*	*per cent*	*mm. Hg*	*grams*	*per cent*
23.1	0.031	33.4	12.8	1.641	15.7
22.6	0.156	32.0	11.8	1.702	15.0
22.6	0.259	30.9	10.9	1.760	14.4
22.1	0.352	29.8	9.9	1.825	13.6
21.8	0.498	28.2	9.3	1.869	13.2
21.2	0.623	26.9	8.7	1.902	12.8
21.0	0.647	26.6	8.0	1.961	12.1
20.6	0.722	25.8	7.0	2.027	11.4
19.9	0.856	24.3	5.9	2.112	10.5
19.5	0.934	23.4	5.3	2.143	10.1
19.0	1.020	22.5	4.0	2.283	8.6
18.5	1.072	21.9	2.8	2.363	7.7
18.1	1.134	21.2	1.8	2.478	6.5
17.3	1.200	20.5	1.0	2.583	5.3
16.6	1.280	19.6	0.0	3.069	0.0
15.7	1.368	18.7			
15.4	1.459	17.7	Additional point by desiccator method		
14.1	1.560	16.6			
13.2	1.619	15.9	23.2		35.4

TABLE 2

Relation between the vapor pressure and water content of the Carrington colloid at 25°C.
Sample No. 10084. Dry weight of sample = 8.977 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
mm. Hg	*grams*	*per cent*	*mm. Hg*	*grams*	*per cent*
25.7	0.019	26.9	10.1	1.621	9.0
23.1	0.137	25.6	6.5	1.819	6.8
22.4	0.298	23.8	5.3	1.898	6.0
22.1	0.499	21.6	1.4	2.130	3.4
20.7	0.731	19.0	1.2	2.158	3.1
19.0	0.974	16.6	0.0	2.432	0.0
16.4	1.233	13.4			
15.8	1.343	12.2	Additional point by desiccator method		
12.2	1.492	10.5	23.3		26.2

tions of high rainfall and temperature, where the hydrolysis has been severe.

The colloid was so extracted that the upper limit of particle size was

TABLE 3

Relation between the vapor pressure and water content of the Miami colloid at 25°C.
Sample No. 10342. Dry weight of sample = 9.437 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
mm. Hg	*grams*	*per cent*	*mm. Hg*	*grams*	*per cent*
24.9	0.134	19.9	11.4	1.443	6.0
22.7	0.212	19.1	10.4	1.456	5.8
22.7	0.296	18.2	9.6	1.515	5.2
21.8	0.346	17.6	7.8	1.561	4.8
21.7	0.403	17.0	6.3	1.597	4.4
21.9	0.523	15.8	4.7	1.659	3.7
21.5	0.606	14.9	4.4	1.672	3.6
20.9	0.692	14.0	3.6	1.703	3.3
20.3	0.820	12.6	3.0	1.737	2.9
20.3	0.895	11.8	2.5	1.744	2.8
19.6	0.956	11.2	1.9	1.781	2.4
18.8	1.062	10.0	1.1	1.845	1.8
18.0	1.125	9.4	0.0	2.013	0.0
16.9	1.181	8.8			
15.7	1.257	8.0	Additional point by desiccator method		
15.2	1.309	7.4			
13.7	1.376	6.7	23.3		25.0

TABLE 4

Relation between the vapor pressure and water content of the Cecil colloid at 25°C.
Sample No. 9415. Dry weight of sample = 9.910 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
mm. Hg	*grams*	*per cent*	*mm. Hg*	*grams*	*per cent*
24.3	0.096	22.3	10.2	2.014	3.0
22.7	0.274	20.5	8.3	2.055	2.5
22.7	0.394	19.3	7.0	2.085	2.3
22.4	0.529	17.9	5.9	2.106	2.0
22.1	0.669	16.5	5.0	2.130	1.8
22.1	0.794	15.3	3.7	2.162	1.5
22.1	0.947	13.7	2.9	2.182	1.3
21.7	1.071	12.5	2.3	2.187	1.2
21.2	1.223	11.0	1.4	2.214	1.0
20.4	1.360	9.6	1.1	2.229	0.8
20.0	1.469	8.5	0.9	2.246	0.6
19.8	1.587	7.2	0.9	2.262	0.4
18.2	1.708	6.0	0.0	2.309	0.0
17.1	1.803	5.1			
14.3	1.909	4.0	Additional point by desiccator method		
12.3	1.966	3.4	23.3		27.9

about 0.3 micron in diameter (6). The colloid was air-dried at room temperature to avoid any irreversible dehydration at the elevated temperature.

The apparatus used for determining the detailed vapor pressure–water composition curves is essentially that used by Wales and Nelson (15). A diagrammatic representation of it is shown in figure 1.

After a 10-g. sample of air-dry colloid ground to pass a 100-mesh sieve had been placed in an evacuated desiccator over 3.3 per cent sulfuric acid for a period of five days, the sample was weighed and transferred to the bulb of the apparatus shown in figure 1. The apparatus was then evacuated through the phosphorus pentoxide tube until about 0.1 g. of water was collected. The stopcocks were closed and the whole apparatus allowed to stand until equilibrium was reached. The phosphorus pentoxide tube was then weighed, and the difference in level of the two legs of the manometer read by means of a cathetometer. The apparatus was again evacuated and the process repeated. The experimental data obtained by this method are given in tables 1 to 4. Also given in these tables is the value for water held, at 25°C., by the colloid in an evacuated desiccator containing aqueous sulfuric acid, with a water vapor pressure of 23.3 mm. Hg. Most of the values were taken after allowing twenty-four hours for equilibrium to be reached. Although this may not be a real equilibrium point, no further change in pressure could be noted by allowing three or four days time.

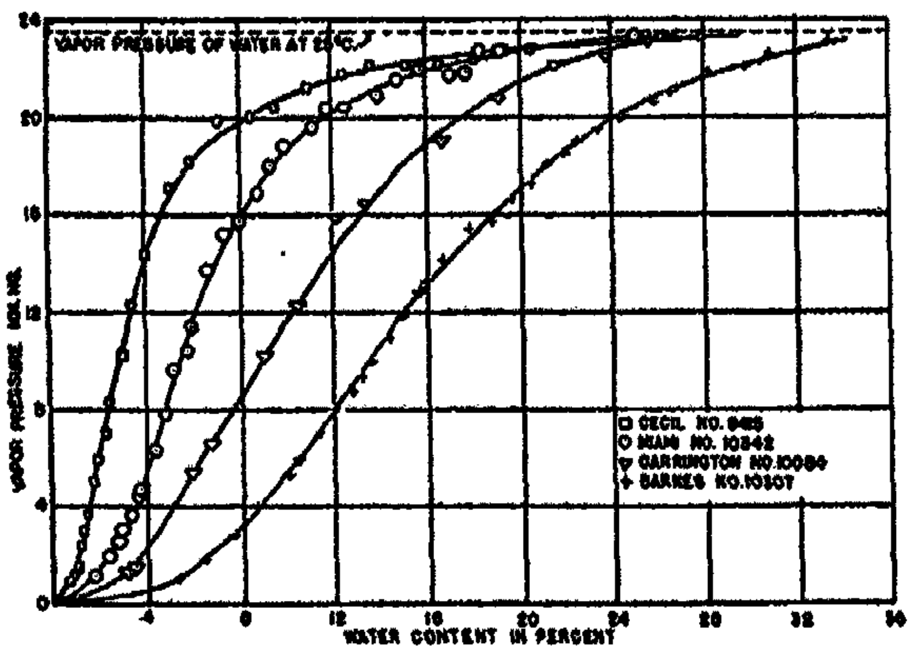

Fig. 2. Water content relation for soil colloids at 25°C.

The curves for the four soil colloids are shown in figure 2. These are all of the same general form. They are similar to the curves for gelatin given by Katz (7) and to those for wood found by Stamm and Loughborough (12). They are also similar to that for aqueous sulfuric acid. Data are available in the International Critical Tables for the sulfuric acid. The first few values on each curve are undoubtedly too high because of removal of adsorbed air. The very low ones are a bit uncertain because the mercury manometer was not sensitive to small changes in pressure in the very low range.

MATHEMATICAL EXPRESSIONS FOR THE CURVES

Katz (7) expressed the vapor pressure–water content relation for an elastic gel by the equation

$$-\frac{RT}{V_0}\ln h = \frac{\alpha\beta}{(\beta - a)^2}$$

where α and β are empirical constants, h is the ratio of the vapor pressure of the gel to that of pure water at the same temperature, a is the water content in grams, per gram of dry colloid, V_0 is the specific volume of water, and R and T have their usual significance.

This equation was tested to see if it would fit the curves for the soil colloids studied. The results were not satisfactory. However, a satisfactory equation for two of the colloids may be obtained as follows. Consider the reaction

$$\text{Soil colloid} \cdot \text{xH}_2\text{O} + \text{water} \rightarrow \text{soil colloid} \cdot \text{yH}_2\text{O}$$

where x is always less than y. The decrease in free energy for this reaction may be obtained from

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

where M is the molecular weight of water, P is the equilibrium pressure of the system, P_0 is the vapor pressure of water at the same temperature, and ΔF is the free energy decrease at this temperature when 1 g. of water is added to an infinite amount of soil colloid (xH_2O).

These values have been calculated for vapor pressures taken from the curves of figure 2, and are presented graphically in figure 3.

As a rule such curves (figure 3) will be found to fit an equation of the type

$$y = ae^{-bx} \tag{2}$$

where a and b are constants and y and x represent the ordinates and abscissae, respectively, and $e = 2.7183$. Letting x = percentage of water in sample and $y = \Delta F$, we have

$$\Delta F = ae^{-bx} \tag{3}$$

Equating equation 1 and equation 3

$$\frac{RT}{M}\ln\frac{P}{P_0} = ae^{-bx} \tag{4}$$

Since R, T, M, and a are constants, we may combine them with the conversion factor to Briggsian logarithms and obtain

$$\log \frac{P}{P_0} = a'e^{-bx} \tag{5}$$

a' and b may be evaluated by throwing the equation into the logarithmic form

$$\log \log \frac{P}{P_0} = \log a' - bx \log e \tag{6}$$

$$\log \log \frac{P}{P_0} = \log a' - 0.4343\, bx \tag{7}$$

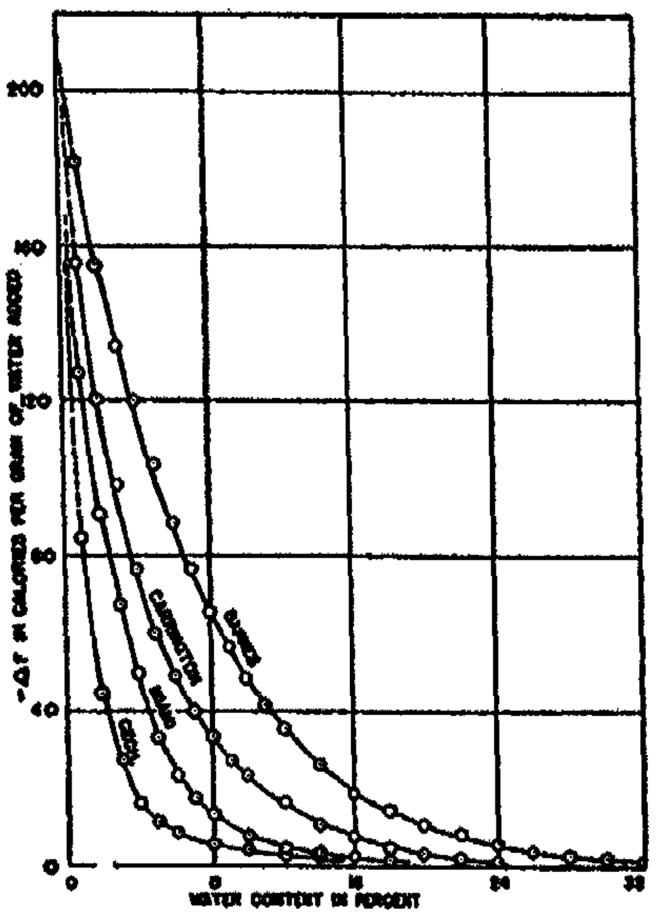

FIG. 3. Change in free energy of soil colloids as a function of water content at 25°C.

a' of course $= \dfrac{Ma}{2.303RT}$; a' (and therefore a) and b may then be evaluated by plotting $\log \log \frac{P}{P_0}$ against x or by plotting $\log \frac{P}{P_0}$ on semi-log paper against x. Log a' will be the intercept on the y axis and $-0.4343b$ the slope. Curves for the four soil colloids studied, plotted by the first method, are given in figure 4. Straight portions are found for all the types, especially at lower water percentages. Equations for the straight portions of each are given below. They are valid, naturally, only for colloids of water content lying on the straight portion.

$$\log \frac{P}{P_0} = 2.82e^{-0.148x} \qquad \text{(Barnes)}$$

$$\log \frac{P}{P_0} = 2.32e^{-0.205x} \qquad \text{(Carrington)}$$

$$\log \frac{P}{P_0} = 2.21e^{-0.311x} \qquad \text{(Miami)}$$

$$\log \frac{P}{P_0} = 1.15e^{-0.491x} \qquad \text{(Cecil)}$$

Possible explanations for the failure to obtain straight lines at higher water contents will be offered later.

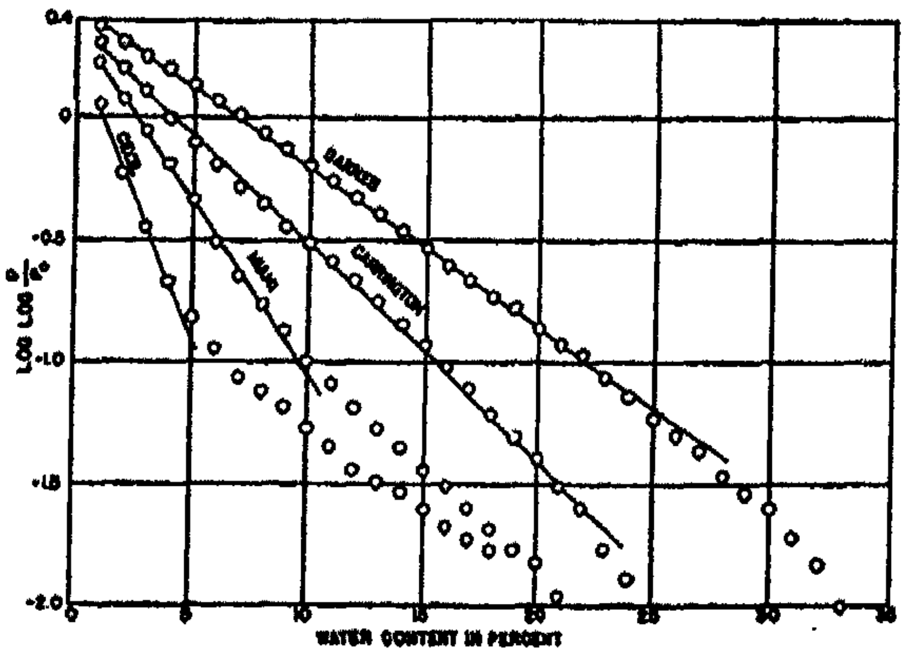

FIG. 4. Log log of vapor pressure ratio as a function of water content at 25°C.

We may obtain the total free energy change for an addition of an amount of water corresponding to 99 per cent of saturation. These values are obtained by determining the area under the curves shown in figure 3. The values obtained are given below.

	ΔF IN CALORIES PER GRAM OF COLLOID	ΔH IN CALORIES PER GRAM OF COLLOID
Barnes	14	22
Carrington	9	17
Miami	6	14
Cecil	3	6

The values for ΔH were obtained by measuring the heat of wetting of the soil colloids according to the method of Anderson (1), except that the samples were dried over concentrated sulfuric acid at 25°C. instead of in the oven at 105°C.

RELATION TO COLLOID COMPOSITION

In recent years chemists have discovered an important relation between the chemical composition of the colloid of a soil and its field characteristics. This relation is sometimes obscured by the presence of unweathered minerals in the extracted colloid. Such minerals are abundant in most soils (9).

Since unweathered ground minerals such as orthoclase do not hold water appreciably in the hygroscopic range, they should, if present as an impurity, serve merely as a diluent, and hence affect the vapor pressure curves only slightly. An examination of the curves in figure 2 shows that the Miami falls nicely into its proper relation between the Carrington and Cecil and not between the Barnes and Carrington as its silica sesquioxide and silica alumina ratios would predict.

The differentiation shown by this family of curves between the four groups of soils covered in this investigation is sharp and of even distribution. It appears that the hygroscopic moisture of the colloid is a characteristic function of the factors which determine the field characteristics of the soil. Further investigation may reveal some curves out of place, just as some of the ratios are out of place, but this will not invalidate the use of these curves as criteria of soil properties.

THE NATURE OF THE HYGROSCOPIC WATER

The data shown in this paper indicate that the hygroscopic water of the soil colloids is held in a similar manner to water of swelling in gelatin and in wood.

Probably the most illuminating treatment of hygroscopic water in elastic gels is that of Peirce (10). He proposes a "two-phase" theory of absorption of water by cotton cellulose, which has water content–vapor pressure isothermals very similar to those of soil colloids.

According to the Peirce theory the hygroscopic water can be considered as occurring in two different phases, or states, on the cellulose. The first of these is the *a* phase which is held to be chemically bound by the hydroxyl groups of the hexose units of the cellulose. The second or *b* phase is made up of the water molecules attracted by the water molecules of the *a* phase and by the colloid surface which is not reactive toward water. From theoretical considerations he arrives at the following formula for the vapor pressure–water content isotherms for cotton and starch

$$1 - \frac{P}{P_0} = (1 - kC_a)e^{-BC_b}$$

where P is the water vapor pressure of the cellulose (xH_2O), P_0 is the vapor pressure of water at the same temperature, k is a constant characteristic for each sample, C_a is the concentration of moisture in the a phase, B is another constant characteristic of each sample, and C_b is the concentration of water in the b phase.

This equation is similar in many respects to the equation arrived at on page 201 for the soil colloids. Peirce pointed out that the equation would be applicable only to pure substances. It is probable that the failure of the vapor pressure–water content curves to rectify, as shown in figure 4, is due to some contaminating colloid which does not exert a noticeable lowering of the vapor pressure in the lower moisture content ranges, but which does make itself noticeable in the higher moisture content ranges. Iron oxide is a contaminant to which we might attribute this behavior.

If then we apply the two-phase theory of Peirce to soil colloids, we may picture the a phase water as being combined with the alumino silicic acid complex, with the tendency toward further hydration as the attracting force. The b phase water is held on the surface of the colloid not occupied by a phase water and as outer layers on the a phase water.

Concerning the a phase water, one must conclude that in the little hydrolyzed soils of the chernozem group the tendency to hydrate is very great, and that in the lateritic Cecil series the tendency is very small. The b phase water does not appear to be so much a function of the chemical composition of the colloid as of the surface. Further investigation is necessary to determine the quantitative relations between these two kinds of hygroscopic water.

This idea of the two kinds of hygroscopic water is easily harmonized with the work of Anderson (2) and of Baver and Horner (4) on the effect of exchangeable ions on the hygroscopicity of colloids. It is interesting to note that the colloids having high base exchange capacities are the ones having much attraction for the a phase water. It is possible that the base exchange phenomena and absorption of a phase water are due to the same chemical affinity, that is, secondary valence, or it may be that the base exchange bases are held by primary valence bonds. Further investigations along this line would be necessary to decide which of these is responsible for the phenomena.

SUMMARY

1. A study has been made of the vapor pressure–water content curves of four typical soil colloids. The curves are shown to be characteristically different for the different soil groups.

2. The change of free energy as a function of water content has been calculated, and the total free energy change on wetting has been determined approximately.

3. An attempt has been made to correlate vapor pressure curves with soil classification.

4. Peirce's two-phase theory of water absorption by cellulose is used to picture the nature of the hygroscopic water of soil colloids.

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STREAM POTENTIALS AND D. C. SURFACE CONDUCTIVITIES IN SMALL CAPILLARIES[1,2]

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A few years ago (8) we reported that the stream potentials of glass capillaries decrease with capillary diameter, being for 5-micra capillaries from 0 to 25 per cent of the normal with 2.5 and 5×10^{-4} *M* potassium chloride, the normal being defined as that found with large capillaries. These findings are believed to be more nearly correct than the earlier report (6) that the stream potential of 5-micra capillaries was, with 5×10^{-4} *M* potassium chloride, about 75 per cent of normal; the earlier findings were presumably due to technical imperfections. We are now reporting on a larger series of measurements on capillaries from 333- to 4.1-micra diameter, with solutions ranging from water to 10^{-2} *M* potassium chloride. The present findings confirm, with some qualifications, and extend those of White, Urban, and Van Atta.

METHODS

The condenser arrangement used in the earlier work was replaced by a vacuum tube amplifier (FP54) for measuring both stream potentials and capillary resistances. The apparatus is shown in figure 1. The amplifier is shielded by its metal box, the remainder of the apparatus by a large copper screen cage. Due precautions as to insulation were observed. With the top of switch A to the left, grid grounded, the plate current is balanced to zero by adjustment of R_2 and R_4. With the switch in the middle position the plate current is again brought to zero by the potentiometer, whose reading gives the potential to be measured, in this case the stream potential. With the top of switch A to the right the voltage drop across R_6 is measured, and from this is calculated the resistance of the capillary. One or more dry cells of known voltage may be put in series with R_6 and the capillary to measure capillary resistance, or the stream potential alone may be used; the same result is obtained with both methods. If a dry

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[2] Aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

cell of known voltage is put into the electrode circuit with switch A in the middle position, the measured voltage is the sum of stream potential and added voltage; this procedure was frequently used as a check. The galvanometer G has a current sensitivity of 1.85 × 10^{-8} amperes per millimeter; the voltage sensitivity of the amplifier is about 0.002 volt per millimeter with the lower resistances, and about 0.006 volt per millimeter with the highest (above 10^{11} ohms).

The standard high resistances, R_s, are of two types,—gold or platinum films sputtered on glass rods (5) and carbon impregnations; a series ranging from 2.18 × 10^{8} to 1.03 × 10^{11} ohms was employed. They were supplied by the Department of Physics, and we are indebted to Dr. G. M. Webb of that department for their initial measurements. The carbon type usually show some change in resistance with change in applied voltage; we have therefore calibrated them for the range of voltages employed. For each determination a standard was chosen as near the value of the unknown as possible; the ratio was usually less than 2 and never more than 3. Our stream potential measurements are in error by not more than 0.002 volt, and the capillary resistances by not more than 1 per cent with resistances less than 10^{10} ohms and not more than 2 per cent with resistances above 10^{10} ohms.

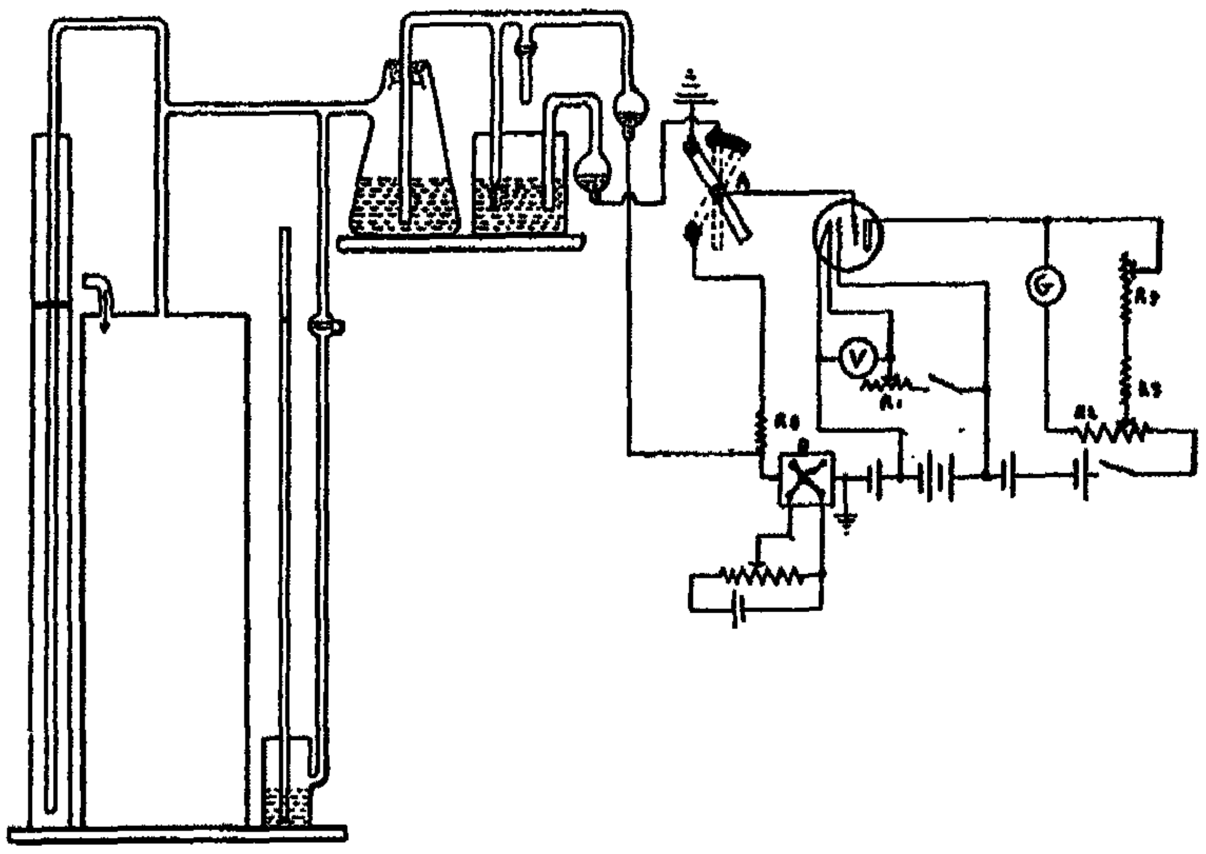

FIG. 1. Apparatus for measuring stream potentials and conductivity. A, high resistance switch; B, reversing switch; V, voltmeter; G, galvanometer; R_1, 20 ohms; R_2, 400 ohms; R_3, 20,000 ohms; R_4, 11,000 ohms; R_s, standard high resistance.

Capillary lengths were measured with micrometer calipers; their cross-sectional area was calculated from the observed resistance when filled with $M/10$ potassium chloride. In some cases diameters were checked by microscopic measurement; agreement with the other method was usually within 1 or 2 per cent, but in all cases the results of the first method were taken. Using the data of capillary dimensions and of observed capillary resistance with dilute solutions the net specific conductivity of the latter in the capillaries was calculated, designated κ_{cap} in the tables.

Two methods of treatment were used with the capillaries. With the first, treatment a, the capillaries were left in chromic acid overnight and then subjected to prolonged rinsing with distilled water. With the second, treatment b, the capillaries were immersed in boiling distilled water for one hour and then washed in distilled water. No consistent differences in the results of these two treatments were observed. The water used in treating the capillaries and in making up the potassium chloride solutions was double distilled, first from an electrical laboratory still and then from an all-Pyrex still to which was added a little Nessler's solution. The specific conductivity of this water ranged from 0.9 to 2.0 × 10^{-6} mhos.

RESULTS

Stream potentials

In the first series capillary resistances were not measured, and therefore specific conductivities in the capillaries not determined. These will not differ significantly from specific bulk conductivities, κ_{sol}, with the larger capillaries and higher concentrations of table 1, since here surface conductivity is negligible. With the lower concentrations, however, there will be an appreciable surface conductivity except with the largest (333 micra) capillary, the ratio of surface to bulk conductivity of course increasing as capillary diameter decreases. Therefore zeta is shown in table 1 with concentrations of 1 × 10^{-4} M and less only for the largest capillary; with the other capillaries at these low concentrations, specific conductivity in the capillary, κ_{cap}, is to an increasing degree greater than κ_{sol} as capillary diameter decreases. Table 1 shows that the stream potential, E/P, falls with decreasing capillary diameter and that the effect of diameter is greater the more dilute the solution. With concentrations of 5 × 10^{-4} M and greater the size effect is no longer appreciable above diameters of 18 micra. While we cannot make a positive statement as regards these particular experiments, since we do not have resistance measurements here, it seems probable, on the basis of many other measurements of surface conductivity, that the size effect on E/P here is due largely to the effect of increased conductivity in the smaller capillaries.

The reproducibility of results with the smallest capillaries is not sufficiently close to permit an evaluation of the effect of electrosmotic retardation of velocity in the double layer, as discussed by Reichardt (4), which would be a further contributing factor in the lowering of E/P.

The κR effect, discussed by Müller and Abramson (1) in connection with electrophoresis and later applied by Komagata (2) to the stream potential problem, is so small as not to be measurable. Komagata's statement (ref. 2, p. 37) that this effect could explain the observed drop in stream potential with diminishing capillary size is invalid for three reasons. First, his table of limiting values of radius, i.e., radius of capillary below which the effect becomes significant, shows all the figures with ten times the cor-

TABLE 1

Stream potentials without resistance measurements

DATE	SOLUTION	κ_{sol}	CAPILLARY DIAMETER	E/P	PER CENT OF NORMAL	ZETA
		mhos × 10^{-6}	*micra*	*mv./cm. Hg*		*mv.*
Nov. 6	Water	1.87	333	734	100	132
			85.4	555	76	
			39.0	258	35	
			12.0	157	21	
			5.78	25	3	
Nov. 7	10^{-6} *M* KCl	3.71	333	201	100	107
			85.4	268	89	
			39.0	132	44	
			12.0	96	32	
			5.78	6	2	
Nov. 8	10^{-4} *M* KCl	16.6	333	71.2	100	114
			85.4	71.4	100	
			39.4	68.1	95	
			12.0	48.3	68	
July 18	5 × 10^{-4} *M* KCl	76.7	333	14.0		
			97.6	15.2		
			58.0	14.5		103
			40.5	13.3		(average)
			18.6	14.0		
July 14	10^{-3} *M* KCl	149	97.6	6.8		99
			58.0	7.2		(average)
			40.5	7.2		
			18.6	6.7		
July 20	10^{-2} *M* KCl	1413	58.0	0.28		36
			40.5	0.26		(average)

rect value, as can readily be seen by substituting values for κ. Thus, where he says a capillary of 24.6-micra radius would show a fall of 1.5 per cent in stream potential with 10^{-4} *M* potassium chloride, this is really true for a 2.46-micra radius. Since no one ever has been able to measure stream potentials on capillaries of 5-micra diameter with a reproducibility within 1.5 per cent, the matter is not at present susceptible

TABLE 2

Results with 1 × 10^{-4} M potassium chloride

CAPILLARY DIAMETER	DATE	TREATMENT	κ_{sol}	E/P	κ_{cap}	ZETA	κ_s
micra			*mhos* × 10^{-5}	*mv./cm. Hg*	*mhos* × 10^{-5}	*mv.*	*mhos* × 10^{-9}
38.6	May 9	a	1.65	68.7	1.80	117	1.50
	May 10	a	1.67	73.0	1.81	125	1.39
	May 13	a	1.67	64.8	1.83	112	1.58
	May 15	a	1.71	70.2	1.84	122	1.34
	May 16	a	1.71	68.1	1.81	117	1.01
	May 22	b	1.66	60.0	1.76	100	1.10
	May 23	b	1.66	65.4	1.76	109	1.10
12.0	May 9	a	1.65	56.2	2.00	106	1.03
	May 13	a	1.67	14.4	1.97	31	0.89
	May 16	a	1.71	17.0	2.04	33	0.98
				15.9	2.03	31	0.95
	May 22	b	1.66	13.1	1.92	23	0.77
5.4	May 31	a	1.77	2.2	3.26	7	1.85
	June 1	b	1.77	>1	2.90	>1	1.44
4.1	May 9	a	1.65	42.2	3.23	129	1.65
	May 10	a	1.67	38.4	3.23	117	1.63
	May 11	a	1.67	35.0	3.11	103	1.50
	May 17	a	1.71	24.2	2.85	65	1.19
	May 18	a	1.69	20.6	2.50	49	0.85
				18.4 eq	2.40	42	0.74
	May 21	a	1.67	34.1	2.92	94	1.30
				32.8	2.87	89	1.25
				32.2	2.82	86	1.20
				31.1	2.73	80	1.10
				29.9	2.71	77	1.07
				29.5	2.71	76	1.07
				28.3	2.60	70	0.97
	May 22	b	1.66	26.8 eq	2.66	68	1.04
	June 1	b	1.77	31.0			
				17.7 eq	2.34	39	0.60

to experimental investigation. Second, he quotes White, Urban, and Krick as having used 5×10^{-5} *M* potassium chloride, where the effect would be somewhat greater, whereas we used 5×10^{-4} *M* potassium chloride. Third, we now know that the stream potential in 5-micra capillaries is usually reduced to an even greater extent than reported by White, Urban, and Krick. The matter may be summed up by the statement that the Komagata effect is entirely negligible and in no way able to account for the observed diminution in stream potential with decreasing capillary size. Of course, with pores of ultramicroscopic size, as in collodion and cellophane membranes, the effect no doubt is important, particularly with dilute solutions.

In the experiments of tables 2 and 3 capillary resistances were measured, making possible calculation of κ_{cap} and of zeta. *E/P* of the smaller (4.1 and 12 micra) capillaries is originally reduced to about the extent that

TABLE 3

Results with 5×10^{-4} M potassium chloride

CAPILLARY DIAMETER	DATE	TREATMENT	κ_{sol}	*E/P*	κ_{cap}	ZETA	κ_s
micra			*mhos* $\times 10^{-5}$	*mv./cm.* Hg	*mhos* $\times 10^{-5}$	*mv.*	*mhos* $\times 10^{-9}$
5.4	June 3	a	7.67	>1	8.80	>1	1.39
	June 6	b	7.67	>1	8.70	>1	1.28
4.1	May 2	a	7.66	12.6	9.45	109	1.87
	May 3	a	7.66	12.0	9.20	104	1.63
	May 8	a	7.66	11.5	9.13	99	1.55
	June 3	a	7.67	5.7	7.97	43	0.31
	June 6	b	7.67	4.5	7.89	37	0.23

κ_{cap} is increased over κ_{sol}, i.e., zeta is about normal. In general, however, *E/P* and zeta fall with time; this tendency appears to be greater the smaller the capillary, although the large ones also show some fall with time. The "eq" after some of the figures in table 2 designates that these were stable or equilibrium values for these dates, i.e., that no further fall occurred during several hours. Some exceptions may be found to almost any general statement about capillary behavior if one makes enough measurements. Some small capillaries, as the 5.4-micra capillary of tables 2 and 3, never show much stream potential, even when new. This may be because of a localized constriction which cannot be recognized by our methods of measurement. It thus appears that cylindrical small capillaries may early in usage show a normal zeta, which means for a 5-micra capillary with 1×10^{-4} *M* potassium chloride an *E/P* of about 50 per cent the normal value, but that zeta usually falls with time so that *E/P* becomes from 5 to 30 per cent of normal. The operation of factors which might be expected to lower zeta by not more than 10 or 15 per cent could hardly be recognized.

Surface conductivity

Data on specific surface conductivity are also given in tables 2 and 3. The calculated values of the capillary resistances with the dilute solutions are obtained from the capillary dimensions and the observed specific bulk conductivities of the dilute solutions, which of course include the conductivity of the water. From these data and from the observed capillary resistances with the dilute solutions the specific surface conductivities are calculated. The results are more reliable with 1×10^{-4} than with 5×10^{-4} *M* potassium chloride, since with the former surface conductivity is a considerably higher fraction of total conductivity. While the tables show that the normal specific surface conductivity with 1×10^{-4} *M* potassium chloride is only slightly less than with 5×10^{-4} *M*, we do not insist that this represents the real truth, because of the probable error in the latter measurements. We believe, however, that the findings permit the conclusion that within this range of concentrations changes in specific surface conductivity must be considerably less than changes in bulk conductivity. The magnitude of the present values for specific surface conductivity with 5×10^{-4} *M* potassium chloride agrees well with the value of 2.2×10^{-9} mhos per cm.^{2} reported by White, Urban, and Van Atta (7).

Many measurements of surface conductivity have been made while the solution was being forced through the capillary under pressure up to 60 cm. of mercury, and many others with no applied pressure, the liquid in the flask and in the outer beaker in this case being carefully brought to the same level. We have never seen any evidence that the flow of liquid has any effect on surface conductivity. Surface conductivity remains the same, for at least an hour after pressure is released, as it was while the pressure was on.[3] Whatever effect electrosmotic movement may have in disturbing the structure of the double layer, as postulated by McBain and Foster (3), would of course still be operative with the pressure released.

Correlation between surface conductivity and zeta

The findings on the smaller capillaries, other than the 5.4-micra capillary show a correlation between the magnitudes of zeta and of surface conductivity. No correlation exists with the 5.4-micra capillary because it was incapable at any time of showing anywhere near a normal stream potential, probably because of a localized constriction. It appears that

[3] This, of course, does not answer McBain and Foster's (3) objection that under these conditions surface conductivity, although present, is masked by a corresponding depletion of bulk solution in the capillary. We feel that the question must remain open for the present.

variations in double layer charge density, due to spontaneous variations in the properties of the surface, are reflected both in stream potential and in surface conductivity. This correlation in a given capillary was not detected by White, Urban, and Van Atta (8), because determinations both of stream potential and of surface conductivity were not made on capillaries smaller than 18 micra, where no great accuracy in surface conductivity measurements can be attained with 5×10^{-4} *M* potassium chloride.

SUMMARY

1. The stream potential, E/P, of glass capillaries falls off with decreasing capillary diameter. This effect is due largely to the increased specific conductivity in the smaller capillaries, due to surface conductivity. While a retarding effect due to electrosmosis is no doubt present, the data do not permit its evaluation.

2. The κR effect, as applied by Komagata to stream potentials, is negligible except with pores of ultramicroscopic size.

3. The value of E/P with most capillaries falls with time; this is not due to an increase in conductivity but presumably to a decrease in zeta.

4. The normal specific surface conductivity, measured with direct current, of 1×10^{-4} *M* potassium chloride at a Pyrex surface is about 1.5×10^{-9} mhos per cm.^{2} and of 5×10^{-4} *M* potassium chloride about 1.7×10^{-9} mhos per cm.^{2}

5. Variations in zeta in a given capillary, as shown by variations in E/P, are also reflected in variations in specific surface conductivity.

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ADSORPTION BY DIATOMACEOUS FILTERS[1]

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While attempting to use a Berkefeld filter candle to remove mother liquor from a crystalline solid, it was found extremely difficult to draw air through the candle by means of a vacuum pump after it was wetted by the aqueous mother liquor. Then it was observed that after washing the wetted filter with acetone it passed air readily; the acetone did not dissolve out a determinable amount of solid. It was thought that an investigation of this phenomenon might yield better insight into the behavior of these diatomaceous filters, and perhaps reveal why pore size determinations by the bubble method are erratic (1). Despite the extensive use of diatomaceous earth (3), few studies of its adsorptive power appear to have been made.

All of the experiments were carried out with Berkefeld "N" diatomaceous candles, which are supposedly of medium pore size. The apparatus chain consisted of a vacuum pump connected to a 4-liter round-bottom flask which was in turn connected, by means of a T-tube, to a manometer and a 1-liter suction flask; between pump and suction flask was a by-pass which allowed evacuation of the suction flask without disturbing the 4-liter flask. The candle and its glass reservoir were fitted into the top of the suction flask by means of a one-hole rubber stopper. In some experiments an air-tight connection was made between the open end of the candle reservoir and a Friederichs' gas-washing bottle to control partially the water vapor content of the air entering the diatomaceous candle. Each unit of the apparatus was separable from the rest by stopcocks.

The experiments were made by evacuating the system up to the Berkefeld candle, closing off the vacuum pump, opening the candle to the evacuated system, and reading the height of the mercury in the open arm of the manometer at regular intervals of time. From the height of the mercury in the open arm of the previously calibrated manometer and the atmospheric pressure, the pressure within the system was determined for each interval of time. The 4-liter flask was used in order to provide a reliable and duplicable pressure difference between the open side of the

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[1] Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20–22, 1935.

candle and the evacuated side. In this manner runs were made using different candles and the same candle under different conditions.

The first run was made using a new candle which had not been in contact with water, in order to determine the rate of flow of air through dry diatomaceous earth for comparison later with the rate through moist earth. This is candle No. 1. The next four runs with candle No. 1 were made using water, absolute ethanol, absolute methanol, and carbon tetrachloride. The data are given in table 1. The candle was completely dried each time before tests were made; and it was soaked thoroughly with the liquid to be tested, in addition to running 100 cc. of the liquid through it in each case. The gas-washing bottle did not contain any liquid during the runs of table 1. In this and the other tables representative data only are presented. In each run from twenty-five to fifty observations were made; all of these points were used in plotting the curves of figures 1 and 2, and formed smooth curves.

TABLE 1

Adsorption of liquids by candle No. 1

AIR		CARBON TETRACHLORIDE		ABSOLUTE ETHANOL		ABSOLUTE METHANOL		WATER	
Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure
seconds	*mm.*	*seconds*	*mm.*	*seconds*	*mm.*	*seconds*	*mm.*	*seconds*	*mm.*
15	184	10	54	10	46	10	73	30	94
30	241	20	88	20	90	20	128	210	38
45	464	30	118	30	129	30	168	510	57
60	545	40	148	40	161	40	202	810	84
75	607	50	181	50	190	50	235	1005	103
90	649	60	211	60	216	60	265	1200	124
105	680	70	245	70	241	70	291	1410	152
120	696	80	277	80	263	80	320	1605	169.5
135	709	90	312	90	292	90	348	1800	208
150	718	100	344	100	318	100	371	2010	240

Using candle No. 2, which was new at the start, a study was made of the differences in rate of air flow through candles wetted by aqueous solutions. The data are given in table 2. Distilled water was used in all cases. All solutions were 1.23 *M*, and in each case the gas-washing bottle was filled with the solution being tested and connected with the candle reservoir to guard against clogging the filter by deposition of solid salt in the pores. Just before each run the candle was kept in the boiling test liquid until no more air bubbles escaped from it, cooled to room temperature, and placed in the system. From the time of immersion in the boiling test liquid until the start of the run the candle was kept constantly in contact with the liquid, 50 cc. of the test liquid being run through the candle into the suction flask immediately prior to the start of the run. Using the by-pass around the 4-liter flask the suction flask was quickly evacuated again. The remaining liquid in the reservoir was then poured out and the run started. After each run hot distilled water was passed through the candle until the filtrate gave no test for the solute just used; then 1 liter more of hot distilled water was run through the candle, thus assuring the absence of the electrolyte.

The data from table 2 are plotted in figure 1, the pressures being the pressures within the system at the given times. The differences in the pressures for the various liquids at any given time are taken as measures

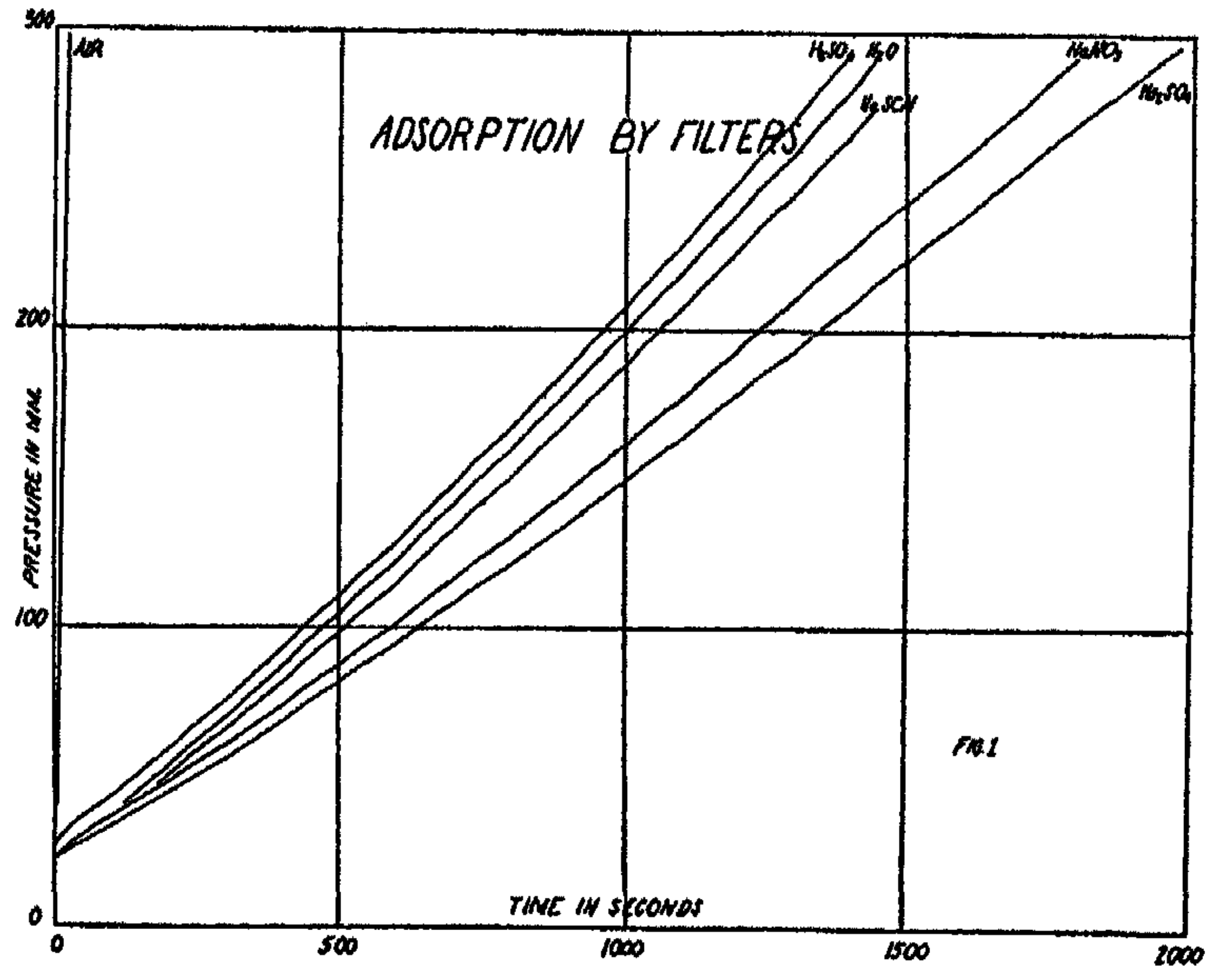

FIG. 1. Adsorption by filters

of the relative amounts of adsorption by the diatomaceous filters. The differences shown in figure 1 cannot be due to differences in vapor pressure, density, or viscosity, because they are not nearly in the correct order. The order of "clogging" of the candle was: sodium sulfate > sodium nitrate > sodium thiocyanate > water > sulfuric acid. If the effect were due entirely to changes in the water equilibrium, the order would either have to be the reverse of the above or the water curve would have to fall considerably further to the right. Experimental error is not a factor, because check runs made agreed to within 1.3 per cent.

Probably owing to the small amounts of electrolytes adsorbed by silica, few data are found in the literature. Gore (6) determined the amounts of adsorption of a number of salts and acids at different concentrations by silica. Since diatomaceous earth is largely silica, it may be expected to behave roughly like silica. So far as one can determine from Gore's results, when recalculated for approximately molar solutions, the order of increasing adsorption for sodium salts is: sulfate < chloride < bromide < iodide. The molar sodium sulfate solution increased in concentration by 1.09 per cent. The other salts showed positive adsorption.

In so far as it is permissible to reason from silica to diatomaceous earth, the experiments of Gore provide what appears to be the soundest explanation of the present results. On this basis, sodium sulfate decreases the permeability of the candles to air mainly by an increase in the amount of water adsorbed by the diatomaceous earth. The effects produced by sodium nitrate and sodium thiocyanate appear to be due to adsorption of electrolyte superimposed on the adsorption of water; potassium nitrate was adsorbed considerably more (data not obtained for sodium nitrate) than the corresponding halogen salts in Gore's experiments. The position of the sulfuric acid curve in figure 1 is about what one would expect from the fact that Gore observed no effect with a molar solution of this acid; it falls closer to the water curve when a correction is introduced for a slight difference in temperature which existed. In all other cases the maximum difference in temperature was one degree from 27°C.

TABLE 2

Adsorption of liquids by candle No. 2

WATER		SODIUM NITRATE		SODIUM THIOCYANATE		SODIUM SULFATE		SULFURIC ACID	
Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure
seconds	*mm.*	*seconds*	*mm.*	*seconds*	*mm.*	*seconds*	*mm.*	*seconds*	*mm.*
60	31.5	180	46.5	60	29.5	60	28.5	60	37.5
180	49.5	360	68.5	180	46.5	240	48.5	180	55.5
360	79.5	540	93.5	360	75.5	420	70.5	360	86.0
540	111.5	720	120.5	540	105.5	600	94.5	540	118.0
720	146.5	900	147.5	720	136.5	900	134.5	720	152.0
900	181.5	1080	175.5	900	170.5	1200	179.5	900	189.0
1080	217.5	1260	206.5	1080	207.5	1500	224.5	1080	227.0
1260	255.5	1440	234.5	1260	240.5	1800	268.5	1260	265.5
1440	291.5	1620	262.5	1380	262.5	1920	288.5	1380	291.5
1380	279.5	1800	292.5	1440	274.5	2040	306.5	1500	320.0

The data from table 1 are plotted in figure 2, curves 1, 2, and 3. Curve 1 was obtained by plotting the data for methanol, while curve 2 represents the data for ethanol and carbon tetrachloride, the two being so close together that they are represented by one curve. Curve 3 was obtained by plotting the data for water in candle 1. Check runs agreed within 1 per cent. The main point of interest is the large difference between the curves for the organic liquids and that for water, the amounts of adsorption being of entirely different orders. Also there appears to be some specific adsorption as between the organic liquids, since vapor pressure differences do not entirely account for the results. In a differently arranged experiment, toluene and acetone behaved similarly to the above three organic liquids, did not differ much between themselves and, by comparison with water under those conditions, were only slightly adsorbed. Since the vapor pressure of toluene is about that of water, the differences between the behavior of the organic liquids and water cannot be accounted for on that basis. The air curve falls to the left of curve 1, of course.

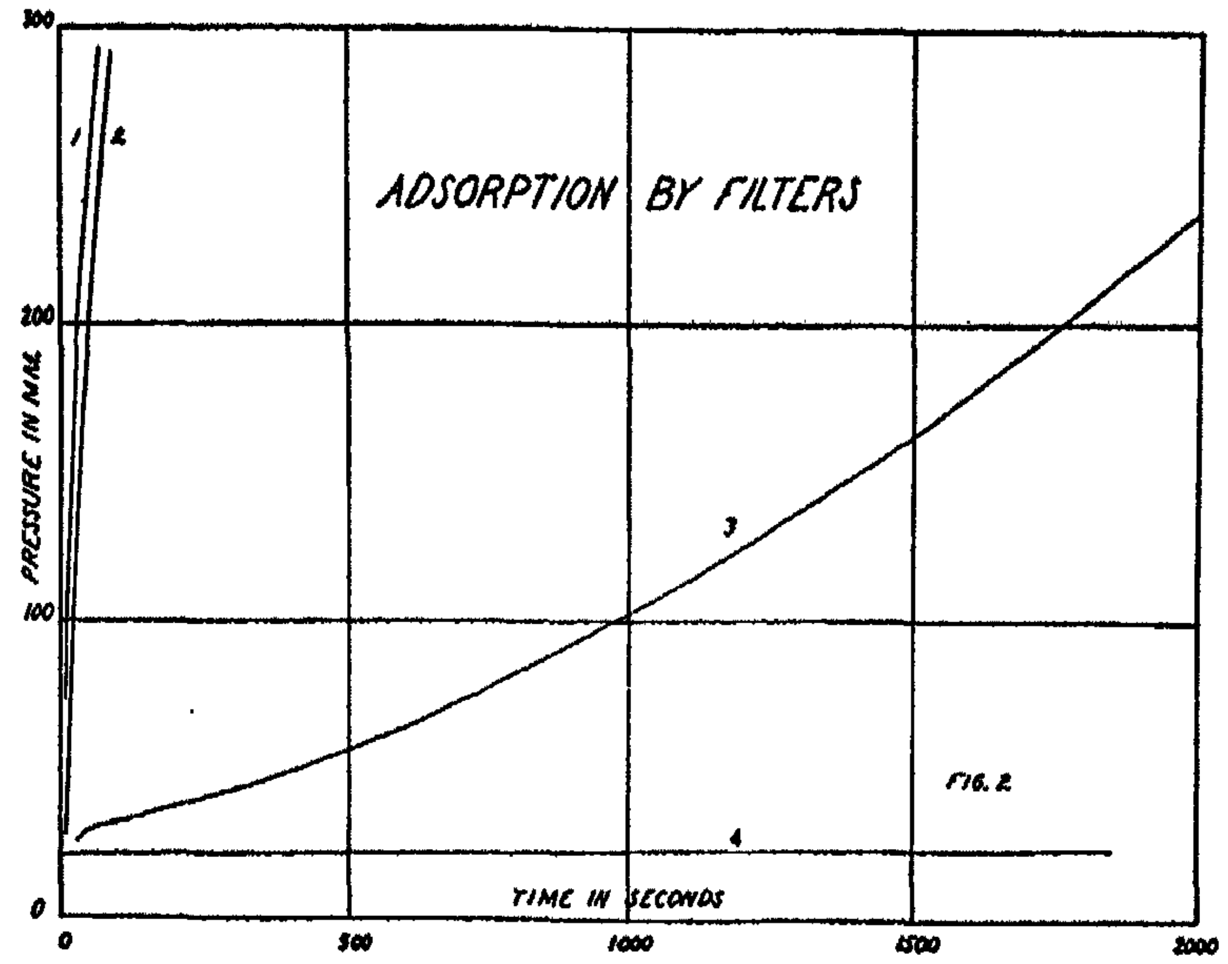

FIG. 2. Adsorption by filters

Ewe (5) points out that filters for sera prepared from the same sample of kieselguhr treated in the same way show considerable variability in performance. This is probably due to differences in pore size and consequent differences in amounts of adsorption. Table 3 contains interesting data on the behavior of candle No. 3, also an "N" candle, toward water. The data are plotted in figure 2, curve 4. There is a tremendous difference in the adsorption of water by this candle and candle No. 2. With candle No. 3 the pressure in the system was below the vapor pressure of water at that temperature for over thirty minutes. The candle was virtually plugged by adsorbed water. The water curve in figure 1 is different again, there being less adsorption than in either of the other two cases. These results were duplicated. From this it appears that identity of behavior is not to be expected as between any two given Berkefeld candles. It might be worthwhile for the bacteriologist to standardize his candles by the amount of water they will adsorb, using the above method.

Microscopic examination of candles No. 1, 2, and 3 revealed the reason for the differences in the amount of water adsorbed by them. It was found that with increasing adsorption of water there had been an increasing amount of destruction of the diatoms, probably during the process of manufacture. In other words, the fragments of the diatoms were smaller with increasing adsorption, which probably means smaller pore size and which certainly means an increased specific adsorbing surface.

TABLE 3

Adsorption of water by candle No. 3

TIME	PRESSURE	TIME	PRESSURE
seconds	*mm.*	*seconds*	*mm.*
15	20.5	1200	23.5
90	21.5	1800	23.5
240	21.5	3000	26.5
600	21.5	4500	28.0
900	22.5	7200	29.0

We can now see why pore size determinations in ultrafilters are erratic. Bechhold (2) gives two methods for the determination of pore sizes of ultrafilters, which he calls the air transpiration method and the rate of transfusion of water method, respectively. The air transpiration method falls down in such filters as the Berkefeld, where the water is strongly adsorbed; two different liquids would give two different values depending on their relative adsorptions, and two different filters would give different values which would express both a difference in pore size and a difference in adsorption. Measurements such as those of Einstein and Muhsam (4), in which ether was used instead of water, are probably free from this objection, because it is not to be expected that the ether is strongly adsorbed by the Berkefeld filter. In the rate of transfusion method no account is taken of the effect of adsorption. This method is defective to that extent. It seems clear that more concordant results on pore size should be obtained by the use of a non-adsorbed or slightly adsorbed liquid, and the pore size should be greater the less the adsorption.

The general results of this paper are as follows:

1. Diatomaceous earth adsorbs water strongly.

2. Berkefeld filters of the same rating show great variation in behavior when wetted by water, probably because the diatoms are crushed to different degrees.

3. Salts are adsorbed by diatomaceous earth, sodium thiocyanate being less strongly adsorbed than sodium nitrate.

4. There is quite strong negative adsorption of a sodium sulfate solution by the Berkefeld filter.

5. Organic liquids tested were adsorbed less than water.

6. A method is suggested for the evaluation of Berkefeld filters for bacteriological work.

7. Certain pore size determinations on ultrafilters are shown to be defective.

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ADSORPTION AND DIFFUSION IN ZEOLITE CRYSTALS

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Zeolites are silicates of calcium, sodium, or potassium together with some aluminum in the anion structure. They occur as minerals in certain volcanic rocks and often form very large and beautiful crystals. Artificial zeolites are made technically for use in water-softening processes, but these substances are not nearly as well defined or well crystallized as the natural minerals.

It has been known for a long time that zeolite crystals show some very unusual properties. (For complete literature references see ref. 2.) They are capable of exchanging reversibly both the cations in the structure against others (for example, Ca against 2Na, and so on), and the water of crystallization against other substances, like ammonia, carbon dioxide, and hydrogen. The cation exchange is the basis of the technical use of zeolites in water-softening. It is quite remarkable that the exchange processes, if performed carefully, leave the crystal lattice unspoiled, as x-ray measurements have shown. Only slight modification of the parameters may occur, corresponding to shrinking or expansion of the lattice. Even the crystal itself may be left entirely intact, transparent, and without cracks. The reverse process gives a crystal which cannot be distinguished from an untreated specimen.

During the last five or ten years our knowledge of the lattice structures of silicates has increased enormously, thanks to the work of W. L. Bragg and his collaborators, especially W. H. Taylor (1). Their studies include a number of the simplest zeolite minerals, and their results give a very good explanation of the remarkable behavior of this class of crystals. For a recent survey of the work on zeolites see the paper by W. H. Taylor (4). It has been found that the zeolite lattice is built up of a very rigid framework of SiO_4 and AlO_4 anions, forming a sort of giant anion. This framework contains channels of sufficiently large diameter to admit cations, water molecules, and other substances of not too big molecular size. The cations and water molecules are not placed at random in the framework, but are fixed to definite positions, which can be determined. The water molecules seem to be most closely associated with the cations of the structure.

The vapor pressure over a dehydrated zeolite crystal, partially saturated with water, ammonia, or other gas, varies continuously with the amount bound by the crystal. In fact, the curve looks very much like an ordinary adsorption isotherm (see figure 1). There are no sharp discontinuities corresponding to certain molar ratios, as one gets with crystal hydrates and ammoniates.

The study of the adsorption properties of these crystals is of great interest since few, if any, adsorbents possess such a well-defined character. We know that for these adsorbents, the molecules held in the lattice take up definite positions which, in some cases, can be determined. We also know the number of lattice positions available in the crystal. Being silicates, these substances are chemically inert and stable, and therefore give results which are quite reproducible as compared with adsorbents such as charcoal, whose adsorption capacity varies with the origin and previous treatment of the material.

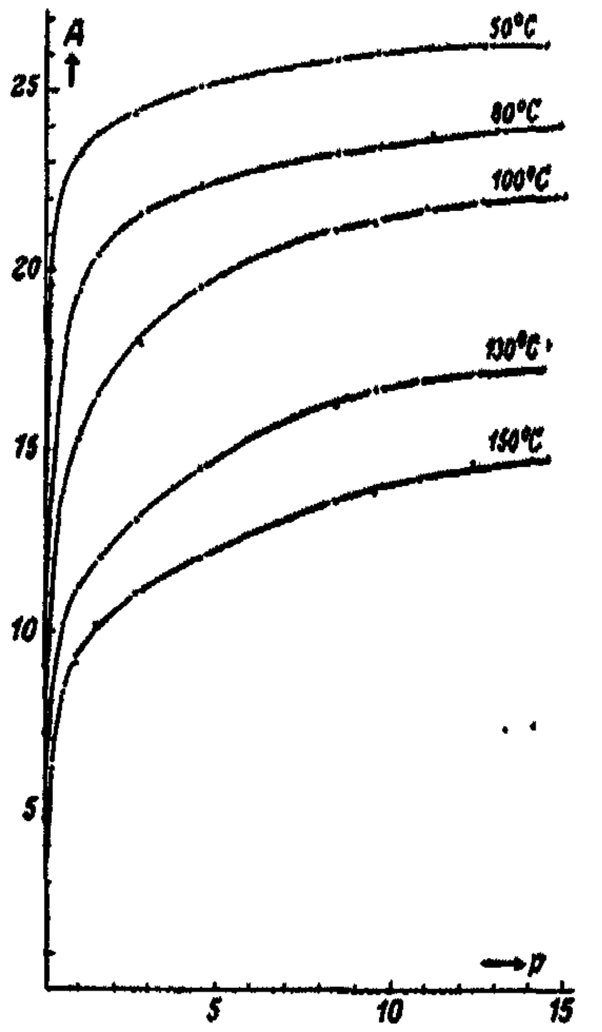

FIG. 1

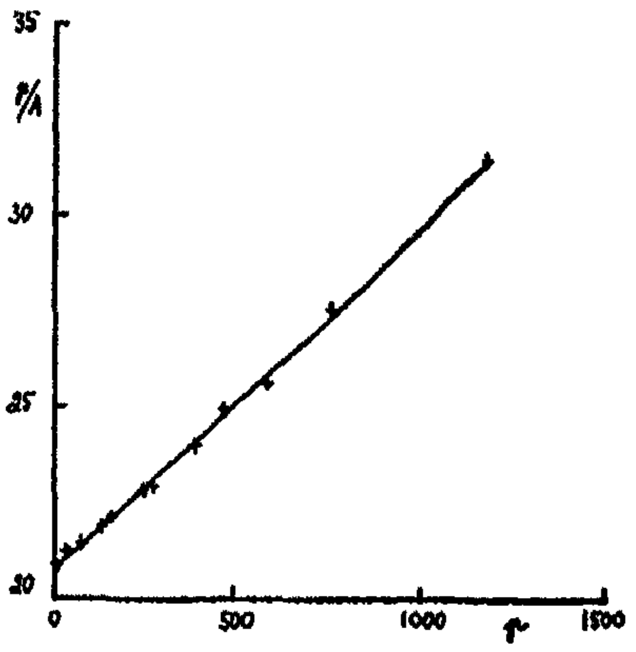

FIG. 2

FIG. 1. Adsorption of water vapor by chabasite (measurements by Tiselius and Brohult). p = pressure in mm. of Hg; A = adsorbed quantity in grams per 100 grams of dehydrated material.

FIG. 2. Adsorption of ammonia by analcite. p = pressure in mm. of Hg; A = adsorbed quantity in cc. at N.T.P. per gram of dehydrated material.

The zeolite structure described above explains an interesting characteristic of zeolite adsorption: there seems to be a certain maximum size of molecules above which no adsorption takes place. Chabasite, for example, adsorbs readily helium, hydrogen, oxygen, nitrogen, carbon dioxide, water, ammonia, methyl alcohol, and ethyl alcohol, but not benzene, ether, the higher alcohols and larger molecules (3, 7). Charcoal, on the other hand, having pores of all sizes, adsorbs very large molecules especially strongly. This may also be a reason for the good reproducibility of zeolite adsorbents: since they admit only quite small molecules which are easily volatilized, they can be freed completely from foreign contaminations by heating in a vacuum.

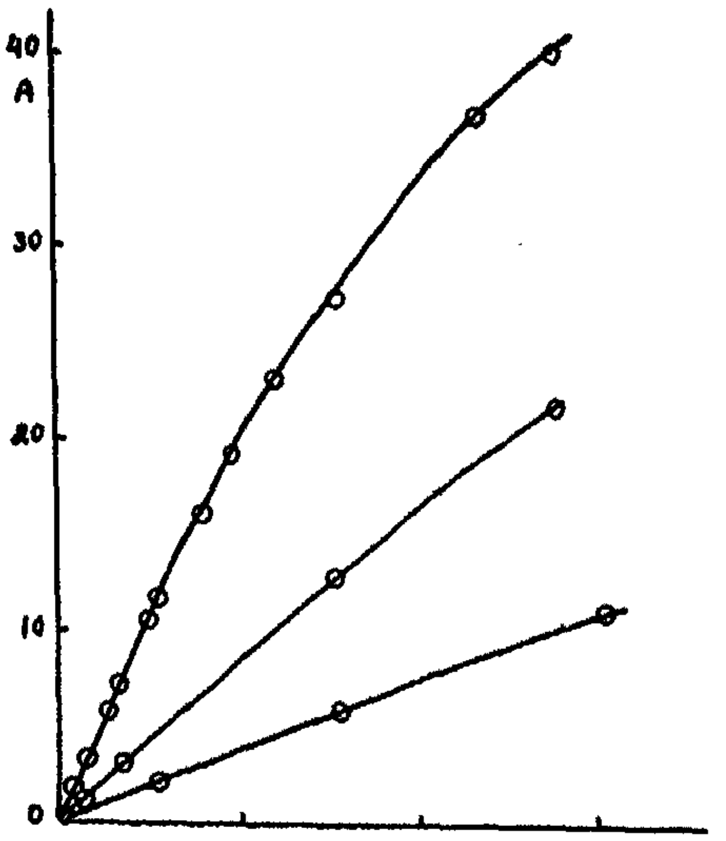

FIG. 3. Adsorption of ammonia by analcite plotted according to Langmuir

Since the molecules in a zeolite lattice are bound to definite positions, one would expect Langmuir's theoretical considerations on adsorption to be applicable. It makes no difference, of course, that we have to deal with a three-dimensional instead of a two-dimensional case. The assumptions made by Langmuir in the simplest cases were that all the adsorbed molecules be bound with the same energy and that there be no interaction between adsorbed molecules. As regards the first point we may obtain some information from x-ray data. W. H. Taylor (4) found that in some cases, for example, thomsonite, there are three different kinds of equivalent positions for the water molecules; in others, for example, scolecite and chavassite (8), there are two kinds; but in two of the cases investigated hitherto, natrolite and analcite, there is only one kind. Most of the work on zeolite adsorption has been made with chabasite, which is the most convenient to work with experimentally, the adsorption capacity being very high (like that of activated charcoal) and the equilibria being established rapidly.

From the results mentioned, however, analcite and natrolite should be expected to show the simplest behavior. The author has recently measured the adsorption of ammonia on dehydrated analcite, and similar work is being carried on at Upsala by S. Brohult. These measurements are difficult, since the rate of adsorption is low, and it is possible to get equilibria within a reasonable time only at high temperatures (about 250°C.). Some results are shown in figures 2 and 3. The isotherms obey the Langmuir law quite well up to an adsorbed quantity of about 25 cc., as shown by figure 3. Still more important is the fact that the heat of adsorption, calculated in the usual way from the isotherms by the Clapeyron equation, is constant over a wide range, as shown by the results given in table 1. This is not usually the case, the heat of adsorption often being much larger for the first amounts adsorbed than for later amounts. It is certainly not true for the system chabasite–water. Still this is a necessary condition for the validity of Langmuir's law. The other condition is the lack of interaction between adsorbed molecules. The deviation of the curve in figure 3 from a straight line for higher concentrations indicates that such an interaction takes place under such conditions, although no determinations of heats of adsorption could be made. The constant a in the Langmuir equation

TABLE 1

Heats of adsorption of ammonia on analcite, calculated by use of the Clapeyron equation on the 302°- and the 341.3°-isotherms in figure 2

AMOUNT ADSORBED A cc. PER GRAM OF DEHYDRATED MATERIAL	HEAT OF ADSORPTION Q CALORIES
5	16880
10	16530
15	16860
20	16700
25	16350
Average	16640

$$A = \frac{abp}{1 + bp}$$

calculated from the isotherms in figure 2, is 124 cc. at 302°C. and 125 cc. at 341.3°C. The value calculated from the number of spaces available in the crystal is 118 cc., in good agreement with the experimental value. Usually the constant decreases rapidly with temperature, on account of a wide variation in the energy of adsorption over the surface. As regards the nature of the binding forces in these crystals, the x-ray measurements by W. H. Taylor referred to above (4) show that the water molecules are placed in a more or less deformed tetrahedron, with two sodium ions (for analcite and natrolite) and two oxygen ions at the corners. Evidently the molecule is held in a sort of "dipole hole" and therefore in a strong electrostatic field. This explains why molecules with permanent moments like water and ammonia are so strongly adsorbed. As far as the water molecules are concerned, the arrangement is very similar to that found in ordinary crystal hydrates like $CaSO_4 \cdot 2H_2O$.

The following experiment also indicates that coördination valencies play a rôle. A thin section of a transparent chabasite crystal was completely transformed into copper chabasite by keeping the crystal for several days in a copper sulfate solution at 100°C. The crystal, now showing the characteristic blue color of copper salts, was dehydrated and ammonia let in. An absorption spectrum was taken, using the quartz vacuum chamber described below. This spectrum proved to be identical with that obtained from a solution containing copper ammonium ions.

Zeolites form a very suitable material for investigating the mechanism of the kinetics of adsorption. The rate of adsorption, as measured in the usual way on powders, varies from fractions of one second to almost infinite time. With the same zeolite different substances are adsorbed at very different rates; chabasite takes up hydrogen and water vapor at room temperature in a few minutes, whereas iodine or mercury are taken up at a measurable speed only at temperatures above 100–200°C. Different zeolites also differ toward one and the same substance. Analcite does not adsorb any water or ammonia at room temperature, but when heated above 100°C. it takes up slowly large amounts of these gases, although the rate becomes sufficiently high to make measurements of equilibria within a reasonable time, only above 250°C. One may obtain some insight into the mechanism of these processes by measurements on powders. Much more detailed information, however, can be obtained by using a direct optical method of observing what happens in a single, evacuated zeolite crystal when a gas, for example, water vapor, is being adsorbed. It has been mentioned already that some zeolite crystals remain transparent after dehydration and readsorption, at least if the operations are performed very slowly and care is taken to avoid too high temperatures or sudden temperature changes. These empty or partially saturated crystals show, when investigated under the polarizing microscope, some very interesting changes in optical properties which can be ascribed to a continuous change of double refraction and extinction angle with the variation of the amount of water or any other substance in the crystal. Measurements of these quantities can therefore be used as an accurate method of determining the concentration of the adsorbed substance in any part of the crystal and make it possible to observe directly on a single crystal how it is penetrated by a substance being adsorbed.

To make observations of this kind, a small chamber was constructed of optical quartz, fused together vacuum-tight, which could be connected to a vacuum apparatus by a ground joint. The chamber could be placed in a microfurnace under the microscope, and it was thus possible to make observations in a vacuum or any gas pressure desired at temperatures up to about 500°C. The first investigation of this kind was made with the zeolite heulandite, which is especially easy to obtain in optical samples (6). The experimental arrangement is shown in figure 4. K is the quartz chamber, enclosed in the microfurnace, P is the polarizing microscope, and the rest is an arrangement for maintaining a constant water vapor pressure. Figure 5 shows a series of exposures of a heulandite crystal adsorbing water. They were taken between crossed nicols in monochromatic (sodium) light. The first exposure shows the partially dehydrated crystal before starting the experiment; the others show the changes taking place after water vapor has been admitted. Two black interference bands, parallel to the surface, migrate slowly into the crystal. In white light a similar series of brightly colored bands is observed. The effect depends, of course, upon the change in double refraction produced by the adsorbed water, the positions of the black bands at any time corresponding to water concentrations giving a double refraction that extinguishes sodium light

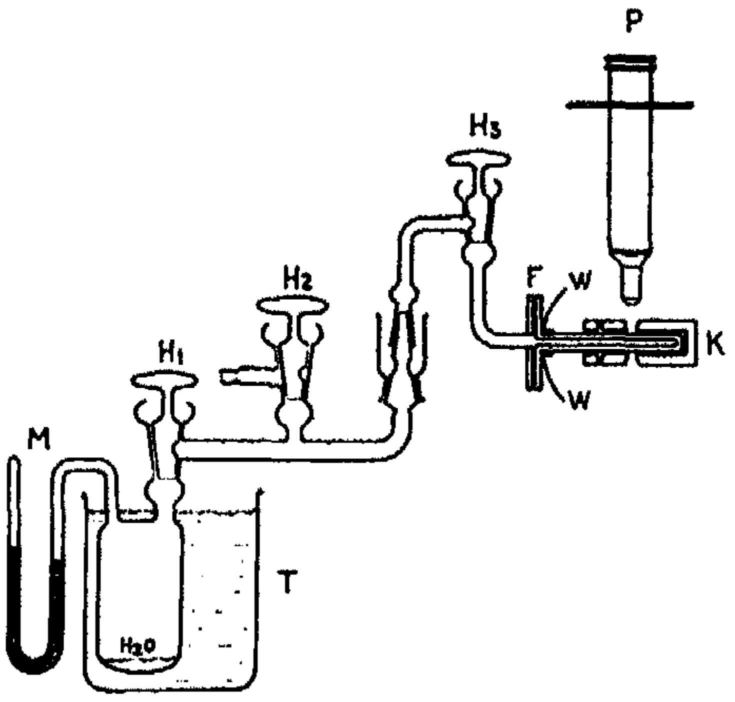

FIG. 4. Experimental arrangement for direct optical observation of diffusion of substances adsorbed in single zeolite crystals.

for the thickness of the crystal plate employed. More bands are observed (figure 6) if a more strongly dehydrated crystal is used, so that the interval of water concentration becomes greater.

The distance travelled by each band is proportional to the square root of time (figure 7), which is in agreement with the requirements of the theory of diffusion. The measurement of these distances forms a convenient method for determining the diffusion constant, if the relation between double refraction and water concentration in the crystal has been determined. By using a compensator with the microscope one can follow also the change of double refraction with time at a point a fixed distance from the surface.

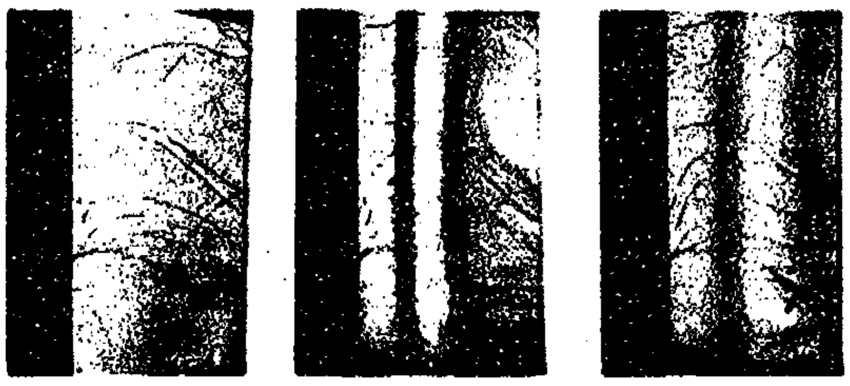

FIG. 5

FIG. 6

FIGS. 5 AND 6. Microphotographs of the diffusion of water adsorbed in a heulandite crystal, exposed between crossed nicols in sodium light.

These methods reveal a strong anisotropy of diffusion, as figure 8 demonstrates. Furthermore, the diffusion in the direction of observation (perpendicular to the plane of the paper in figures 5, 6, and 8) is immeasurably small.

The results show that the migration of the water molecules in the crystal follows the ordinary diffusion laws for solutions. This is, however, true only for small concentration intervals. Measurements over wider intervals show that Fick's law is still valid, but the diffusion constant is strongly dependent on the concentration, at least for low concentrations, as shown by the results in table 2. The probable reason for this abnormal behavior is the fact that adsorption is thermodynamically not a case of ideal solution; instead, the vapor pressure increases faster than proportional to the concentration. Moreover, for heulandite, the first amounts of water adsorbed are exceptionally firmly bound by the lattice, making it more difficult for the molecules to jump to an adjacent position. Since we know that the molecules take up definite positions in a lattice, the most plausible mechanism of diffusion is that of "hopping" from one position to another, already assumed by Langmuir and others for describing surface diffusion phenomena. The chance of hopping, and hence the diffusion constant D, should in such a case be proportional to the exponential $e^{-q/RT}$, where q is the energy of activation of diffusion. Plotting log D against $1/T$ should give a straight line, which is actually the case (figure 9). The different crystallographic directions give different temperature coefficients. For diffusion perpendicular to (201), q = 5400 cal.; for diffusion perpendicular to (001), q = 9140 cal. It is interesting to compare the values of q thus

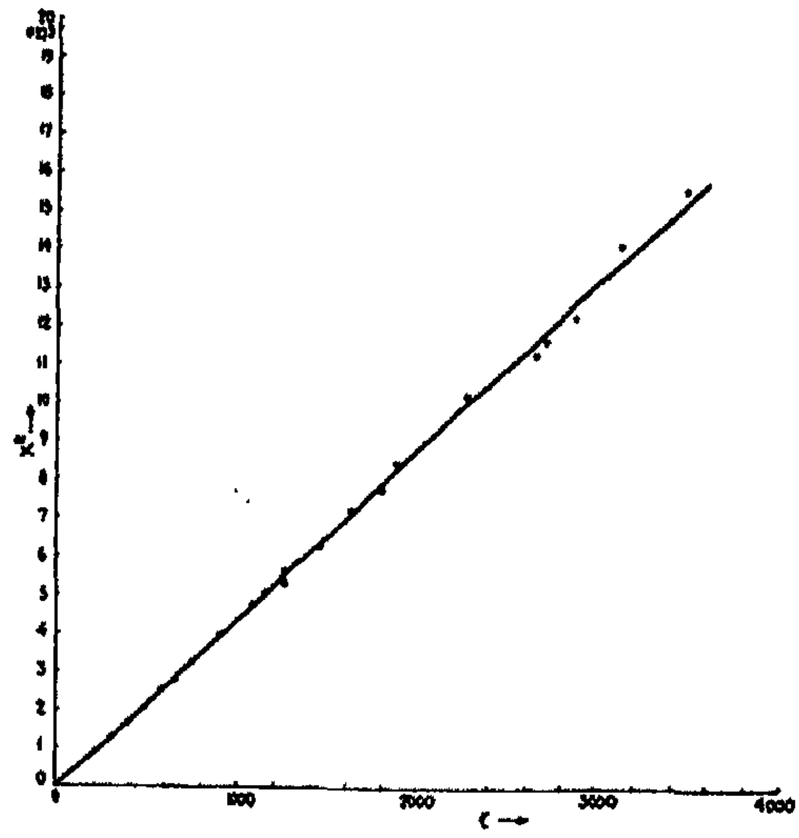

FIG. 7. The square of the travelled distance of each interference band is proportional to t

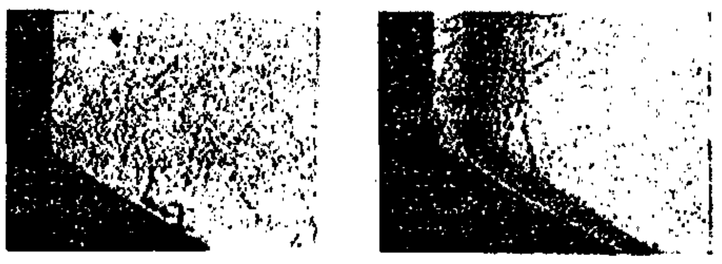

FIG. 8. Anisotropy of diffusion of adsorbed water in a crystal of heulandite

obtained with the heat of adsorption, which for water in heulandite is 14,100 cal. at the concentration where the temperature coefficients were determined. For making a diffusion jump, therefore, only 0.4 to 0.65 of the energy required to jump entirely out of the lattice is necessary. One may imagine this as a result of the adsorption spaces being so near to each other that their force fields partially overlap.

TABLE 2

Diffusion constants for water in heulandite at 20.0°C., in the direction perpendicular to (201)

WATER CONCENTRATION	$D \times 10^7$	WATER CONCENTRATION	$D \times 10^7$
per cent	*cm.²sec.⁻¹*	*per cent*	*cm.²sec.⁻¹*
10	about 0.04	15	2.7
11	about 0.2	16	3.6
12	0.7	17	4.0
13	1.3	18	4.0
14	2.0	19	3.3

The diffusion constants in the direction perpendicular to (001) are 11.6 times smaller.

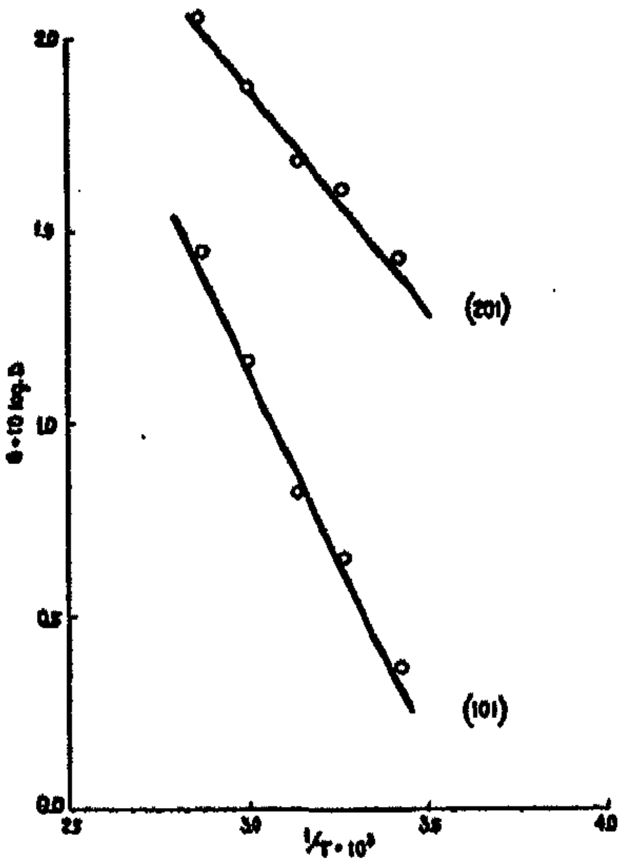

FIG. 9. Temperature dependence of the diffusion constant for water adsorbed in heulandite

Recently the author has made similar experiments on the system analcite and ammonia. Although the work has not yet been concluded, it is quite evident that the diffusion constant is very much lower and the activation energy is very high, equal to or even larger than the heat of adsorption, which in this case is 16,600 cal. One reason for this may be that the adsorption spaces in analcite are very widely separated (as is known from its crystal structure and water content).

The kinetics of adsorption, especially the slow or activated adsorption, has attracted much attention during recent years. The experiments have so far been made exclusively on powders or conglomerates of crystals by volumetric methods. However, in the investigations just described it is certain that the diffusion in the crystal is the rate-determining factor. This is evident from the fact that the concentration at the surface all the time during the adsorption process is constant and equal to the saturation value, as can be observed directly under the microscope. This may not always be the case for adsorption in zeolites, and it is therefore valuable to be able to get additional information by the optical method described.

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22-33.

THE SORPTION OF BROMINE AND IODINE BY ACTIVATED CHARCOAL

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In a previous publication (1) a method was described which made it possible to study the sorption of bromine and iodine by porous adsorbents over a rather wide pressure range at several temperatures. At that time the sorption of bromine and iodine by silica gel at several temperatures was reported. Equilibria for adsorption and desorption were established rapidly in the case of silica gel. In the present study on charcoal equilibrium was reached slowly, so that rates of sorption were measured in addition to the determination of the amounts taken up at equilibrium.

The charcoal used in this investigation was prepared from coconut shells. Broken coconut shells were cleaned and then placed in a large Soxhlet extractor where they were successively extracted for prolonged periods with ether, alcohol, and finally water. The extracted shells were coked in a covered iron crucible in a sand bath. The temperature was raised slowly to 550–575°C. and held there for half an hour after the last flammable vapors came off. After cooling the charcoal was crushed and sieved. A portion of 25 g. that passed a 10-mesh and was retained by a 20-mesh sieve was taken for activation. This was packed in a clean silica combustion tube and heated to 850°C. in an electric furnace. Superheated steam from a small boiler was passed over the charcoal for thirty minutes. After cooling, the average loss in weight on activation by steam was found to be 25 per cent of the initial weight. The steam-activated charcoal was then placed in a silica tube and heated to 700°C. while it was evacuated with a pair of Langmuir condensation pumps. The charcoal was protected from mercury vapor by a liquid air trap. After a 24-hour evacuation the charcoal was cooled to room temperature and oxygen admitted. After standing some time in an atmosphere of oxygen the charcoal was again heated and evacuated for a period of 48 hours. The charcoal was then cooled in an atmosphere of nitrogen. On ashing in a platinum crucible the following results were obtained: ash, 0.185 per cent; ash as sulfate, 0.233 per cent; silica, 0.026 per cent.

The charcoal was crushed in an agate mortar and that portion used which passed a 60-mesh and was retained by a 100-mesh screen. About 0.2 g.

TABLE 1

Sorption of bromine by charcoal

PRESSURE IN MM. CORRECTED	X/M MILLIMOLES PER GRAM OF SORBENT	HOURS FOR READING
Isotherm at 58.0°C.		
0.63†	4.155	9.0
3.0†	4.607	4.5
11.4†	4.972	14.0
68.8	5.358	20.0
140.4	5.554	21.5
265.7	5.665	23.0
473.0	5.779	24.0
691.8	5.849	22.0
474.1	5.804*	22.0
265.8	5.702*	14.0
140.4	5.579*	25.0
67.4	5.459*	27.0
11.4†	5.149*	10.5
1.8†	4.787*	13.0
0.63†	4.445*	16.0
0.03†	3.904*	35.0
Check isotherm at 58.0°C. after determining isotherms at higher temperatures recorded in this same table		
0.03†	3.431	72.0
70.6	5.456	23.5
695.6	5.836	24.0
68.3	5.456*	25.0
0.00‡	3.163*	24.0
Isotherm at 98.1°C.		
0.03†	3.044	22.0
3.0†	4.088	24.0
18.6	4.729	27.0
68.3	5.048	24.0
266.2	5.311	21.0
792.3	5.527	29.0
Isotherm at 98.1°C.—*concluded*		
266.2	5.335*	22.0
68.9	5.076*	22.0
18.2	4.776*	25.0
3.0†	4.124*	10.0§
0.03†	3.121*	22.0
Isotherm at 137.6°C.		
0.03†	2.611	20.5
1.8†	3.355	23.5
19.2	4.207	24.0
68.1	4.629	19.0
265.8	4.990	23.0
791.5	5.217	24.0
266.7	5.013*	24.0
69.5	4.671*	32.0
20.3	4.244*	21.0
1.8	3.377*	25.5
0.03	2.623*	24.5
Isotherm at 178.4°C.		
0.03†	2.250	38.0
3.0	3.016	33.0
16.8	3.619	25.0
67.2	4.143	20.0
266.8	4.628	23.5
787.8	4.899	26.0
266.7	4.645*	20.0
69.2	4.186*	27.0
17.8	3.652*	26.5
3.0†	3.054*	23.5
0.03†	2.247*	72.0

* Desorption readings.

† Values derived from vapor pressure function.

‡ High vacuum with charcoal at 58.0°C.

§ Thermostat had to be reset on temperature.

TABLE 2

Rates of sorption of bromine by charcoal at 137.6°C.

TIME IN MIMUTES	SPRING LENGTH IN MM.	MILLI-MOLES PER GRAM
Pressure = 0.03 mm.;* temperature = 98.1°C. 137.7°C.		
0	60.031	3.120
20	59.597	2.956
65	59.252	2.755
195	59.125	2.678
990	59.009	2.600
1230	59.001	2.587
Pressure = 1.8 mm.		
0	59.001	2.587
20	59.829	3.086
45	60.043	3.220
240	60.221	3.304
430	60.249	3.339
1260	60.276	3.361
1355	60.267	3.355
Pressure = 19.2 mm.		
0	60.267	3.355
15	61.289	3.951
20	61.457	4.073
25	61.491	4.069
40	61.564	4.112
100	61.633	4.146
645	61.703	4.176
1425	61.715	4.174
Pressure = 68.1 mm.		
0	61.715	4.174
5	62.034	4.370
10	62.303	4.529
15	62.357	4.566
30	62.370	4.586
60	62.395	4.607
140	62.413	4.612
245	62.415	4.613
495	62.425	4.619
1100	62.443	4.623

TIME IN MINUTES	SPRING LENGTH IN MM.	MILLI-MOLES PER GRAM
Pressure = 265.8 mm.		
0	62.443	4.623
5	62.950	4.906
10	62.985	4.932
25	62.999	4.946
180	63.037	4.974
400	63.040	4.976
730	63.055	4.985
1390	63.064	4.990
Pressure = 791.5 mm.		
0	63.064	4.990
5	63.370	5.153
10	63.396	5.179
30	63.405	5.184
170	63.420	5.193
410	63.433	5.201
830	63.448	5.216
1420	63.450	5.217
Pressure = 266.7 mm.*		
0	63.450	5.217
5	63.166	5.050
15	63.146	5.038
60	63.111	5.018
270	63.107	5.015
520	63.103	5.013
760	63.104	5.014
1330	63.102	5.012
Pressure = 69.5 mm.*		
0	63.102	5.012
5	62.656	4.757
15	62.620	4.739
60	62.540	4.692
520	62.520	4.680
670	62.517	4.678
885	62.516	4.678
1935	62.504	4.671

TIME IN MINUTES	SPRING LENGTH IN MM.	MILLI-MOLES PER GRAM
Pressure = 20.3 mm.*		
0	62.504	4.671
15	61.900	4.313
25	61.877	4.293
85	61.824	4.271
195	61.796	4.255
1070	61.780	4.242
1280	61.779	4.241
*Pressure = 1.8 mm.**		
0	61.779	4.241
10	61.110	3.851
20	60.831	3.687
30	60.688	3.597
55	60.532	3.511
420	60.361	3.411
1090	60.828	3.391
1600	60.302	3.376
Pressure = 0.03 mm.*		
0	60.302	3.376
5	60.234	3.324
10	60.082	3.241
20	59.901	3.122
60	59.518	2.909
120	59.340	2.807
195	59.222	2.720
250	59.184	2.713
910	59.110	2.657
1460	59.021	2.617

* Desorption readings.

of this charcoal was weighed into the little glass bucket of the McBain balance. The experimental procedure was the same as previously described (1).

Table 1 gives the results obtained for the sorption of bromine by charcoal at 58°, 98.1°, 137.6°, and 178.4°C. Table 2 gives the complete data at 137.6°C. for the rates of adsorption and desorption of bromine by the charcoal. Table 3 records the results of the sorption studies of iodine on charcoal. It should be noted that during desorption it was never possible to completely remove the bromine or iodine which had been adsorbed by the activated charcoal.

TABLE 3

Sorption of iodine by charcoal

PRESSURE IN MM. CORRECTED	X/M MILLIMOLES PER GRAM OF SORBENT	HOURS FOR READING
Isotherm at 178.4°C.		
0.03†	0.07492	5.5
10.6	0.2341	2.0
80.0	0.2774	12.5
169.0	0.2897	3.0
234.0	0.2963	1.5
368.0	0.3036	1.2
100.0	0.2815*	4.0
26.0	0.2614*	10.5
4.3	0.2205*	2.5
0.03†	0.0759*	30.0
Isotherm at 218.8°C.		
0.03†	0.0416	17.0
10.6	0.1881	3.5
80.0	0.2525	1.2
169.0	0.2671	12.0
Isotherm at 218.8°C.—*concluded*		
234.0	0.2721	2.2
423.5	0.2829	2.2
560.0	0.2882	2.7
317.5	0.2784*	2.2
100.0	0.2593*	11.0
26.0	0.2315*	5.0
2.0†	0.1470*	6.0
0.03†	0.0539*	22.0
0.00‡	0.0073*	8.0
Isotherm at 178.4°C.		
2.0†	0.2064	1.0
79.7	0.2889	18.0
168.4	0.3011	3.0
420.0	0.3175	2.0
315.5	0.3141*	14.0
118.5	0.2963*	4.0

* Desorption readings.

† Value derived from vapor pressure function.

‡ High vacuum at 525°C., spring measured at 37°C.

In a previous paper in this journal (2) figures were given for the data here presented. They are not therefore repeated here. The data are given as a matter of record for other investigators.

SUMMARY

1. Data are given for the sorption of bromine by activated charcoal at 58°, 98.1°, 137.6°, and 178.4°C.

2. Data are given for the rates of adsorption and desorption of bromine by charcoal at 137.6°C.

3. Data are given for the sorption of iodine by activated charcoal at 178.4° and 218.8°C.

REFERENCES

(1) Cameron, A. E., and Reyerson, L. H.: J. Phys. Chem. 39, 169 (1935).
(2) Reyerson, L. H., and Cameron, A. E.: J. Phys. Chem. 39, 181 (1935).

STUDIES OF POLARIZATION DISCHARGES IN MULTIPLE ELECTRODE SYSTEMS

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Each of two identical exploring electrodes, in equilibrium with an electrolytic solution, immersed between the current electrodes of an electrolytic cell, will conduct approximately the same amount of current. The current passing through two such exploring electrodes in the same direction will build up a positive pole and an equal negative pole on each electrode. The two exploring electrodes will form two concentration polarization storage batteries that will rapidly discharge when the polarizing current is stopped because each battery is shorted by the metal of the electrode. A definite current will continue to flow through the solution between the two exploring electrodes, if one tries to measure the potential difference between the two electrodes immediately after the applied current is stopped. Under these circumstances, we have observed currents that last for minutes and have measured these currents in various electrodes and cell systems.

The current electrodes become polarized during the passage of current. Also it has been pointed out that each current electrode becomes polarized differently at different points on its surface. We have observed currents that last for minutes midway between two electrodes twenty inches apart, when the only possible source of these currents was the two polarized current electrodes behaving as two shorted storage batteries connected together. There was no metallic connection between these electrodes, only the electrolytic connection.

Since the effect shows up with alternating current also, such currents will obviously affect the measurement of the conductivity and dielectric constant of electrolytes if electrodes are used. Therefore, the second part of this study was made to investigate the source of these currents and, if possible, their magnitude under various conditions. The variables cannot all be accurately controlled and the currents measured cannot be used to correct existing data, but it is pointed out that in the future apparatus should be designed that will eliminate any possibility of having these

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currents when they are important. The experimental part will indicate that the latter precaution is imperative.

EXPERIMENTAL

Electrodes and cells

Calomel, hydrogen, mercury–mercuric oxide, mercury–mercurous sulfate, silver, silver–silver chloride, and copper electrodes, all prepared by standard procedures, were used with solutions that would be in equilibrium with the electrodes. The most satisfactory chloride electrodes were made by uniformly coating pure silver wire or silver foil with the chloride, by electrolysis in a concentrated solution of the chloride to be studied. Electrodes whose potentials varied by less than a tenth of a millivolt could be prepared by this method. Two shapes were used, straight wires (size 16) with about two inches immersed vertically in the solution, as in figure 1, and electrodes with the same amount of surface exposed, but bent as in figure 2. The current electrodes, prepared in the same way, are designated as A and C; the exploring electrodes as E_a and E_c.

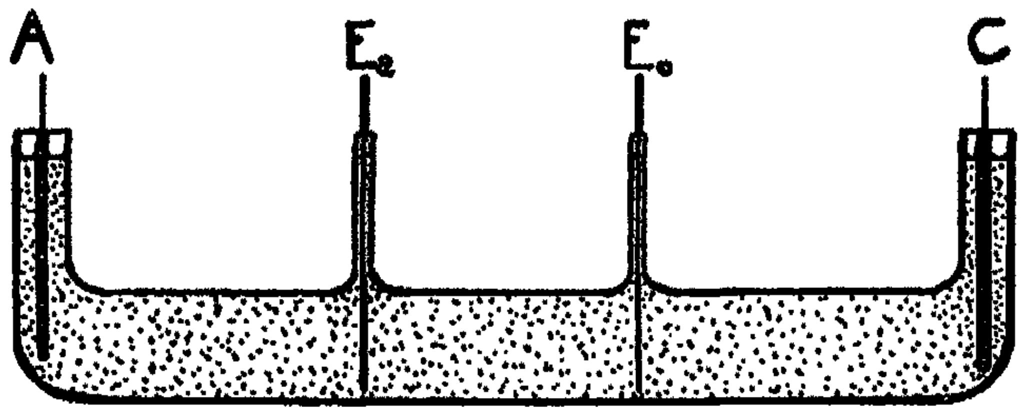

FIG. 1. The simple cell. A, anode; C, cathode; E_a and E_c, exploring electrodes

Measuring instruments

A Leeds and Northrup galvanometer (Type HS) of 2×10^{-8} amperes per millimeter current sensitivity and of very low resistance was used to measure the current. A vacuum tube voltmeter (Tube No. 30), with high resistance, was used for a part of the measurements.

Switch

A double, double pole, single throw switch on Bakelite with platinum to mercury contacts was employed. It was capable of breaking both sides of the charging current and connecting the measuring instrument 0.001 of a second later. A walking beam was attached to the switch to manipulate the protecting glass shield (I in figure 2).

Procedure

The experimental procedure involved the arbitrary control of the time the applied current was allowed to flow, the magnitude of the current, the resistance of the solution between the exploring electrodes, the frequency of the current if alternating current is used, the size and shape of the exploring electrodes, the solvent, the solute, the size and shape of the vessel containing the electrodes, the time elapsing between cutting off the applied current and measuring the produced current, the position of E_a and E_c with respect to A and C, and the temperature of the solution. The time of passage of current through the solution was taken as thirty seconds. An average effect independent of imperfections in construction was obtained by reversing the current.

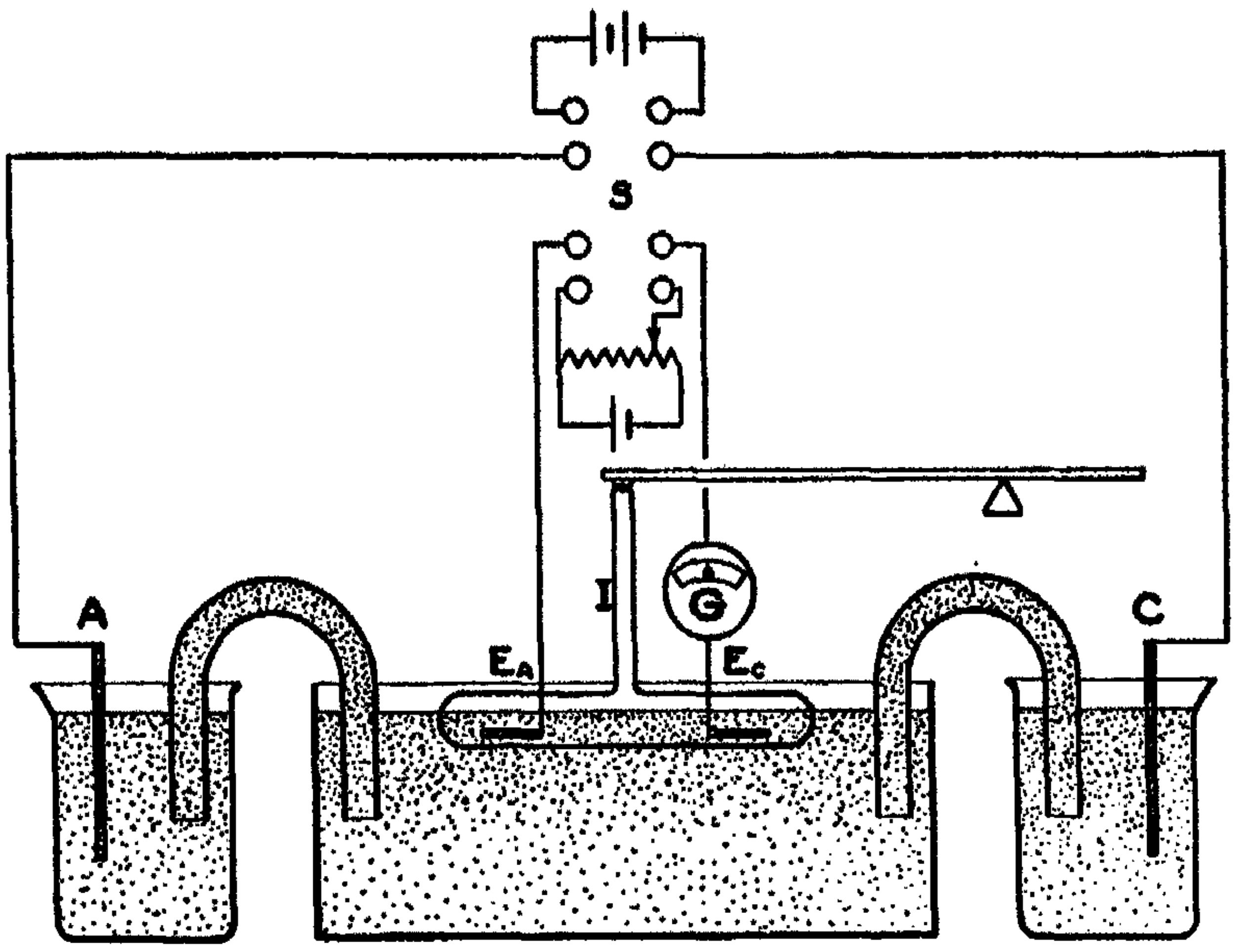

FIG. 2. The complete cell

During experiments of the first type, the apparatus shown in figure 2 was used with some one of the above mentioned solution–electrode systems. The switch was thrown after thirty seconds, thereby disconnecting the applied current, lowering the shield from around E_a and E_c in order to expose them to the solution through which a current had passed, and connecting the measuring apparatus. No current was detected in the solution between E_a and E_c.

In the second type of experiment the same procedure, without the glass shield, was followed. Then a current of 1 × 10^{-4} to 1 × 10^{-2} milliamperes was found flowing through the measuring instruments; the current was flowing in the same direction in which it would flow if the instruments were connected while the applied current was flowing.

In the third type of experiment the current electrodes were placed inside the trough, about six inches outside E_a and E_c, which were four inches apart. The glass shield protecting E_a and E_c from the charging current was replaced, the solution was violently stirred, and the regular procedure was repeated to stop the current and to expose E_a and E_c. (a) If the current electrodes were placed vertically in the cell, a current of 1 × 10^{-5} to 1 × 10^{-2} milliamperes was found flowing through the instruments in the same direction as in the previous experiment (figure 4). (b) If the current electrodes were placed horizontally in the cell, a similar current was found flowing in the opposite direction (figure 5).

The fourth type of experiment was a repetition of the third, except that the shield was not used, and the current electrodes were polarized in a beaker completely outside of the system, washed in distilled water, and then transferred to the cell (figure 2). The presence of the polarized electrode produced a current of 1 × 10^{-3} milliamperes in the measuring instruments in the same directions as in the third type of experiments, which means that the polarization is in the surface of the electrodes and is not uniform over the surface of the same electrode.

The above group of experiments gives us some definite information concerning the nature of the phenomena. The observed current has nothing to do with general concentration polarization of the electrolyte. It is not a phenomenon of some peculiar dielectric polarization, nor an external condenser in the electrical system.

In the fifth type of experiment the current electrodes A and C were returned to the beakers, and the electrodes E_a and E_c were rotated at a high rate of speed (more than 100 R.P.M.). The results were very similar to the results obtained in the second type of experiment, except that the currents measured were much smaller than when the electrodes E_a and E_c were stationary. If only one electrode was rotated, we obtained electrokinetic phenomena about which we will report later.

The above experiment seemed difficult to interpret except in the light of the fact that the phenomenon exists even though the direction of the applied current through E_a and E_c may be reversed rapidly. In the sixth type of experiment E_a and E_c were left exposed to alternating currents of frequency varying from 20 to 12,000 cycles per second (General Radio beat frequency oscillator). Again there was a current flowing after the applied current was stopped, which varied in sign and magnitude. The maximum effect using the alternating current appeared to have a peak value at about 200 cycles per second, but definitely existed at as high a frequency as 12,000 cycles. The effect was 1×10^{-3} milliamperes and greater between the electrodes of a conductivity cell (Washburn, Type A, electrodes platinized) in dilute solutions, using a 500-cycle applied current.

In experiments of type seven, either A or C was a circular electrode, and the other electrode was placed at its center. If E_a and E_c were somewhere in between these electrodes a small effect was obtained. If E_a and E_c were outside a large effect was obtained, a current of 1 milliampere or more, the direction of which can be reversed by rotating the circular electrode through 180°. These results, with E_a and E_c outside, were not obtained if the circular electrode was a metal cylinder that contained no electrolytic connection between the solution inside and the solution outside of it. One small electrolytic connection, 1 mm. in diameter or less, was sufficient.

The results of these last experiments are supplementary evidence that an electrode is polarized by a current passing across the interface but a small fraction of a second. Alternating the current does not periodically restore the original situation, but increases the sharpness of the differential polarization. Unfortunately, the authors are not able to reproduce their data quantitatively on account of the difficulty of controlling all the variables. Therefore they do not feel that the actual figures need be published. However, they can point out a number of the variables and their influence on the current.

The apparatus and procedure being the same (the current electrodes not interfering), the magnitude of the effect, as indicated by the current in the measuring instruments, increases with the following: an increase in the current through the cell, an increase of the resistance of the electrolyte, an increase in the ratio of the resistances of the possible current paths, an increase in the viscosity and decrease of the dielectric constant of the solvent, an increase in size, especially the length, of the electrodes E_a and E_c that are responsible for the effect; it also increases the greater the difference in potential between any two points on the polarized electrodes. The effect decreases with an increase in the resistance of the measuring instrument, an increase in the temperature, and withdrawal of the exploring electrodes into side tubes out of the current path, as is possible in the apparatus of figure 1. When the current electrodes are capable of giving their effect also, the effect is quite dependent on the size and shape of these electrodes, but it is independent of the rate of stirring of the electrolyte up to the limit of stirring with a rod. Care is used to make sure that E_a and E_c, if straight wires, are always parallel to each other and perpendicular to the central lines of force between A and C, otherwise a double effect with opposite signs may be observed. Two positive and two negative currents have been observed with one period of polarization. The depth of the solution in the cell of figure 2 permits currents to flow that are not detectable in the cell shown in figure 1. We are only able to measure the resultant current in each case, and not even it at its maximum value, *since the effect decays very rapidly at first.*

DISCUSSION OF RESULTS

In order to explain all of the phenomena they must be treated as being made up of two effects: firstly, an effect due to the polarization at the ends of the exploring electrodes, E_a and E_c; secondly, an effect due to the differential polarization of each of the current electrodes at different points on their surface. The current measured in the first case is illustrated in figure 3 as the resultant of four currents, 1, 1′, 2, and 3 caused by the polarization of E_a and E_c. If no metallic connection is made between E_a and E_c, then currents 1, 1′, and a modified form of 2 will discharge the polarization. Current 2, in this case, would flow in both directions *through the solution from E_c to E_a. If the galvanometer connects the two* electrodes we have currents 2 and 3. Current 2 will not be equal to 3 unless the resistances in the two circuits are the same, and they obviously are not. This action of the currents sets up a resultant current in the galvanometer in the direction indicated by I. Experiments of the first and second type without exception bear out this mechanism.

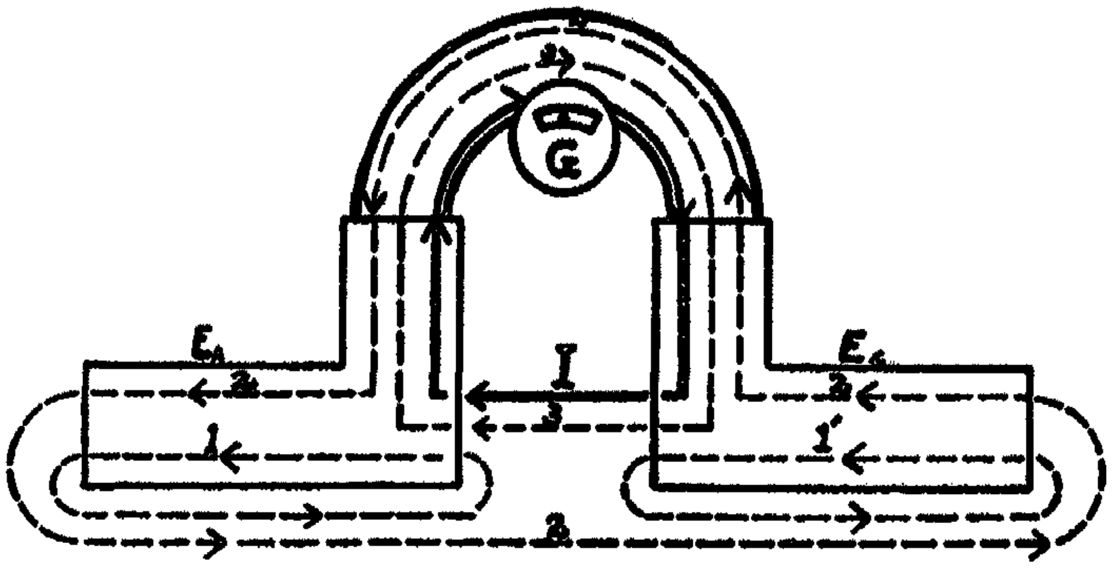

FIG. 3. Discharge circuits

When the exploring electrodes are protected while the current passes, and only the effects of the current electrodes are obtained, the path of the effective current is shown for each of the typical cases in figures 4 and 5. In the case of the horizontal electrodes the point of maximum polarization is at the end of the current electrodes. On discharge, the current follows *the path indicated in figure 5. In the case of the vertical electrodes the* point of maximum polarization is at the bottom of the electrodes (1). On discharge the current follows the path indicated in figure 4. The experiments of the third and fourth type without exception substantiate the above mechanism.

These experiments are of value in that they demonstrate some very simple principles in systems where there has been a tendency to overlook their significance. They demonstrate (1) that a resultant current is produced in a solution between two shorted batteries dipping into the same solution, if the electrical lines of force are not symmetrical and if metallic connection is made between the shorted batteries; (2) that a polarized electrode must be treated as a number of spot electrodes of widely varying polarization potentials, i.e., it is at least one shorted battery; (3) that the use of alternating current for polarizing the electrodes does not change the situation, probably because the current in the two directions crosses the electrode interface at different points; and (4) that the polarization potential of an electrode measured in any of the usual ways gives some sort of a weighted average of all of the polarization potentials.

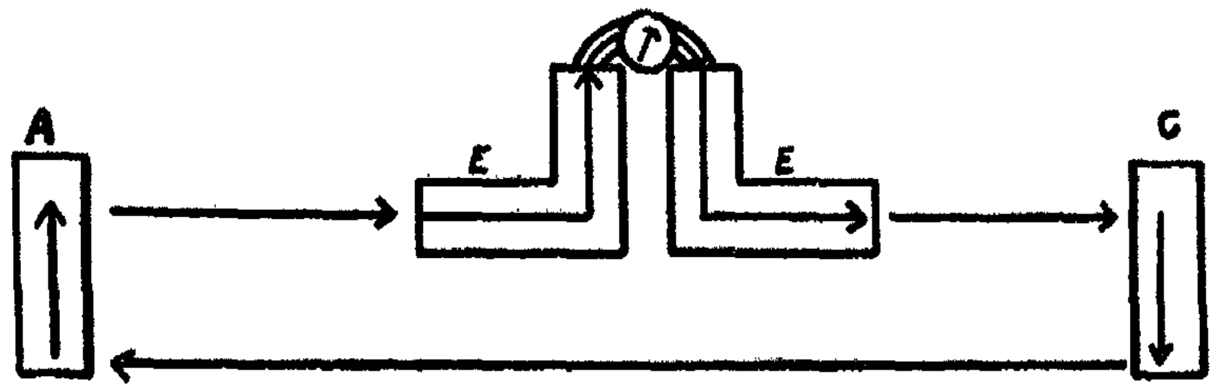

Fig. 4. Discharge circuit

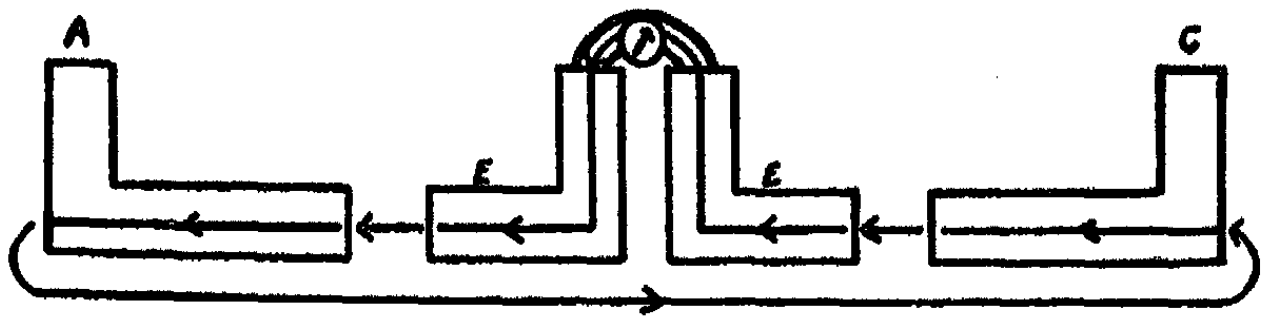

Fig. 5. Discharge circuit

SUMMARY

Currents in an electrolytic solution that are produced by the presence of polarized electrodes have been discussed. The importance of considering them when dealing with electrolytic phenomena has been pointed out.

REFERENCE

(1) Ferguson and Dubpernell: Trans. Electrochem. Soc. 63, 221 (1933).

THE OXIDATION POTENTIAL OF THE SYSTEM POTASSIUM MOLYBDOCYANIDE-POTASSIUM MOLYBDICYANIDE, AND THE EFFECT OF NEUTRAL SALTS ON THE POTENTIAL

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Collenberg (1) determined the oxidation-reduction potentials of molybdocyanide and molybdicyanide solutions. His measurements, however, were made in the presence of potassium chloride, the concentration of which was not known. In the preparation of his solution of potassium molybdicyanide an excess of potassium chloride was used to decompose precipitated silver molybdicyanide in order to form the soluble potassium molybdicyanide and insoluble silver chloride. His data do not allow an extrapolation of the potential to an ionic strength of zero. For this reason we have determined the oxidation-reduction potentials at increasing dilutions in order to find the potential at an ionic strength of zero. In addition the effects of neutral salts on the potential were studied.

MATERIALS USED

Potassium molybdocyanide

This product was prepared according to the method of Olsson (5) and recrystallized three times from water by the addition of ethyl alcohol. The water content of the air-dried product was determined by heating in the electric oven at a temperature of 105°C. for five hours. The loss in weight from two samples gave 1.993 and 2.006 moles of water, respectively. Two other samples were titrated at the same acidity as in the potentiometric method described below, with a permanganate solution standardized against Kahlbaum's sodium oxalate, and the results agreed with the formula $K_4Mo(CN)_8 \cdot 2H_2O$ within 0.5 per cent. Erio-grün was used as an indicator in the permanganate titration, since the golden-yellow color of the potassium molybdicyanide formed masks the permanganate endpoint. The volume of permanganate used to obtain the endpoint with erio-grün was found to be identical with that found in the potentiometric method.

In figure 1 the change in potential is given in the potentiometric titration of a mixture of 100 ml. of 0.007 molar molybdocyanide and 2 ml. of concentrated sulfuric acid with 0.1 normal permanganate, the saturated calomel electrode being used as the reference electrode.

Aqueous solutions of potassium molybdocyanide are relatively stable, as shown by the fact that the titer was constant for at least two days. In our work fresh solutions were prepared every second day.

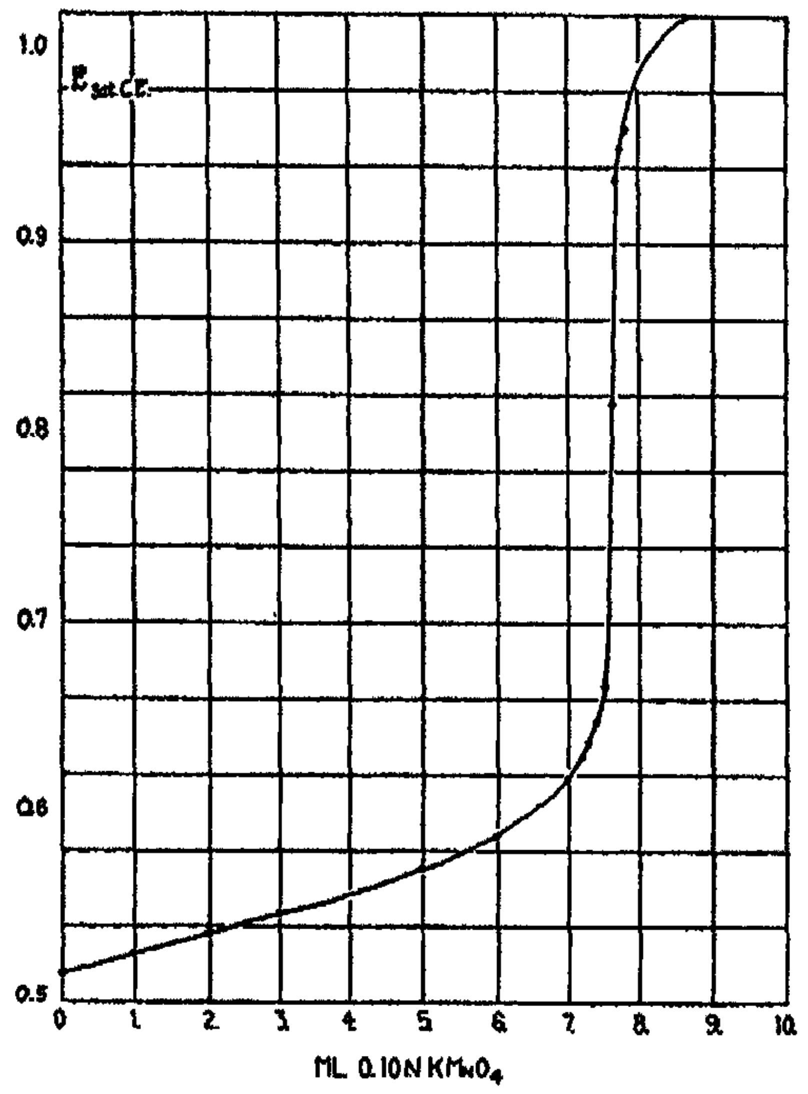

FIG. 1. Titration curve for $K_4Mo(CN)_8$

Potassium molybdicyanide

Solutions of potassium molybdocyanide, acidified with sulfuric acid, were oxidized with potassium permanganate until a pink color persisted. An excess of silver nitrate was then added to precipitate silver molybdicyanide. The precipitate was filtered off on a Buchner funnel and washed until no test for the silver ion was obtained in the washings. The moist silver molybdicyanide was suspended in water and shaken with somewhat less than the equivalent quantity of potassium chloride, leaving some silver molybdicyanide undecomposed. The filtered solution was used as a stock solution, its concentration being determined by electrometric titration with a standard solution of potassium ferrocyanide.

Fieser (2) used the same procedure for the determination, but does not state the conditions for the titration. We found good results in neutral or weakly alkaline medium, but no distinct jump was observed in acid medium. This is easily explained by the fact that the oxidation potential of the ferrocyanide–ferricyanide system increases much more with increasing hydrogen-ion concentration than that of the molybdocyanide–molybdicyanide system. Figure 2 shows the change of potential in the titration of 100 ml. of 0.016 molar molybdicyanide with potassium ferrocyanide in the presence of 1 ml. of concentrated sulfuric acid and in neutral medium.

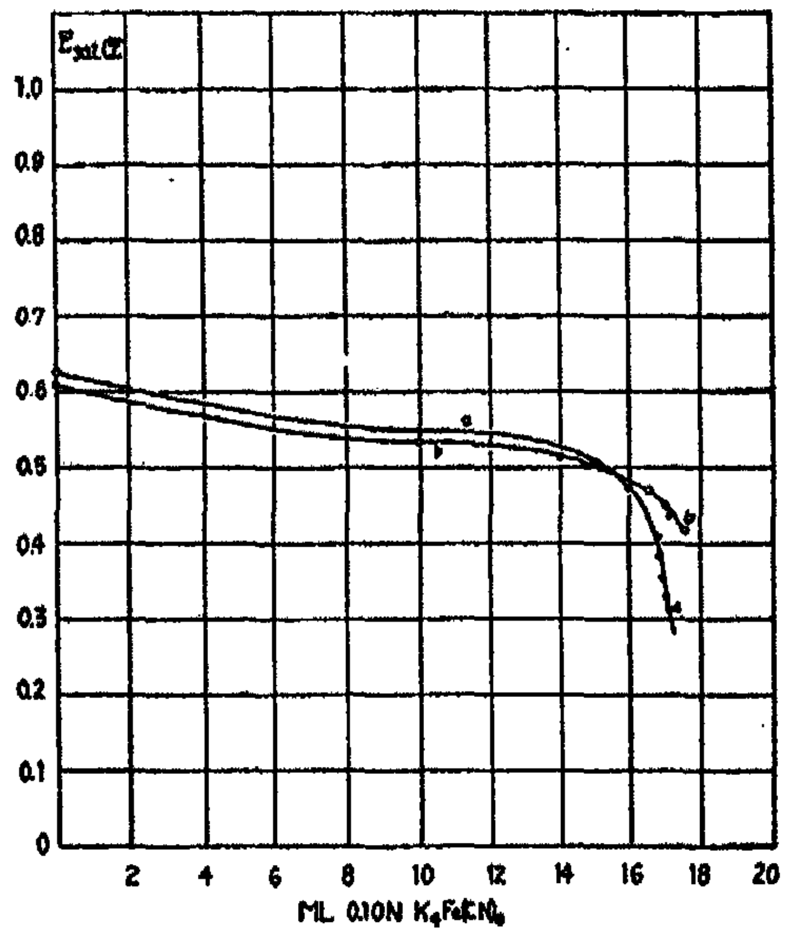

FIG. 2. Titration curve for $K_4M_o(CN)_8$. a = neutral medium; b = acid medium

TABLE 1

Decrease in strength of potassium molybdicyanide in per cent after six days

ACID SOLUTIONS		NEUTRAL SOLUTIONS		BASIC SOLUTIONS	
Diffuse light	Dark	Diffuse light	Dark	Diffuse light	Dark
19.3	1.3	23.4	2.2	29.3	3.3

Solutions of potassium molybdicyanide were found to be extremely sensitive to light. A 0.016 molar solution analyzed in the dark and then placed in the window in direct sunlight was found to change in titer by 22 per cent in two hours. Solutions kept in the dark changed approximately

1 per cent in six days. Hydrogen ions have a stabilizing influence on solutions of potassium molybdicyanide. The effects of acetic acid and sodium carbonate on the decomposition of potassium molybdicyanide are shown in table 1. The light to which the solutions were exposed was diffuse sunlight in a north room of the laboratory.

TABLE 2

Oxidation-reduction potentials of potassium molybdocyanide–potassium molybdicyanide solutions at 25°C.

$K_3Mo(CN)_8$	$K_4Mo(CN)_8$	RATIO MOLYBDI / MOLYBDO	TOTAL μ	$\sqrt{\mu}$	$E_{Q.H.}$	$E_{N.H.E.}$	ϵ_0'
M	*M*						
0.03012	0.02888	1.0430	0.4695	0.6852	0.2155	0.7919	0.7908
0.003012	0.002888	1.0430	0.04695	0.2167	0.1800	0.7564	0.7553
0.001205	0.001155	1.0430	0.01878	0.1371	0.1697	0.7461	0.7450
0.000602	0.000577	1.0430	0.00938	0.0968	0.1638	0.7402	0.7391
0.02696	0.02872	0.9390	0.44896	0.6701	0.2131	0.7895	0.7911
0.00539	0.00574	0.9390	0.08974	0.2996	0.1870	0.7634	0.7650
0.002696	0.002872	0.9390	0.04489	0.2119	0.1776	0.7540	0.7556
0.001080	0.001150	0.9390	0.01798	0.1341	0.1675	0.7439	0.7455
0.00054	0.000574	0.9390	0.00898	0.0950	0.1615	0.7379	0.7395
0.000270	0.000287	0.9390	0.00449	0.0670	0.1577	0.7341	0.7357
0.000108	0.000115	0.9390	0.00180	0.0424	0.1553	0.7317	0.7333
0.02112	0.03044	0.6940	0.43212	0.6574	0.2045	0.7809	0.7903
0.00422	0.006088	0.6940	0.08622	0.2936	0.1786	0.7550	0.7644
0.00211	0.003044	0.6940	0.04311	0.2076	0.1688	0.7452	0.7546
0.00084	0.001218	0.6940	0.01725	0.1313	0.1585	0.7349	0.7443
0.000422	0.000609	0.6940	0.00862	0.09285	0.1526	0.7290	0.7384
0.000211	0.000304	0.6940	0.00431	0.06566	0.1485	0.7249	0.7343

ϵ_0' refers to the potential of an equimolecular solution of molybdocyanide and molybdicyanide calculated from the figures in columns 3 and 7.

$E_{Q.H.}$ is the E.M.F. as measured against the quinhydrone electrode in a solution being 0.01 *N* in hydrochloric acid and 0.09 *N* in potassium chloride.

$E_{N.H.E.}$ is the E.M.F. referred to the normal hydrogen electrode as calculated from $E_{Q.H.}$ (see ref. 4).

EXPERIMENTAL PROCEDURE

To a solution of potassium molybdicyanide, prepared as described above, was added a weighed quantity of potassium molybdocyanide. The solution was then analyzed for molybdocyanide and molybdicyanide by titration with potassium permanganate and potassium ferrocyanide, respectively, and used as a stock solution for the dilution measurements. All flasks and apparatus used to contain the solutions were coated with black lacquer and kept in the dark. The measurements were made in a darkened room. For details regarding the experimental technique reference is made to a previous paper (3). Table 2 gives the results of measurements of various dilutions of three stock solutions containing different ratios of molybdocyanide and molybdicyanide. By "Total μ" is meant the sum of the ionic strengths of molybdocyanide and molybdicyanide.

The values of ϵ_0' found in table 2 were plotted against $\sqrt{\mu}$ on large cross section paper and extrapolated to determine the value of the normal potential at zero ionic strength. The extrapolated value was found to be 0.7260 volt, referred to the normal hydrogen electrode. The curve is shown in figure 3. The straight line in the figure represents the values of ϵ_0' calculated on the basis of the limiting Debye-Hückel equation:

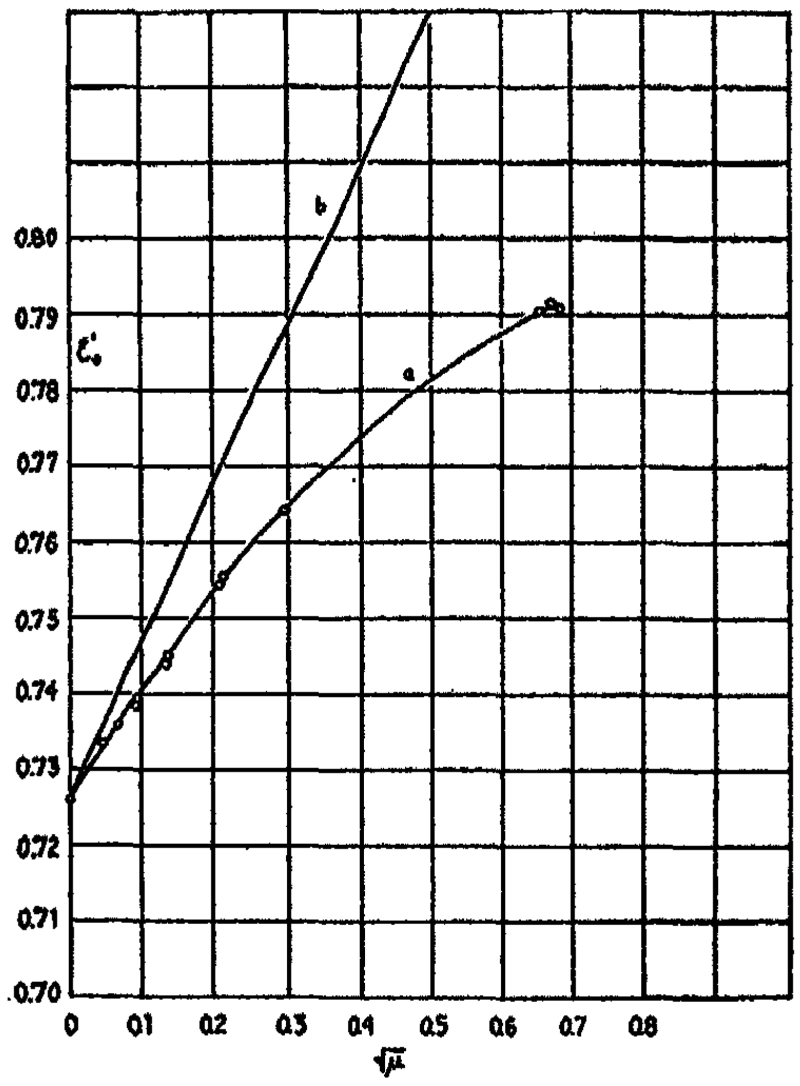

FIG. 3. Change of normal potential ϵ_0' with increasing ionic strength μ. a = experimental data (table 2); b = calculated values

$$\epsilon_{0\,\text{calculated}}' = \epsilon_0 + 0.0591 \log \frac{c_{\text{MoCn}_8^{---}}}{c_{\text{MoCn}_8^{----}}} \cdot \frac{f_3}{f_4} \text{ (at 25°C.)}$$

where $\epsilon_0 = 0.7260$ volt, and f_3 and f_4 are the activity coefficients of the molybdicyanide and molybdocyanide, respectively.

Since ϵ_0' refers to the value for equimolecular concentrations of molybdocyanide and molybdicyanide, then the calculated value of ϵ_0' is

$$\epsilon_0' = \epsilon_0 + 0.0591 \log \frac{f_3}{f_4}$$

in which, according to the limiting Debye-Hückel expression, $\log \frac{f_3}{f_4} = 3.5 \sqrt{\mu}$.

TABLE 3

$Log \frac{f_3}{f_4}$ in dilute solutions of molybdo-molybdicyanides in the presence of various electrolytes

μ	$\sqrt{\mu}$	$\text{LOG} \frac{f_3}{f_4}$	μ	$\sqrt{\mu}$	$\text{LOG} \frac{f_3}{f_4}$
	KCl			HCl	
0.01	0.1365	0.4068	0.0104	0.1380	0.3796
0.025	0.1833	0.5695	0.0522	0.2466	0.6305
0.05	0.2421	0.7322	0.10	0.3296	0.7779
0.1	0.3295	0.9118			
0.25	0.5080	1.1950			
0.5	0.7132	1.4373			
	NaCl			NH_4Cl	
0.01	0.1317	0.3756	0.0107	0.1343	0.4136
0.025	0.1797	0.5166	0.0269	0.1850	0.5813
0.10	0.3276	0.8288	0.1075	0.3390	0.9237
0.5	0.7123	1.3254	0.5374	0.7448	1.4525
	LiCl			$CaCl_2$	
0.01	0.1317	0.3813	0.01	0.1317	0.6100
0.025	0.1797	0.5085	0.025	0.1797	0.8050
0.1	0.3276	0.8085	0.1	0.3276	1.1322
0.25	0.5073	1.0593	0.5	0.7123	1.5340
	$SrCl_2$			$BaCl_2$	
0.01	0.1317	0.6186	0.01	0.1317	0.6610
0.025	0.1797	0.8390	0.025	0.1797	0.8813
0.1	0.3276	1.1814	0.1	0.3276	1.2203
0.5	0.7123	1.6814	0.5	0.7123	1.7085

The effects of various salts and of hydrochloric acid on the potential of dilute solutions of molybdocyanide–molybdicyanide are shown in table 3. Instead of reporting the measured values of the E.M.F., the figures are given for $\log \frac{f_3}{f_4}$ calculated from the equation:

$$E = \epsilon_0 + 0.059 \log \frac{c_{\mathrm{MoCn_8}^{---}}}{c_{\mathrm{MoCn_8}^{----}}} \cdot \frac{f_3}{f_4}$$

where E is the measured potential referred to the normal hydrogen electrode and ϵ_0 is the potential at infinite dilution (0.7260 volt). For the sake of brevity the composition of the very dilute molybdocyanide–molybdicyanide solution is omitted. Since these solutions were not stable, fresh solutions had to be prepared for each set of measurements. $\sqrt{\mu}$ represents the square root of the total ionic strength of the mixtures, whereas μ_s designates the ionic strength of the added salts.

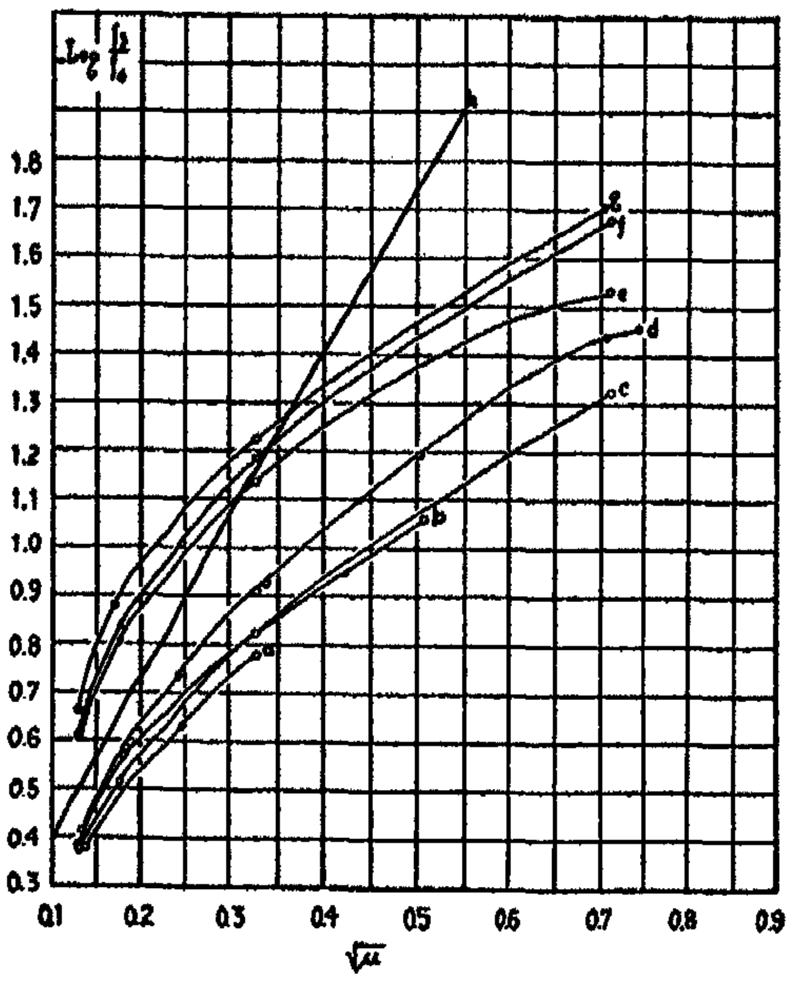

FIG. 4. Ratio of activity coefficients as a function of ionic strengths. a = HCl; b = LiCl; c = NaCl; d = KCl and NH_4Cl; e = $CaCl_2$; f = $SrCl_2$; g = $BaCl_2$; h = calculated values.

The values of $\log \frac{f_3}{f_4}$ are found plotted against $\sqrt{\mu}$ in figure 4. The straight line in figure 4 represents the theoretical values of $\log \frac{f_3}{f_4}$ calculated on the basis of the limiting Debye-Hückel equation.

The effect of various anions on the potential of a dilute solution of molybdocyanide-molybdicyanide was investigated, using potassium chloride, potassium bromide, and potassium nitrate at a concentration of 0.25 molar, respectively, in the mixtures. The values of ϵ_0' in the presence of the three salts were calculated from the measured E.M.F. as described above, and gave 0.7965, 0.7957, and 0.7950 volts, respectively. These results are in accordance with the results obtained in solutions of ferrocyanide-ferricyanide, the various univalent anions having virtually the same effect on the potential.

An attempt was made to determine the effect of sodium hydroxide on the potential of dilute solutions of molybdocyanide-molybdicyanide. Two solutions were measured, one containing 0.01 molar and the other 0.1 molar sodium hydroxide. The solutions were exceedingly unstable and no constant readings could be obtained. The potentials decreased very rapidly, but initial readings agreed with the values for ϵ_0 obtained with hydrochloric acid.

DISCUSSION OF THE RESULTS

The oxidation-reduction potential of the molybdocyanide-molybdicyanide system, starting at an ionic strength of zero, changes with increasing ionic strength markedly different from that of the ferrocyanide-ferricyanide system (3). In the latter case it was found that up to an ionic strength of 0.04, the normal potential was greater than that calculated on the basis of the limiting Debye-Hückel expression. With molybdocyanide-molybdicyanide, however, the experimental values were lower than the calculated ones at all ionic strengths. This behavior is normal in dealing with a system, the potential-determining ions of which are of such a high valence type. On the other hand, it should be stated that even at the greatest dilutions the slope of the experimental curve is decidedly less than that of the line calculated on the basis of the limiting Debye-Hückel expression. For this reason no attempt has been made to calculate average ionic sizes using the more extensive Debye-Hückel equation.

As was to be expected, neutral salts were found to increase the oxidation-reduction potential of dilute molybdocyanide-molybdicyanide solutions to a very large extent. With the univalent cations the effect decreases in the order $K^+ = NH_4^+ > Na^+ > Li^+ > H^+$. In all these cases the values of $\log \frac{f_3}{f_4}$ calculated from the experimental data were less than those derived from the simple Debye-Hückel expression. In the case of ferrocyanide-ferricyanide, however, the experimental figures at lower ionic strengths were less than the ones calculated from the Debye-Hückel equation.

The divalent cation salts, at the same ionic strengths, have a much greater effect, the latter decreasing with decreasing ionic size: $Ba^{++} >$

$Sr^{++} > Ca^{++}$. At lower ionic strengths the experimental figures for log $\frac{f_3}{f_4}$ were found to be greater than those calculated on the basis of the simple Debye-Hückel expression. Hydrogen ions have an effect similar to that of other univalent cations, the former being comparable to the lithium ion. From this behavior one may infer that both molybdocyanic and molybdicyanic acids behave as strong electrolytes. In this respect molybdocyanic acid is entirely different from ferrocyanic acid, since it has been found that the fourth ionization constant of the latter is equal to 5.6×10^{-5} (4). This explains why the oxidation–reduction potential of the ferrocyanide–ferricyanide system increases much more with increasing hydrogen-ion concentration than that of the molybdocyanide–molybdicyanide system.

SUMMARY

1. The normal potential of the molybdocyanide–molybdicyanide system was extrapolated to an ionic strength of zero and found to be 0.7260 volt at 25°C.

2. The effect of various salts upon the oxidation–reduction potential at various ionic strengths has been determined. The univalent anions investigated have the same effect at corresponding ionic strengths.

3. At the same ionic strengths divalent cations exert a greater effect than univalent cations, the effect decreasing with decreasing size of the ion.

4. From the effect of hydrogen ions upon the potential, it is concluded that molybdocyanic acid is a strong electrolyte.

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THE ACTION OF POTASSIUM *n*-AMYL XANTHATE ON CHALCOCITE

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In the flotation concentration of ores, water-soluble substances such as xanthates, generally termed collecting agents, are used to prepare the surface of the minerals to be floated so that attachment will take place between air bubbles and the mineral particles. Very small quantities of xanthates (of the order of 0.05 lb. per ton of ore) are found entirely adequate to impart to the mineral particles a surface at which air will displace water to such an extent that efficient flotation is possible. At the present time the nature of the mechanism of this action is for the most part an unsettled matter.

In previous work with potassium *n*-amyl xanthate and chalcocite, Dewey (1, 3) found that cuprous xanthate and several other organic copper compounds could be leached from the surface of chalcocite which had been treated with potassium *n*-amyl xanthate under various conditions. He explained the formation of the organic copper compounds other than cuprous xanthate by "decomposition" and "association" hypotheses. In long-time grinding tests of potassium *n*-amyl xanthate and chalcocite nothing could be leached from the mineral. No effort was made to find the cause of this phenomenon and its relation to other results. Dewey also made experiments which indicated that oxygen is necessary for the reaction between xanthate and chalcocite, and unnecessary if dixanthogen is substituted for the potassium xanthate. In Dewey's work as a whole, the experimental variables, time of grind, time of xanthate treatment, and amount of xanthate, had values far above those encountered in flotation practice. Also the desirability of working out and applying a quantitative technique to the determination of the reaction-products of amyl xanthate and chalcocite was strongly indicated.

In the present investigation the primary aim has been to establish a sound experimental basis for the explanation of the mechanism of the collecting action of xanthates on chalcocite. For the xanthate treatment of chalcocite an experimental technique has been used which allows reasonably close laboratory reproduction of actual flotation operation procedure and conditions, and at the same time makes possible an accurate accounting of all the reaction products. The influence of several experimental variables on the reaction product relationships was found, and the results were correlated with the flotative properties of the mineral. A group of tests was conducted to ascertain whether cuprous xanthate is adsorbed from benzene solution by chalcocite. For comparative purposes a few of the experiments were repeated using the oxidized mineral malachite instead of chalcocite.

EXPERIMENTAL

Materials

Chalcocite (Cu_2S) was obtained from a coarse, relatively pure Kennecott jig concentrate by consecutive hand picking, crushing, table concentration, sizing (−28 +65 mesh), then finally chemical cleaning with 1:1 hydrochloric acid, then concentrated aqua ammonia. This "cleaned chalcocite" was found to be quite pure, containing minute quantities of bornite (Cu_4FeS_4), chalcopyrite ($CuFeS_2$), and somewhat more covellite (CuS). A small batch of "cleaned chalcocite" was melted in a crucible, crushed, and sized (−28 +65 mesh) to give a product suitable for use. This artificial chalcocite has been termed "furnace chalcocite."

Potassium *n*-amyl xanthate was prepared from *n*-amyl alcohol (Sharples Solvents Corporation), carbon disulfide, and potassium hydroxide. The crude preparation was purified by recrystallization from an acetone–ether mixture, followed by a thorough washing with ether. Prepared in this way the xanthate is very slightly yellowish in color, practically odorless, and very voluminous. Iodometric titration of an aqueous solution showed the purity to be 99.5 per cent.

Cuprous *n*-amyl xanthate was prepared from potassium xanthate and cupric chloride in water or alcoholic solution according to the following reaction:

$$4KX + 2CuCl_2 \rightarrow Cu_2X_2 + 4KCl + X_2$$

(In this and other equations in this paper, X is used to denote the amyl xanthate radical, $-SC(S)OC_5H_{11}$.) It was found that the pure substance could be prepared by washing the yellow precipitate very carefully with alcohol and ether to remove the dixanthogen (X_2, also known as amyl thioformate disulfide) also formed by the reaction. The cuprous *n*-amyl xanthate prepared in this way appeared non-crystalline, even under the microscope, but it was found that very small yellow prismatic crystals could be crystallized from pyridine.

General experimental procedure

The procedure used may be summarized as follows: (*1*) A 200-g. charge of chalcocite was ground in a 500-g. capacity Abbé porcelain pebble mill

(4000 g. of pebbles) with 200 cc. of distilled water. (The empty space in mill was about 3 l., containing about 85 milliequivalents of oxygen at 615 mm. and 20°C.) (*2*) The pulp from (*1*), after dilution to 400–450 cc., was agitated with an accurately weighed amount of potassium *n*-amyl xanthate in a closed 2.5-l. reagent bottle. (*3*) The treated pulp was filtered and the mineral washed with water on a Buchner funnel, diluting the filtrate to 500 cc. for analysis. (*4*) The mineral was leached with acetone, ether, and warm benzene, in the order named. (*5*) The aqueous filtrate and the leach products were analyzed.

Analytical methods

The aqueous filtrate from the treatment of the chalcocite with xanthate was analyzed iodometrically for reducing ions and excess xanthate by the procedure of Taylor and Knoll (11). In some of the experiments titrations with 0.02 *N* hydrochloric acid were made to determine the total hydroxide plus carbonate. The total potassium in solution in several experiments was determined as potassium sulfate (12). Sulfate was determined by precipitation as barium sulfate (9).

As cuprous xanthate was found (as described later) to be the major leach product, an iodometric method was developed for its determination in benzene solution, utilizing the following reaction:

$$Cu_2X_2 + I_2 \rightarrow Cu_2I_2 + X_2$$

It was found that an accurate determination can be made on a 25-cc. aliquot portion of a benzene leach solution containing cuprous xanthate by titration with a 0.005 *N* solution of iodine in benzene, using a special technique. As the reaction is too slow to be practicable at ordinary temperatures, the titrations must be made near the boiling point of benzene, allowing 1–2 minute intervals with occasional shaking between 5-, 2-, or 1-cc. additions of iodine solution, the amount of iodine added depending upon the proximity to the end point as judged by experience. Titrating in this manner, the pink color of excess iodine becomes very noticeable with an excess of 0.5–1.0 cc. of 0.005 *N* iodine. This small excess may be quite accurately measured by color matching of the solution after removal of the cuprous iodide by filtration. Apparently the above reaction takes place in more than one step, as a dark brown solution is formed on first addition of the iodine, and no precipitate of cuprous iodide is formed until later stages in the titration.

REACTION PRODUCTS FOUND WITH THE CHALCOCITE

Leachable products

Dewey (1, 3), in his previous work on the reactions of potassium xanthate and chalcocite, was able to leach from the treated mineral a series of six substances having different solubility properties. In the present work, with experimental conditions maintained as closely as possible within the limits of practical flotation operation, only two substances were leached from chalcocite treated with xanthate, as described in the following: (*1*) cuprous *n*-amyl xanthate, a yellow substance insoluble in ether, slightly soluble in acetone, and fairly soluble in benzene, forming a yellow solution; and (*2*) a red substance, soluble in acetone, ether, and benzene, forming orange to red solutions depending on the concentration. This substance was designated as "ether-soluble" to distinguish it from cuprous xanthate. Attempts were made to synthesize the "ether-soluble" compound in several ways from xanthate and monothiocarbonate, but no substance with the same solubility properties was obtained.

In all experiments it was found that the major portion of the leach products consisted of cuprous xanthate. From 100 to 1500 cc. of benzene were required for removal of the cuprous xanthate from the mineral, depending upon the amount present. As cuprous xanthate, even in an extremely weak solution, imparts a yellow color to benzene, the leaching was continued until the extract was colorless. The end point was quite definite, and little washing was required to finish the operation after the bulk of the cuprous xanthate had been removed.

The acetone leach, containing a little cuprous xanthate and perhaps a large part of the "ether-soluble," was evaporated (using a fan), and the "ether-soluble" and the cuprous xanthate in the residue separated by means of ether. The "ether-soluble" was combined with the main ether leach solution, evaporated, and the residue taken up with benzene for iodometric titration by the method used for the cuprous xanthate. The cuprous xanthate separated from the acetone extract was combined with the bulk of the cuprous xanthate for determination of the total cuprous xanthate.

Film at mineral surface unleachable by acetone, ether, and benzene

Using the leaching agents, acetone, ether, and benzene, a considerable portion of the xanthate abstracted by the chalcocite from an aqueous potassium amyl xanthate solution remained with the mineral in an unleachable state. This unleachable film decomposed, producing a pleasant ester-like odor, when the treated mineral was allowed to stand for a few days in a loosely stoppered bottle. On agitation with water of the treated chalcocite which had developed the characteristic odor, an appreciable frothing was noted, indicating the presence of a soluble surface-active organic compound.

It was found that by heating the xanthate-treated and leached chalcocite to about 220°C. in a distillation apparatus suitable for the distillation of very small quantities, a colorless, pleasant-smelling liquid could be distilled off. Potassium amyl xanthate and other xanthate derivatives gave the same distillation product when heated in the presence of finely ground, untreated chalcocite, which presumably contained a little moisture not removed by the drying after grinding. The distillate was not a sulfur compound. The refractive index and boiling point checked those of amyl alcohol quite closely.

Attempts were made to remove the unleachable film with most of the common laboratory reactants and solvents, and a few rather uncommon ones. Except for pyridine, all the agents tried met with no success. The pyridine extract of xanthate-treated and leached (acetone, ether, and benzene) chalcocite was yellow. Evaporation of the yellow pyridine solution showed the substance removed to be cuprous xanthate. Thus, the unleachable film *appears* to be cuprous xanthate so intimately associated with the chalcocite that a chemically active agent is necessary to break it away.

THE EFFECT OF QUANTITY OF XANTHATE

The effect of quantity of xanthate on products of treatment

A series of experiments was made using the experimental procedure previously described to find the effect of quantity of xanthate added on the products of the action of potassium *n*-amyl xanthate on chalcocite. The grinding time and xanthate treatment time in this series were kept constant at one hour and at fifteen minutes, respectively. Results are given in table 1, and graphically represented in figures 1 and 2.

In this group of experiments the "ether-soluble" leach product was quite small in quantity in comparison with the cuprous xanthate, having from 1 to 4 per cent of the iodine equivalent of the cuprous xanthate leached. Enough of the red "ether-soluble" substance for an analysis was not obtained. Since the amount was so small, it was included with the cuprous xanthate in the table of results. As a matter of fact, in most of the tests only the total amount was determined by titration of the combined leach products, as the very small quantity of "ether-soluble" material was not observed and differentiated from cuprous xanthate until some of the tests with larger quantities of xanthate had been conducted.

Two experiments were made using "furnace chalcocite" in place of the "cleaned chalcocite." Under like conditions the proportion of products was roughly the same as for the unmelted mineral. The little difference was probably due to the difference in grinding properties between the natural and artificial copper sulfides. These two experiments showed that porosity or some other property peculiar to the chemically cleaned mineral was not an important determinative factor in the results.

In this series of tests it is seen that the xanthate added may be accounted for as excess xanthate in solution, leachable compounds (practically all

TABLE 1

The effect of quantity of xanthate added on the reaction products

200 g. of cleaned chalcocite, 1-hour grind in 500-g. pebble mill with 4000 g. of pebbles, conditioned 15 minutes on mechanical rolls in 2.5-l. bottle with 0.5 l. of water and potassium *n*-amyl xanthate as indicated. Amounts expressed as milliequivalents per 200 g. of chalcocite. The symbol X is used for the xanthate radical.

KX ADDED	Cu_2X_2 EXTRACTED	EXCESS X IN SOLUTION	TOTAL X^- ABSTRACTED	UNLEACHABLE X ON CHALCOCITE*	TOTAL OH^-, CO_3^{--} IN SOLUTION	SO_4^{--} IN SOLUTION	TOTAL ANIONS IN SOLUTION	K^+ IN SOLUTION
0.25	0.007		0.25	0.24				
0.50	0.058		0.50	0.44				
1.10	0.46	0.01	1.09	0.63				
1.61	0.81	0.01	1.60	0.79				
2.67	1.80	0.02	2.65	0.85				
2.66	1.65	0.02	2.64	1.00	2.12	0.20	2.34	
4.21	2.86	0.02	4.19	1.33				
4.21	2.80	0.02	4.19	1.39				
6.31	4.64	0.09	6.22	1.58	5.50			6.31
8.55	6.00	0.95	7.60	1.60	6.35			8.34
10.64	6.52	2.42	8.22	1.70	7.13			10.50
12.90	7.02	4.19	8.71	1.69	8.00	0.30	12.57†	12.73

* Obtained by difference.

† Including reducing ions, $(S_mO_n)^{--}$. In most of the tests the reducing ions were negligible, increasing with xanthate added to a maximum of 0.08 milliequivalent for 12.90 milliequivalents of xanthate added.

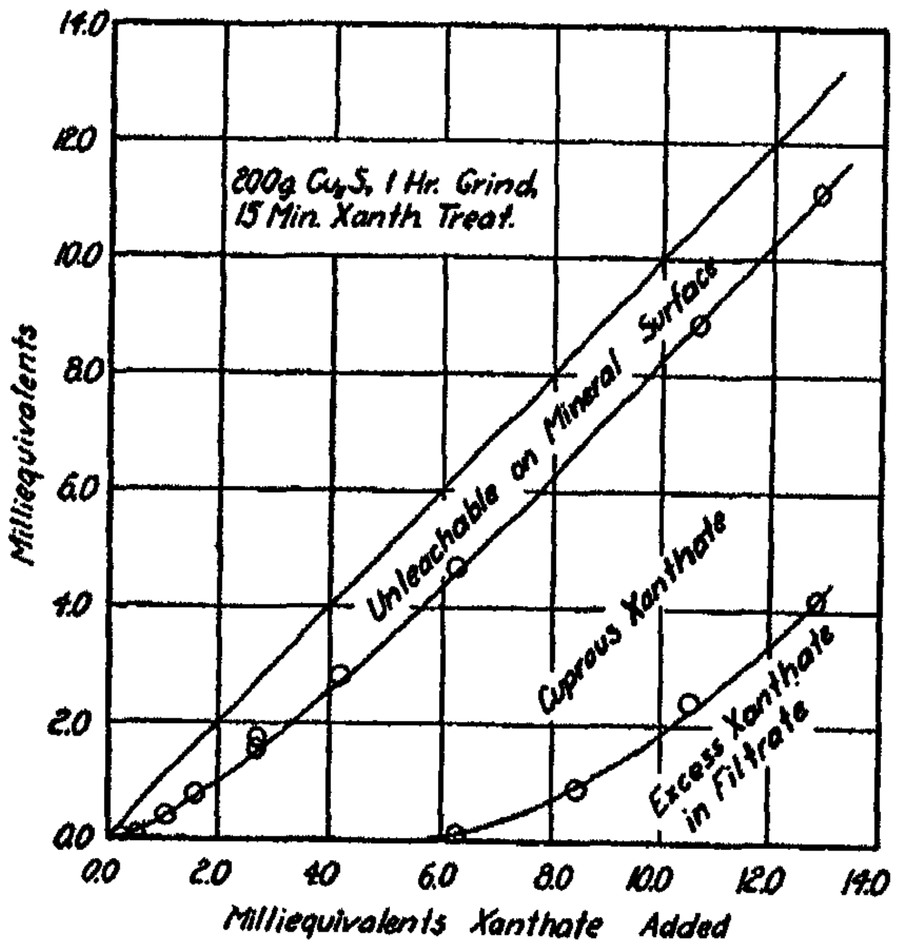

FIG. 1. The effect of quantity of xanthate added on the reaction products

cuprous xanthate), and unleachable xanthate, the proportions of these three being dependent on the quantity of xanthate added. The unleachable portion tends to approach a maximum with increasing amount of xanthate added.

All the potassium of the collector remains in solution, and hydroxide, carbonate, and sulfate are thrown into solution to make a total equivalent to the xanthate taken out of solution, within the limits of experimental error. Under the conditions of these tests, reducing ions $(S_mO_n)^{--}$ thrown into solution were practically negligible, in no experiment amounting to over 0.08 milliequivalent per 200 g. of chalcocite.

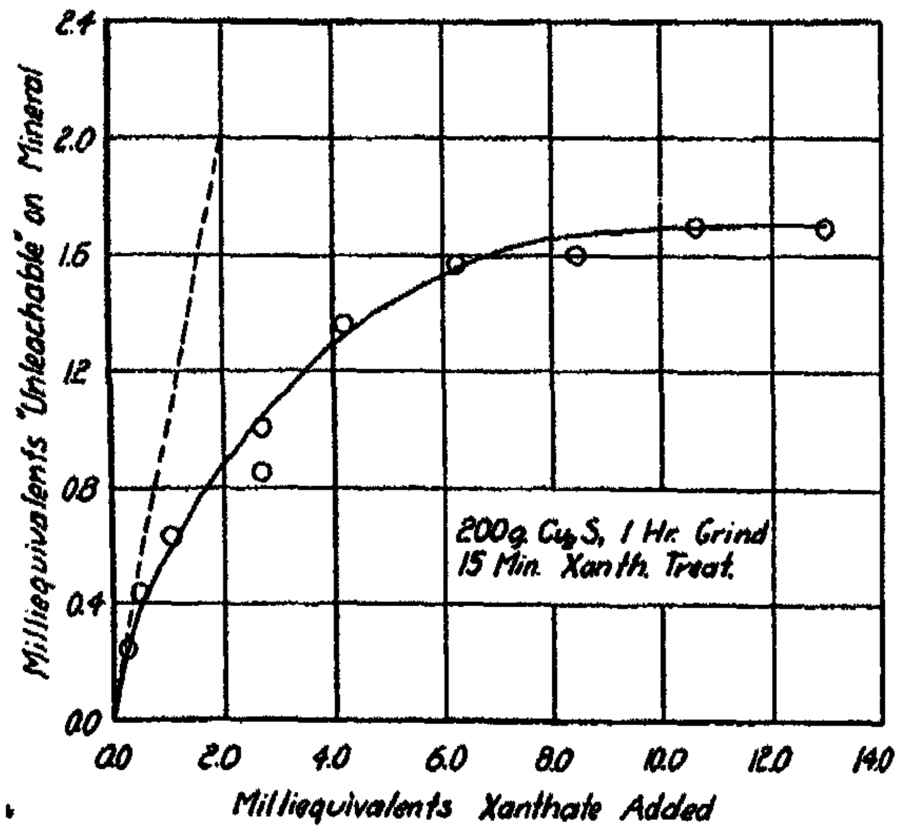

FIG. 2. The effect of quantity of xanthate added on the unleachable xanthate on the chalcocite

Flotation tests were made on leached and unleached treated chalcocite. These tests were made in a 50-g. celluloid cell with no further addition of reagent, either frother or collector. They showed that the removal of leachable products had no appreciable effect on the floatability of the xanthate-treated mineral; 95 to 100 per cent recovery could be obtained in all the tests but that involving the smallest amount of xanthate. In the tests involving larger amounts of xanthate the froth was very dry and the chalcocite seemed to float very peculiarly, more as a "dust" than as a mineralized froth. In the tests in which the maximum unleachable quantity was closely approached, the mineral floated immediately upon addition to the machine as an apparently dry mass which could be literally blown out of the machine. Gaudin and Malozemoff (4) observed this phenomenon of an extremely dry froth with both galena and chalcocite under certain conditions. This condition might correspond to an air-solution–mineral contact angle in the neighborhood of 90°, the result perhaps of a complete filming on the mineral particles by the unleachable xanthate.

The effect of quantity of xanthate on flotation recovery

Flotation tests on 40-g. samples of ground chalcocite were made in a 50-g. capacity celluloid "University of Utah" cell with the addition of terpineol, 0.05 lb. per ton, and varying amounts of potassium *n*-amyl xanthate. The chalcocite was ground in 200-g. batches according to the procedure previously described, flotation data being obtained for two grinding times, fifteen minutes and one hour, respectively. Mohr pipettes were used to add a standard xanthate solution directly to the pulp in the cell. Two minutes after the xanthate collector addition the frother was added and the froth raked off for 6 to 8 minutes. Concentrates and tailings were weighed and the recoveries calculated. Results are given in table 2 and graphically represented in figure 3.

TABLE 2

The effect of quantity of xanthate added on the flotation recovery

40-g. samples floated in 50-g. celluloid cell with terpineol, 0.05 lb. per ton, for 6–8 minutes after 2 minutes conditioning with amount of potassium *n*-amyl xanthate as indicated.

LBS. OF XANTHATE PER TON OF CHALCOCITE	MILLIEQUIVALENTS OF XANTHATE PER 200 G. OF CHALCOCITE	RECOVERY PER CENT
15-minute grind		
0.00	0.00	13
0.025	0.013	31
0.14	0.07	65
0.28	0.14	83
0.41	0.20	85
1-hour grind		
0.00	0.00	7
0.005	0.0025	10
0.055	0.027	31
0.11	0.053	41
0.16	0.08	54
0.21	0.10	66
0.25	0.12	70
0.39	0.20	75
0.51	0.26	85

From the data for the chalcocite ground for one hour it is seen that 0.26 milliequivalent of potassium *n*-amyl xanthate per 200 g. of chalcocite is sufficient for substantial flotation. From table 1 it is seen that if this amount of xanthate is added to 200 g. of chalcocite ground for one hour, practically all of the xanthate abstracted by the mineral is unleachable. Also, under these conditions the amount of unleachable product on the mineral is only about one-seventh of the maximum possible unleachable amount for the quantity of mineral and time of grind in question, as indicated by the curve of figure 2. If this unleachable entity corresponds to a monomolecular film (as will be shown hereafter), it can thus be said that only a fraction of a monomolecular film is necessary for flotation of a particle. Comparison of the data for the two times of grind confirms this line of reasoning by showing that the quantity of xanthate required for a given flotation recovery is dependent upon the fineness of grinding, and therefore, on the area of mineral surface.

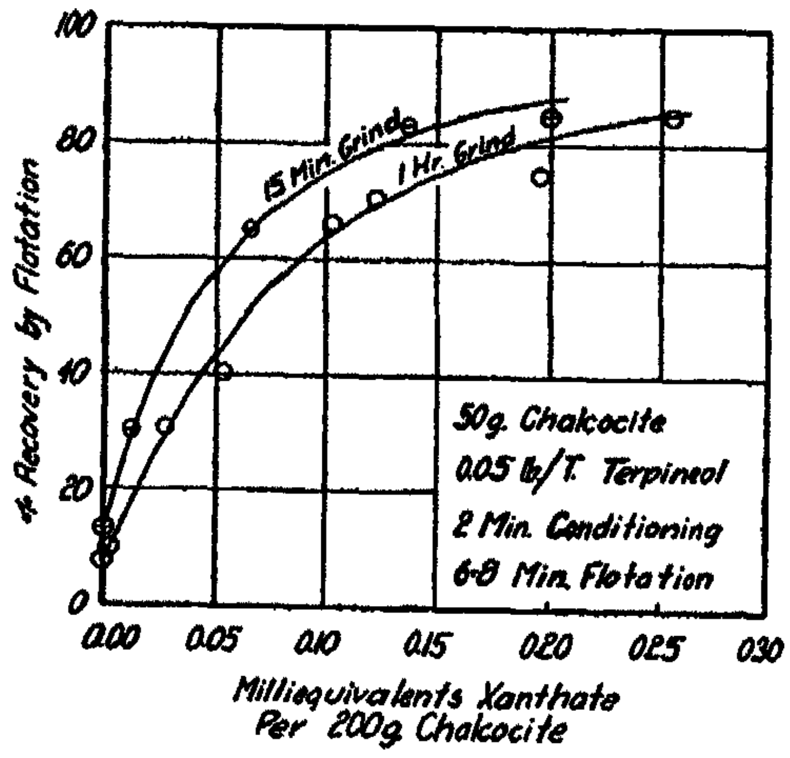

FIG. 3. The effect of quantity of xanthate on the flotation recovery

The froth dryness–contact angle analogy previously suggested gives weight to the idea of only a partial monomolecular film with a surface of relatively low contact angle being necessary for high flotation recovery. To use another terminology, the mineral particles do not have to be treated to the maximum degree of non-wettability but only to a certain fraction of that degree, the value of that fraction being dependent upon particle size, shape, and specific gravity. Mathematical calculations of the theoretical order of magnitude of the contact angle necessary for flotation made by Gaudin (2) led to the conclusion that particles are floatable with contact angles under 10°; whereas Wark and Cox (13) experimentally found the maximum contact angle of minerals in contact with amyl xanthate solution to be of the order of 90°.

THE EFFECT OF TIME OF XANTHATE TREATMENT

Several experiments were made varying the time of treatment with potassium *n*-amyl xanthate. The time of grind was one hour in all of this group of experiments. Results are given in table 3.

In the experiments involving long-time agitation with xanthate, appreciable amounts of the "ether-soluble" substance in addition to the cuprous xanthate were obtained by leaching. This red substance was apparently the same as the "ether-soluble" leach product observed in previous work with fifteen minutes treatment; in long-time agitation tests this substance was present in somewhat greater quantities. It seems likely that the "ether-soluble" material is a reaction product, possibly containing the monothiocarbonate radical, formed slowly in long-time treatment from cuprous xanthate, free hydroxide, and chalcocite, as suggested by Dewey in his "decomposition" and "association" hypotheses. Oxygen may also enter the reaction.

TABLE 3

The effect of time of xanthate treatment on the reaction products

Tests using general experimental procedure, grinding for 1 hour. Amounts expressed in milliequivalents per 200 g. of chalcocite. The symbol X is used for the xanthate radical.

KX ADDED	TIME OF TREATMENT	Cu_2X_2 EXTRACTED	EXCESS X^- IN SOLUTION	TOTAL X^- ABSTRACTED	I_2 EQUIVALENT OF "ETHER-SOLUBLE"	UNLEACHABLE X ON CHALCOCITE*	TOTAL OH^-, $CO_3^{=}$ IN SOLUTION
2.62	1 min.	1.58	0.02	2.60		1.02	2.16
2.66	6 min.	1.56	0.02	2.64		1.06	2.12
2.66	15 min.	1.65	0.02	2.64		1.00	2.12
2.68	24 hrs.	0.95	0.02	2.66	0.28	†	1.63
10.70	1 min.	5.13	4.00	6.70		1.57	5.88
10.64	15 min.	6.52	2.42	8.22		1.70	7.13
10.63	20 hrs.	7.75	0.15	10.48	0.30	†	9.23

* Obtained by difference.

† The formula of the "ether-soluble" product is unknown, hence there is no basis for a calculation of the unleachable quantity when an appreciable quantity of "ether-soluble" is found.

Evidently the reactions to produce the unleachable film and the cuprous xanthate occur immediately on mixing the reagent with the pulp. However, from the results with the larger quantity of xanthate it seems that the cuprous xanthate formation slows up as more cuprous xanthate coating is produced on the mineral, probably owing to difficulty of diffusion of free xanthate ions through the coating to react with the mineral.

RELATION OF EFFECTIVE MINERAL SURFACE AREA TO PRODUCTS

Effect of time of grinding

A series of experiments was made to determine the effect of time of grinding on the reaction-product relationships. The usual experimental procedure was used, the quantity of xanthate being kept constant at 5.4 milliequivalents and the xanthate treatment time being kept constant at

TABLE 4

The effect of time of grinding on the reaction products

Tests using general experimental procedure, treating with 5.4 milliequivalents of potassium *n*-amyl xanthate for 15 minutes. Amounts expressed as milliequivalents per 200 g. of chalcocite. The symbol X is used for the xanthate radical.

HOURS OF GRIND	Cu_2X_2 EXTRACTED	I_2 EQUIVALENT OF "ETHER-SOLUBLE"	EXCESS X⁻ IN SOLUTION	UNLEACHABLE X ON CHALCOCITE*	MILLIEQUIV. HCl TO YIELD A pH OF 7	REDUCING IONS IN SOLUTION
¼	3.80	0.06	1.04	0.80	2.96	0.03
1	From curve of figure 2			1.48		
2	3.52	0.11	0.02	1.81	3.59	
4	2.67	0.18	0.02	2.63	3.44	0.11
12	1.09	0.19	0.04	4.13	2.97	0.22
48	0.03†		0.01	4.46	0.37	

* Obtained by difference.

† The small quantity of "ether-soluble" in this run did not justify its separate determination, and it was added to the cuprous xanthate solution before titration.

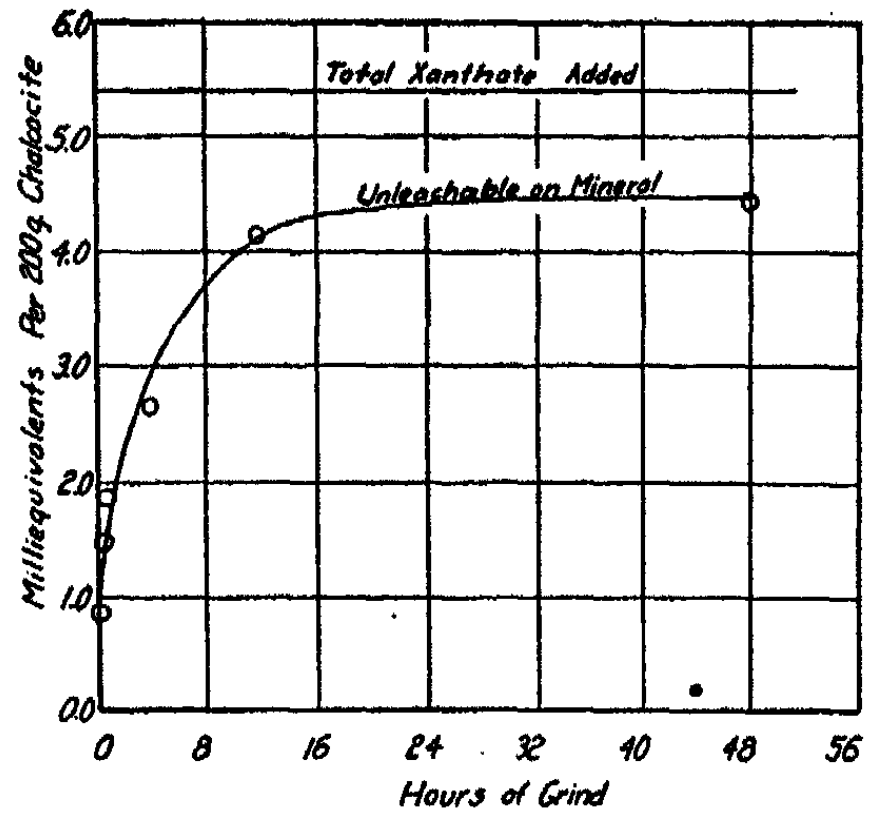

FIG. 4. The effect of time of grinding on the reaction products

fifteen minutes. Experimental results are given in table 4 and plotted in figure 4.

In the longer grinding tests a considerable vacuum was noted on opening the pebble mill, indicating reaction of oxygen with the mineral during grinding. Increasing difficulty in filtration of the treated pulp was encountered with increasing fineness of grinding. Silicate in the ground pulp, worn off the pebbles, increased to about 10 to 15 per cent of the weight of the mineral for the longest grinding time.

The data from these runs show that the unleachable portion definitely increases with increase in surface of the mineral particles with longer grinding, and in long grinds approaches the total amount of xanthate added. The titration figures on the filtrate show that the hydroxide decreases, while the reducing ions $(S_mO_n)^{--}$ increase with increase in surface. Although no determinations were made, it is expected that the sulfate in the filtrate also increases with increase in time of grinding.

TABLE 5

Size analysis of deslimed ground chalcocite

SIZE	AVERAGE SIZE	THEORETICAL SPECIFIC SURFACE‡	WEIGHT, PER CENT	THEORETICAL SURFACE‡
microns	*microns*	*cm.^{2} per gram*		*cm.^{2} per gram*
−74 (+200 mesh)	80	140	0.5	0.7
−74, +37 (−200, + 400 mesh)	50	220	5.0	11
−37, + 15	21*	520	25.4	184
−15, + 7.5	10*	1100	57.9	637
−7.5	2†	5500	1.2	66
Total			100.0	899

* The accuracy of the average size figures from sedimentation analysis is probably of the order of 10 per cent. The figures are calculated assuming Stokes' law for spheres falling in a liquid; the irregularity in shape of ground mineral particles limits the accuracy of the method.

† This is an estimate, as no further separation was made of the −7.5μ portion. The figure is purposely low, to be on the safe side. The weight per cent of this portion is so small that the soundness of the estimate has no great effect on the accuracy of the total surface figure.

‡ Assuming all particles to be cubes.

Estimation of thickness of unleachable film

As the phenomena associated with the formation and presence of the unleachable entity on the mineral surface seemed to be indicative of an irreversible adsorption, it seemed desirable to make a quantitative comparison of the extent of mineral surface and the maximum amount of unleachable attainable with that surface. The mineral which had been ground in the pebble mill contained too large a percentage of extremely fine material for accurate surface measurement; accordingly for this work the mineral, after grinding, was carefully "deslimed" by water sedimentation in buckets. A sample of the deslimed mineral was then sized by combined screening and acetone sedimentation, and from the sizing analysis the surface was estimated. Results of this operation are given in table 5. In other work with the determination of surface area by sizing (5) it has been shown that a correction factor should be applied to the theoretical surface figure to correct for irregularity in shape of particles, cracks, etc. A factor of 1.5 was used, giving an actual surface figure of 1350 $cm.^2$ per gram (1.5 × 899). The factor used is possibly accurate to within 10 per cent; and as the theoretical surface figure is estimated to be accurate to about 10 per cent, the accuracy of the actual surface figure may be roughly 15 per cent ($\sqrt{0.10^2 + 0.10^2} = 0.141$).

Two samples of the sized chalcocite were agitated with a large excess of xanthate (2.5 and 1.5 milliequivalents per 150 g., respectively) and the products determined, using the general experimental procedure. The unleachable xanthate figures were 0.16 and 0.13 milliequivalents per 150 g., respectively. Using the average figure, 0.145 milliequivalent,

$$0.145 \times 10^{-3} \times 6.06 \times 10^{23} = 8.8 \times 10^{19} \text{ molecules of xanthate per 150 g. of chalcocite}$$

$$1350 \times 150 = 2.02 \times 10^{5} \text{ cm.}^2 \text{ of surface per 150 g. of chalcocite}$$

Assuming a monomolecular film,

$$\frac{2.02 \times 10^{5}}{8.8 \times 10^{19}} = 23 \times 10^{-16} \text{ cm.}^2 = 23 \text{ A.U.}^2\text{, the area occupied by one xanthate group}$$

Adam and Müller (10), by two independent methods, estimated the area of a hydrocarbon chain to be 20.5 A.U.², which agrees well with the figure of 23 A.U.² found here for the area occupied by one xanthate radical. The difference between these figures is well within the limits of experimental error of the method used in this work for the estimation of the surface of the chalcocite. Also the polar group of the xanthate radical may have some effect on the area which it occupies. Thus the result of the calculation justifies the assumption of a monomolecular film, and it can be said that the maximum amount of unleachable xanthate attainable on a chalcocite surface is equivalent to a complete monomolecular film.

ADSORPTION OF CUPROUS XANTHATE FROM BENZENE

Tests were run to determine if cuprous xanthate is adsorbed from benzene solution by chalcocite. 200-g. samples of chalcocite were ground in a pebble mill for one hour with 500 cc. of benzene solutions of cuprous xanthate of various concentrations. Results of four such tests are given in table 6.

The chalcocite after these tests was found to be quite floatable in water. No cuprous xanthate could be removed from it by leaching with benzene. Pyridine, however, removed cuprous xanthate. Thus an "unleachable" film similar to that of the potassium xanthate treatment experiments, to which high mineral floatability is due, is also formed by the adsorption of cuprous xanthate from benzene. Also, the maximum unleachable figures for the two types of experiments seem to check, although this benzene adsorption series is too incomplete for a definite assertion. More detailed work of this nature might lead to interesting and significant results.

TABLE 6

Adsorption of cuprous xanthate from benzene by chalcocite

MILLIEQUIVALENTS OF Cu_2X_2 ADDED	MILLIEQUIVALENTS OF Cu_2X_2 LEFT IN SOLUTION	MILLIEQUIVALENTS OF Cu_2X_2 ADSORBED
0.40	0.00	0.40
0.89	0.23	0.66
1.34	0.54	0.80
3.43	1.73	1.70

COMPARATIVE TESTS WITH MALACHITE

A few semiquantitative experiments of the same nature as some of the chalcocite experiments were repeated with malachite, ($CuCO_3 \cdot Cu(OH)_2$). Two tests were made on 200-g. samples, using the general experimental procedure for grinding, treatment, and determination of reaction products. It was found that malachite abstracts xanthate from aqueous potassium *n*-amyl xanthate solution, forming cuprous xanthate and dixanthogen. The malachite after the leaching procedure, contrary to experience with chalcocite, was entirely non-floatable. Thus, with malachite, an *unleachable* water-repellent coating is not formed in an aqueous xanthate solution.

Several tests with a benzene solution of cuprous xanthate showed that malachite does not appreciably adsorb the cuprous xanthate from benzene solution under the conditions under which chalcocite exhibits a marked adsorption.

DISCUSSION

On the basis of the results presented in this paper it seems that the collecting action of xanthate is essentially different for chalcocite and for malachite. Apparently, the flotation of the sulfide mineral is caused by the formation of an oriented monomolecular film tightly "anchored" to the mineral; whereas flotation of the oxidized mineral seems to be due to the formation of a much thicker coating of base-metal xanthate (and dixanthogen), not "anchored" to the mineral, but merely adjacent to the mineral surface. This comparison offers a rational explanation for the fact that in actual flotation operation the quantity of xanthate required for flotation of malachite is many times that required for flotation of chalcocite.

The "anchored" monomolecular film formed on chalcocite does not possess the same solubility properties as any known xanthate or xanthate derivatives. Although, as evidenced by its complete insolubility in benzene, the film does not consist of cuprous xanthate, cuprous xanthate may be removed from the surface by means of pyridine. On the whole, all the observed properties of this film seem to be analogous in many ways to the properties of films of adsorbed gases on solids, which were observed and clarified by Langmuir (6). Quoting from his discussion of the adsorption of oxygen on tungsten: "It is very evident from this work that the oxygen layer has totally different properties from those we should expect, either with a layer of oxide or a film of highly compressed gas. The facts are in good accord, however, with the theory that oxygen atoms are chemically combined with the tungsten atoms." On the basis of these and other similar results Langmuir advanced the theory that in the adsorption of gases on solids, the adsorptive forces are chemical forces of the primary valence type. Carrying this conception over to the present work, it appears that the "unleachable" film consists of xanthate groups chemically attached to copper atoms of the chalcocite by primary valence bonds.

The adsorbed film is formed on the chalcocite from potassium xanthate solution by reaction of the xanthate ions with the surface of the mineral. As suggested by Frumkin (8) for adsorption of electrolytes by charcoal, hydroxide ions are produced at the surface from adsorbed oxygen; these hydroxide ions are replaced by xanthate ions and enter the solution, as follows:

$$\boxed{Cu_2S} + \tfrac{1}{2}O_2 \rightarrow \boxed{Cu_2S}\,O$$

$$\boxed{\begin{array}{c}Cu_2S\\ \end{array}}\,O + H_2O + 2X^- \rightarrow \boxed{\begin{array}{c}Cu_2S\\ \end{array}}\begin{array}{l}X\\X\end{array} + 2OH^-$$

Carbonate ions may be formed from hydroxide and the carbon dioxide present in the system.

During grinding and other treatment, a certain amount of adsorbed or "anchored" reducing ions and sulfate ions are produced at the mineral surface by oxidation reactions, as suggested by Taylor and Knoll (11) for galena. These ions are also replaced by xanthate and enter the solution, as follows: (A *denotes* adsorbed anion, sulfate ion, reducing ion, etc.)

$$\boxed{\begin{array}{c}Cu_2S\\ \end{array}}\begin{array}{l}A\\A\end{array} + 2X^- \rightarrow \boxed{\begin{array}{c}Cu_2S\\ \end{array}}\begin{array}{l}X\\X\end{array} + 2A^-$$

Cuprous xanthate is formed by reaction of xanthate ions with that part of the chalcocite surface already covered with an adsorbed xanthate film, as follows:

$$\boxed{x\mathrm{Cu_2S}}\begin{matrix}\mathrm{X}\\ \mathrm{X}\end{matrix} + \tfrac{1}{2}\mathrm{O_2} + \mathrm{H_2O} + 2\mathrm{X}^- \rightarrow 2\mathrm{OH}^- + \mathrm{Cu_2X_2} + \boxed{\begin{matrix}(x-2)\mathrm{Cu_2S}\\ 2\mathrm{CuS}\end{matrix}}\begin{matrix}\mathrm{X}\\ \mathrm{X}\end{matrix}$$

The cuprous amyl xanthate so formed is leachable with benzene, and its removal does not appreciably affect the flotative properties of the mineral. With the amounts of xanthate used in flotation practice only a relatively small fraction of the amount of reagent may be accounted for as cuprous xanthate.

THEORETICAL FORMULATION

Applying the kinetic theory of reaction to the suggested reaction mechanism, a mathematical interpretation of the reaction-product relationships given in table 1 may be obtained. The following symbols are used in the derivation:

A = milliequivalents of xanthate ions in solution at any time,
A_0 = total milliequivalents of xanthate extracted by the mineral from solution in a given reaction,
B = milliequivalents of adsorbed xanthate on mineral at any time,
B_0 = total adsorbed xanthate formed in a given reaction,
C = milliequivalents of cuprous xanthate on mineral at any time,
t = time,
S = effective mineral surface, expressed as milliequivalents of "elementary spaces" (see Langmuir (7)),
x = fraction of elementary spaces on which xanthate is adsorbed at any time,
x_0 = fraction of elementary spaces on which xanthate is adsorbed after completion of the given reaction, and
k_1, k_2, k_3 = constants.

First, the rate of decrease in free xanthate ions is equal to the sum of the rates of formation of adsorbed xanthate and of cuprous xanthate, as the loss in free xanthate in solution must be accounted for either as cuprous xanthate or as adsorbed xanthate.

$$-\frac{dA}{dt} = \frac{dB}{dt} + \frac{dC}{dt} \qquad (1)$$

The rate of formation of adsorbed xanthate is proportional to the area of bare, unreacted surface and to the concentration of xanthate.

$$\frac{dB}{dt} = k_1(1 - x)SA \qquad (2)$$

The rate of formation of cuprous xanthate is proportional to the covered surface and to the concentration of xanthate.

$$\frac{dC}{dt} = k_2xSA \tag{3}$$

Substituting equations 2 and 3 in equation 1,

$$-\frac{dA}{dt} = k_1(1 - x)SA + k_2xSA \tag{4}$$

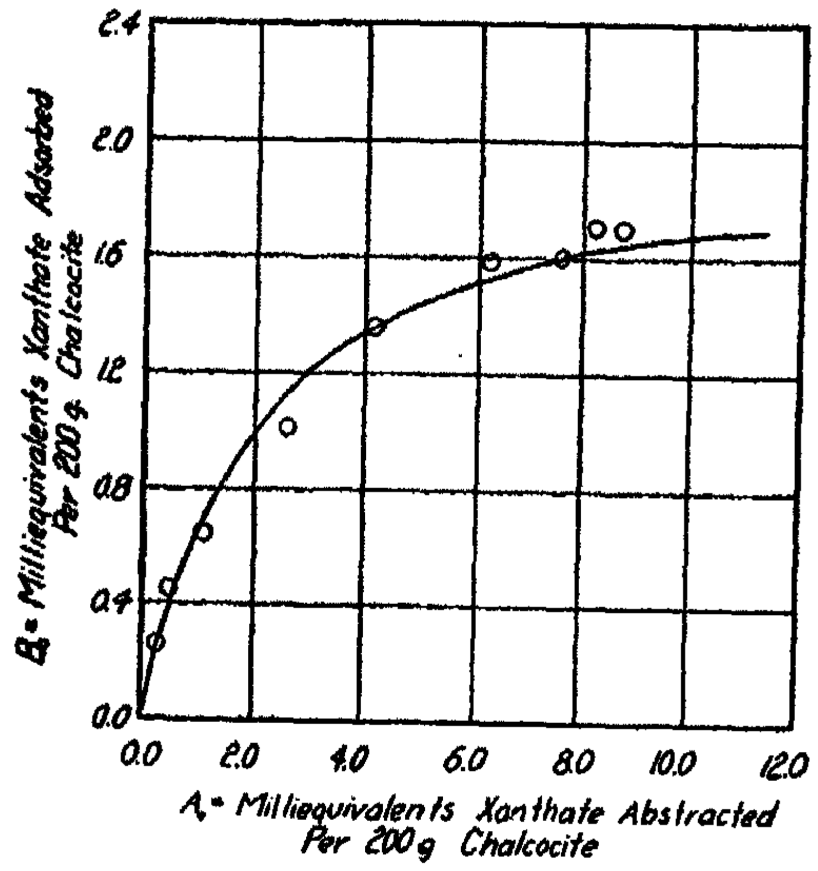

FIG. 5. Adsorption curve, $A_0 = -1.25B_0 - 9.1 \log (1 - B_0/1.75)$. Experimental points from table 1 plotted as circles

The rate of increase in adsorbed xanthate is equal to the rate of increase in adsorbed surface, expressed in the same units.

$$\frac{dB}{dt} = \frac{Sdx}{dt} \tag{5}$$

From equations 2 and 5,

$$\frac{dx}{dt} = k_1(1 - x)A \tag{6}$$

Dividing equation 4 by equation 6,

$$\frac{dA}{dx} = -S - \frac{k_2xS}{k_1(1 - x)} = -S\left(1 + k_3\frac{x}{1 - x}\right) \tag{7}$$

Integrating and substituting limits,

$$\frac{A_0}{S} = x_0(1 - k_3) - k_3 \log_e(1 - x_0) \tag{8}$$

Substituting data from table 1, $B_0 = x_0S = 1.36$ when $A_0 = 4.19$, and assuming S, the surface for 1-hour grind, to be 1.75 milliequivalents as indicated by the maximum of the curve of figure 2, solving for the constant k_3, and converting logs to base 10, the equation becomes:

$$A_0 = -2.19x_0 - 9.1 \log (1 - x_0) \tag{9}$$

Substituting $x_0 = B_0/S$

$$A_0 = 1.25B_0 - 9.1 \log (1 - B_0/1.75) \tag{10}$$

The curve of this equation is plotted in figure 5, with the experimental points from table 1 shown as circles. It is seen that the experimental points check this theoretical curve quite closely, especially as the experimental results for the adsorbed or "unleachable" entity were determined by difference from three experimental values: namely, the total xanthate added, the cuprous xanthate extracted, and the excess xanthate in solution.

SUMMARY AND CONCLUSIONS

In this work the following results have been obtained:

1. In short-time treatment of chalcocite with xanthate the xanthate abstracted by the mineral may be accounted for as cuprous xanthate and as an entity unleachable with ordinary solvents. The formation of these two products occurs practically instantaneously, although with larger quantities of xanthate the reaction to form cuprous xanthate slows up with increase in quantity of cuprous xanthate on the mineral.
2. In long-time treatment of chalcocite with xanthate, leachable products other than cuprous xanthate are formed relatively slowly, possibly by reaction of cuprous xanthate and hydroxide in solution.
3. All the potassium of the potassium xanthate remains in the solution.
4. Hydroxide, carbonate, sulfate, and reducing ions $(S_mO_n)^{--}$ are thrown into the solution in a total amount metathetically equivalent to the xanthate abstracted from the solution.
5. Leaching off the leachable products from xanthate-treated chalcocite has no appreciable effect on the flotative properties of the chalcocite.
6. Pyridine extracts cuprous xanthate from xanthate-treated and leached chalcocite, that is, from chalcocite having the "unleachable" film.
7. The "unleachable" product increases with increase in xanthate added, approaching a maximum in a manner suggestive of adsorption.
8. The maximum amount of unleachable xanthate attainable with a given sample of chalcocite corresponds to a complete monomolecular film on the chalcocite.

9. If a quantity of xanthate just sufficient for effective flotation is added, it may be almost completely accounted for as the unleachable product. Only a relatively small fraction of a monomolecular film of "unleachable" is necessary for efficient flotation. The fraction of the surface filmed determines the dryness of the mineralized froth.

10. Increasing the surface of the mineral by longer grinding increases the unleachable portion and decreases the cuprous xanthate portion of the reaction products.

11. The unleachable water-repellent film may be produced by the adsorption of cuprous xanthate from benzene solution by the chalcocite.

12. There is an essential difference between the collecting actions of xanthate on chalcocite and on malachite, respectively. An unleachable, water-repellent film is not formed on malachite by xanthate.

From these experimental facts it appears that the collecting action of xanthates in the flotation of chalcocite is a result of the production of an oriented, partial-monomolecular film of xanthate groups, chemically adsorbed in the Langmuirian sense. This film is formed by reaction of xanthate ions with the surface of the mineral which contains various adsorbed entities as a result of oxidation during grinding and other treatment. The formation of the adsorbed film is accompanied by reaction of a portion of the xanthate to form cuprous xanthate and perhaps small amounts of other substances separable from the mineral by means of organic solvents. Application of kinetic theory principles to the suggested reaction mechanism gives an adsorption–reaction curve which checks the experimental data well within the limits of experimental error.

This work is being continued with other xanthates and other minerals.

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A STUDY OF THE SORPTION OF ACID SODIUM OLEATE[1]

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The colloid theory of liquid-liquid systems has been envisaged in a broad, general formulation by Cofman (2), who redefined the classical thermodynamic variables and then applied them in the classical manner to colloid systems. One of the consequences of this approach is the statement that colloids are characterized by energy changes of a potential rather than a thermal nature. In other words, the energy exchanges of molecularly dispersed systems involve a heat effect which originates in the haphazard kinetic motion. On the contrary, the energy transfers of colloidally dispersed matter which, by definition, possesses a restricted degree of motion, must be associated with chemical or electrochemical processes. The same opinion had been expressed earlier by Einstein (2).

It is true that classical thermodynamics in the form of Gibbs' adsorption equation has proved to be both "infertile and incomplete" (16) for the liquid-liquid interface. Several reasons have been given for this failure, among which are the following: entropy changes in the adsorbing region contingent upon adsorption (10), inadequacy of the analytical methods employed to check the theory (10, 4), and the use of the equation in a questionably valid form (11).

The investigation reported here is a further study of the liquid-liquid interface by a method already outlined (15). The influence of some hydrocarbon oils on interfacial free energy is the subject of inquiry. The data are considered in the light of Cofman's theory.

METHOD

The method employed consisted of a study of the kinetics of sorption[3] at the interface between sodium oleate solutions and hydrocarbon oils.

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[1] Condensed from the dissertation presented to the Faculty of the Massachusetts State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[2] Present address: Worcester State Hospital, Worcester, Massachusetts.

[3] McBain (11) applied the term "sorption" to surface effects that are not distinguishably adsorption or absorption.

Briefly the technique depends on the hydrolytic equilibrium

$$\underset{\text{Colloid micelles}}{(NaOl)_x} \rightleftharpoons NaOl + H_2O \rightleftharpoons NaOH + \text{Acid sodium oleate}$$

which has been worked out by McBain and his students (12, 14). It is evident that acid sodium oleate has the greatest escaping tendency of all the components of the equilibrium and, therefore, should be sorbed most readily. In the event of such sorption the equilibrium is displaced in the direction of formation of additional free sodium hydroxide.

The measurements of increments of sodium hydroxide were made at 25 ±0.01°C. with a conductivity apparatus. A 10-cc. volume of aqueous sodium oleate solution was introduced into a Freas type conductivity cell with attendant care to avoid frothing. Half an hour later the resistance of this solution was determined with a Wheatstone-Kohlrausch bridge sensitized with a two-stage audio frequency amplifier. Then, a 5-cc. aliquot of the hydrocarbon oil under investigation was allowed to run down the inside wall of the cell and to become an unbroken layer on the surface of the sodium oleate solution. The ground glass stopper of the conductivity cell was sealed with molten paraffin. Determinations of the resistance of the sodium oleate solution were recorded at specified intervals with time reckoned from the formation of the liquid–liquid interface.

MATERIALS

Sodium oleate was prepared from oleic acid of the best quality. Approximately molar equivalents of oleic acid and freshly made sodium alcoholate, both in absolute alcohol, were poured together. The precipitated sodium oleate was washed on a suction filter with cold absolute alcohol. The partially purified product was precipitated again from absolute alcohol, washed, and finally dried at reduced pressure and low temperature to avoid decomposition.

Solutions of sodium oleate were prepared by a special procedure in order to avoid foams, exposure in transference, and contamination from soft glass. The calculated quantity of dry sodium oleate was weighed and introduced into a dry glass-stoppered Pyrex bottle and the necessary amount of conductivity water added. Like the sodium oleate solutions of Du Noüy (3), solutions treated as described remained clear almost indefinitely, provided they were sealed with paraffin and stored in the dark.

Sodium hydroxide solutions were obtained from the dilution of 20 *M* sodium hydroxide with the proper amount of conductivity water (1).

The hydrocarbon oils—*o*-, *m*-, and *p*-xylenes, toluene, benzene, *n*-hexane, *n*-heptane, *n*-octane, 95 per cent *n*-nonane, *n*-decane, and kerosene—were purified by double distillation from metallic sodium through an all-glass Pyrex distilling apparatus. The fraction of kerosene which distilled between 180 and 240°C. was taken as representative. The 95 per cent n-nonane was made available through the courtesy of the Bureau of Standards, American Petroleum Institute Project No. 4.

EXPERIMENTAL

New data have demonstrated that benzene, used in the previous study (15), is not a good standard of reference for the hydrocarbons. For this reason the sorption phenomenon was examined over a range of concentrations of sodium oleate with m-xylene superimposed. The layer of hydrocarbon oil on the surface of the dilute sodium oleate solution displaces the hydrolytic equilibrium in the direction of greater hydrolysis. The magnitude of the displacements can be estimated accurately as *increments* of the equivalent conductance of the aqueous phase.

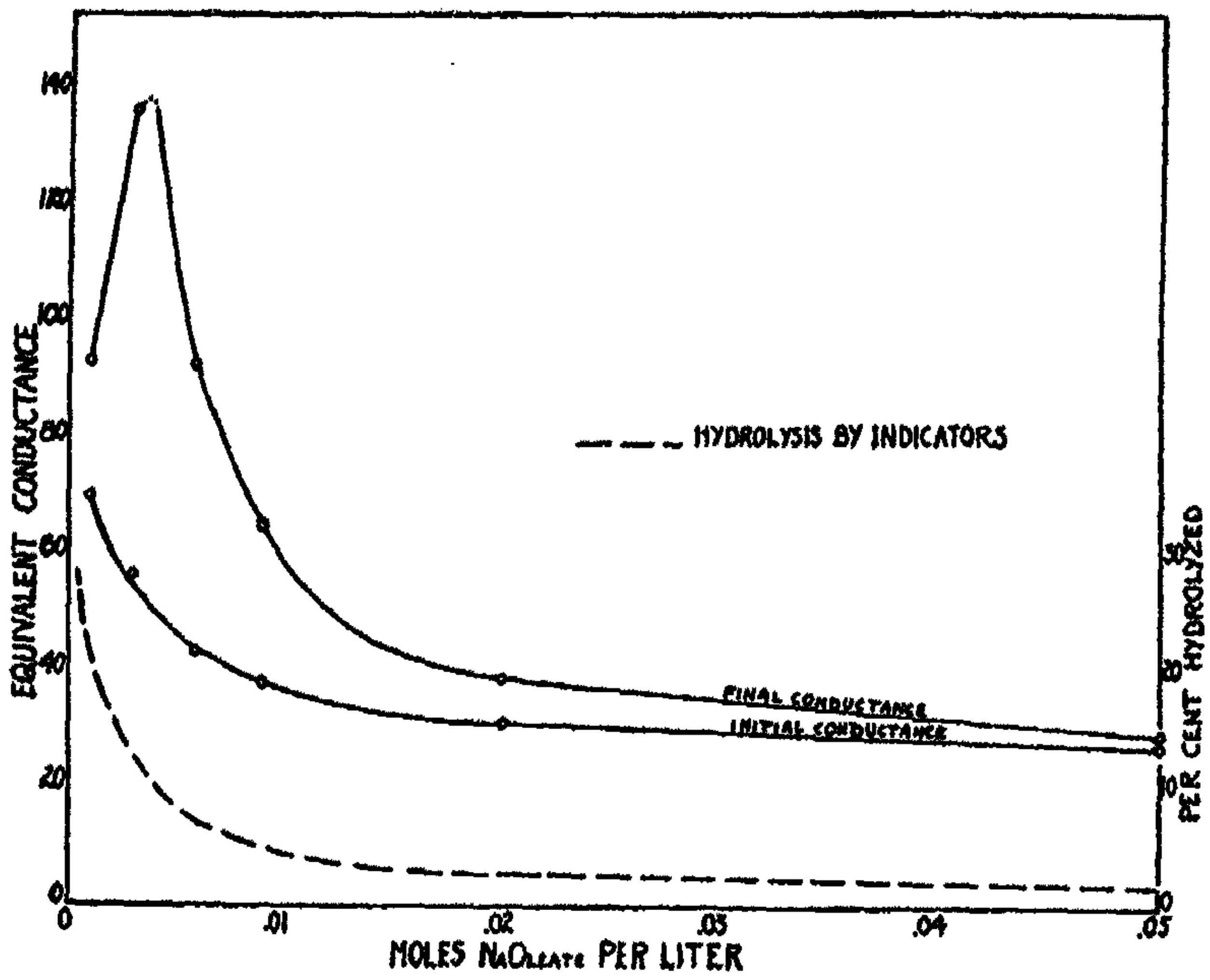

FIG. 1. Variations of the conductance induced by m-xylene with concentration of sodium oleate. Dotted line shows hydrolysis found by indicators

The initial and final conductances of sodium oleate solutions over a range of concentrations are given in graphical form (figure 1), together with the percentages of normal hydrolysis obtained through indicators by McBain and Hay (13) in the same concentration interval. The final conductance was read after twenty-two hours.

Although the curve of percentages of sodium oleate hydrolyzed shows a rapid and continuous increase with dilution, the curve of final conductances under *m*-xylene is not symbatic. If the conductance increments were a measure simply of the phase distribution of oleic acid, the equivalent conductance of sodium hydroxide (240 mhos) should be approached. This is, however, not the case. After passing through a maximum, the final conductance begins to decrease in spite of the fact that normal hydrolysis increases.

These data indicate that the effect measured is not simply the extraction of free oleic acid by the oil phase but, rather, is a true adsorption at the interface.

TABLE 1

The sorption potentials of some hydrocarbons at 25°C.

OIL	INITIAL CONDUCTANCE	FINAL CONDUCTANCE	INCREMENT	SORPTION POTENTIAL
Hexane	36.72	49.33	12.61 12.65	0.509
Heptane	38.30	50.77	12.47	0.503
Octane	38.20	50.56	12.36	0.498
Nonane	38.20	49.97	11.77	0.476
Decane	38.20	48.69	10.49	0.424
Benzene	36.51	55.15	18.64 19.81	0.753? 0.801?
Toluene	36.10	58.00	21.90	0.885
o-Xylene	36.55	60.96	24.41	0.987
m-Xylene	36.35	61.12	24.77 24.77	1.000
p-Xylene	36.59	60.16	23.57	0.952
Kerosene	36.84	48.36	11.52	0.466

Sorption potentials of hydrocarbon oils

The conductance increments of a series of hydrocarbon oils have been determined. The hydrocarbons were investigated two at a time in closely similar cells. Simultaneously, with each pair a control determination was made on *m*-xylene. Aliquot parts (10 cc.) of the same $M/100$ sodium oleate solution were used for all of the hydrocarbons given in table 1. The ratio of the total conductance increment for a given hydrocarbon to that for *m*-xylene is tabulated as the relative sorption potential.

Rates of sorption of the hydrocarbons

The rate of sorption during the first few minutes of the process is an important datum for any hydrocarbon oil. This initial velocity is an approximate measure of the potential gradient for acid sodium oleate between the aqueous solution and the liquid–liquid interface. In each portion of the same sodium oleate solution the thermodynamic potential of acid sodium oleate is the same; hence, the relative potential gradient is determined solely by the free interfacial energy. Therefore, the rate of sorption at the outset of the process is proportional to the free interfacial energy. The free sodium hydroxide which accumulates as a result of the displacement of the hydrolytic equilibrium complicates the subsequent rates and alters the thermodynamic potential of the acid soap.

The initial rate of sorption for each hydrocarbon oil has been calculated. The conductance increment for the first quarter of an hour of the velocity process was multiplied by four in order to convert it to mhos per hour.

TABLE 2

Relative initial free interfacial energies and total conductance increments in contact with M/100 aqueous sodium oleate solution

OIL	RELATIVE INTERFACIAL ENERGY AS MHOS PER HOUR	TOTAL CONDUCTANCE INCREMENT
Hexane	3.68	12.6
Kerosene	2.56	11.5
Benzene	1.32	18.6
p-Xylene	4.40	23.6
Toluene	4.60	21.9
m-Xylene	6.72	24.8
o-Xylene	11.52	24.4

The first part of the conductance–time curve may be assumed to be linear without much error. These initial slopes or relative interfacial free energy values are given in table 2 for a few hydrocarbons.

The complete conductance–time data are given in figure 2 for all of the hydrocarbons except the alkanes heptane, octane, nonane, and decane. These alkanes differ only slightly from hexane; therefore they are omitted.

The curves demonstrate clearly that a disturbing factor exists in the case of benzene. The data in both tables 1 and 2 indicate a peculiarity also. Closer inspection of figure 2 has led to the suspicion that the same disturbance influences the toluene and *p*-xylene curves, although to a lesser degree.

The interpretation of these results is greatly simplified when the structure of surfaces given by Harkins, Clark, and Roberts (5) and Harkins, Davies, and Clark (6) is employed. These authors and Langmuir (9) have shown that the benzene ring, uniformly polarized by its double bonds, lies flat in the surface of pure water. Harkins and his collaborators have stated also that toluene molecules are slightly tilted as a result of the polarizing influence of the methyl group; *m*- and *o*-xylene make larger and larger angles respectively with the plane of the interface. The intensity of the stray fields of these molecules varies with the angle of tilt.

The order of intensity of these stray electric fields adjudged from structure only should be *o*-xylene > *m*-xylene > toluene > *p*-xylene > benzene. The evidence given above (table 2) is in complete agreement with these conclusions of Harkins and Langmuir, and seems to indicate that the initial slope of the time–sorption curve is a measure of the free interfacial energy present subject to the conditions imposed.

The work of McBain (14) and Walker (17) has elucidated the nature of the aqueous sodium oleate solutions. At the concentration ($M/100$) used in the present experiments sodium oleate is largely in the form of micelles. These micelles are rather highly polar as a consequence of their structure. Surface tension measurements (7) show that colloid micelles of sodium oleate exert a much smaller surface pressure than molecular soap does. As concentration increases, the surface pressure of sodium oleate decreases after a maximum has been passed. It may be concluded, therefore, that the surface of a $M/100$ sodium oleate solution is somewhat polar in nature because the surface solute is principally in the form of polar micelles. Under these conditions the stray fields of the impinging hydrocarbons probably exist in almost the same relationship to the sodium oleate interface as they do to pure water.

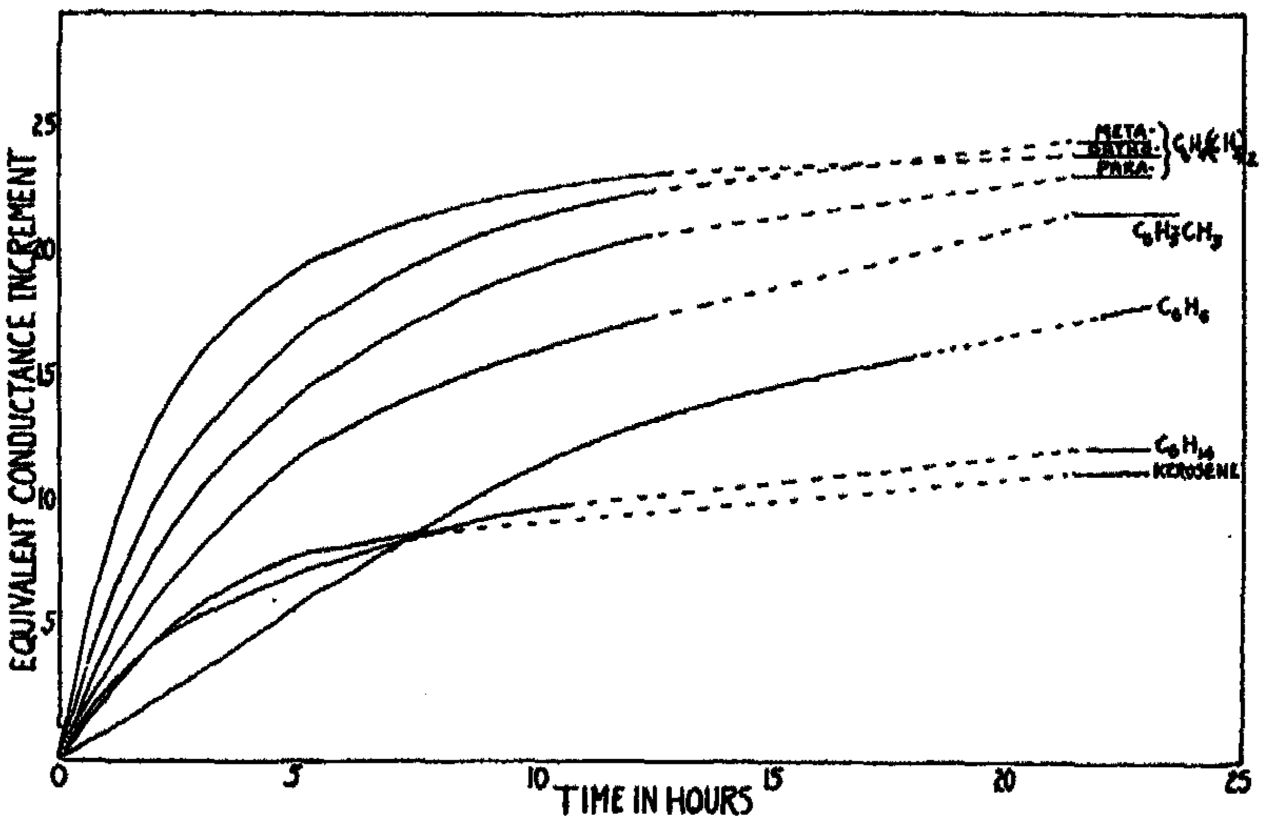

FIG. 2. The time increments of equivalent conductance for a few pure hydrocarbons. The solid lines indicate the readings taken

The conductance measurements reported here are evidently due to the selective sorption of acid sodium oleate. The selective sorption and orientation of molecular soap must of necessity destroy the polar nature of the aqueous surface, and create in its place a non-polar surface of oleate chains on which the hydrocarbon oil impinges. The end result, then, must be a re-orientation of the benzene rings and a straightening of the tilted rings to the perpendicular. The previously mentioned flattening of the time–conductance curves seems to be evidence of this phenomenon. The fact that benzene and all of its derivatives tend to nearly the same total increment regardless of initial slope, bears out this statement also. In accordance with Gibbs' minimum free energy principle any changes in surface structure must be in the direction of increases of potential energy. These re-orientation effects seem, therefore, to indicate "changes of entropy" in the adsorbing layers of the hydrocarbon oil.

Storage of potential energy

It has been suggested (2) that energy transfers in colloid systems involve chemical or electrochemical processes. Some support for this statement is contained intrinsically in the data above, but an experiment was designed to yield more direct proof. To the same $M/100$ sodium oleate solution known amounts of sodium hydroxide were added stepwise and aliquots of the sodium oleate–sodium hydroxide mixture were removed between additions. An accurately measured amount of each aliquot was investigated with *m*-xylene at 25°C. The data are plotted in figure 3.

The additional alkali suppresses normal hydrolysis. Some of the added sodium hydroxide disappears by combination with the acid sodium oleate. The straight line in figure 3 is the conductance–concentration curve expected if none of the sodium hydroxide combined. The shaded area shows the amount and limit of normal hydrolysis.

m-Xylene induces hydrolysis even in the presence of added alkali which has reduced normal hydrolysis to a negligible degree. It is probable, then, that Cofman's idea is wholly tenable. Free energy in the system is converted to potential energy. In this induced hydrolysis water is broken up into its constituent ions; free energy is thereby stored as electrochemical potential.

Acid sodium oleate and surface tension

The increments of equivalent conductance at different concentrations of sodium oleate are plotted in figure 4 for comparison with the surface pressure measurements of Johlin (8). Surface pressure is the force exerted by the surface solute against the surface tension of the pure solvent; numerically, it is the difference between the surface tension of the pure solvent and that of the solution.

The similarity of the two curves suggests that a part of the surface pressure exerted by sodium oleate is a function of hydrolysis as measured by conductance. In concentrations of 0.02 *M* and greater, sodium oleate exists largely in the form of micelles. It appears, therefore, that the micelles alone exert a surface pressure of about 46 dynes and that greater surface pressures are exerted by acid sodium oleate. It follows then, that the surface pressure of a sodium oleate solution which impinges on its vapor has a very limited value when that datum is applied to the liquid–liquid interface between that same sodium oleate solution and an oil phase.

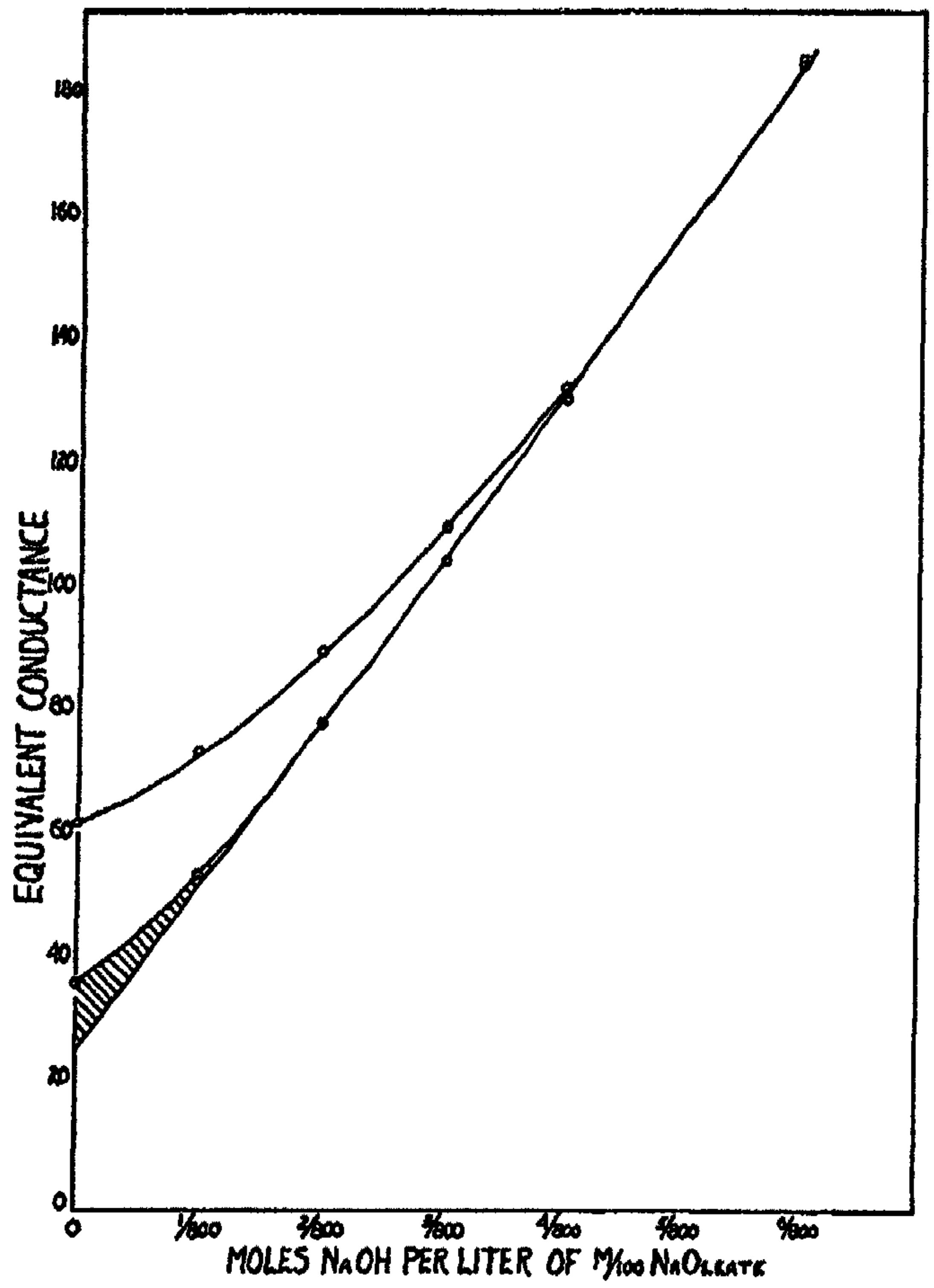

FIG. 3. The effect of sodium hydroxide on the increment of conductance due to *m*-xylene

Owing to the fact that acid sodium oleate exerts the greater surface pressure, together with the fact that the hydrocarbon phase increases the quantity of it by selective adsorption and the resultant hydrolysis, the surface pressure of solute for a given sodium oleate solution in contact with an oil phase can exceed the surface pressure which obtains when the same solution impinges on its vapor.

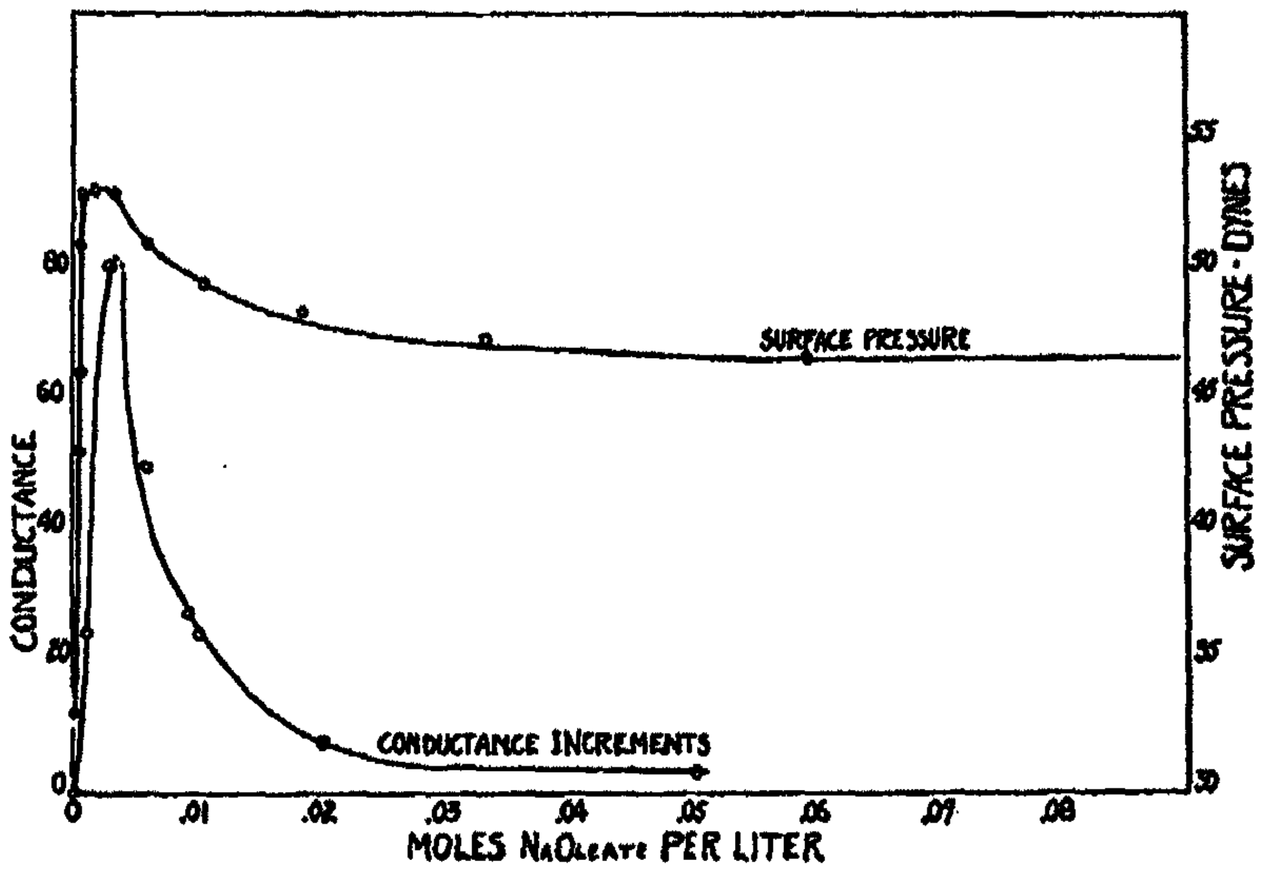

FIG. 4. A comparison of surface pressures with *m*-xylene conductance increments at different concentrations

CONCLUSIONS

The failure of Gibbs' equation must be attributed at least in part to a lack of knowledge of the processes involved. The inflexion points and negative slopes in the surface pressure–concentration relationship for sodium oleate are probably due to changes in the solute. If the concentration function were differentiated and each of the various forms of aggregates considered as a separate solute with individualistic properties, negative values of Γ would probably not arise.

Moreover, it seems that changes in the structure of surfaces not covered by the theory of orientation take place during and as a result of adsorption. There is probably a molecular re-orientation in the surface configuration of some oils at the plane of contact. As a consequence free and potential surface energies of the interface are altered. These changes must be included in Gibbs' equation.

The selective adsorption of acid sodium oleate by hydrocarbon oils alters the surface pressure by an amount not predictable from surface tension measurements. The characteristics of the oil phase must be considered.

Relative sorption potentials, which should be useful data in the quantization of emulsions, are tabulated.

Some evidence in support of the idea that colloids involve potential energy changes has been given. In the case of sodium oleate and hydrocarbon oils free interfacial energy is stored in the cleavage of water.

The author is indebted to Dr. Paul Serex, whose sustained interest was invaluable to the progress of the work.

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NEW BOOKS

Optical Rotatory Power. By T. Martin Lowry. 21.5 x 13.5 cm.; xiii + 483 pp. London: Longmans, Green and Co., 1935. Price: 30/- net.

It would require more space than is available to enumerate all the subjects which Professor Lowry deals with in this book, and it must suffice to say that in addition to an outline of the historical development of each theme, he gives valuable details of most of the apparatus used in polarimetric work, and a comprehensive treatment of the main problems at present under discussion, especially those to which his own investigations have been directed, or are related. Mostly the treatment is adequate, but in a number of cases it is incomplete, work quite relevant to the question dealt with being ignored; and it may be noticed that the diagram on p. 330 really represents the behavior not of nicotine but of ethyl tartrate (see Z. physik. Chem. **60**, 652 (1907)), whilst in the diagram on p. 154, the curve of ellipticities ought to be inverted (J. phys. [3] **7**, 84 (1898)).

In the theoretical parts of the book, the treatment is speculative, and often unsatisfactory from a logical point of view. Thus since quartz, and tartaric acid in solution, exhibit anomalous rotation dispersion, and the phenomenon in the latter case is attributed to the existence of dynamic isomers, it might be expected, by parity of reasoning, that quartz ought also to consist of several dynamic isomerides, a logical conclusion which there is, however, some reluctance to adopt.

This modern tendency towards deductive reasoning seems more than a little premature in regard to optical activity, considering that the very outlines of the subject have not yet been satisfactorily investigated, even in a qualitative sense. There is in fact, on account of the remarkable sensitiveness of the phenomena in question to various external and internal factors, hardly any subject which so little lends itself to such treatment. Nevertheless, Professor Lowry's book, representing as it does the attitude of a large school of investigators, will quickly become, on that account, as well as by its many valuable qualities, indispensable to workers in this field.

T. S. Patterson.

Colloid Symposium Monograph. Papers presented at the Eleventh Symposium on Colloid Chemistry, Madison, Wisconsin, June, 1934. Edited by H. B. Weiser. Baltimore: The Williams & Wilkins Company, 1935.

The Colloid Symposium since its birth has afforded an open forum where the somewhat artificial distinctions separating chemistry, physics, and physiology can be disregarded. Also it has been generally possible to achieve an elasticity of discussion not usual under the alarm-clock and stop-watch ridden sessions of major conventions. The publication of its proceedings as an annual monograph is generally justified, more particularly when as in the present volume one finds a feature subject rallying to it a number of papers. In this case the feature was cellulose. A sort of snails' race between colloid and cellulose chemists as to which should be the last to take notice of the other appears ended. In this collection the paper by W. D. Bancroft and J. B. Calkin entitled "Adsorption of Caustic Soda by Cellulose" does not appear to contain much new over their papers in *Textile Research*, but sums up clearly their evidence and arguments against any stoichiometric combination.

E. O. Krämer and W. D. Lansing contribute a valuable review of methods and data available for determining molecular weights of cellulose and its derivatives; S. E. Sheppard and P. T. Newsome a comparison of the properties of the cellulose (tri)-esters of the homologous fatty acids. The papers of A. Stamm and collaborators on the diffusion and sorption of water in wood and cellulose are rich in data and suggestive in argument. Papers on adsorption deal with both the experimental side and the theoretical—an interesting example of the latter being a critique by G. E. Cunningham of the Langmuir equation for the adsorption isotherm, and a proposed substitute. Several papers deal with electrokinetics in various applications. A technical paper by F. L. Browne on the behavior of paint as affected by gel changes of the vehicle, and a semi-technical one by W. D. Bancroft and P. H. Miller on cold vulcanization should be mentioned. The latter is remarkable as admitting that data which can be represented by a smooth adsorption curve may actually derive from stoichiometric combination.

S. E. Sheppard.

Orthohydrogen, Parahydrogen and Heavy Hydrogen. By Adalbert Farkas. 14.5 x 22 cm.; xiv + 215 pp. Cambridge: The University Press. New York: The Macmillan Company, 1935. Price: $3.50.

This important addition to the Cambridge Series of Physical Chemistry will be welcomed by all investigators who are interested in hydrogen. The book is timely and is especially valuable because it combines the different phases of the subject in one volume. It is divided into two parts. Part I is devoted to ortho- and parahydrogen and its chapters are as follows: I. The Discovery of Orthohydrogen and Parahydrogen; II, Theory; III, The Properties of the Hydrogen Modifications; IV, The Kinetics of the Ortho-parahydrogen Conversion; V, Applications; VI, Ortho and Para Systems in other Molecules. Part II discusses heavy hydrogen in chapters entitled as follows: I, The Discovery of Heavy Hydrogen; II, The Preparation and Determination of Heavy Hydrogen; III, The Properties of Heavy Hydrogen; IV, The Chemistry of Heavy Hydrogen (1. Equilibria, 2. Kinetics).

The author, who personally has contributed much to the development of our knowledge of the subject, amply fulfills the purpose for which the book was written. This can best be stated as the author does when he says, "the purpose of this book is to describe the preparation, properties and chemical behavior of these different kinds of the same element and to illustrate how the investigations connected with this subject have contributed to the solution of some chemical and physical problems." The author gives a very complete review of the theoretical as well as the experimental work which has been completed since the discovery of ortho- and para-hydrogen in 1929. There is not much to be said in criticism of the book, for any lack of completeness must be attributed to the present state of development of the subject and not to omissions on the part of the author. Part I is therefore more complete than Part II. The combination of the theoretical with the experimental work seemed to the reviewer to be particularly well done. The book is heartily recommended to advanced students in physical chemistry as well as to those who are working in the field.

L. H. Reyerson.

The Principles of Experimental and Theoretical Electrochemistry. By Malcolm Dole. xiii + 549 pp. New York: McGraw-Hill Book Co., Inc., 1935. Price: $5.00.

This is one of the most valuable books written on the subject of electrochemistry. During recent years the field has broadened so rapidly and new material, both experimental and theoretical, has appeared in such amounts that students have been unable to keep up-to-date by reading original publications. In this book the author has analyzed most of the recent work and organized it and condensed it in a masterly manner. It is primarily a reference book, though it might be used as a text in a graduate course or, more especially, a seminar.

Several topics which are entirely omitted or briefly mentioned in other texts are given extensive treatment. Among these are: the Wien effect and Debye frequency effect, 11 pages; dielectric constants and electric moments, 35 pages; molecular rays, 27 pages; phase-boundary and semipermeable-membrane potentials, 20 pages; and the glass electrode, 16 pages. Especially interesting is the chapter entitled "Quantum Mechanics and Electrochemistry."

The author assumes a pronounced modern point of view. There are nearly seven hundred literature references, of which more than five hundred are to articles that have appeared during the last ten years, and more than three hundred since 1930.

The book is unusually free from errors. It is written in a clear, understandable style. Complex mathematical derivations have been omitted, though ample references are given to original sources for those who wish to follow through such derivations. Care is taken, however, to point out the assumptions involved in the mathematical developments, so that the reader may understand the limitations of applications of the final simple expressions included in the text. There are many curves and figures and many tables of data that assist the reader materially in following the discussions. One might be misled by the term "experimental" in the title of the book. It is in no sense a laboratory manual, but the experimental side of each topic is emphasized and actual data are extensively used in the discussion of theories.

Naturally there are several points about such a book that conflict with the views of each individual reader. The reviewer regrets that the author did not see fit to use some of the conventions and methods of attack that have become so generally accepted by the authors of the most popular texts in physical chemistry in the discussion of thermodynamics and electromotive force. Several instances might be mentioned where exceedingly elementary material is introduced that tends to detract from the high tone of the book as a whole. Among such topics may be mentioned the following: series and parallel circuits, the electrolysis of simple substances, and the Faraday and the coulometer, presented between pp. 29 and 33; the direct-current Wheatstone bridge, pp. 42-3; the voltmeter, potentiometers of the Poggendorf type, indicating devices (the moving-coil galvanometer), pp. 211-5; standard cells, and some useful electrodes, pp. 220-5. The material presented on these pages is found in the most elementary texts of physics and physical chemistry and must be familiar to any person interested in this book. And yet the subject of conductometric titrations, which has received such extensive development during the last few years that H. T. S. Britton published a book on the subject in 1934, is given only one page.

On the whole the book represents a difficult task remarkably well done. No person interested in electrochemistry or the theories of electrolytic solutions can afford to be without it.

ALFRED L. FERGUSON.

Electrons (+ and −), Protons, Neutrons and Cosmic Rays. By ROBERT A. MILLIKAN. 490 pp. Chicago: The University of Chicago Press, 1935. Price: $3.50.

As the author explains in the preface, the present book is a direct outgrowth of the volume entitled *The Electron* published in 1917 (University of Chicago Press), which was revised in 1924 and further expanded when he delivered the Messenger Lectures at Cornell University.

Besides the small amount of revision necessary in the earlier parts, six entirely new chapters have been added on waves and particles, discovery and origin of cosmic rays, the spinning electron, the positron, the neutron and the transmutation of elements, and the nature of cosmic rays.

The name of the author is intimately associated with most of these new fields. The positron was discovered in his laboratory. He has been one of the leaders in the investigation of cosmic rays. The treatment as one might have expected is interesting, thorough and authoritative.

In the section on the divisibility of the electron the conclusion is reached that there is up to the present no evidence whatsoever of a sub-electron.

The work is splendidly illustrated with figures and photographs of cloud tracks and of apparatus.

S. C. LIND.

Absolute thermische Daten und Gleichgewichtskonstante. By R. DOCZEKAL (in collaboration with H. Pitsch). 23 x 15 cm.; 69 pp.; three diagrams in pocket. Vienna: Julius Springer, 1935. Price: 6.60 RM.

This book contains a summary of the thermodynamic equations used in the calculation of energies, entropies, and free energies of substances, with data for hydrogen, oxygen, nitrogen, carbon monoxide, carbon, water, carbon dioxide, methane, and benzene given in tables and curves. These data are applied to the determination of equilibrium constants of some reactions of technical interest. The evaluation of equilibrium constants in dissociation reactions is then considered, the tables provided furnishing the values when the degree of dissociation is known. Since the data, particularly the specific heats of gases, are only very approximate, the results are in general more suitable for application in industrial conditions than in the research laboratory. The symbols used are not those employed in England or America and are printed in Gothic type. Within its limitations the book is likely to be very useful and the authors appear to have taken pains in selecting the data. It should be particularly useful in works laboratories where problems of the type it deals with must frequently call for solution.

J. R. PARTINGTON.

THE THERMODYNAMIC PROPERTIES OF CADMIUM SULFATE IN WATER-ETHYL ALCOHOL SOLUTIONS

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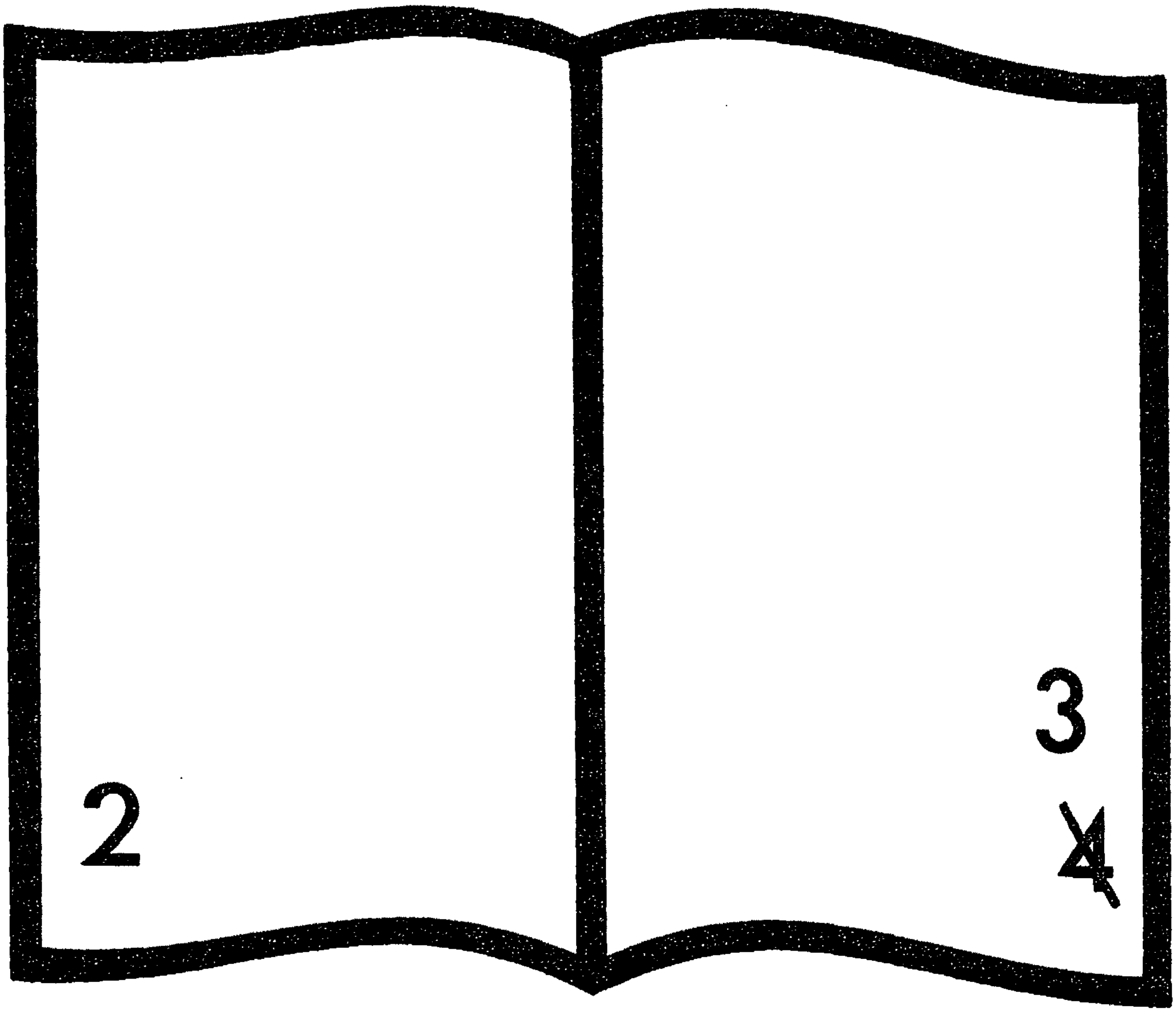
INTRODUCTION

The purpose of this research was to investigate how the partial free energy, heat content, and heat capacity of a typical bivalent electrolyte, cadmium sulfate, are affected on lowering the dielectric constant by the addition of ethyl alcohol to its aqueous solution.

It can be demonstrated (7, 20) that the electric free energy of an ion can be computed from the work of reversibly charging the ion from a reference potential to its actual potential ψ. The latter is composed of two parts: first, a part ψ_0 which exists in the absence of any surrounding ions and arises by virtue of its own charge; and second, a part ψ^* which arises from the unequal distribution of the surrounding ions as interpreted by the Debye-Hückel interaction theory. The interaction effect depends upon $D^{-3/2}$ as a limiting first approximation, and upon a parameter a which represents in terms of the model the distance of closest approach of the ions. The interaction effect can be eliminated exactly when the experimental results at finite concentration permit of an unequivocal extrapolation to infinite dilution.

The potential, ψ_0, which generally is of greater magnitude, should, according to Born (3), vary inversely with the radius of the ion and the dielectric constant. Born's equation for the solvent effect assumes the same simple model, namely, that the ions may be represented by spheres of radius r_i, and the medium by a continuous dielectric having the macroscopic value D. All chemical processes of solvation are ignored.

One aspect of this investigation was to ascertain in how far this simple model can account for the experimental results obtained with a bi-bivalent salt, where the electric effects are of greater magnitude than with a uni-univalent salt, by comparing the radii of the ions as computed from the Born equation with the value a as given by the interaction theory. Although a number of investigators (6, 10, 11, 19, 23) have utilized galvanic cells to study medium effects in terms of the free energy of transfer of electrolytes, no systematic investigation of temperature coefficients in non-aqueous solvents has been made. Such studies are of importance since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they furnish accurate data for the calculation of changes in the heat content and heat capacity of the cell process from which the thermal properties of the electrolyte can be readily obtained. Owing to the highly reproducible behavior of cadmium amalgam and mercurous sulfate electrodes, cells containing these electrodes are most suitable for attacking this problem.

Since the requisite data for aqueous cadmium sulfate are available from the studies of LaMer and Parks (17) on the amalgam cell:

Cd (2 phase), $CdSO_4$ (M, H_2O), $PbSO_4$(S), Pb (2 phase) Cell I

for which the cell process is:

Cd (satd. Hg) + $PbSO_4$(S) = $CdSO_4$ (M, H_2O) + Pb (satd. Hg)

we first investigated this cell by replacing the water progressively with ethyl alcohol. Equilibrium, however, was attained so slowly in the presence of alcohol that cell I was abandoned in favor of the amalgam cell using mercurous sulfate instead of lead sulfate:

Cd (2 phase), $CdSO_4$ (M, a per cent EtOH), Hg_2SO_4(S), Hg Cell II

Cd (satd. Hg) + Hg_2SO_4(S) = $CdSO_4$ (M, a per cent EtOH) + 2Hg

The limited success which the mercurous sulfate electrode has achieved in aqueous solution is due primarily to the uncertainty arising from the relatively large corrections for its solubility, which must be applied when the concentration of the more soluble sulfate (cadmium sulfate) is less than 0.005 M. Fortunately, the solubility of mercurous sulfate is greatly reduced by the addition of alcohol. In 33.3 weight per cent ethyl alcohol, using Hulett's method (14) of precipitating the mercury as chloride by the addition of hydrochloric acid, we find $S_{Hg_2SO_4} = 1.8 \times 10^{-6}$ moles per liter. The same value was obtained in experiments in which the alcohol was first evaporated and the chloride precipitated from aqueous solution. The solubility product of mercurous sulfate in 33 weight per cent alcohol is consequently so small that no correction for sulfate ion is necessary in calculating the observed normal potentials $E^{0\prime}$, even for concentrations as low as 0.001 M cadmium sulfate. Furthermore, cell II yielded highly reproducible potentials and hence is well suited for our purpose, even though its use is limited to rather narrow ranges of concentration as a result of the decreased solubility of both cadmium sulfate and mercurous sulfate. In 15 per cent ethyl alcohol the lower limit for precise work is 0.01 M cadmium sulfate; in 33 per cent ethyl alcohol the limits are 0.001 M extending to saturation (about 0.01 M); above 33 per cent ethyl alcohol the internal resistance of the cell is so high that 0.01 M is the practical lower limit; above 50 per cent alcohol cadmium sulfate becomes too insoluble for precise measurements.

To compare the results in water using cell I with those in alcohol using cell II, it is necessary to know the thermal properties of cell III:

$$\text{Pb (2 phase), PbSO}_4\text{(S), Hg}_2\text{SO}_4\text{(S), Hg} \qquad \text{Cell III}$$

$$\text{Pb (satd. Hg)} + \text{Hg}_2\text{SO}_4\text{(S)} = \text{PbSO}_4\text{(S)} + 2\text{Hg}$$

Subtracting cell III from cell II yields

$$\text{Cd (2 phase), CdSO}_4\ (M,\ a \text{ per cent EtOH), PbSO}_4\text{(S), Pb (2 phase)} \qquad \text{Cell IV}$$

$$\text{Cd (satd. Hg)} + \text{PbSO}_4\text{(S)} = \text{CdSO}_4\ (M, a \text{ per cent EtOH}) + \text{Pb (satd. Hg)}$$

It will be observed that cell IV is identical with cell I except that the solvent contains *a* per cent ethyl alcohol. By comparing results with cell I and cell IV, the free energy of transferring cadmium sulfate from water to alcohol can be computed without involving the troublesome and uncertain solubility corrections for mercurous sulfate.

Henderson and coworkers (12, 13) have measured cell III at 18°, 25°, and 30°C., but as this temperature range was not sufficient, and no precautions were reported for the removal of oxygen from the solution, we have reinvestigated cell III over the range 0° to 50°C.

APPARATUS

The electrical apparatus described in detail previously by LaMer and Parks (17) was used. The potentiometer was recalibrated. The Eppley Cell No. 74017, calibrated by the Bureau of Standards, was checked frequently against other standard cells in the laboratory.

PREPARATION OF MATERIALS

The best C.P. grades of salts were further purified by repeated crystallization as described previously, using conductivity water and Nonsol bottles for storage. The preparation and storage of the amalgams was identical with previous description. The cadmium sulfate solutions were prepared by diluting a master solution (approximately 0.1 molal) by weight, the exact concentration of which was known to 0.05 per cent by the quantitative deposition of cadmium by electrolysis.

Ethyl alcohol. We have corroborated the work of Stout and Schuette (24), who showed that the method in which ethyl alcohol is distilled from aluminum and potassium hydroxide is more effective in removing the aldehydes than the more common method using silver oxide. Ten grams of potassium hydroxide was added per liter of 95 per cent alcohol. The next day 6 to 8 g. of aluminum turnings per liter of alcohol was added, the reaction mixture refluxed for one hour, and finally distilled in an atmosphere of nitrogen in glass apparatus having an efficient fractionating column. The middle and last fractions were found to be aldehyde-free when tested with fuchsin-sulfite reagent as described by Woodman (26). The specific gravity of the alcohol was then taken at 25°C. The weight per cent of the alcohol was determined from the density.

Mercurous sulfate. Mercurous sulfate was prepared electrolytically by the Hulett method (15), in which purified mercury served as the anode and a platinum wire dipping into sulfuric acid of density 1.15 was the cathode. The product was gray, owing to the presence of finely divided mercury, which is a distinct advantage in checking any tendency of the mercurous ion to be oxidized to mercuric ion. Vosburgh and Eppley (25) have shown that samples of mercurous sulfate prepared by three different methods—the reduction of mercuric sulfate by mercury, direct current electrolysis, and the reaction of mercurous nitrate and sulfuric acid—give E.M.F.'s agreeing within 0.01 mv. Åkerlöf (1) also obtained satisfactory results with mercurous sulfate prepared electrolytically in his study on the alkali sulfates. The mercurous sulfate was stored in the dark under 2 molal sulfuric acid in a Nonsol bottle.

EXPERIMENTAL METHOD

The cell vessel used for cells I and II was the same as that developed by Cowperthwaite and LaMer (5) for their study of zinc sulfate. This type of cell vessel permits the entire filling operation to be carried out in an atmosphere of nitrogen, and the cell can then be sealed off under mercury. The reader should consult their paper for the diagram and details of manipulation.

The type of cell vessel used by LaMer and Parks was found to be more suitable for cell III, where two solids are involved. Their cell vessel is composed of six electrodes divided by three large bore stop-cocks into two groups of three each. On one side three similar lead-lead sulfate electrodes and on the other side three similar mercurous sulfate–mercury electrodes are set up. This type of vessel has the particular advantage that measurements to check the constancy and reproducibility of each leg of the three electrodes forming the one half-cell as well as the measurements of the three total cells can be made without disturbing the contents or the vacuum.

EXPERIMENTAL DATA

To test the reproducibility and freedom from hysteresis of cell II in alcohol solutions, three sets of five cells each were made up on different days. The concentrations of cadmium sulfate and ethyl alcohol were respectively 0.01 M and 33.3 per cent. The average deviation at 25°C. was ±0.0064 mv. For two of these sets, the readings were taken at different temperatures in the order: 25°, 30°, 20°, 15°, 10°, 0°, 10°, 20°, 25°, and 30°C. The combined averages of the values obtained at descending and ascending temperatures of the two sets never had an average deviation greater than ±0.02 mv.; usually much less. Cell II is not only reproducible but it exhibits little, if any, temperature hysteresis.

Henderson and Mellon (12), using both a saturated and an unsaturated solution of sodium sulfate as the conducting medium, found that cell III gave an E.M.F. of 0.96466 at 25°C. They also demonstrated that the E.M.F. was independent of the conducting medium by using saturated and unsaturated solutions of nickel, zinc, manganese, and cobalt sulfates in place of sodium sulfate.

TABLE 1

Observed E.M.F. *of cell III*

TEMPERATURE t°C.	NO. OF CELLS MEASURED	$E = E^{0'} = E^{0}$
0.0	3	0.96051
12.5	3	0.96262
25.0	6	0.96471
37.5	3	0.96680
50.0	3	0.96891

TABLE 2

Values of E for 0.01 M cadmium sulfate

t°C.	E (I) (H_2O)	E (II) (33.3 PER CENT ALCOHOL)	E (II) (50 PER CENT ALCOHOL)	E (IV) (33.3 PER CENT ALCOHOL)	E (IV) (50 PER CENT ALCOHOL)
0.0	0.14651	1.04526	1.02425	0.08475	0.06374
10.0	0.14720	1.04780	1.02596	0.08561	0.06377
15.0	(0.14673)	1.04870	1.02659	0.08567	0.06356
20.0	0.14588	1.04942	1.02707	0.08555	0.06320
25.0	(0.14476)	1.04997	1.02744	0.08526	0.06273
30.0	0.14346	1.05032	1.02774	0.08477	0.06219

t°C.	$E^{0'}$ (I) (H_2O)	$E^{0'}$ (II) (33.3 PER CENT ALCOHOL)	$E^{0'}$ (II) (50 PER CENT ALCOHOL)	$E^{0'}$ (IV) 33.3 PER CENT ALCOHOL)	$E^{0'}$ (IV) (50 PER CENT ALCOHOL)
0.0	0.03812	0.93687	0.91586	−0.02364	−0.04465
10.0	0.03485	0.93545	0.91361	−0.02674	−0.04858
15.0	(0.03239)	0.93436	0.91225	−0.02867	−0.05078
20.0	0.02956	0.93310	0.91075	−0.03077	−0.05312
25.0	(0.02645)	0.93166	0.90913	−0.03305	−0.05558
30.0	0.02317	0.93003	0.90745	−0.03552	−0.05810

* ( ) interpolated values.

In table 1 are given our results for cell III over a wider temperature interval, using as solvents 0.33 M sodium sulfate and 0.002 M sulfuric acid (to prevent hydrolysis in water), and 0.01 M sodium sulfate in 33.3 per cent ethyl alcohol. The measurements of the two sets agreed within ±0.02 mv. and checked Henderson and Mellon's value at 25°C. to 0.05 mv.

In table 2 are recorded the observed values of E for the respective cells for 0.01 M cadmium sulfate in the solvents water (column 2), and 33.3 per cent and 50 per cent ethyl alcohol (columns 3 and 4) at various temperatures. Each value represents the average of at least five cells; the average deviation was never greater than ±0.02 mv., and in many cases only ±0.01 mv. The values for the cell process IV, obtained by subtracting the temperature-interpolated values of E (III) from E (II), are given for purposes of direct comparison with cell I with which they are equivalent except for the presence of alcohol.

In table 3 are given the observed values for cell II for different concentrations of cadmium sulfate in 33 per cent ethyl alcohol at 25°C. Each value represents the average of at least five cells; the average deviation was never greater than ±0.04 mv. The values for cell I in water were taken from a large scale graph of LaMer and Parks' (17) $E^{0\prime}$ values after they had been interpolated to 25°C. using an equation of the third degree in t.

TABLE 3

E for cells I, II, and IV as function of concentration of cadmium sulfate and per cent of alcohol at 25°C.

M	0 PER CENT ALCOHOL	33 PER CENT ALCOHOL	
	I	II	IV
0.01	0.14476	1.04997	0.08526
0.008	0.14877	1.05249	0.08778
0.006	0.15404	1.05577	0.09106
0.004	0.16158	1.06017	0.09546
0.002	0.17424	1.06686	0.10215
0.001	0.18840	1.07386	0.10915

15 per cent alcohol at 0.01 M; E (II) = 1.07908; E (IV) = 0.11437.

THEORETICAL

When a mole of salt is transferred from an aqueous solution of dielectric constant D_2 to an alcoholic solution of dielectric D_1, the reversible work of transfer arises from two sources. The excess electrical free energy, which the ions possess by virtue of their unequal distribution as interpreted by the Debye-Hückel interaction theory, changes somewhat with the change in the dielectric constant. Secondly, the individual ions of radius r_i possess a greater electrical free energy in the medium of low dielectric constant by virtue of the greater amount of work which is necessary to charge reversibly these ions for such a medium. Born's equation for this solvent medium effect is

$$\Delta \bar{F}_0 = \frac{(z\epsilon)^2 N}{2}\left(\frac{1}{D_1} - \frac{1}{D_2}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (1)$$

$\Delta \bar{F}_0$ is the free energy change at infinite dilution, where the effects of interaction are absent.[1]

The activity coefficient often is a more convenient quantity to use in the numerical treatment of experimental data than is the free energy. Any activity coefficient whose standard state of reference is taken as unity for infinite dilution in pure water will be designated by the symbol f. When the activity coefficient is referred to the standard state of infinite dilution in a particular water–alcohol medium, an asterisk will be used (f^*). A subscript zero indicates that the concentration of electrolyte is zero, and when the medium is pure water, a superscript zero will be used (f^0; $f_0^0 = 1$, etc.). All concentrations of cadmium sulfate are expressed in moles per kilogram of solvent; the concentration of alcohol in weight per cent.

TABLE 4

"Total medium effect" log f/f^0 for cadmium sulfate at 25°C.

WEIGHT PER CENT ETHYL ALCOHOL	D	0.01 M	0.008 M	0.006 M
15.0	70.14	0.5138		
33.3	59.16	1.0059	1.0311	1.0647
50.0	48.93	1.3867		

WEIGHT PER CENT ETHYL ALCOHOL	D	0.004 M	0.002 M	0.001 M
33.3	59.16	1.1178	1.2187	1.3398

In terms of these definitions, the total medium effect is log f/f^0 and is composed of two parts, the solvent effect = log f_0/f_0^0 = log f_0, since $f_0^0 = 1$, plus the interaction medium effect log f^*/f^0. Thus

$$\log f/f^0 \quad \log f_0 + \log f/f^0 \qquad (2)$$

Owen (21) uses the terms "primary" and "secondary" medium effects, but we prefer the more descriptive terms "solvent" and "interaction." They are obviously related to the potentials ψ_0 and ψ^* mentioned in the introduction.

The total medium effect is obtained directly from the E.M.F. of the double cell I–IV by the relation

$$E = E\,(\mathrm{IV}) - E\,(\mathrm{I}) = 0.05915\, f/f^0 \qquad (3)$$

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[1] $Z\epsilon$ is the charge on the ion, N is Avogadro's number, and r_+ and r_- are the radii of the cation and anion.

The results are given in table 4 for the concentrations of cadmium sulfate and alcohol studied.

Calculation of the solvent medium effect and the interaction coefficient f^* requires a knowledge of E^0 for cell II in alcohol. In figure 1 we have plotted the values of $E^{0\prime}$; defined as

$$E^{0\prime} = E + \frac{\nu RT}{n\mathfrak{F}} \ln M; \quad E^{0\prime} = E^0 - \frac{\nu RT}{n\mathfrak{F}} \ln f^* \quad (\nu = n = 2) \quad (4)$$

against the square root of the molality for 33.3 per cent ethyl alcohol. The data obviously do not approach the limiting slope of the Debye-Hückel theory at concentrations as low as 0.001 M. This behavior has been observed (4, 9) previously for the solubility data of salts in methyl and ethyl alcohol-water mixtures.

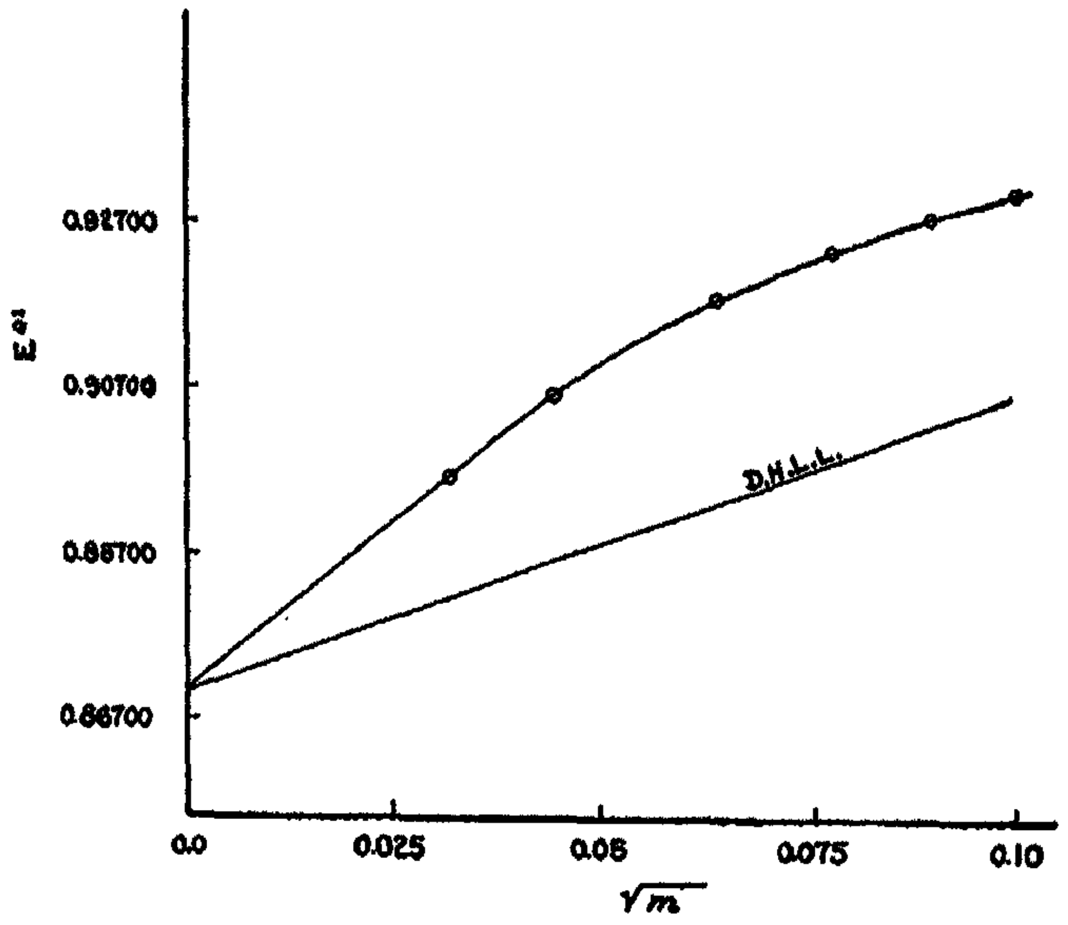

FIG. 1

Fortunately, a precise value of E^0 is not necessary, since a comparatively large error in $\log f^*$ results in only a small error in $\log f_0$, f^* never being greater than 1 per cent of f_0. In table 5 we give the calculation of E^0 using the Gronwall, LaMer, and Sandved (8) equation for the activity in equation 4 for $a = 2.92$ A.U., which proved to give the best fit.

It will be noticed that the individual values fluctuate more from the average than they do for cadmium sulfate in water solution. This is due to the fact that the higher terms do not converge rapidly in the case of the alcohol solution ($D = 59.16$), whereas they do converge with sufficient rapidity in the case of water ($D = 78.54$). LaMer and Parks obtained a constant E^0 when an ion size of 3.6 A.U. units was used. Whether the decrease in a from 3.6 A.U. in water to 2.92 A.U. in 33.3 per cent alcohol is real, or arises from insufficient convergence, or is due to theoretical weaknesses in the Debye-Hückel theory cannot be determined at present. It is gratifying that the E^0 calculated over the range from 0.01 M to 0.001 M, agrees within 0.16 mv. of the value obtained by the linear graphical extrapolation. We estimate that E^0 is known to ±0.0005 volt, which fortunately introduces an uncertainty in the calculation of the solvent medium effect of only ±0.5 per cent. Using the average value $E^0 = 0.87033$, the solvent medium effect for 33.3 per cent ethyl alcohol in the absence of any interaction effects equals 1.6246.

According to the Born equation, the solvent medium effect, log f_0, should be proportional to the reciprocal of the dielectric constant of the solvent, a prediction which Åkerlöf (2) found to hold fairly well for sodium, potassium, lithium, and hydrogen chlorides up to 80 per cent methyl alcohol in water ($D = 42.3$). The dotted line in figure 2 has been drawn on this assumption. The distance from any point on the solid line to the dotted line at the same value of $1/D$ is equal to the interaction medium effect, which, it will be noted, rapidly becomes of greater importance as the dielectric constant decreases.

TABLE 5

Calculation of E^0 by the Gronwall, LaMer, and Sandved extension; $a = 2.92$ A.U.

CONCENTRATION	E^0	DEVIATION FROM MEAN
0.01	0.87075	0.00044
0.008	0.86994	−0.00047
0.006	0.86966	−0.00075
0.004	0.87006	−0.00035
0.002	0.87095	0.00054
0.001	0.87107	0.00065
Average..................	0.87041 ± 0.0005	
Graphical extrapolation...	0.87025	

From the slope of the dotted line we calculate that

$$\frac{2}{r} = \left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

corresponds to a value of $r = 1.24$ A.U. If the ions are spherical and no forces of deformation intrude, $a = 2r = 2.48$ A.U. The disagreement with $a = 2.92$ A.U., calculated from the Gronwall, LaMer, and Sandved form of the interaction theory, while outside experimental error, is not serious considering the highly simplified character of the model which completely neglects any influence of solvation.

In column 2 of table 6 are given the values of f^*, the interaction activity coefficient for cadmium sulfate in 33 per cent ethyl alcohol and referred to unity at infinite dilution in this solvent and in column 3, f^0, the corresponding activity coefficients in aqueous solution. The last column gives the interaction medium effect $\log f^*/f^0$.

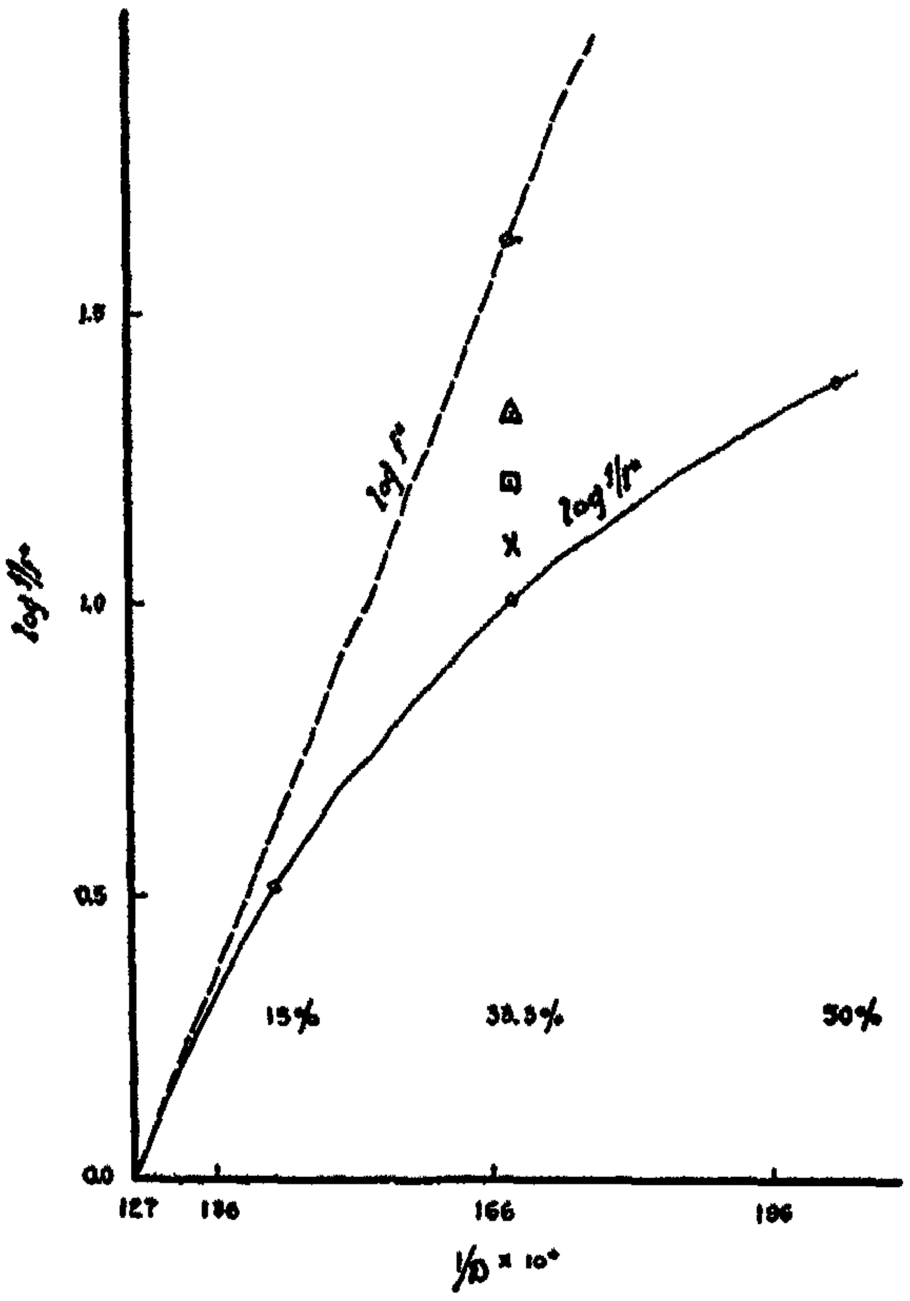

FIG. 2

○, 0.000 M; △, 0.001 M; ⊡, 0.002 M; ×, 0.004 M; ⊙, 0.010 M

The decrease in molal heat content ($-\Delta H$) and the increase in molal heat capacity (ΔC_p) are related to the E.M.F. of the cell process by the relations:

$$-\Delta\text{H} = n\mathfrak{F}\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right] \tag{5}$$

$$\Delta\text{C}_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p = n\mathfrak{F}T\left(\frac{\partial^2 E}{\partial T^2}\right)_p \tag{6}$$

It can be shown that if $E^{0\prime}$ is plotted (17) against $1/T$ the slope of the curve at any point is a measure of the magnitude of $(-\,\Delta\text{H})$ corresponding to the temperature and composition of the solvent at that point. Similarly, the curvature is a measure of the value of ΔC_p for the cell process.

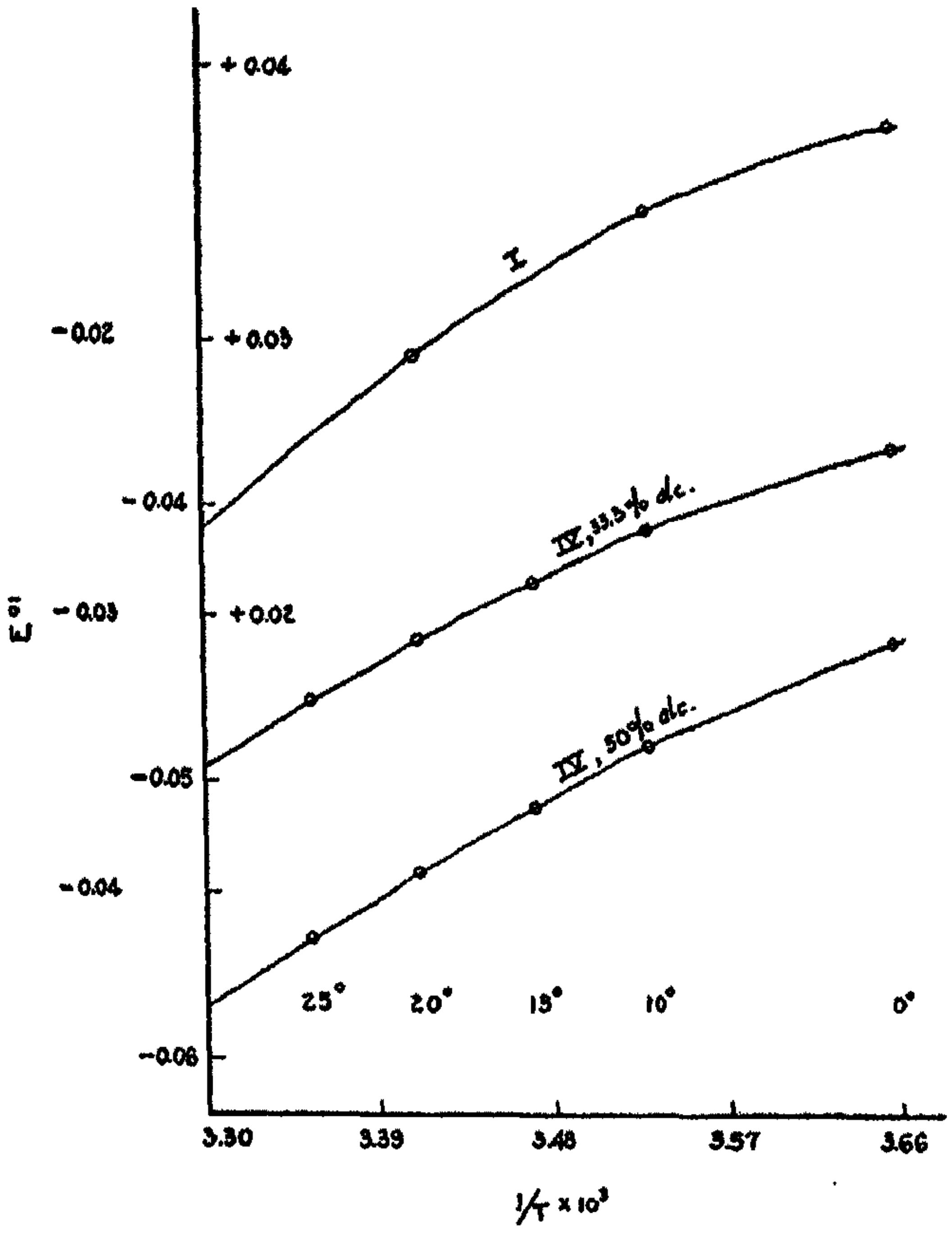

FIG. 3

Scale of ordinates reading from left to right refers to cell IV (50 per cent alcohol), cell IV (33 per cent alcohol), and cell I (water).

If $E^{0\prime}/T$ is plotted against $1/T$, the slope is directly related to $-\Delta H$ and the curvature directly to Δc_p.

The values of $E^{0\prime}$ for cells I and IV are thus plotted in figure 3, from which it is evident that with increasing alcohol content $-\Delta H$ decreases and Δc_p becomes less negative, i.e., it increases.

To facilitate the numerical computation of these quantities we have expressed E for the different cell processes at 0.01 M cadmium sulfate as polynomials of the third degree in terms of t°C.:

$$E = A + Bt + Ct^2 + Dt^3 \qquad (7)$$

using the experimental values of the E.M.F. at 0°, 10°, 20°, and 30°C. To test the reliability of the derived equation, the computed values of E for the two temperatures, 15° and 25°C., were compared with the experimental values. The calculated and experimental values checked in all cases within ±0.02 mv. The empirical equation may accordingly be relied upon to give the correct derivatives within the limits of accuracy of the data. Such a check is not obtained if a second degree equation is employed. The coefficients of equation 7 are given in table 6a.

TABLE 6

Interaction activity coefficients of cadmium sulfate at 25°C.

M	f^* (33 PER CENT EtOH)	f^0 (H_2O)	$-\log f^*/f^0$
0.001	0.363	0.698	0.285
0.002	0.238	0.606	0.406
0.004	0.154	0.496	0.507
0.006	0.122	0.443	0.560
0.008	0.104	0.408	0.594
0.010	0.092	0.382	0.619

TABLE 6a

Coefficients × 10^5 for equations 10 and 11

CELL PROCESS	A	B	C	D
I (0 per cent, M = 0.01)	14651	19.9833	−1.46	0.015167
III (Independent of solvent)	96051	16.8000	0.0	0.0
IV (33.3 per cent, M = 0.01)	8475	13.8607	−0.56	0.003333
IV (50 per cent, M = 0.01)	6374	3.8333	−0.38	0.002667

ΔH and Δc_p, calculated by substituting the proper analytical expressions of the derivatives of equation 7 in equations 5 and 6 are given in table 7 for 15°C., for which temperature the higher derivatives should be most reliable. Column 5 for $\frac{\partial \Delta c_p}{\partial T}$ is included to preserve consistency with the experimental values of E at the various temperatures, but no claim is made for accuracy since this quantity depends upon the third derivative $\partial^3E/\partial T^3$.

Since Parks and LaMer (22) have measured the E.M.F. and its temperature derivatives of the cell for which the process is

$$\text{Cd(S)} = \text{Cd (two-phase amalgam)} \qquad \text{V}$$

ΔH and Δc_p for the process

$$\text{Cd(S)} + Hg_2SO_4 = CdSO_4\ (M, a \text{ per cent EtOH}) + 2Hg \qquad \text{VI}$$

were computed by the relation VI = II + V.

TABLE 7

Summary of results for 15°C. (288.1°K) in calories

PROCESS	PER CENT EtOH	$-\Delta H$	Δc_p	$\frac{\partial \Delta c_p}{\partial T}$
III Pb (satd.Hg) + Hg_2SO_4(S) = $PbSO_4$ + 2Hg		42,208	0	0.
IV Cd (satd.Hg) + $PbSO_4$ = $CdSO_4$ (0.01 M) + Pb (satd.Hg)	0.0	8,577	−207	11.4
	33.3	4,045	−109	2.3
	50.0	3,670	−69	2.2
VI Cd(S) + Hg_2SO_4(S) = $CdSO_4$(0.01 M) + 2Hg	0.	56,041	−220	17.4
	33.3	51,509	−122	8.3
	50.0	51,134	−82	7.8
VII Cd(S) + $PbSO_4$(S) = $CdSO_4$(0.01 M) + Pb (satd.Hg)	0.	13,833	Same as process VI	
	33.3	9,301		
	50.0	8,926		

In a similar way the same quantities for process VII, involving solid cadmium instead of the two-phase amalgam, can be computed from the relation VII = IV + V.

HEAT CONTENTS AND HEAT CAPACITIES OF DILUTION

The values[2] for

$$\Delta\bar{H} = \bar{H}(0.01\ M, a \text{ per cent EtOH}) - \bar{H}\ (0.01\ M, H_2O)$$

and

$$\Delta\bar{c}_p\ (0.01\ M) = \bar{c}_p\ (0.01\ M, a \text{ per cent EtOH}) - \bar{c}_p\ (0.01\ M, H_2O)$$

arising from the transfer of a mole of cadmium sulfate from a 0.01 molal solution in water to a 0.01 molal solution in 33.3 and 50 per cent ethyl

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[2] The partial molal quantities, designated by the bar, always refer to the solute. The customary subscript 2 has been omitted as unnecessary in this paper.

alcohol are given in table 8 for the temperatures 10°, 15°, and 20°C. The values of $\bar{L}$ (0.01 M) and $\bar{c}_p$ (0.01 M) are tabulated for the different temperatures in table 9. $\bar{L}$ is defined by the equation

$$\bar{L} = \bar{H}\,(0.01\ M, a \text{ per cent EtOH}) - \bar{H}^0\,(M = 0, \mathrm{H_2O})$$

$$\bar{c}_p = \Delta c_p\,(\mathrm{VI}) + c_p(\mathrm{Cd}) + c_p(\mathrm{Hg_2SO_4}) - 2c_p(\mathrm{Hg})$$

using the values as given in the International Critical Tables for solid cadmium, mercurous sulfate, and liquid mercury. The values for $\bar{L}$ (0.01 M) and $\bar{c}_p$ (0.01 M) for cadmium sulfate in water (22) are also listed for comparison. Table 9 shows that c_p (0.01 M) for cadmium sulfate is very nearly a linear function of the weight per cent of alcohol.

TABLE 8

Values of $\Delta\bar{H}$ and $\Delta\bar{c}_p$

a PER CENT EtOH	$\Delta\bar{H} = \bar{H}$ (0.01 M, a PER CENT EtOH) − $\bar{H}$ (0.01 M, $\mathrm{H_2O}$)			$\Delta\bar{c}_p = c_p$ (0.01 M, a PER CENT EtOH) − c_p (0.01 M, $\mathrm{H_2O}$)		
	10°C.	15°C.	20°C.	10°C.	15°C.	20°C.
33	3931	4532	4906	143	98	52
50	4073	4907	5446	185	138	89

TABLE 9

Values of $\bar{L}$ and $\bar{c}_p$

a PER CENT EtOH	$\bar{L} = \bar{H}$ (0.01 M, a PER CENT EtOH) − $\bar{H}^0$ (M = 0, $\mathrm{H_2O}$) FOR $\mathrm{CdSO_4}$			$\bar{c}_p$ (0.01 M, a PER CENT EtOH) FOR $\mathrm{CdSO_4}$		
	10°C.	15°C.	20°C.	10°C.	15°C.	20°C.
0.0	526	621	752	−280	−195	−106
33.3	4457	5153	5658	−137	−98	−54
50.0	4599	5528	6198	−95	−58	−17

In order to obtain an estimate of the probable error in these values, 0.02 mv., which was the average deviation of the experimental results, was added to or subtracted from the measurements, and new values calculated. In the case of the heat content, it was found that the maximum error was obtained if the 0.02 mv. was alternately added to and subtracted from the measurements. This amounted to ±1.3 per cent (±62 cal.). In the case of the heat capacity, the maximum error was obtained if the 0.02 mv. was added to the first measurement and subtracted from the third. This amounted to ±2.4 per cent (±2.6 cal. per degree). The probable error in $\bar{L}$ may be twice as large as the error in $\Delta\bar{H}$ of transfer, since it involves the subtraction of one $\Delta\bar{H}$ from another. The error in $\bar{c}_p$ may also be twice as large as the error in Δc_p, as it is necessary to add the change in the heat capacity involved in the transfer of a mole of solid cadmium from the solid state to a two-phase amalgam to Δc_p from process II. The heat capacities of the solids, cadmium and mercurous sulfates, and that of liquid mercury are accurate to about 0.1 cal. per degree.

Henderson and Stegeman (13) measured the E.M.F. of cell III at 18°, 25°, and 30°C. From their empirical second-degree equation one would expect that Δc_p (III) = 10.5 cal. per degree. Although our measurements upon the same cell at 0°, 12.5°, 25°, 37.5°, and 50°C. yield a value of ΔH (III) at 18°C. which checks their value within 0.2 per cent (69 cal.), we find $\partial^2E/\partial T^2$ (see table 7) to be equal to zero. Consequently, Δc_p (III) should be zero. This prediction can be checked, using the calorimetric heat capacity data for the respective solids given in International Critical Tables, Vol. V, pp. 85–97. The calorimetric data require Δc_p (III) equal to 0.1 cal. This agreement furnishes further evidence that the changes in heat capacity in chemical processes may be accurately calculated from precise E.M.F. measurements, provided the data extend over a wide range of temperature and an empirical equation of sufficient power for accurate representation is employed.

These data show that for 15°C. the molal heat of dilution in water of 0.01 M cadmium sulfate is 621 cal., whereas the heat effect involved in transferring one mole of cadmium sulfate at 0.01 molal from 33 per cent alcohol to water is 4532 cal., i.e., the thermal effect of interaction in water is about 12 per cent of that of transfer, which is essentially a pure solvent effect.

Perhaps the most striking result of this investigation is the almost linear increase (i.e., to less negative values) which the partial heat capacity of the salt undergoes on the addition of alcohol. The large negative values for $\bar{c}_p$ which salts exhibit in water is ascribed by Zwicky (27) to compression of the solvent in the neighborhood of the ion and to a loss in degrees of freedom of the solvent as result of electrostriction. In a solvent of lower dipole moment such effects are less and hence a less negative value of $\bar{c}_p$ is observed.

SUMMARY

1. E.M.F. measurements are reported for the cell:

Cd (two-phase amalgam), $CdSO_4$ (M, a per cent EtOH), Hg_2SO_4(S), Hg for M = 0.01 in 33.3 and 50 per cent ethyl alcohol at 0°, 10°, 15°, 20°, 25°, and 30°C.; as a function of M in 33.3 per cent alcohol at 25°C.; and for M = 0.01 in 15 per cent alcohol at 25°C.

The cell: Pb (two-phase amalgam), $PbSO_4$(S), Hg_2SO_4(S), Hg has been measured at 12.5°C.-intervals over the range 0° to 50°C.

2. The partial heat contents, and the partial heat capacities of cadmium sulfate have been calculated in the alcoholic solutions for comparison with the corresponding aqueous solutions.

3. The total medium effect for 0.01 molal cadmium sulfate in 15, 33.3, and 50 per cent alcohol, and the solvent and interaction medium effects in 33.3 per cent alcohol, have been evaluated. The results have been considered in the light of the Born transfer equation and the extended form of the Debye-Hückel interaction theory.

4. The value of *r*, the mean ionic radius of the cadmium and sulfate ions as calculated from the Born equation, is in fair agreement with the value of *a*, the distance of closest approach of two ions, calculated by means of the extended theory of Debye and Hückel.

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THE SOLUBILITY OF LEAD SULFATE IN AQUEOUS SOLUTIONS OF SULFURIC ACID AT HIGH CONCENTRATIONS

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Crockford and Brawley (1) have determined the solubility of lead sulfate in aqueous sulfuric acid solution up to 80 per cent acid at 0°, 25°, 35°, and 50°C. Donk (2) has made a systematic study of the same system up to approximately 100 per cent acid at 0°, 50°, 100°, 150°, and 200°C. His work was concerned principally with the composition of the solid phases and his actual solubility data are quite meager, in some cases being completely lacking. A complete discussion of the relationships in the binary system sulfuric acid–water is given by Mellor (3).

The purpose of the work reported in this paper was to add to the data of the ternary system, particularly at the higher acid concentrations. To this end solubility data have been determined at acid concentrations up to approximately 104 per cent sulfuric acid, corresponding to 80.5 per cent sulfur trioxide, at 0°, 25°, 35°, and 50°C. The eutectic temperature in the binary system lead sulfate–sulfuric acid has also been determined.

EXPERIMENTAL

The usual procedure employed for solubility measurements was followed. Various mixtures were allowed to come to equilibrium in glass-stoppered bottles, properly agitated in constant temperature baths. The temperatures were constant to ±0.02°C. at the three higher temperatures. For the 0°C. isotherm the temperature was never over 0.1°C. Equilibrium was rapidly attained in those cases in which lead sulfate was the only solid phase. When sulfuric acid or one of its hydrates was a solid phase, considerable trouble from supercooling was experienced.

The materials employed were prepared and purified according to the methods used by Crockford and Brawley (1). The analytical procedures were likewise the same.

The compositions of the solid phases were obtained by the method of intersecting tie-lines. For the determination of the lead sulfate–sulfuric acid eutectic temperature, the usual cooling curve method was used.

DATA AND CONCLUSIONS

The data obtained for the 25°, 35°, and 50°C. isotherms were plotted on large coördinate paper and the best curve drawn through the points. The concentrations given in table 1 are taken from these curves. It was not thought worthwhile to give the data for the wet residues. The results agree with those of Donk, in that lead sulfate is the only solid phase at these temperatures.

TABLE 1

Solubility of lead sulfate in aqueous sulfuric acid at 25°, 35°, and 50°C.

CONCENTRATION OF ACID IN WEIGHT PER CENT	LEAD SULFATE, IN MILLIGRAMS PER 1000 G. OF SOLUTION, AT		
	25°C.	35°C.	50°C.
80	11.5	24.0	42.0
85	60.0	100.	130.
90	200	318	380
95	800	1,060	1,260
100	18,000	22,000	27,600
101	31,000	36,000	42,000
102	47,000	52,000	56,000
103	63,000	68,000	72,000

TABLE 2

Data for the 0°C. isotherm

NO.	ACID CONCENTRATION IN WEIGHT PER CENT	LEAD SULFATE IN MG. PER 1000 G. OF SOLUTION	SOLID PHASES
1	77.48	4.2	Lead sulfate
2	79.10	8.6	Lead sulfate and sulfuric acid monohydrate
3	89.44	42.0	Lead sulfate and sulfuric acid monohydrate
4	91.69	272	Lead sulfate
5	94.03	680	Lead sulfate
6	96.52	2200	Lead sulfate
7	97.08	3000	Lead sulfate and sulfuric acid

In table 2 are given the data for the 0°C. isotherm as actually determined. No solutions exist above 97.08 per cent.

The lead sulfate–sulfuric acid eutectic temperature was found to be 5.4°C.

If all the data available on the ternary system are plotted it is found that lead sulfate exists as the only solid phase over the major part of the diagram. On the lead sulfate–water side of the diagram the binary eutectic is of course at practically 0°C. On the lead sulfate–sulfuric acid side is the one eutectic whose temperature is given above. On the sulfuric acid–water side are found three hydrates of sulfuric acid. Two of these have definite melting points. Only the monohydrate exists above 0°C. Within the diagram will be four ternary eutectics, all of which will occur very close to the sides of the diagram.

The 0°C. isotherm shows the existence of five solubility curves. On two of these the solid phase is lead sulfate; on two others it is the monohydrate of sulfuric acid; on the other it is anhydrous sulfuric acid. The values of the acid concentrations at the intersections of these curves (solutions 2, 3, and 7), are essentially the same as the values given by Donk.

SUMMARY

The solubility of lead sulfate in various solutions of sulfuric acid at concentrations above 80 per cent and at 0°, 25°, 35°, and 50°C. has been determined.

The solid phase at 25°, 35°, and 50°C. is always lead sulfate. At 0°C. sulfuric acid and sulfuric acid monohydrate also exist as solids

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COLLOIDAL SOLUTIONS IN CONCENTRATED ELECTROLYTES[1]

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INTRODUCTION

If concentrated sulfuric acid be electrolyzed with a direct current of high current density and a potential difference of, for instance, 100 volts, using electrodes of noble metals, such as gold, platinum, or palladium, after some time there will suddenly be observed in the liquid a dark color, which seems to proceed from the anode. It was thought that this phenomenon might be ascribed to the formation of a colloidal solution of palladous sulfide. In order to test this assumption, experiments were carried out which soon proved its exactness. Experiments were then performed in order to find out whether other substances are colloidally dispersed in sulfuric acid and in other concentrated electrolytes.

EXPERIMENTAL

1. Concentrated sulfuric acid as a dispersion medium

a. Colloidal sulfides

The palladium sulfide sol may be prepared as follows: A solution of about 200 mg. of palladous sulfate in 1 liter of commercial concentrated sulfuric acid (about 96 per cent) is heated to about 100°C., after which 100 to 200 mg. of flowers of sulfur is added. On stirring the liquid, a darkening is soon observed. After cooling, the sol is filtered through a glass filter to remove small quantities of coarser particles.

The sol formation may be represented by the following reaction:

$$PdSO_4 + 2S \rightarrow PdS + 2SO_2$$

The particle size has been determined by the usual ultramicroscopic method. If the particle is supposed cubic, the edge of the cube is found to be 97 $m\mu$. This number is, without doubt, too high, owing to the polydispersity of the sol.

The sol may remain stable for several weeks. Finally little flakes are formed, which adhere to one another and at last sink to the bottom. This flocculate exhibits a remarkable behavior. On shaking the flakes dis-

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[1] This paper is part of a thesis presented at the University of Amsterdam.

appear, and the original sol is restored completely. After a few days the flakes appear again, but can be dispersed anew by shaking. The same behavior is exhibited on centrifuging. The flakes appear on the bottom of the vessel, but disperse at once on shaking. The velocity of flocculation increases on heating, but the reversibility of the flocculate is not influenced. An "aging" phenomenon of the flocculate could not be observed; more than a year later the reversibility of the flakes was unchanged. The reversible flocculation is clearly different from a reversible sedimentation, as in the latter case the particles only sink to the bottom, while in the former case little visible flakes are formed throughout the liquid, which constantly grow and at last sink to the bottom.

On diluting the sol with water, an irreversible coagulate immediately appears.

The gold and platinum sulfide sols can be prepared in the same way and have practically the same properties. The silver sulfide sol is formed by mixing a solution of silver sulfate in the concentrated acid with a sol of sulfur in the same liquid (see below). At a temperature of about 40° to 50°C. the sol formation is observed, but at 60° to 70°C. the particles dissolve completely in the dispersion medium. When electrolyzing concentrated sulfuric acid with silver electrodes André (1) observed a brownish liquid, which he mistook for a silver sol. As a matter of fact a silver sulfide sol had been formed.

b. Colloidal metals

Colloidal metals may be prepared by reducing the dilute solutions of the salts in sulfuric acid with reducing agents such as a concentrated, freshly prepared solution of white phosphorus in ether or in carbon disulfide. The palladium sol is formed at room temperature, while sols of platinum and gold result on heating to 30° to 40°C. Reduction can also be accomplished with hydrogen at a higher temperature, but the resultant sols are less stable, owing to secondary coagulation. The palladium sol is a dark brown stable sol, which does not flocculate on heating. On dilution of the sol with water an immediate flocculation ensues. The influence of dilution on the stability of the sol is shown in table 1. Upon dilution with alcohol the sol does not coagulate, but dissolves slowly in the course of a few days.

Ultramicroscopic examination shows a fairly good monodisperse sol with slowly moving particles. The particle size has been determined for several specimens. Usually the value of the length of the edge of the supposed cubic particle is found to be between 30 and 40 mμ.

Different colors are exhibited by the gold sols, from red to yellow, brownish, and blue, apparently owing to slight modifications in the manner of preparation. The most stable are the red sols, which can be prepared by reducing at the lowest possible temperature, while immediate cooling after the beginning of the reduction is necessary.

The particle size of a gold sol has been determined by the ultramicroscopic method; the length of the edge of the supposed cubic particles is found to be 44.5 mμ.

The gold sols are less stable than the palladium sols and generally flocculate within a week. On heating the sols, the color changes from blue to red and yellow, and finally the sols become almost colorless. Observations of the Tyndall effect, which becomes more intense, prove that the sol flocculates.

The platinum sol is a brownish-black sol, the properties of which are practically the same as those of the gold sol.

c. Colloidal silver halides

A silver chloride sol is formed on mixing a solution of 2 or 3 milliequivalents of silver sulfate in sulfuric acid with an equivalent quantity of hydrochloric acid. It is a white opalescent liquid, which resembles a silver chloride sol in water. After a few days the sol flocculates. The stability is not influenced if exactly equivalent quantities of silver sulfate and hydrochloric acid be mixed, or if one of these components be slightly in excess of the other.

TABLE 1

Influence of dilution on the stability of the sol

NO.	COMPOSITION OF THE MEDIUM		CONDITION OF THE SOL
	Sulfuric acid	Water	
	cc.	cc.	
1	25	0	Stable
2	20	5	Flocculation in one day
3	15	10	Flocculation in a few hours
4	10	15	Instant flocculation
5	5	20	Instant flocculation

The silver bromide and silver iodide sols are formed when a halide is added to an excess of a silver sulfate solution in sulfuric acid. In this case the formation of the silver halides takes place much more rapidly than the decomposition of the hydrobromic and hydrochloric acids. The colloidal silver bromide is whitish-yellow, the silver iodide yellow, in color. The halide sols in sulfuric acid flocculate on dilution with water and have practically the same properties.

d. Colloidal sulfur

The sulfur sol may be prepared by adding a drop of a concentrated solution of sodium sulfide to concentrated sulfuric acid, while stirring the liquid steadily. The sol formation is due to decomposition of the polysulfide which is always present in sodium sulfide. The slow decomposition of the hydrogen sulfide thus formed causes a gradual increase in the sol concentration.

e. Colloidal organic substances

If an organic substance be brought into contact with concentrated sulfuric acid, it is carbonized in many cases, while the acid is colored brown to black. Ultramicroscopic examinations show that a sol has been formed.

If a drop of a dilute sucrose solution be mixed with sulfuric acid and the mixture be kept at 150°C. for some time, a dark brown sol results, which shows a number of intensely light-scattering, slowly moving particles. On dilution with water, the sol flocculates. The analysis of the flakes gave the following results: C = 64.73 per cent, H = 3.18 per cent, no ash. Sulfur was detected only qualitatively. It is evident that the dispersed phase is a sulfurated product of sucrose.

Sabbatini (4) prepared a sol in water (which he mistook for a carbon sol) by pouring the reaction product of sucrose and sulfuric acid into water and dialyzing. As a matter of fact the original solution in sulfuric acid was already a colloidal system.

f. Colloidal carbon

A carbon sol may be obtained by electrolyzing sulfuric acid with carbon electrodes, using a direct or alternating current with a potential difference of 100 volts. To remove the coarser particles the sol is filtered through a glass filter. The sol is stable for some time, but on dilution with water it flocculates immediately.

2. Other dispersion media

a. Phosphoric acid

Colloidal sulfides may be obtained by passing hydrogen sulfide through a dilute solution of salts of the respective metals in commercial concentrated phosphoric acid, which contains about 89 per cent of the acid, while other sols are prepared as in the sulfuric acid medium and generally show the same properties.

A different behavior is exhibited by the silver halide sols, which show nearly the same stability if the quantities of silver and halide be exactly equivalent or if a slight excess of halide be present, but which are much more stable if silver be slightly in excess.

The results of a determination of the particle size of a gold sulfide (Au_2S_3) sol gave a value of 67 mμ for the length of the edge of a supposed cubic particle.

All these sols flocculate on dilution with water and in several cases with organic liquids, as is shown in tables 2 and 3 for a gold sulfide sol.

b. Saturated salt solutions as dispersion media

Generally all saturated solutions of very souble salts have a stabilizing action on colloids, but there are only a few salts of which the saturated solution has been found to be a medium for stable colloids, for instance, saturated solutions of the acetates of potassium and ammonium, or the chlorides of calcium and magnesium. A more extensive study has been made of the potassium acetate and calcium chloride solutions, which can be media for several stable metal, sulfide, and other sols. In most cases the sols can be stabilized by very small quantities of gelatin. On dilution, as well as on dialysis, stabilized and non-stabilized sols flocculate.

TABLE 2

Effect of dilution with water on a gold sulfide sol

NO.	COMPOSITION OF THE DISPERSION MEDIUM		CONDITION OF THE SOL
	Phosphoric acid	Water	
	cc.	cc.	
1	25	0	Stable
2	20	5	Flocculates slowly
3	15	10	Flocculates more quickly
4	10	15	Instant flocculation
5	5	20	Instant flocculation

TABLE 3

Effect of dilution with alcohol on a gold sulfide sol

NO.	COMPOSITION OF THE DISPERSION MEDIUM		CONDITION OF THE SOL
	Phosphoric acid	Alcohol	
	cc.	cc.	
1	25	0	Stable
2	20	5	Flocculates slowly
3	15	10	Flocculates more quickly
4	10	15	Instant flocculation
5	5	20	Instant flocculation

3. *Physical properties*

a. Conductivity

The concentrated electrolyte solutions which have been used as dispersion media have a very high conductivity as compared with ordinary sols. The specific conductivity of sols in water or in organic media seldom exceeds a value $K = 3 \times 10^{-4}$. Table 4 shows the specific conductivity of the different media.

b. Electrokinetic potential

The usual methods for the determination of the electrokinetic potential of the particles cannot be applied, owing to the high conductivity of the medium. In a few cases it was possible to overcome this difficulty, making use of the property of sulfuric acid that mixtures of it with other substances sometimes have a low conductivity. A solution of sulfur trioxide in sulfuric acid has been made, containing about 65.1 per cent free sulfur trioxide, which has a very low conductivity. Cataphoresis has been carried out with a palladium sulfide sol in this medium in a specially modified Burton apparatus. No movement whatever of the boundary could be detected. The same phenomenon has been observed with a palladium sol in a mixture of about equal volumes of sulfuric acid and glacial acetic acid.

TABLE 4

Specific conductivity of the different media

MEDIA	$K_{16°} \times 10^4$
Sulfuric acid, 96 per cent	940
Phosphoric acid, 87 per cent	710
Calcium chloride, saturated	950
Potassium acetate, saturated	520

TABLE 5

Relative viscosity of the dispersion media

MEDIA	RELATIVE VISCOSITY AT 25°C. WATER = 1
Sulfuric acid, 96 per cent	20.4
Phosphoric acid, 89 per cent	55.2
Calcium chloride, solution saturated at room temperature	5.89
Potassium acetate, solution saturated at room temperature	11.91
Phosphoric acid, 44.5 per cent	6.15

c. Relative viscosity

The relative viscosity of these sols has been determined with a viscosimeter of the Jones-Veazy type (3) in a thermostat at 25°C. No difference in the viscosity of the sols and the dispersion media could be detected.

DISCUSSION

According to the current views, the stability of a sol is ascribed to a potential difference between the particle and the medium or to a solvation of the particle. As neither a movement in the Burton apparatus nor a high relative viscosity could be detected, both of these explanations seemed to be out of the question. It might be supposed that the particles are discharged by the electrolyte, but that the very great viscosity of the dispersion medium is the cause of an extremely slow flocculation and therefore of the apparent stability of the sol. Inspection of table 5 shows at once, however, that this assumption is not correct. The maximum viscosity reaches the value 55.2, in relation to water, but the proportion between the stability of sols in concentrated phosphoric acid and in dilute aqueous solution is much higher, since the time necessary for flocculation is in the latter case measured in seconds and minutes, but in the former in days and weeks. Other observations lead to the same conclusion. A sol in phosphoric acid which has been diluted to twice its volume is flocculated within a short time, yet the table shows that the viscosity of this medium is higher than the viscosity of a saturated solution of calcium chloride, which can be a medium for a stable sol. A red gold sol can be made in a concentrated solution of sucrose, which has a high viscosity. Yet a small quantity of electrolyte turns the color from red to blue within a short time. In this case the high viscosity does not stabilize.

On the other hand it must be considered that, owing to the very small concentration of the sols, their relative viscosity will, according to Einstein's law (2), not differ from unity by an observable amount, even if a larger quantity of solvent should adhere to the particle.

Again, the phenomenon of reversible flocculation may be brought forward, which is in some respects analogous to the reversible isothermal sol–gel transformation usually called thixotropy. This phenomenon is exhibited by some colloids which have a more or less lyophilic character, such as the ferric oxide sol, the vanadium pentoxide sol, etc., and is explained by assuming a very weak bond between the particles which are surrounded by layers of adhering liquid. Now in this case the concentration of the colloid is so high that all the liquid is enclosed within the large gel complex, and the free dispersion medium has completely disappeared. However, this behavior may also be exhibited by a dilute colloid. In this case the quantity of liquid is too large to be totally enclosed, but solvated flakes are formed, the thixotropy of which is shown by a total dispersion on shaking. This phenomenon has been observed by H. Werner (5), who studied a suspension of *Bolus alba*. This clay suspension flocculated after some time, but the flakes, which were covered by a liquid layer, could be dispersed by shaking.

This picture is quite identical with the reversible flocculation exhibited by the palladium sulfide sol in sulfuric acid and by other sols mentioned in the experimental part. It is therefore assumed that the particles of these sols, which show thixotropy in dilute solution, are covered by a layer of adhering liquid medium and possess in some degree lyophilic properties.

The conception of thixotropy will have to be extended and defined as a reversible isothermal transition from a sol to a conglomerate, while, moreover, the latter may equally well be a gel as a flocculate. This point of view can be proved by the observation that some colloids show thixotropy in concentrated solution, but reversible flocculation when diluted. This typical behavior is clearly shown by bentonite.

In accordance with this hypothesis it may be assumed that in concentrated salt solutions an adsorption of the salt will ensue. The hydration of the adsorbed salt will hydrate the particle, which therefore will be stabilized. This hypothesis is supported by the observation that, in general, the more hydrated the ions of the salt are, the higher is the stability of the colloidal systems.

The protective action of proteins is explained by a hydration which stabilizes the particle. Thus the hydrating action of the salt in concentrated solution can be partially supplied by gelatin. Now it is clear that with small concentrations of electrolytes more gelatin will be needed to stabilize the colloids if the salt concentration is increased, while in concentrated salt solutions the reverse is true. In the former case the hydrating gelatin is necessary to obtain the minimum stability, which is decreased by the action of the electrolytes; in the latter case the hydration of the adsorbed salt acts as a substitute for the hydration of the protein.

CONCLUSION

From this study it may be concluded that the influence of electrolytes on colloids is more complicated than was formerly thought. A hydrophobic sol which is perfectly free of electrolytes is generally unstable, as a small quantity of electrolyte is necessary to form the double layer. This quantity is stabilizing. A somewhat larger quantity produces flocculation. Finally a very high concentration of electrolytes has again a stabilizing influence. In general, a colloidal system, according to the electrolyte concentration, has two stable and two unstable zones.

SUMMARY

1. A colloidal solution may be stable in solutions of concentrated electrolytes.

2. Methods of preparation have been described for sols of metals, sulfides, silver halides, sulfur, carbon, etc. in dispersion media such as concentrated sulfuric acid and phosphoric acid and saturated solutions of salts, such as calcium chloride and potassium acetate.

3. Sols in solutions of concentrated electrolytes do not show any electrokinetic potential difference, nor an increase in relative viscosity.

4. Some colloids in concentrated electrolytes exhibit thixotropy.

5. The hypothesis that the stability of colloidal systems in concentrated electrolytes is caused by solvation is supported by several arguments.

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THE SOLUBILITY OF LEAD BROMATE AND ITS ACTIVITY COEFFICIENTS IN SOLUTIONS OF ELECTROLYTES

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INTRODUCTION

This investigation was undertaken in order to study the effect of nitrates of certain uni- and bi-valent metals on the solubility and activity coefficients of a bi-univalent salt, and to compare observed results with those computed on the basis of modern theories of electrolyte solutions. For this purpose the solubility of lead bromate was determined at 25°C. in aqueous solutions of various concentrations of the nitrates of sodium, potassium, lithium, calcium, strontium, and lead.

W. Böttger (1) determined the solubility of lead bromate in water and found it to be 13.37 g. (0.0289 mole) per liter of solution at 19.96°C. From conductance data he calculates that the saturated solution is 72 per cent ionized. We find the solubility of lead bromate in water at 25°C. to be 0.03437 mole per liter. The density of this saturated solution is 1.0112.

MATERIALS AND PROCEDURE

Water. The solutions were prepared with "conductivity" water which was obtained by the distillation of distilled water over sodium hydroxide and potassium permanganate in a tin-lined vessel.

Lead bromate. The lead bromate was prepared by the following method: A solution of sodium bromate heated to 30°C. was added to a solution of lead nitrate at the same temperature with constant stirring. The lead bromate was allowed to settle, and the solution was cooled. The supernatant liquid was then decanted, and the lead bromate was washed several times by decantation, filtered, and washed again on the filter. The lead bromate was then washed thoroughly with pure 95 per cent alcohol and absolute ether and dried in a vacuum desiccator over magnesium perchlorate at room temperature. Attempts to dry the lead bromate by heating resulted in decomposition as described by Rammelsberg (5).

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[1] This paper gives the essential portions of the thesis presented by E. J. Hoffman in June, 1935, to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Nitrates. The nitrates were of the best quality available. They were crystallized once and sometimes twice from conductivity water. They were then dehydrated thoroughly.

Sodium thiosulfate solution. The sodium thiosulfate solution used for analysis was prepared by the method of Watson (6).

Preparation of solutions. Conductivity water was added by means of an accurately calibrated pipet (100-cc. capacity) to glass-stoppered bottles containing previously weighed quantities of the nitrate and an excess of lead bromate. All weighings were corrected for buoyancy. A heavy coat of paraffin was applied to the stoppers of the bottles after the solutions were prepared, and the bottles were then mechanically rotated in a water-bath at 25.00 ± 0.05°C. for several hours until equilibrium was established.

Method of analysis. After equilibrium had been established, the bottles were removed from the rotator and, still immersed almost completely, were held stationary in the water-bath to allow the excess lead bromate to settle. The clear solution was then drawn off by means of vacuum into an Erlenmeyer flask almost completely immersed in the water-bath (4). A small plug of absorbent cotton was placed in the end of the delivery tube to prevent the passage of any solid particles of lead bromate during the transfer of the solution from the bottle to the flask. Four 10-cc. samples of the solution were withdrawn from the flask by means of an accurately calibrated pipet and transferred to previously weighed weighing bottles. These samples were then accurately weighed in order to determine the densities of the solutions. These solutions were then washed into 500-cc. glass-stoppered Erlenmeyer flasks containing a solution of potassium iodide acidified with hydrochloric acid, and were titrated with 0.3 M sodium thiosulfate prepared by the method described above. A 0.2 per cent starch solution, containing 0.1 per cent salicylic acid as preservative, was used as indicator. Analysis of each concentration of nitrate solution was thus run in quadruplicate. It was possible from a knowledge of the weight of each constituent of the solution and the density to determine the concentrations as molality, molarity, or mole fraction.

EXPERIMENTAL RESULTS

Tables 1 to 6 list the solubilities at 25°C. of lead bromate in aqueous solutions of the nitrates at various concentrations. We denote in general the molality and molarity of a solute in a solution by m and c, respectively. The normalized mole-fraction, $\bar{x}$, of Pb^{++} is calculated on the assumption of complete ionization of the dissolved salts. Normalized mole-fraction (4) is equal to the mole-fraction multiplied by the factor 55.51. The ionic strength, S, given in these tables is calculated on the basis of complete

TABLE 1

Solubility, equilibrium constants (K_1 and K_2), and activity coefficients of lead bromate in the presence of potassium nitrate at 25°C.

c KNO_3	d SATURATED SOLUTION	c $Pb(BrO_3)_2$	$\bar{z}$ $Pb(BrO_3)_2$	A	α	K_1	f_1^2	f'	γ'
0.	1.0112	0.03437	0.03447		0.4660	0.01980	0.574	0.365	0.364
0.04883	1.0156	0.03924	0.03938	0.6348	0.5222	0.01975	0.471	0.320	0.318
0.09934	1.0181	0.04378	0.04405	0.5720	0.5610	0.01987	0.406	0.286	0.284
0.1956	1.0286	0.05104	0.05129	0.5650	0.6162	0.01985	0.330	0.245	0.243
0.2950	1.0378	0.05798	0.05828	0.5400	0.6569	0.01987	0.280	0.216	0.213
0.3901	1.0456	0.06396	0.06434	0.5313	0.6878	0.01983	0.246	0.196	0.192
0.4857	1.0547	0.07003	0.07042	0.4481	0.7129	0.01983	0.220	0.179	0.175
0.5784	1.0608	0.07577	0.07636	0.4522	0.7330	0.01986	0.200	0.165	0.161
0.7671	1.0776	0.08734	0.08805	0.5886	0.7662	0.01987	0.169	0.143	0.138
0.9339	1.0906	0.09818	0.09921	0.4587					
1.1850	1.1127	0.1134	0.1146	0.4181	Av. = 0.01984				
1.4419	1.1327	0.1293	0.1293	0.4363					
1.8314	1.1664	0.1550	0.1576	0.4058	A = 0.30; K_2 = 0.01452; $\bar{z}_0$ = 0.02441; α_0 = 0.3120				
2.0352	1.1833	0.1685	0.1717	0.3845					
2.2469	1.2011	0.1782	0.1815	0.3973					
2.4449	1.2161	0.1799	0.1830	0.4164					
2.6423	1.2220	0.1732	0.1769						

TABLE 2

Solubility, equilibrium constants (K_1 and K_2), and activity coefficients of lead bromate in the presence of sodium nitrate at 25°C.

c $NaNO_3$	d SATURATED SOLUTION	c $Pb(BrO_3)_2$	$\bar{z}$ $Pb(BrO_3)_2$	A	α	K_1	f_1^2	f'	γ'
0.	1.0112	0.03437	0.03447		0.4610	0.01992	0.581	0.365	0.364
0.04833	1.0141	0.03884	0.03900	0.7294	0.5137	0.01988	0.483	0.323	0.321
0.1013	1.0184	0.04317	0.04335	0.6789	0.5523	0.01995	0.418	0.290	0.289
0.1991	1.0266	0.04984	0.04997	0.6483	0.6036	0.01997	0.345	0.252	0.249
0.2963	1.0334	0.05580	0.05602	0.6329	0.6397	0.02003	0.299	0.225	0.222
0.3938	1.0424	0.06144	0.06157	0.6143	0.6683	0.02006	0.265	0.204	0.201
0.4892	1.0465	0.06430	0.06454	0.6585	0.6959	0.01959	0.241	0.195	0.191
0.5874	1.0564	0.07112	0.07122	0.6003	0.7121	0.01998	0.220	0.177	0.172
0.7776	1.0697	0.08024	0.08033	0.4830	0.7430	0.01997	0.189	0.157	0.152
0.9655	1.0837	0.08899	0.08899	0.5709	0.7667	0.01996	0.168	0.141	0.136
1.1970	1.1000	0.09967	0.09962	0.5535					
1.4241	1.1158	0.1098	0.1097	0.5406	Av. = 0.01993				
1.8655	1.1460	0.1295	0.1292	0.5050					
2.2921	1.1754	0.1487	0.1484	0.5009	A = 0.385; K_2 = 0.01453; $\bar{z}_0$ = 0.02456; α_0 = 0.3110				
2.6860	1.2010	0.1651	0.1648	0.4911					
3.4672	1.2530	0.1990	0.1986	0.4725					
4.8546	1.3378	0.2536	0.2546	0.4546					
6.0912	1.4172	0.3026	0.3041	0.4420					
7.1770	1.4824	0.3416	0.3446	0.5327					

TABLE 3

Solubility, equilibrium constants (K_1 and K_2), and activity coefficients of lead bromate in the presence of lithium nitrate at 25°C.

c LiNO$_3$	d SATURATED SOLUTION	c Pb(BrO$_3$)$_2$	$\bar{z}$ Pb(BrO$_3$)$_2$	A	α	K_1	f_1^s	f^s	γ^s
0.	1.0112	0.03437	0.03447		0.4542	0.02007	0.590	0.365	0.364
0.04925	1.0135	0.03849	0.03864	0.8663	0.5043	0.02001	0.496	0.326	0.325
0.09873	1.0158	0.04224	0.04244	0.7837	0.5369	0.02014	0.438	0.297	0.295
0.2049	1.0244	0.04874	0.04880	0.7643	0.5870	0.02021	0.363	0.258	0.255
0.3012	1.0293	0.05365	0.05379	0.7500	0.6192	0.02025	0.320	0.234	0.231
0.3933	1.0348	0.05800	0.05812	0.7366	0.6434	0.02029	0.290	0.217	0.213
0.4929	1.0399	0.06206	0.06217	0.7333	0.6655	0.02026	0.266	0.202	0.198
0.5815	1.0446	0.06517	0.06525	0.7373	0.6828	0.02015	0.248	0.193	0.188
0.7751	1.0549	0.07225	0.07226	0.7226	0.7117	0.02014	0.218	0.174	0.169
0.9644	1.0649	0.07867	0.07849	0.7102					
1.4259	1.0880	0.09337	0.09310	0.6814	Av. = 0.02017				
1.8680	1.1084	0.1061	0.1057	0.6623					
2.3032	1.1302	0.1190	0.1184	0.6412	A = 0.50; K_2 = 0.01453; $\bar{z}_0$ = 0.02498; α_0 = 0.3079				
2.7213	1.1507	0.1310	0.1300	0.6257					
3.5192	1.1887	0.1534	0.1518	0.5919					
4.9703	1.2562	0.1930	0.1904	0.5685					

TABLE 4

Solubility of lead bromate in the presence of strontium nitrate at 25°C. Values of α and A calculated for saturated solutions of lead bromate in the presence of strontium nitrate

c Sr(NO$_3$)$_2$	d SATURATED SOLUTION	c Pb(BrO$_3$)$_2$	$\bar{z}$ Pb(BrO$_3$)$_2$	A	α	A*
0.	1.0112	0.03437	0.03447			
0.005566	1.0117	0.03581	0.03595	0.8342	0.476	0.478
0.01031	1.0129	0.03702	0.03717	0.8929	0.490	0.485
0.01958	1.0144	0.03893	0.03911	0.9257	0.511	0.518
0.05020	1.0226	0.04455	0.04471	0.8892	0.563	0.530
0.09944	1.0332	0.05180	0.05199	0.8441	0.617	0.529
0.1975	1.0548	0.06339	0.06354	0.7972	0.680	0.530
0.2949	1.0741	0.07301	0.07318	0.7676	0.719	0.529
0.3903	1.0933	0.08177	0.08191	0.7427	0.749	0.525
0.4856	1.1107	0.08939	0.08961	0.7281	0.768	0.525
0.5804	1.1301	0.09739	0.09750	0.7092	0.785	0.520
0.7614	1.1627	0.1110	0.1113	0.6842	0.811	0.514
0.9446	1.1971	0.1249	0.1253	0.6608	0.831	0.505
1.3742	1.2748	0.1535	0.1542	0.6297	0.862	0.495
1.7789	1.3438	0.1765	0.1781	0.6127	0.880	0.480
2.1599	1.4084	0.1955	0.1979	0.6031		
2.5197	1.4668	0.2105	0.2140	0.5980		
2.8704	1.5261	0.2228	0.2267	0.5976		

* Calculated from equations 24 and 25.

TABLE 5

Solubility of lead bromate in the presence of calcium nitrate at 25°C. Values of α and A calculated for saturated solutions of lead bromate in the presence of calcium nitrate

c $Ca(NO_3)_2$	d SATURATED SOLUTION	c $Pb(BrO_3)_2$	x $Pb(BrO_3)_2$	A	α	A*
0.	1.0112	0.03437	0.03447			
0.006271	1.0099	0.03565	0.03584	1.2263	0.475	0.541
0.01116	1.0117	0.03640	0.03656	1.4195	0.483	0.636
0.02156	1.0135	0.03921	0.03941	0.9559	0.514	0.533
0.05162	1.0195	0.04298	0.04314	1.1370	0.549	0.676
0.1215	1.0313	0.05387	0.05409	0.8693	0.630	0.556
0.1975	1.0425	0.06202	0.06231	0.8353	0.674	0.558
0.3352	1.0643	0.07497	0.07522	0.7874	0.726	0.551
0.4920	1.0869	0.08769	0.08808	0.7513	0.764	0.544
0.5764	1.0997	0.09473	0.09496	0.7318	0.780	0.537
0.7780	1.1283	0.1105	0.1108	0.6945	0.810	0.522
0.9524	1.1457	0.1194	0.1204	0.6908	0.825	0.528
1.3805	1.2090	0.1435	0.1437	0.6753	0.852	0.527
1.7872	1.2607	0.1647	0.1653	0.6502		
2.1719	1.3074	0.1813	0.1823	0.6408		
2.5361	1.3489	0.1944	0.1963	0.6354		
3.1950	1.4215	0.2118	0.2154	0.6347		

* Calculated from equations 24 and 25.

TABLE 6

Solubility of lead bromate in the presence of lead nitrate at 25°C.

c $Pb(NO_3)_2$	d SATURATED SOLUTION	c $Pb(BrO_3)_2$	$\sqrt[3]{\frac{L_c}{4}}$	x $Pb(BrO_3)_2$	$\sqrt[3]{\frac{L_x}{4}}$	A
0.	1.0112	0.03437	0.03437	0.03447	0.03447	
0.004947	1.0104	0.03371	0.03529	0.03388	0.03546	0.8167
0.009921	1.0118	0.03332	0.03635	0.03348	0.03651	0.7564
0.01990	1.0132	0.03258	0.03819	0.03277	0.03841	0.7697
0.04981	1.0219	0.03161	0.04333	0.03176	0.04354	0.7707
0.09940	1.0356	0.03145	0.05058	0.03160	0.05083	0.7533
0.1978	1.0643	0.03264	0.06262	0.03318	0.06366	0.6973
0.2955	1.0936	0.03457	0.07333	0.03465	0.07352	0.6942
0.3882	1.1120	0.03657	0.08283	0.03697	0.08372	0.6603
0.4871	1.1480	0.03876	0.09245	0.03887	0.09272	0.6501
0.5804	1.1735	0.04102	0.1015	0.04119	0.1017	0.6330
0.7672	1.2290	0.04572	0.01193	0.04583	0.1196	0.6027
0.9470	1.2786	0.05046	0.1364	0.05069	0.1371	0.5770
1.1663	1.3402	0.05613	0.1568	0.05648	0.1577	0.5544
1.3807	1.4011	0.06183	0.1767	0.06226	0.1779	0.5397

ionization of the dissolved salts. The ionic strength is defined by the equation

$$S = \tfrac{1}{2}\Sigma c_i z_i^2 \tag{1}$$

where c_i is the molar concentration and z_i is the valence of an ion of the i^{th} kind.

It will be observed that in general the solubility of lead bromate increases with increasing concentration of added nitrate. In the presence, however, of lead nitrate, the solubility of the bromate diminishes to a minimum and then increases. The data obtained with lead nitrate as added salt can be best compared with those found with other salts by means of the quantity $\sqrt[3]{\frac{L_c}{4}}$, where L_c is the ionic product of lead bromate, i.e.,

$$L_c = [\mathrm{Pb^{++}}]\,[\mathrm{BrO_3^-}]^2 \tag{2}$$

calculated on the assumption of complete ionization. When the added salt has no ion in common with lead bromate, it is readily seen that

$$\sqrt[3]{\frac{L_c}{4}} = [\mathrm{Pb^{++}}] = c = [\mathrm{Pb(BrO_3)_2}] \tag{3}$$

When the added salt is lead nitrate of concentration c_s,

$$\sqrt[3]{\frac{L_c}{4}} = \sqrt[3]{(c + c_s)c^2} \tag{4}$$

We have accordingly included in table 6 the values of $\sqrt[3]{\frac{L_c}{4}}$ which are seen to increase in the normal way with increasing ionic strength of the solution.

The solubility data are represented graphically in figure 1. It will be seen that, at a given ionic strength, the increase in the solubility (or solubility product, L_c) due to added nitrate diminishes in the order, potassium nitrate, sodium nitrate, lead nitrate, lithium nitrate, strontium nitrate, calcium nitrate.

The solubility data obtained were used to test the applicability of the Debye-Hückel (2) equation, which becomes for a bi-univalent salt in aqueous solution at 25°C.,

$$\begin{aligned} -\log f = \log \bar{x} - \log \bar{x}_0 &= \frac{1.009S^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} \\ &= \frac{1.009S^{\frac{1}{2}}}{1 + 0.3283 \times 10^8 aS^{\frac{1}{2}}} \end{aligned} \tag{5}$$

In this equation $\bar{x}_0$ is the normalized activity and $\bar{x}$ is the normalized mole-fraction of lead ion (or of bromate ion) for an ionic strength S, and a is the mean ionic diameter parameter. It is seen that $\bar{x}_0$ may be looked on as the value of $\bar{x}$ (the normalized mole-fraction of Pb^{++} in a saturated solution of lead bromate) extrapolated to a value of $S = 0$. This extrapolated value of $\bar{x}$ is equal to m_0 and approximately equal to c_0, the extrapolated values of the molality and molarity, respectively, of a saturated solution of lead bromate.

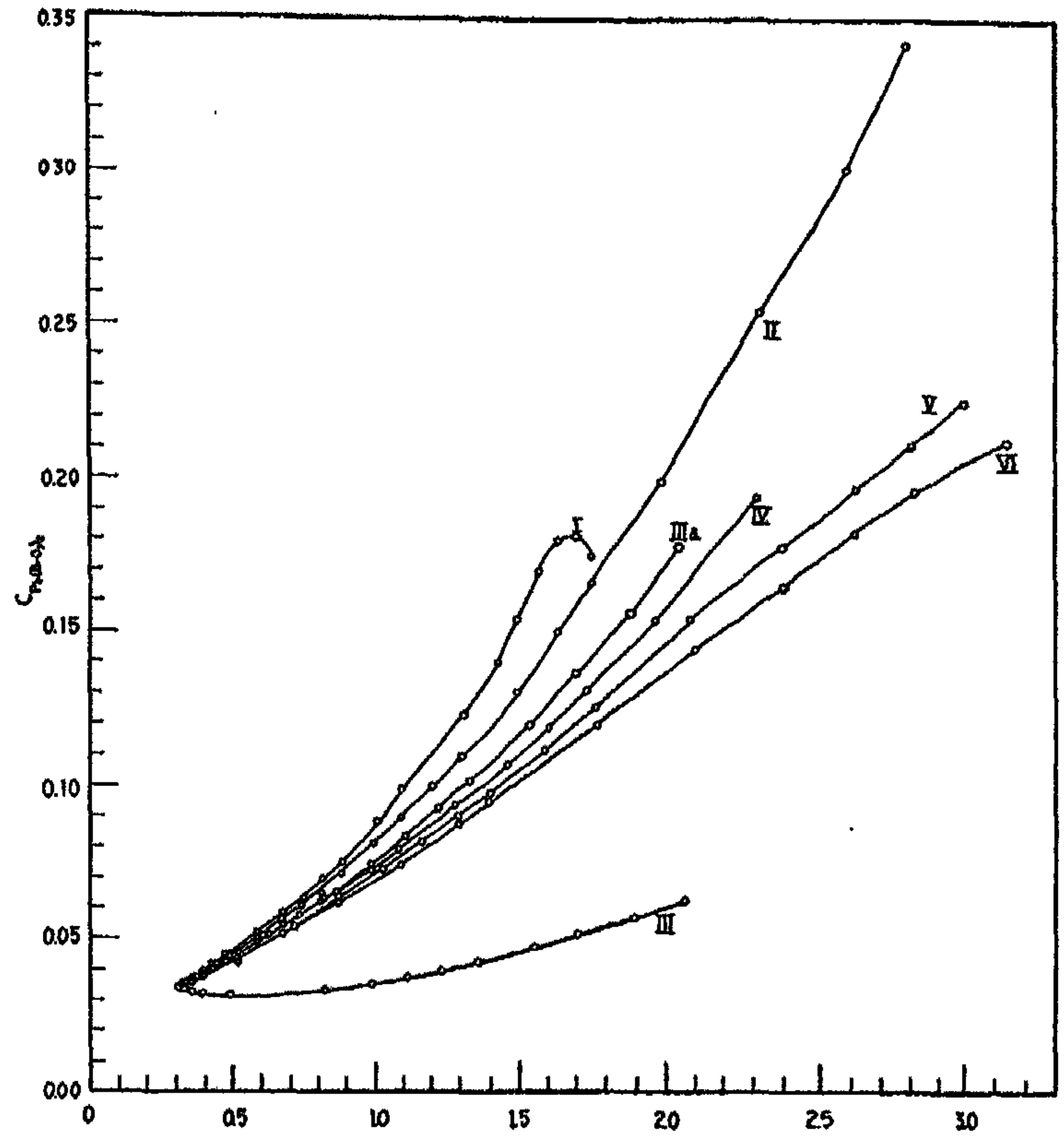

FIG. 1. Solubility of lead bromate in the presence of electrolytes. I, KNO_3; II, $NaNO_3$; III, $Pb(NO_3)_2$; IIIa, values of $\frac{\sqrt[3]{L_s}}{4}$ for lead nitrate solutions; IV, $LiNO_3$; V, $Sr(NO_3)_2$; VI, $Ca(NO_3)_2$.

The two unknowns, $\bar{x}_0$ and A (or a), can be calculated by means of equation 5 from two sets of corresponding values of $\bar{x}$ and S. In each case the values of $\bar{x}$ and S for lead bromate in pure water were combined successively with the corresponding values of these quantities for solutions containing increasing concentrations of added nitrate. If, for a given added electrolyte, a fairly constant series of values of A (or of x_0) is obtained, especially for the more dilute solutions, we may conclude that the postulates of the Debye theory are satisfied. These include the assumption that the electrolytes dealt with are virtually completely ionized.

In column 5 of tables 1 to 5 and in column 7 of table 6 are given the values of A and $\bar{x}_0$ calculated in the manner described for each series of solutions. It will be observed that in each case the values of A are far from being constant. There is a marked decrease in A with increasing ionic strength. We can conclude, therefore, that, if we postulate that lead bromate and the added salts are completely ionized, equation 5 is *not* applicable to aqueous solutions of lead bromate in the presence or absence of other electrolytes. We shall examine later the consequences that follow from the assumption that, in saturated solutions, lead bromate is only partially ionized.

THE HÜCKEL EQUATION

In an extension of the Debye and Hückel treatment, E. Hückel (3) took into account a possible variation of the dielectric constant of a solution with the concentration of the dissolved substances. The equation he derived, as applied to the present problem, may be written,

$$\log \bar{x} = \log \bar{x}_0 + \frac{1.009S^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} + CS \qquad (6)$$

where C is a constant. For our purpose we may consider equation 6 to be an interpolation formula. The constants of the equation, $\bar{x}_0$, A, and C, can be found by the solution of three simultaneous equations of the form 6, using the corresponding values of $\bar{x}$ and S. The usefulness of equation 6 can then be tested by calculating values of $\bar{x}$ for various values of S and comparing the calculated with the observed values. We shall omit the details of these calculations, which showed that equation 6 can reproduce with a fair degree of accuracy our experimental results. We give in table 7 the appropriate values of the constants of the Hückel equation.

INCOMPLETE IONIZATION OF TERNARY ELECTROLYTES

Since the Debye-Hückel equation has been found to be applicable to aqueous solutions of numerous simple electrolytes up to an ionic strength of at least unity, the question arises whether the failure in the present case is apparent rather than real. Now the Debye-Hückel equation has been applied to the solubility data of lead bromate on the assumption that all the salts concerned are completely ionized. This assumption was made in calculating the ionic strength S and the concentration of Pb^{++} or of BrO_3^- in any solution.

Referring to the data given in any of the tables from 1 to 6, we see that the calculated value of A decreases with increasing concentration of added nitrate. This result may be expressed in the statement that the solubility of lead bromate *increases* more rapidly with increasing concentration of added electrolyte than would be predicted by the Debye-Hückel equation, using a value of A obtained from solutions of low ionic strength. In other words, the effective activity coefficient of lead bromate *decreases* more rapidly with increasing concentration of added salt than the theory predicts. The assumption that the *added* nitrate is only partially ionized will not, by itself, account for this behavior; in fact, if the added nitrate in the more concentrated solutions is ionized to a smaller degree than we have supposed, the solubility of lead bromate should increase less, instead of more, rapidly with increasing concentration of the added salt.

Let us suppose, however, that lead bromate in solution is either incompletely ionized or that it exists in the form of the ions $PbBrO_3^+$, Pb^{++}, and BrO_3^-. It will be recalled that, in calculating A of equation 5, two solutions are compared, one containing only lead bromate and water, the second containing in addition some soluble nitrate. If we assume that the dissolved lead bromate is not entirely in the form of Pb^{++} and BrO_3^- ions, the ionic strengths of the two solutions referred to will, of course, be less than the values calculated on the basis of complete ionization, but it is readily seen that the *decrease* in the calculated ionic strength due to our new assumption of incomplete ionization of lead bromate will be relatively greater for the first than for the second solution. Hence it follows that as we go from a solution of lead bromate only to solutions containing in addition a soluble nitrate, the activity coefficient of any ion present will decrease more rapidly than if we assume complete ionization. This is qualitatively in agreement with the observed behavior. To simplify to some extent the treatment of the problem, we make the following assumptions:

TABLE 7

Values of the Hückel constants for lead bromate in aqueous solutions of various nitrates

SOLUTION	A	$\bar{a}_0$	C
$Pb(BrO_3)_2$-KNO_3	0.8158	0.01860	0.1116
$Pb(BrO_3)_2$-$NaNO_3$	0.8143	0.01876	0.07132
$Pb(BrO_3)_2$-$LiNO_3$	0.8638	0.01904	0.04084
$Pb(BrO_3)_2$-$Sr(NO_3)_2$	1.0564	0.01948	0.05906
$Pb(BrO_3)_2$-$Ca(NO_3)_2$	1.1041	0.01961	0.05624
$Pb(BrO_3)_2$-$Pb(NO_3)_2$	0.9215	0.01910	0.06225

(a) Lead bromate in aqueous solution ionizes in two stages, as given by the scheme,

$$\text{I. } Pb(BrO_3)_2(s) \rightleftharpoons Pb(BrO_3)_2 \rightleftharpoons PbBrO_3^+ + BrO_3^- \qquad (7)$$

$$\text{II. } PbBrO_3^+ \rightleftharpoons Pb^{++} + BrO_3^- \qquad (8)$$

(b) The ionization according to the first stage is analogous to the ionization of a uni-univalent salt. We assume therefore that the ionization of lead bromate into $PbBrO_3^+$ and BrO_3^- is virtually complete.

(c) We restrict our calculations at the present time to the case that the added nitrate is a uni-univalent salt (e.g., potassium nitrate) which we assume to be completely ionized.

(d) In solutions containing added nitrate, it is probable that a certain amount of the intermediate ion, $PbNO_3^+$, will be formed. In this preliminary treatment we assume that the amount of $PbNO_3^+$ formed can be neglected.

(e) We assume that the Debye-Hückel equation is applicable to our solutions when the correct value of the ionic strength is used. It follows from this equation that in a given solution all ions having numerically equal charges have approximately equal activity coefficients and that the activity coefficient of a divalent ion is approximately equal to the fourth power of that of a univalent ion. We shall suppose that these relations are exact.

MATHEMATICAL TREATMENT

If c and c_s are the analytically determined molarities of lead bromate and of added uni-univalent salt (e.g., potassium nitrate) and if α is the degree of dissociation of the intermediate ion, $PbBrO_3^+$, according to equation 8, we find

$$\begin{aligned}[\mathrm{Pb^{++}}] &= c\alpha \\ [\mathrm{PbBrO_3^+}] &= c(1-\alpha) \\ [\mathrm{BrO_3^-}] &= c(1+\alpha) \\ [\mathrm{K^+}] = [\mathrm{NO_3^-}] &= c_s\end{aligned} \tag{9}$$

The ionic strength, S, of the solution is given by the equation

$$S = c(1 + 2\alpha) + c_s \tag{10}$$

Equations analogous to equation 9 may be written in terms of molalities instead of molarities.

The *actual*, normalized mole-fraction of Pb^{++}, $\bar{x}_{Pb^{++}}$, is given by the equation

$$\bar{x}_{Pb^{++}} = \frac{55.51m\alpha}{55.51 + (2+\alpha)m + 2m_s}$$

Within at least one part in 3000, this expression may be replaced by

$$\bar{x}_{Pb^{++}} = \frac{55.51m\alpha}{55.51 + 3m + 2m_s} \tag{11}$$

on substituting 3 for the term $(2 + \alpha)$ in the denominator of the previous equation. Defining $\bar{x}$ (without subscript) by the equation

$$\bar{x} = \frac{55.51m}{55.51 + 3m + 2m_s} \tag{12}$$

we may write

$$\begin{aligned} \bar{x}_{Pb^{++}} &= \bar{x}\alpha \\ \bar{x}_{PbBrO_3^+} &= \bar{x}(1 - \alpha) \\ \bar{x}_{BrO_3^-} &= \bar{x}(1 + \alpha) \end{aligned} \tag{13}$$

The quantity $\bar{x}$ defined by equation 12 might be called the analytical (normalized) mole-fraction of lead bromate (or of lead ion).

In connection with the equilibria given in equations 7 and 8, we define the constant K_1 by the equation

$$K_1^3 = a_{Pb^{++}}a^2_{BrO_3^-} = f_2f_1^2(\bar{x})^3\alpha(1 + \alpha)^2 \tag{14}$$

where f_1 and f_2 are activity coefficients of univalent and divalent ions respectively. Since we assume $f_2 = f_1^4$, equation 14 becomes

$$K_1 = f_1^2\bar{x}[\alpha(1 + \alpha)^2]^{\frac{1}{3}} \tag{15}$$

Similarly we define K_2 by the equation

$$K_2 = \frac{a_{Pb^{++}}a_{BrO_3^-}}{a_{PbBrO_3^+}} = \frac{f_2f_1}{f_1}\bar{x}\frac{\alpha(1 + \alpha)}{1 - \alpha}$$

or

$$K_2 = f_2\bar{x}\frac{\alpha(1 + \alpha)}{1 - \alpha} = f_1^4\bar{x}\frac{\alpha(1 + \alpha)}{1 - \alpha} \tag{16}$$

Since we have at 25°C., according to Debye and Hückel,

$$\log f_1 = -\frac{0.5045S^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} \tag{17}$$

equations 15 and 16 may be written (bearing equation 10 in mind),

$$\log K_1 = \log \bar{x} + \tfrac{1}{3}\log[\alpha(1 + \alpha)^2] - \frac{1.009\sqrt{c(1 + 2\alpha) + c_s}}{1 + A\sqrt{c(1 + 2\alpha) + c_s}} \tag{18}$$

$$\log K_2 = \log \bar{x} + \log\frac{\alpha(1 + \alpha)}{1 - \alpha} - \frac{2.018\sqrt{c(1 + 2\alpha) + c_s}}{1 + A\sqrt{c(1 + 2\alpha) + c_s}} \tag{19}$$

Of the four unknowns in equations 18 and 19, K_1 and K_2 are constants for all solutions saturated with lead bromate, A is presumed to be a constant for a series of solutions containing a given added nitrate, and α varies from one solution to another even in a given series.

STOICHIOMETRIC ACTIVITY COEFFICIENT OF LEAD BROMATE

It is readily seen from equation 14 that the mean activity, $a_\mp$, of lead bromate in a saturated solution of this salt is equal to K_1. It follows that the *stoichiometric* activity coefficient, f^s, of lead bromate in a saturated solution is given by the expression

$$f^s = \frac{a_\mp}{4^{\frac{1}{3}}\bar{x}} = \frac{K_1}{4^{\frac{1}{3}}\bar{x}} \tag{20}$$

Similarly it can be shown that the stoichiometric activity coefficient, γ^s, referred to molalities is given by the equation

$$\gamma^s = \frac{a_\mp}{4^{\frac{1}{3}}m} = \frac{K_1}{4^{\frac{1}{3}}m} \tag{21}$$

On comparison of equations 14, 15, and 20, we find

$$f^s = (f_2 f_1^2)^{\frac{1}{3}}\left[\frac{\alpha(1+\alpha)^2}{4}\right]^{\frac{1}{3}} = f_1^2\left[\frac{\alpha(1+\alpha)^2}{4}\right]^{\frac{1}{3}} \tag{22}$$

Only if α were equal to unity would f^s be equal to $(f_2 f_1^2)^{\frac{1}{3}}$ or f_1^2.

SOLUTION OF EQUATIONS 18 AND 19

Equations 18 and 19 were solved by a laborious and time-consuming method of trial which we shall illustrate in the case of the solutions containing potassium nitrate (see table 1). Two of these, that containing 0.09934 N potassium nitrate (solution 1) and that containing 0.7671 N potassium nitrate (solution 2), were selected for study. Let α_1 and α_2 represent the values of α for solutions 1 and 2 respectively. First of all, some arbitrary value for A was selected. Then a value of α_1 was assumed for solution 1. Application of equations 18 and 19 to solution 1, using these values of A and α_1, led to a value of K_1 and a value of K_2. This value of K_1 was then used for solution 2 and by means of equation 18 a value of α_2 was derived. This value of α_2 substituted in equation 19 gave a value of K_2 for solution 2. If this value of K_2 did not agree with the value of K_2 found from solution 1, a new value of α_1 was selected and the calculations were repeated until finally identical values of K_2 were found for both solutions.

Using this value of K_2, equation 19 was then applied to all the other solutions of the potassium nitrate series and a value of α was calculated for each solution. Application of equation 18, using the value of α so found, gave a value of K_1 for each solution of the series. If the values of K_1 found for the various solutions did not agree with those found for solutions 1 and 2, a new value of the parameter A was selected and the whole process was repeated until finally practically identical values of K_1 were calculated for all solutions of the series up to an ionic strength of about unity.

In this way we found for saturated solutions of lead bromate in the presence of potassium nitrate, a value of A equal to 0.30, a value of K_2 equal to 0.01452, and the remarkably consistent values of K_1 (average = 0.01984) given in the seventh column of table 1. Similarly for sodium nitrate solutions, we found $A = 0.385$, $K_2 = 0.01453$, and an average value of K_1 equal to 0.01993 (see table 2). For lithium nitrate solutions, we obtained $A = 0.50$, $K_2 = 0.01453$, and K_1 (average) = 0.02017 (see table 3). The excellent agreement among the three independent determinations of both K_1 and K_2 seems to offer considerable support to the views presented by the authors.

The tables also contain values of α, the degree of ionization of $PbBrO_3^+$, as well as values of f_1^2, the latter calculated by means of the equation

$$\log f_1^2 = \log (f_2 f_1^2)^{\frac{1}{3}} = -\frac{1.009\sqrt{c(1+2\alpha)+c_s}}{1 + A\sqrt{c(1+2\alpha)+c_s}} \qquad (23)$$

The average value of K_1 from the three series is 0.01998. Tables 1, 2, and 3 contain values of the stoichiometric activity coefficients, f^s and γ^s, calculated by means of equations 20 and 21 using $K_1 = 0.01998$. These equations can also be used to calculate the stoichiometric activity coefficients for any of the solutions in tables 1 to 5. For the solutions listed in table 6, in which the added salt is lead nitrate, the stoichiometric activity coefficient, f^s, is given by the relation:

$$f^s = \frac{K_1}{L_s^{\frac{1}{3}}} \text{ or } \frac{K_1}{4^{\frac{1}{3}}\sqrt[3]{\frac{L_s}{4}}}.$$

Similarly the value of γ^s follows from the equation

$$\gamma^s = \frac{K_1}{L_m^{\frac{1}{3}}}$$

IDEAL SATURATED SOLUTION OF LEAD BROMATE

Consider the hypothetical case of a saturated aqueous solution of lead bromate in which the ionic charges no longer make the ions non-ideal solutes; in other words, let us suppose that by some means or other the various molecular species present have unit activity-coefficients. In this ideal solution, let $\bar{x}_0$ be the normalized mole-fraction of the lead bromate and let α_0 be the degree of ionization of the ion $PbBrO_3^+$. It follows from equations 18 and 19 that

$$\log K_1 = \log \bar{x}_0 + \tfrac{1}{3} \log [\alpha_0(1 + \alpha_0)^2]$$

$$\log K_2 = \log \bar{x}_0 + \log \left[\frac{\alpha_0(1 + \alpha_0)}{1 - \alpha_0}\right]$$

From the accepted values of K_1 and K_2, viz. 0.01998 and 0.01453, respectively, we readily calculate

$$\bar{x}_0 = 0.02465$$
$$\alpha_0 = 0.3103$$

Values of $\bar{x}_0$ and α_0, derived from the values of K_1 and K_2 for each of the three series of solutions, are given in tables 1, 2, and 3.

APPLICATION TO CALCIUM NITRATE AND STRONTIUM NITRATE SOLUTIONS

When the added salt is of the calcium nitrate type, we obtain, instead of equations 18 and 19, the expressions

$$\log K_1 = \log \bar{x} + \tfrac{1}{3} \log \alpha(1 + \alpha)^2 - \frac{1.009 \sqrt{c(1 + 2\alpha) + 3c_s}}{1 + A \sqrt{c(1 + 2\alpha) + 3c_s}} \qquad (24)$$

$$\log K_2 = \log \bar{x} + \log \frac{\alpha(1 + \alpha)}{1 - \alpha} - \frac{2.018 \sqrt{c(1 + 2\alpha) + 3c_s}}{1 + A \sqrt{c(1 + 2\alpha) + 3c_s}} \qquad (25)$$

if we assume the added salt to be completely ionized. From equations 24 and 25 we obtain

$$2 \log K_1 - \log K_2 - \log \bar{x} = \tfrac{1}{3} \log \left[\frac{(1 + \alpha)(1 - \alpha)^3}{\alpha} \right] \qquad (26)$$

Using the average values of K_1 and K_2, viz. 0.01998 and 0.01453, obtained previously, we can apply equation 26 to each of the series of solutions (see tables 4 and 5), and calculate for each solution the value of α. Substituting this value of α in equation 24, we can determine the magnitude of the parameter A. The results obtained by these calculations appear in columns 6 and 7 of tables 4 and 5. We include here only solutions which contained an added nitrate.

The values of A so calculated exhibit a remarkable degree of constancy if we except solutions 3 and 5 in the calcium nitrate series. An examination of a large scale plot of figure 1 shows that for solution 5 the point which represents the solubility of lead bromate falls considerably below the best smooth curve through the experimental points; the same thing is observed to a slighter degree in the case of solution 3 ($C_s = 0.01116$).

We were not so successful in dealing with the lead nitrate series except when the concentration of added lead nitrate was very small. When a large excess of lead nitrate is present, our results seem to indicate that not only does an appreciable fraction of the added lead ions combine with BrO_3^- to form $PbBrO_3^+$, but that a considerable amount of undissociated lead bromate is also formed.

SUMMARY

1. We have determined the solubility at 25°C. of lead bromate in pure water and in the presence of potassium nitrate, sodium nitrate, lithium nitrate, calcium nitrate, strontium nitrate, and lead nitrate.

2. The theory of Debye and Hückel is not valid for these solutions if we assume that lead bromate exists in solution as Pb^{++} and BrO_3^- exclusively.

3. We postulate that the ionization of lead bromate occurs in two stages

$$\text{(a)}\ Pb(BrO_3)_2 \rightleftharpoons PbBrO_3^+ + BrO_3^-$$

$$\text{(b)}\ PbBrO_3^+ \rightleftharpoons Pb^{++} + BrO_3^-$$

Of these we assume that the first is virtually complete and that the second is incomplete.

4. These assumptions, when incorporated into the equations of Debye and Hückel, enabled us to determine certain equilibrium constants related to the reactions

$$\text{(a)}\ Pb(BrO_3)_2(s) \rightleftharpoons PbBrO_3^+ + BrO_3^-$$

$$\text{(b)}\ PbBrO_3^+ \rightleftharpoons Pb^{++} + BrO_3^-$$

5. Consistent values of K_1 and K_2 were found by a study of the potassium nitrate, sodium nitrate, and lithium nitrate solutions. Using these values of K_1 and K_2, satisfactorily constant values of the parameter A were calculated for both the calcium nitrate and the strontium nitrate series.

6. The stoichiometric activity coefficient of lead bromate for any of the solutions listed can be easily calculated from the value of K_1. Other activity coefficients are given in the tables.

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THE SOLUBILITY OF LANTHANUM IN MERCURY FROM 0°C. TO 50°C.[1]

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INTRODUCTION

The purpose of this investigation was to determine the solubility of lanthanum in mercury from 0° to 50°C. The need for these data arose in the continuation of an investigation (17) of the theory of Debye and Hückel (5) as extended by Gronwall, LaMer, and Sandved (9) for symmetrical valence type electrolytes and by Gronwall, LaMer, and Greiff (8) for the unsymmetrical types. To test the predictions of the theory for the unsymmetrical high valence type electrolytes by employing free energy measurements obtainable from suitable galvanic cells, lanthanum salts appear to be the most promising. The more common trivalent metal salts such as those of iron and aluminum are extensively hydrolyzed in aqueous solution and therefore undesirable for E.M.F. work.

If the temperature coefficients of the electromotive force are also determined, the partial and integral heats of dilution of the salt may be computed. It is therefore desirable to have the solubility of lanthanum in mercury over the temperature range to be studied. A heterogeneous amalgam is desirable, for then the electrode is easily reproducible without analysis. No data could be obtained in the literature concerning the solubility of lanthanum in mercury except the single statement of Müller (20) that amalgams containing only 1 atomic per cent lanthanum still showed a solid phase. A gravimetric rather than an electrometric method was employed, because even though Müller found a 1 per cent amalgam to be heterogeneous he did not approach a constant E.M.F. until he employed an approximately 5 per cent amalgam. The discrepancy indicated by these observations will be investigated in future work.

The composition of the solid phase in equilibrium with the amalgam at 25°C. was investigated by chemical analysis.

PREPARATION OF MATERIALS

Mercury. Redistilled mercury was stirred under a dilute nitric acid–mercurous nitrate solution for three days. It was then redistilled three

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[1] This paper is based upon a thesis submitted by Joseph L. Campanella to the Faculty of Rhode Island State College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1933.

times in a slow current of air as recommended by Hulett (12), and finally distilled once under high vacuum.

Oxalic acid. The best grade of C.P. oxalic acid was recrystallized three times from distilled water, and the crystals were dried in air.

Lanthanum. C.P. metallic lanthanum prepared by the electrolysis of the fused chloride was obtained. The metal was analyzed by precipitating the oxalate with oxalic acid and igniting to the oxide at 800–850°C. as recommended by Kolthoff and Elmquist (16). The average of two separate determinations showed 99.97 per cent lanthanum. The arc spectrum of this metal was examined in a quartz spectrograph in the laboratory of Professor W. A. Noyes, Jr., at Brown University and found to be exceptionally pure, containing only a trace of iron and aluminum. No further purification was attempted on account of the difficulties involved.

Absolute ethyl alcohol. Commercial 95 per cent alcohol was refluxed for several hours with sufficient lime to remove 10 per cent water and then distilled, discarding the initial and final 200-cc. portions. The middle portion was again distilled from sufficient metallic sodium to remove an additional 5 per cent of water. Density determinations showed the alcohol thus prepared to be 99.89 per cent pure (14).

Lanthanum bromide monohydrate. To a 10 per cent solution of lanthanum chloride which showed no absorption lines in the visible spectrum (the most likely impurities cerium, neodymium, and praseodymium all possess prominent absorption lines in the visible spectrum), an excess of a 5 per cent solution of oxalic acid was added. The precipitated lanthanum oxalate was washed free from hydrochloric acid and ignited to the oxide in a large platinum dish. The oxide was dissolved in C.P. hydrobromic acid; on slow evaporation the solution furnished colorless crystals of heptahydrated lanthanum bromide. The monohydrate was prepared by long dehydration (ten to twelve days) of the more highly hydrated salt *in vacuo* at 90°C. The composition was checked by chemical analysis. The experimental and theoretical values for lanthanum checked to ±0.19 per cent. Temperatures above 90°C. can not be employed because of the formation of insoluble basic compounds (16).

Propylenediamine. Propylenediamine (70–75 per cent) was obtained from the Eastman Kodak Company for the determination of mercury by the method of Spacu and Spacu (25).

EXPERIMENTAL PROCEDURE

The high basicity of lanthanum makes the amalgam very reactive in air and water. This eliminates the electrolytic method of formation of both the metal and its amalgams in aqueous solutions. The amalgams have been prepared with a fair degree of success by the electrolysis of concentrated solutions of $LaBr_3 \cdot H_2O$, $LaCl_3$, or $LaCl_3 \cdot H_2O$ in absolute ethyl alcohol (2, 15, 18). The amalgams employed in this investigation were prepared by two methods: (1) The necessary amounts of lanthanum and mercury to make 0.5 per cent, 1 per cent, 2 per cent, and 3 per cent amalgams were weighed out separately and put into a fused quartz flask. The flask was evacuated, and then heated in an oil bath to approximately 200°C. for eight hours. The lanthanum had by this time disappeared, and a pasty two-phase amalgam resulted. The same phenomenon that Müller (20) reported with respect to the pasty solid phase was observed in all cases. However, this behavior seemed to have no effect on the composition of either the liquid or solid phase. (2) Electrolysis of a concentrated solution of $LaBr_3 \cdot H_2O$ in absolute ethyl alcohol, as recommended by Audrieth and coworkers (2, 15, 18), was the second method employed. A solution of 9 g. of $LaBr_3 \cdot H_2O$ in 25 cc. of absolute ethyl alcohol was used in a test tube type cell having a platinum contact sealed in the bottom. The mercury forming the cathode was slowly stirred by an air-tight stirrer. A current of 0.2 of an ampere per square centimeter was passed through the solution for twenty to twenty-four hours. The cell was cooled continuously by running water.

The heterogeneous amalgam prepared by either method was placed in a fused quartz flask (50-cc. capacity) and evacuated. The flask was placed in a water thermostat at 25 ± 0.01°C. and shaken at intervals for several days. After reaching equilibrium, which was approached from both sides, the flask was opened and samples of the liquid phase withdrawn for analysis by means of a special filter pipet. This pipet was a modified form of that used by Hulett and de Lury (13) in their work on cadmium amalgam. The details of this pipet are shown in figure 1. By means of a vacuum pump attached at B the amalgam was drawn into C through the tight plug of glass wool, A. The filtered amalgam was dropped into a small container and quickly closed for weighing. A supply of these pipets was kept in the thermostat so that they would be at the proper temperature. This method of separating the two phases is considered superior to filtering through chamois leather or sintered Jena glass crucibles, because it is more rapid. With lanthanum amalgams this is important on account of their rapid oxidation in air. Furthermore, Russell (24) found the use of chamois skin unreliable.

After removing the samples at one temperature the next temperature level studied was set and the process repeated. For operating the thermostat at 12.5°C. a modified form of the apparatus recommended by Stier (26) was employed. For operation at 0°C. a bath of ice and water mush was used as described previously (17). The Beckman thermometers were checked at intervals against a standard thermometer recently certified by the Bureau of Standards.

The analysis of the samples presented some difficulty on account of the relatively small amount of lanthanum and large amount of mercury present. None of the ordinary methods of quantitative analysis was found applicable, nor would hydrochloric acid react quantitatively with the amalgam in a special flask similar to that used by Hulett and de Lury (13). It was soon observed, as noted by other investigators (2, 15, 18, 20), that lanthanum, like aluminum, completely separates from the amalgam when left exposed to the air. The lanthanum separates as the greyish white hydroxide with some basic carbonate. Consequently after weighing the samples they were set aside in contact with the air for two weeks. To prevent the possible formation of a protective coating the samples were shaken at regular intervals. At the end of this time a measured quantity of 0.1 *N* hydrochloric acid was added to the amalgam, and after standing a few minutes the excess acid determined by titration with standard carbonate-free sodium hydroxide, using phenol red as an indicator. The analytical weights and burets used were calibrated, and corrections were applied where necessary. It was found that under the conditions employed (approximately 0.1 *N* hydrochloric acid) a negligible quantity of the mercury dissolved. It is interesting to note that the samples lost weight on standing the two weeks in spite of the increase in weight due to compound formation with the oxygen in the air. This was undoubtedly due to evaporation of the mercury. This method of analysis has been found by Jukkola, Audrieth, and Hopkins (15) to check the gravimetric method of precipitation as the oxalate and ignition to the oxide. The solid phase in the amalgam at 25°C. was analyzed for both mercury and lanthanum.

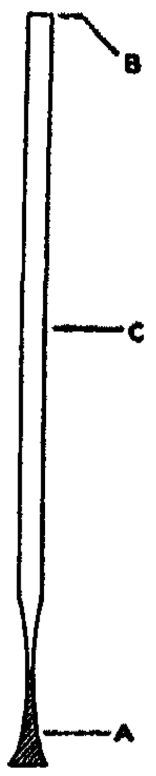

FIG. 1. Filter pipet

After the amalgam reached equilibrium in the thermostat, the liquid and solid phases were quickly separated by filtering through a plug of glass wool. The lanthanum was determined by precipitating the oxalate with oxalic acid and igniting to the oxide. The quantity of mercury present in this case was much smaller, and its precipitation as the oxalate could be prevented by hydrochloric acid. The mercury was determined in the filtrate from the oxalate precipitation by the method of Spacu and Spacu, using propylenediamine (25).

TABLE 1

The solubility of lanthanum in mercury

t	WEIGHT PER CENT LANTHANUM	AVERAGE	ATOMIC PER CENT LANTHANUM
°C.			
0	0.00552	0.00552 ± 0.00008	0.00640
	0.00540		
	0.00544		
	0.00558		
	0.00566		
12.5	0.00899	0.00907 ± 0.00006	0.00934
	0.00909		
	0.00913		
	0.00902		
	0.00916		
25	0.00952	0.00960 ± 0.00006	0.0133
	0.00949		
	0.00965		
	0.00965		
	0.00967		
37.5	0.0134	0.0134 ± 0.0004	0.0182
	0.0139		
	0.0138		
	0.0126		
	0.0133		
50	0.0179	0.0184 ± 0.0005	0.0246
	0.0190		
	0.0178		
	0.0185		
	0.0189		

RESULTS AND DISCUSSION

The solubility of lanthanum in mercury is given in table 1 for the various temperatures studied. The results tabulated represent the average of at least four separate analyses on individual amalgams prepared by the methods previously described. The atomic per cent was calculated from the weight per cent by the graphical method given by Ölander (22) and checked by analytical computation. The results in table 1 are shown graphically in figure 2, where the log of the atomic fraction is plotted against the reciprocal of the absolute temperature. The slope of the line was determined from a large scale plot and the line corresponds to the equation

$$\log N_2 = \frac{-1020}{T} - 0.4575$$

where N_2 is the atomic fraction of lanthanum in the saturated amalgam.

The agreement between the thermal and electrolytic amalgams was not

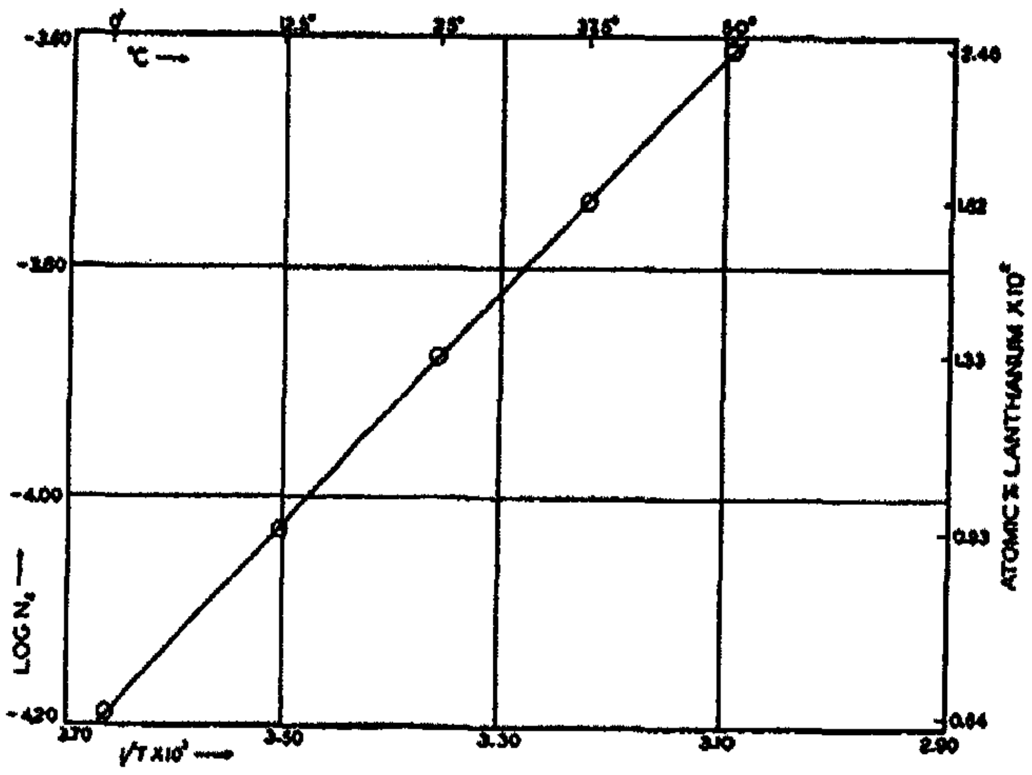

FIG. 2. The solubility of lanthanum in mercury

as good as desired. The per cent of lanthanum in the electrolytic amalgams was consistently higher than in the thermal amalgams. This discrepancy may be investigated by future work. Most of the amalgams here reported were prepared by the thermal method.

The solubility of a sparingly soluble metal in mercury is clearly not likely to be a definite quantity. Some metals, like copper and manganese and unlike zinc, lead, or tin, are known to form aggregates not only with themselves but also with mercury. It has been claimed that iron amalgams (4) and sodium amalgams (23) (up to 0.14 per cent sodium) are definitely colloidal in nature. However, in the case of liquid sodium amalgams, Bent (3) finds no evidence of a colloidal nature. The sizes of the particles in any amalgam may accordingly vary from atomic dimensions upwards, and the quantity which passes through a filter would then depend upon the factors controlling the distribution of particle sizes and the diameter of the filter pores. Until the size of particles in mercury have been determined, the term "solubility" must have a limited meaning. A method other than filtration must be found for determining a homogeneous phase. This is particularly important with lanthanum amalgams on account of the peculiar pasty composition of all amalgams of low lanthanum content. The values reported at least fix the upper limit of the solubility.

In the light of the relationship between the melting point of a metal and its solubility in mercury established by Tammann and Hinnüber (27) our results are not unreasonable. They find that for metals melting at from 300° to 400°C. more than 1 per cent of the metal is soluble in mercury, and this decreases with increasing melting point. For metals melting around 1000°C. (lanthanum melts at approximately 826°C.) the solubility is 0.1 per cent and less.

The low solubility of lanthanum in mercury, together with the general properties of its amalgams, leads us to the conclusion that amalgams of this metal are unsuited for precise electromotive force measurements without considerable difficulty. The analysis of the amalgam can be eliminated by employing a two-phase system, but then a dropping electrode cannot be used and non-aqueous solvents are necessary on account of the activity of the amalgam.

These data may be interpreted in terms of internal pressures and the solubility theory as described by Hildebrand (10). According to the theory, the insolubility of lanthanum and mercury in each other should follow from their position in the table of internal pressures. However, one cannot predict the existence of compounds from internal pressures, and even though a large difference in internal pressures exists, insolubility cannot occur if compound formation takes place.

There are many ways of estimating the internal pressures of metals, but we are handicapped in the case of lanthanum because the necessary physical properties in the liquid state (such as coefficient of expansion and compressibility, surface tension, and heat of vaporization) are not known. If we adopt the method of Gilfillan and Bent (6) and divide the boiling point (19), although it is not accurately known, by the atomic volume (21), lanthanum is placed between bismuth and lead in the table as given by Hildebrand, Hogness, and Taylor (11). This position indicates a rather large difference in the internal pressure of mercury and of lanthanum (approximately 250 per cent increase) and is in accord with the insolubility found in this investigation. Furthermore, the solubility of lead in mercury has been determined by Gouy (7) and found to be 0.013 per cent by weight at 25°C. Andrews and Johnston (1) found the solubility of bismuth in mercury to be very small. Lanthanum should be mutually soluble with lead and with bismuth. However, it should be remembered that this position for lanthanum is based on slightly inaccurate constants.

The results of the analysis of the solid phase in the amalgam at 25°C. are summarized in table 2. In each case the value given is the average of two determinations made on four separately prepared amalgams.

The empirical formula calculated for a compound having the above ratio of lanthanum to mercury is La_2Hg_{11}. To determine whether this compound is a chemical individual, it is necessary to determine the composition at various temperatures to see if the composition is constant and between what limits it exists. Since it is extremely difficult to separate completely the crystalline amalgam from adhering mother liquor, thereby making the analytical results uncertain, we did not attempt this problem at this time.

TABLE 2

Analysis of solid phase in lanthanum amalgam at 25°C.

WEIGHT PER CENT LANTHANUM	WEIGHT PER CENT MERCURY
11.00 ± 0.12	88.99 ± 0.08

SUMMARY

1. Lanthanum amalgams were prepared by direct heating of the metal with mercury and by the electrolysis of $LaBr_3 \cdot H_2O$ in absolute ethyl alcohol.

2. The solubility of lanthanum in mercury is reported at 0°, 12.5°, 25°, 37.5° and 50°C.

3. In the temperature range from 0° to 50°C. the solubility is represented by the equation:

$$\log N_2 = \frac{-1020}{T} - 0.4575$$

4. A brief discussion of the problems affecting the determination of the solubility of a sparingly soluble metal in mercury is given.

5. The low solubility of lanthanum in mercury indicates that lanthanum has a rather high internal pressure, approximately the same as that of bismuth.

6. From the general behavior of lanthanum amalgam we believe it unsuited for precise E.M.F. work without considerable difficulty.

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X-RAY STUDIES OF CRYSTALLITE ORIENTATION IN CELLULOSE FIBERS. II

SYNTHETIC FIBERS FROM BACTERIAL CELLULOSE MEMBRANES[1]

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As partial proof for the conclusions drawn in a previous paper (13), x-ray diagrams of natural fibers were compared with those of fibers synthesized from bacterial cellulose membranes. During the preparation of these "synthetic fibers," certain interesting observations regarding the plastic behavior of the crystallite suggested a further study of the type and degree relationship between deformation and orientation. It is the purpose of the present paper to describe briefly this extended investigation and especially to point out the significance of the results in that they appear to throw additional light on the question raised in the earlier paper (13), namely, what is the nature of the crystallite? Further information in this connection is not only of theoretical interest but also of practical importance, especially in the production of regenerated cellulose sheets and fibers.

Aside from a study of the characteristics of cellulose fiber diagrams themselves—a critical review of which has been given elsewhere (14)—one of the useful methods of investigating the configuration of the crystallite is to observe with x-rays its plastic behavior. Unfortunately, owing to the existence of a complex, ever varying, cylindrical cell wall, harboring numerous non-cellulosic materials, it is extremely difficult to draw definite conclusions when the method is applied to natural fibers. Although bacterial cellulose membranes have little macroscopic resemblance to natural fibers, they offer a unique opportunity for studying certain fundamental problems relating to the fine structure of natural cellulose for the following reasons: (1) they possess a well-formed, natural cellulose, crystalline structure; (2) they exist as a uniform membrane in a highly swollen or gel condition; (3) plastic flow can be readily produced in the

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natural membrane, while with natural fibers it is necessary to use a swelling agent first,—a process which usually changes the native to the mercerized crystalline form; and (4) the size of the membrane specimen allows a direct correlation of the x-ray and other data, while a bundle of natural fibers is necessary for a satisfactory x-ray diagram. These advantages first suggested themselves in the course of confirming with x-rays the chemical results of Hibbert and Barsha (3) regarding the identity of membrane and cotton cellulose.

DESCRIPTION OF MEMBRANES

Membranes prepared by bacterial action from solutions of sucrose, glucose, glycerol, fructose, galactose, and mannitol were used.[3] The method of preparing the membranes and a description of their properties may be found in the publications of Hibbert and coworkers (3, 6, 7, 17). In brief, the "membranes" are synthesized from sugar solutions by the bacterium *Acetobacter xylinus* in the presence of a nutrient medium. As deposited on the surface of the solution by the bacteria, the membranes are in a highly swollen or gel condition. They contain about 1 g. of cellulose to 100 g. of water, a large portion of which can be removed by mechanical pressure. The removal of this water, either by pressure or by drying, is an irreversible process, and the dried membranes are tough dense parchments, very resistant to the penetration of liquids. The membranes are chemically identical with cotton cellulose, as shown by the methylation, acetylation, acetolysis, and hydrolysis experiments of Barsha and Hibbert (3).

Farr and Eckerson (5), from microscopic and microchemical studies, have recently found the membrane to consist of bacteria, and each bacterium to be composed of a protoplast surrounded by a relatively thick cellulose layer, which in turn is coated with a thin layer of pectic substance. They found the membrane to be built up of thin layers of these bacteria, and the uniform color obtained in polarized light (5) indicates directional arrangement of strands of bacteria in these thin layers.

DEFINITION OF TYPES OF ORIENTATION

In the majority of specimens examined there was more or less deviation from the preferred type of orientation present, but, owing to the large number of samples described, the orientation of each will not be represented by distribution curves (16) or face pole diagrams (20). Instead, the preferred orientation of each sample discussed will be classified merely as one of the following types:

Random orientation. The crystallites are arranged in all possible directions, and the same random x-ray diagram is obtained with the sample at any angle to the x-ray beam.

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[3] These membranes were kindly furnished by Dr. Harold Hibbert.

Uniplanar orientation. The only limitation imposed is that the *b*-axes (direction of cellulose chains) of the crystallites lie parallel to a plane. The crystallites lie at random in the plane and have all possible rotations around their *b*-axes. With the plane perpendicular to the x-ray beam, the x-ray diagram is random with all lines present; if the plane is parallel, a fiber pattern is obtained with all lines present.

Selective uniplanar orientation.[4] The orientation is similar to a uniplanar orientation in that the *b*-axes are parallel to and are arranged at random in a plane, but differs in that the (101) planes of the crystallite have a selective orientation parallel to the plane (usually the large surface of the specimen). With the x-ray beam perpendicular to the plane, a random oriented pattern is obtained with the (101) line missing and the $(10\bar{1})$ present. With the beam parallel, the (101) line is present as a dense arc on the equator, while the $(10\bar{1})$ is present only as a faint arc on the meridian.

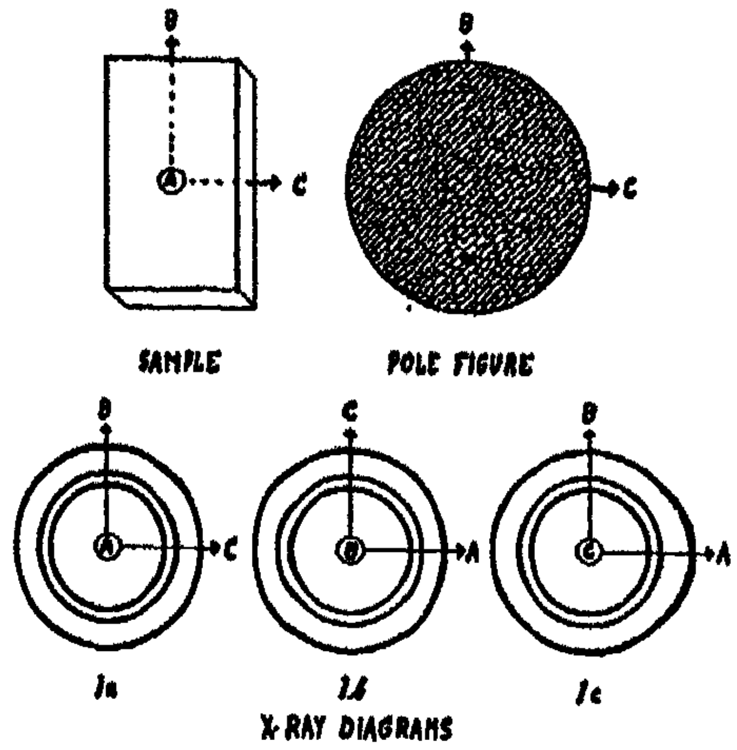

Fig. 1. Random orientation (see text for explanation)

Uniaxial orientation. The only limitation imposed is that the *b*-axes of the crystallite have a preferred orientation parallel to the fiber axis. With the x-ray beam perpendicular to the fiber axis, the (101), $(10\bar{1})$, and (002) lines exist as intensity maxima at the equator, and their relative densities remain constant with rotation of the sample around the fiber axis as long as the fiber axis is perpendicular to the x-ray beam. If the x-ray beam is parallel to the fiber axis, a random pattern is obtained.

Selective uniaxial orientation. The *b*-axes of the crystallites are not only parallel to the fiber axis, but the (101) planes are also parallel to a

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[4] Often referred to as a ring fiber structure.

plane containing the fiber axis—a combination of a uniaxial orientation and a selective uniplanar orientation (equivalent to a biaxial orientation for the cubic system). With the x-ray beam perpendicular to the fiber

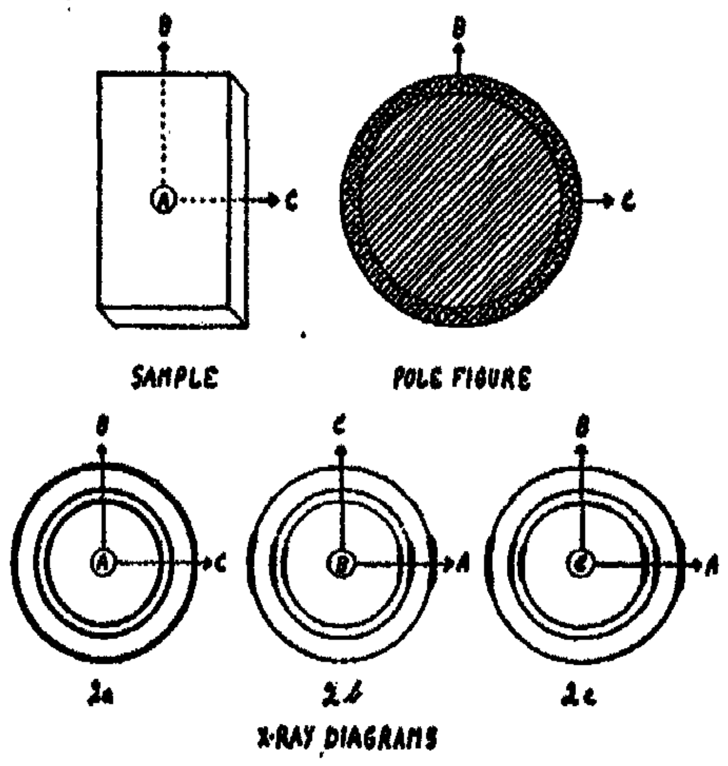


FIG. 2. Uniplanar orientation (see text for explanation)

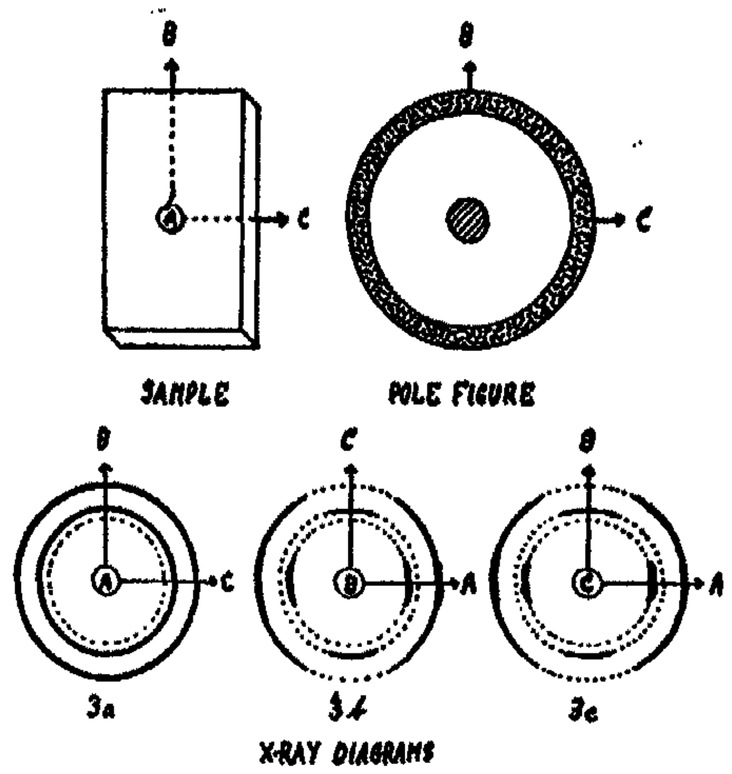


FIG. 3. Selective uniplanar orientation (see text for explanation)

axis, the (101), (10$\bar{1}$), or (002) lines may exist as intensity maxima on the equator, but the relative densities of these lines change if the sample is rotated at different angles around the fiber axis. For example, with the selective plane parallel to the x-ray beam, the (101) line will be present and the (10$\bar{1}$) absent; with the beam normal to the plane the order is reversed. If the fiber axis (also the plane) is parallel to the x-ray beam a fiber pattern is obtained.

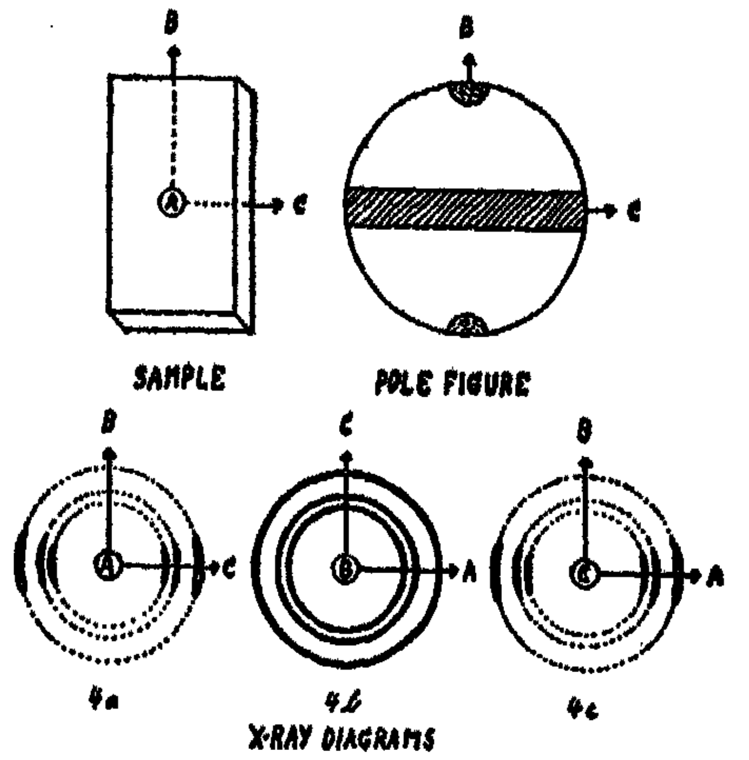


Fig. 4. Uniaxial orientation (see text for explanation)

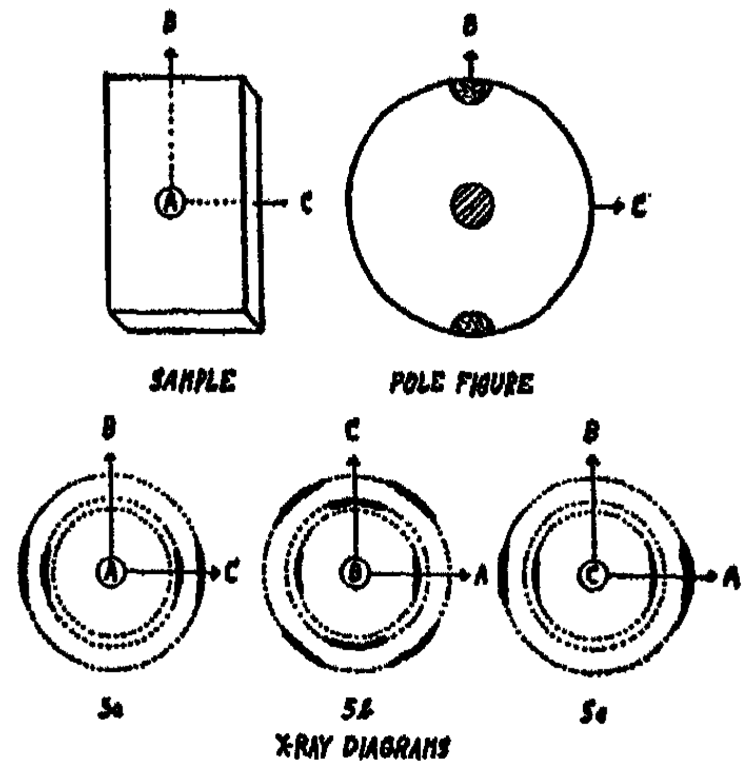


Fig. 5. Selective uniaxial orientation (see text for explanation)

Stereographic projections, or pole figures, representing the various types of orientation and their corresponding x-ray diagrams are illustrated diagrammatically in figures 1, 2, 3, 4, and 5. In the pole figures the dotted areas represent the projection of the *b*-axes and the cross-hatched areas the projection of the [101] directions. A, B, and C represent arbitrary reference axes within the sample. In drawing the x-ray diagrams considerable deviation from the preferred type is assumed.

STUDY OF MEMBRANES NOT MECHANICALLY DEFORMED

Undried membranes. Owing to the large amount of water present, it is impossible to study with x-rays the orientation of the cellulose as it exists in the swollen condition. The cellulose diffraction pattern, if present, is completely masked by the characteristic water haloes, and as the sample dries the water pattern is gradually replaced by the cellulose pattern. It is not indicated from the x-ray data, therefore, whether well-defined cellulose crystallites with a definite orientation exist in the swollen membrane, or whether they are formed during drying. Microscopic observations in polarized light, however, indicate that the cellulose has a definite orientation within each bacterium and that the bacteria are arranged end-to-end to form long strands (5).

Membranes dried in the form of an aerogel. The possibility of using aerogels to study the structure and orientation of gels has been pointed out by S. S. Kistler, who kindly converted a section of the swollen membrane into an aerogel (8). The aerogel was examined with the beam perpendicular and also parallel to the plane of the membrane, and from each direction a crystalline cellulose pattern with a random orientation was obtained. If the aerogel is pressed into a sheet there is a tendency toward the formation of a selective uniplanar orientation.

Assuming the aerogeling process not to disturb the crystallinity or orientation, the random crystalline x-ray pattern would seem to indicate that crystalline cellulose is deposited with the water held between the crystallites (intermicellar). The random orientation which changes to a selective uniplanar orientation when the aerogel is pressed would suggest a honeycomb structure with a selective orientation in the cell walls of the structure. Microscopic examination reveals no visible honeycomb structure, and it is possible that the cellulose walls of the bacteria and the space between the bacteria form the cell walls of the assumed honeycomb structure. This assumption would be in harmony with the microscopic conclusion that the cellulose has a definite orientation within each bacterium.

Dried with plane of membrane parallel to a glass plate. If a large section of the membrane is allowed to dry with the flat surface resting on a horizontal glass plate, the dried sheet peeled off and subjected to x-ray analysis, a selective uniplanar orientation is found, similar to that reported by Mark and Susich for "biosynthetische cellulose" (9). Representative diagrams with the x-ray beam perpendicular and parallel to the plane of the dried membrane are shown in figures 6a and 6b, respectively. If it is assumed that the original orientation in the swollen membrane persists in the dried condition, we are led to conclude that the cellulose is deposited in the membrane with a selective uniplanar orientation more perfect than is possible from a honeycomb structure. It was noticed, however, that upon drying the membrane adheres to the glass plate and that shrinkage occurs only normal to the glass plate. For example, a swollen sheet about 0.5 cm. thick will shrink to about 0.0005 cm. (0.1 per cent of its original thickness), while the width and length remain practically constant. That this unidirectional shrinkage apparently affects the orientation is shown by the following experiment.

Dried with plane of membrane perpendicular to a glass plate. Several slices of the membrane were carefully prepared and placed side by side with the original plane of the membrane perpendicular to the glass surface. Again, as with the membrane parallel, shrinkage of about the same dimensions occurred only normal to the glass and a selective uniplanar orientation was obtained.

Samples were also dried with the plane of the membrane both perpendicular and parallel to a mercury surface. This procedure allowed the membrane to contact freely in all directions while drying, and in most cases an imperfect uniplanar orientation was obtained. In other samples, provided the ratio of top to edge surface was large enough to allow practically all the water to leave from the top surface, a tendency toward a selective uniplanar orientation was found. However, for samples dried on mercury, the orientation was less perfect than for similar samples dried on glass, and the membrane had a tendency to wrinkle or pucker, which made the estimation of orientation difficult.

Membrane dried not in contact with surface. If a rod-like specimen of the membrane is allowed to dry in such a way that evaporation takes place equally in all directions normal to the strip, there is an approximately equal shrinkage in all directions and a resulting slight tendency toward a uniaxial orientation. However, when the sample is allowed to contract freely upon drying, puckering makes it difficult to estimate the orientation. In some cases the samples may be classified as having a random orientation.

These results on drying would seem to indicate that the selective uniplanar orientation of a dried membrane is probably the result of stress produced by a unidirectional shrinkage resulting from the rapid removal of water from one direction only. It is well known that shrinkage is an anisotropic property with a maximum effect perpendicular to the *b*-axis, but the present data would seem to indicate that the direction of shrinkage is still more specific,—it occurs principally normal to the (101) planes, or in the [101] direction. Evidently, a random orientation is the equilibrium state of the swollen membrane, and if a major shrinkage occurs in one direction upon drying the (101) planes assume a position normal to that direction. Orientation and shrinkage appear to be two dependent variables—the result of an anisotropic crystalline property—and if one is fixed the behavior of the other is limited.

In the previous paper (13) it was pointed out that the selective orientation of dried bacterial cellulose sheets is suggestive of a general mechanism of selective cellulose deposition which might be extrapolated to plant cell membranes, but the present results would seem to invalidate the suggestion. Owing to the more rigid condition of natural fibers, it is difficult to predict what influence shrinkage may have on their orientation, but the present experiments would seem to infer that it is a factor which cannot be ignored, and that it may be in part responsible for the non-selective orientation found in spiral fibers (13),—a point which should bear further investigation.

STUDY OF DEFORMED MEMBRANES

If, instead of allowing the membrane to dry on a flat surface, it is stretched, compressed, or in some way deformed during drying, various orientation effects are produced. For studying this relationship between deformation and orientation, specimens of the swollen membrane were carefully prepared, deformed in different ways, allowed to dry, and subjected to x-ray analysis at various angles and positions along the sample.

Stretched membrane. The stretching was accomplished by suspending in a vertical position a strip of the swollen membrane and applying weights attached to the lower end. The amount of tension which could be safely applied without causing rupture was small at first, but became very great as the strip dried. Both broad flat strips and narrow rod-like strips were treated in this way. Stretching in one direction produces a uniaxial orientation which is most pronounced in the rod-like samples, gradually changing toward a selective uniaxial orientation as the strips are made more sheet-like. An x-ray pattern of a rod-like sample with the beam perpendicular to the fiber axis is shown in figure 7. Its similarity to a cotton pattern is illustrated by a comparison of figures 7 and 8.

Rolled membrane. One end of a flat strip was clamped to a glass plate and the strip rolled in one direction. This process tends to produce a selective uniaxial orientation, as illustrated in figure 9.

Drawn membrane. For this experiment a set of standard diameter holes, used for determining wire gauges, sufficed for drawing dies. A tapered end of the membrane strip was started through the die, fastened to a clamp, and pulled through by applying weights to the clamp. Since twenty to forty minutes were often needed for the final passes, precaution was necessary to prevent too rapid drying of the sample. Drawing produces a uniaxial orientation which becomes more perfect with progressive passes through the die. The type of fiber structure obtained by drawing is illustrated in figure 10.

Pressed membrane. A square section of a membrane was placed between two glass plates and pressure applied. X-ray diagrams showed the sample to possess a selective uniplanar orientation, similar to that produced by allowing a sheet to dry on a glass surface.

Membrane dried with ends fixed. A rod-like strip of swollen membrane was stretched across the end of a beaker, the ends taped to the sides of the beaker, and the strip allowed to dry. The shrinkage accompanying drying causes the strip to become very taut. X-ray diagrams show a uniaxial orientation, as illustrated in figure 11.

Flat strips were prepared in the same way with the exception that the middle of the strip rested on a glass rod of 2-cm. diameter placed across the top of the beaker. This arrangement allowed the middle of the strip to be pressed against a smooth surface while under stress. Thus the section of the strip in contact with the glass rod is influenced by both a unidirectional shrinkage and a unidirectional tension acting at right angles to each other. The result was a selective uniaxial orientation for this portion of the strip, while the part not in contact with the glass rod developed only a uniaxial orientation.

The results on deformed membranes show that, in general, three types of orientation were produced. If the plastic flow takes place (a) with reference to an axis, a uniaxial orientation is obtained; (b) if with reference to a plane, a selective uniplanar orientation; or (c) if with reference to an axis and a plane, a selective uniaxial orientation.

Microscopic study. In an effort to throw further light on the nature of the plastic flow, a microscopic study was made of the deformed membranes. From the swollen membranes, by means of suitable solvents (5), it is possible to isolate the bacteria individually or in bead-like strands. These same bacteria linked together in bead-like strands with a definite uniform interior orientation, as indicated by the uniform color in polarized light, may be found in the strongly deformed membranes. Although the isolation of these unchanged bacteria cannot be accepted as definite proof, it would seem to indicate that the bacteria may move as units during plastic deformation.

STUDY OF MERCERIZED MEMBRANES

Action of sodium hydroxide. While studying the effect of substituting the water of the swollen membranes for other liquids, an unusual phenomenon concerning the action of sodium hydroxide was observed. Normally sodium hydroxide swells cellulose materials, but in the membrane it produces a shrinkage. For example, if a swollen membrane is placed in 18 per cent sodium hydroxide it begins to contract rapidly, and in about fifteen minutes the length and breadth shrink to approximately one-fourth the original dimensions, while the thickness remains practically the same. The treated sample gives a random mercerized x-ray pattern.

The failure of several salts to produce the same action would indicate that it is not an osmotic effect. The shrinkage appears to be definitely associated with a crystallographic change to the mercerized form, since the sodium hydroxide must be of sufficient concentration (above about 14 per cent) to produce a mercerized structure before any appreciable shrinkage occurs.

If the membrane is first dried on a glass plate and then treated with sodium hydroxide, it shrinks to only about two-thirds the former width and length, with a slight increase in thickness. This process tends to destroy slightly the original selective uniplanar orientation of the dried specimen. The very compact form of the dried membrane, however, makes it difficult to produce a mercerized crystalline structure.

Specimen dried, then mercerized under stress. A number of fiber specimens previously dried under stress were treated with sodium hydroxide, subjected to the same type of original stress, washed, and allowed to dry. X-ray analysis showed that, in general, the original type of orientation is not changed, but the degree of orientation becomes more perfect. Figure 12 shows the same sample as figure 11 after being replaced over the beaker and treated for a short time with sodium hydroxide. The native crystalline structure is not changed, but the fiber structure is more perfect.

FIG. 6a. X-ray diagram of membrane dried in contact with glass surface. X-ray beam perpendicular to large surface of membrane

FIG. 6b. X-ray beam parallel to surface (same sample as figure 6a)

FIG. 7. Membrane dried with tension in one direction. X-ray beam perpendicular to fiber axis (tension axis)

FIG. 8. Typical x-ray diagram of cotton fibers. X-ray beam perpendicular to fiber axis

FIG. 9. Membrane rolled in one direction. X-ray beam normal to plane and direction of rolling

FIG. 10. Membrane drawn through die. X-ray beam perpendicular to fiber axis (drawing axis)

FIG. 11. Membrane allowed to dry with ends of strip fastened to rigid supports. X-ray beam perpendicular to fiber axis (long direction of strip)

FIG. 12. Same sample as figure 11 after treatment with sodium hydroxide

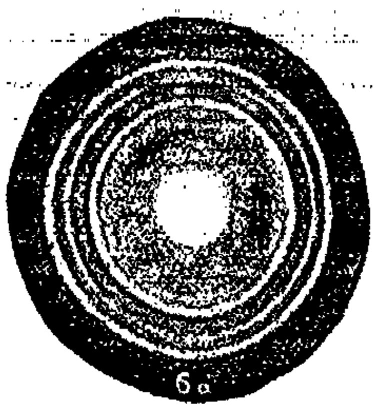
FIG. 13. Typical x-ray diagram of ramie fibers. X-ray beam perpendicular to fiber axis

FIG. 14. Strip of membrane mercerized with ends fastened to rigid supports. X-ray beam perpendicular to fiber axis (long direction of strip)

FIG. 15. Typical x-ray diagram of cuprammonium rayon. X-ray beam perpendicular to fiber axis

FIG. 16. Strip of membrane subjected to combined tension and pressure applied at right angles to each other (see text for explanation). X-ray beam perpendicular to direction of tension (axis of strip) and parallel to direction of pressure (normal to plane of strip).

FIG. 17. Same sample as figure 16 rotated 90° around fiber axis. X-ray beam still perpendicular to fiber axis (direction of tension), but perpendicular to direction of pressure (parallel to plane of strip).



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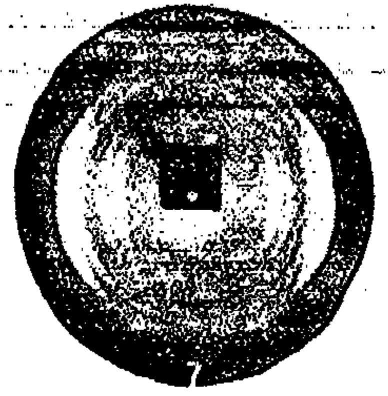

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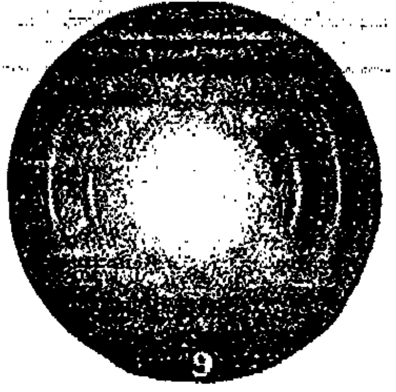

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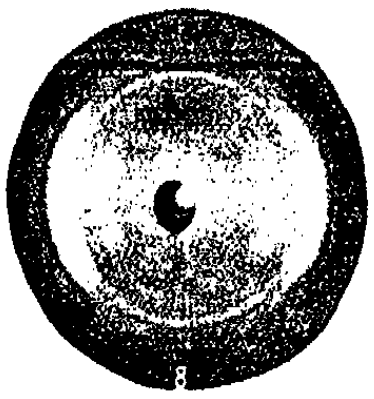
6b



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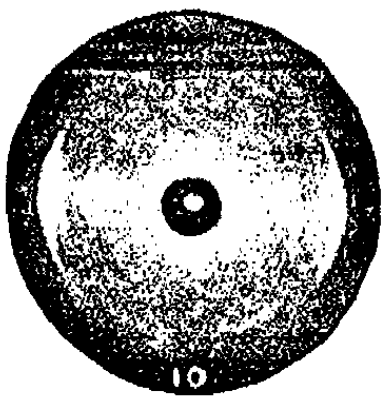

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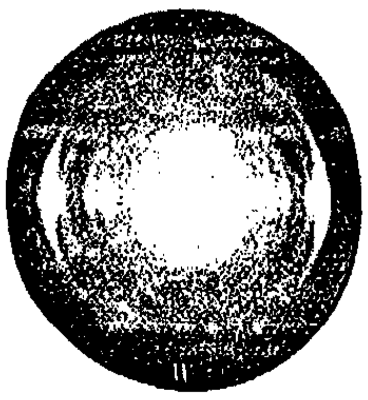

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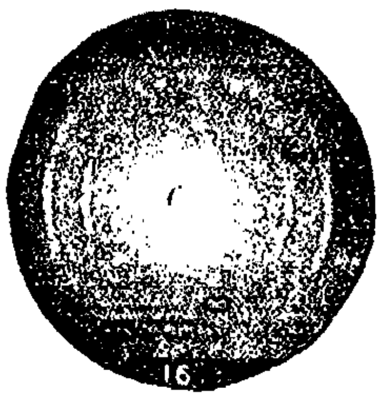

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15

17

Figs. 6a to 17

As shown by comparison of figures 12 and 13, the fiber structure is equal to that of ramie, which is one of the most perfectly oriented natural fibers.

A number of sheets previously dried on glass were treated with sodium hydroxide and subjected to a straight tension pull. With progressive extension the selective uniplanar orientation is gradually replaced by a uniaxial orientation. At the intermediate stage both orientations may be considered as present, which results in an imperfect selective uniaxial orientation.

Specimen mercerized with ends fixed. Strips were mounted over a beaker, as previously described, and kept in contact with 18 per cent sodium hydroxide for 30 minutes, washed for 30 minutes, and allowed to dry. Owing to the shrinkage produced by the sodium hydroxide, the strips become very taut and a mercerized uniaxial fiber structure is produced, as illustrated in figure 14. Its similarity to a well oriented cuprammonium rayon diagram may be seen from a comparison of figures 14 and 15.

If the strip is placed over a glass rod and then treated with sodium hydroxide, the section in contact with the glass rod develops a selective uniaxial orientation, while that not in contact develops a uniaxial orientation.

Specimen dried, mercerized, then subjected to combined tension and compression. Uniaxial fibers, previously prepared by drawing, were placed between two smooth lead sheets and the center of the sample moistened with sodium hydroxide The lead strips with the samples between them were then placed between a smooth steel plate and a steel rod 6 cm. in diameter. If sufficiently wide strips of lead are used and the axis of the steel rod is perpendicular to the fiber axis of the specimen, the circumference of the rod will force the lead to flow parallel to the fiber axis of the specimen when the rod and plate are pressed together by means of a large vise. Thus, simultaneously with the perpendicular pressure produced by the vise, a tension is produced in the sample by the plastic flow of the lead. Spreading of the sample is prohibited by placing thin lead strips on either side. The principle of the process has been successfully used to prepare selective uniaxial oriented specimens of keratin (1), and it is commonly used to draw a thin wire or roll a thin sheet by placing the sample inside of another metal. If thick lead sheets are used a uniaxial orientation may be obtained. However, by proper regulation of the lead thickness, the pressure, etc., specimens may be prepared by this method which show a selective uniaxial orientation, as shown by figures 16 and 17 with the x-ray beam perpendicular and parallel to the flat side of the sample, respectively (x-ray beam perpendicular to the fiber axis). The presence of a selective uniaxial orientation was further confirmed by a fiber pattern when the x-ray beam was made parallel to the fiber axis.

This experiment illustrates the fact that it is possible, by the proper combination of tension and pressure, to prepare a selective uniaxial orientation by forcing the sample to become longer and thinner but not broader or narrower,—a change in dimensions corresponding to that of a rolled sheet metal. The experiment indicates also the possibility of preparing a specimen with an orientation approaching that of a single crystal, from which the relative refractive indices along the *a*- and *c*-axes may be obtained, as well as other fundamental crystallographic information heretofore unattainable, owing to the absence of single crystals of cellulose.

THEORETICAL

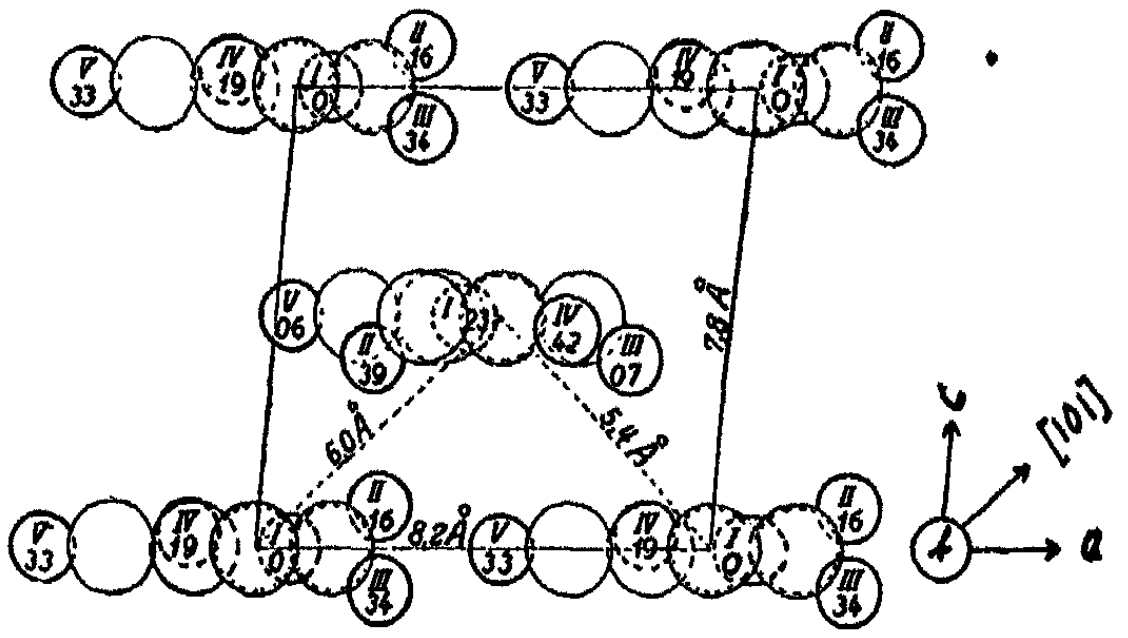
In connection with the selective orienting properties of the crystallite, it is interesting to note that the (101) crystallographic plane of cellulose, in its influence on the type of orientation obtained, appears to play a rôle analogous to that of a glide plane in metals. The mechanism of obtaining the orientation, however, must be quite different for the two materials. Instead of a glide plane slip as for metals, all of the evidence points to a "micellar flow" or movement of the crystallite as a unit for cellulose (14). The equilibrium position for the cellulose crystallite, therefore, must be governed, not by the symmetry of glide planes, but by the external configuration of the crystallite.

The pronounced orienting tendency of cellulose with reference to the *b*-axis—that a rayon filament can be oriented, for example, by stretching—is well known, and this property is usually attributed to rod-like micelles or fibrous bundles of cellulose chains which are oriented parallel to the direction of stretching. If an elongated shape in the direction of the *b*-axis is responsible for the parallel alignment of the crystallites when cellulose is stretched, the question then arises, what configuration of the crystallite is responsible for the selective orienting tendency with reference to the (101) plane?

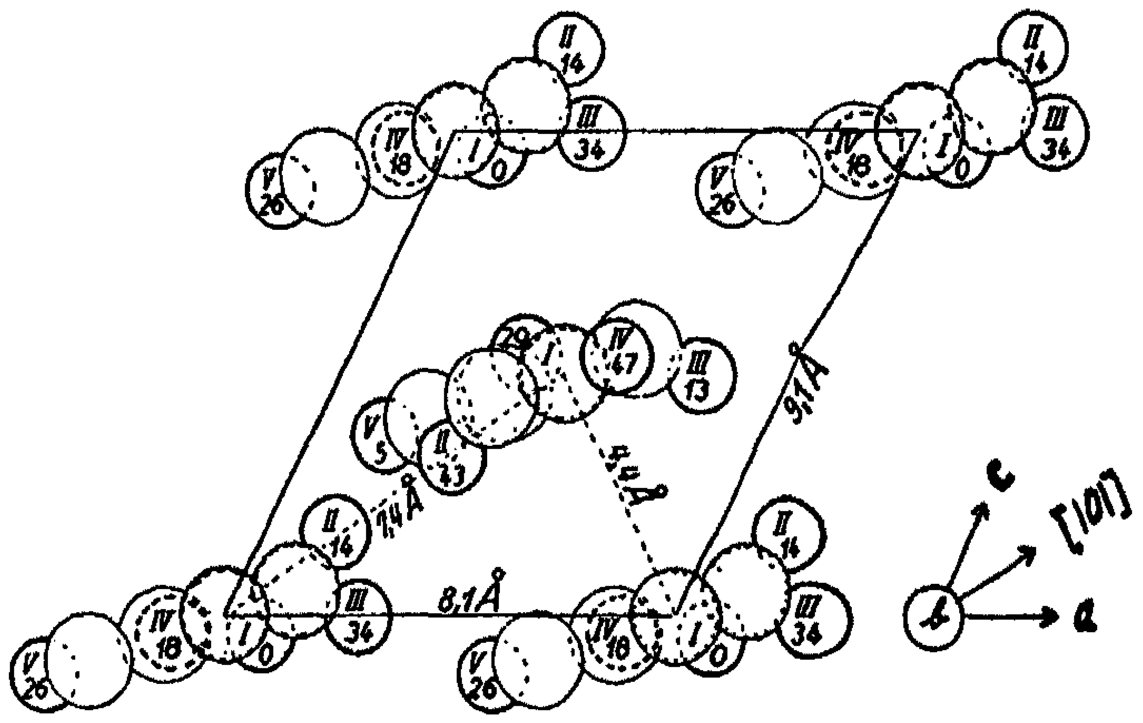
Assuming an elongated cellulose crystallite which moves as a unit during plastic flow, there are two possible external configurations which could account for its selective behavior: (1) it could have a flat or ribbon-like shape; or (2) it could have a greater secondary valence attraction on two sides. In other words, the selective orienting tendency of the crystallites may be due either to their shape or to the cohesive forces between them, or perhaps to a combination of both factors.

It is impossible to predict to what extent cleavage planes may exist in crystalline cellulose, but from analogy to other crystals one would expect a tendency toward cleavage along the (101) planes. If this were true then the conditions would be favorable for the existence of flat or shingle-like crystallites, which, owing to their shape, should behave in the manner experimentally observed.

If it is shape alone that is responsible for the selective orienting tendency of cellulose, then we have reason to believe that the crystallite would have to be rather ribbon-like. In the case of superpolymers, Carothers (4) has estimated that the molecular weight should be above 12,000 and the molecular length above 1000 A.U. before orientation can be produced easily by stretching. On the other hand, oriented films may be produced readily from comparatively short molecules, a property due to the exist-



NATIVE



MERCERIZED

FIG. 18a and 18b. View down the *b*-axis of the cellulose unit cell (after K. R. Andress: Z. physik. Chem. 4B, 190 (1929)) ence of polar groups at the ends of the molecules, and it would seem logical to assume that the polar hydroxyl groups of cellulose may be partly responsible for the orienting properties of cellulose.

As may be seen from figure 18a, the (101) planes of cellulose have the largest number of hydroxyl groups per square unit of surface. Since the secondary valence of cellulose is attributed to hydroxyl groups, the sides of the crystallite parallel to the (101) planes should have the greatest valence forces, owing to the geometrical arrangement of the glucose residues in the crystal lattice, and these hydroxyl groups may assist the selective orienting tendency of the crystallite. In addition to their selective orienting tendency, these hydroxyl groups, and also the ones at the ends of the cellulose chains, should assist the orienting tendency with reference to the *b*-axis.

The selective orienting tendency is not a unique property of bacterial cellulose membranes. Gelatin (18), myosin (2), cellulose acetate and cellulose nitrate films (10), and regenerated cellulose films (15) all show a selective uniplanar orientation when allowed to dry in sheet form. Keratin (1), regenerated cellulose films (15), and cellulose acetate and cellulose nitrate films (10) also show a selective uniplanar or uniaxial orientation when treated under the proper conditions, and it is interesting to note that all of these materials which show a selective orienting tendency have polar groups attached to fibrous molecules which exist as elongated micelles or crystallites.

There are several properties of cellulose which are in harmony with the concept of hydroxyl group influence. For example, since the hydroxyl groups are largely responsible for the sorption of water by cellulose (12), a crystallite studded with hydroxyl groups on two sides would be expected to have a major shrinkage normal to the (101) planes. Furthermore, since the (101) planes of the mercerized lattice have more (about 25 per cent) available hydroxyl groups per unit of surface than the native, as may be seen from a comparison of figures 16a and 18b, this may account in part for the greater sorption of water by mercerized cellulose and its greater selective orienting tendency.

DISCUSSION AND SUMMARY OF RESULTS

In general, the experimental results would lead one to conclude that the major factor in determining the type and degree of orientation found in deformed membranes is the relative direction and extent of the flow, or change in dimensions of the sample, rather than the nature, magnitude, or direction of the forces producing the flow. In other words, *if the sample is elongated in one direction, the b-axes of the crystallites are oriented parallel to that direction; if the sample is constricted in one direction, the (101) planes are oriented normal to that direction.* This general rule would seem to apply to both mercerized and unmercerized membranes, regardless of whether the changes in dimensions are produced by shrinkage or by plastic flow due to mechanical force. It appears less difficult, however, to prepare a selective oriented fiber structure from the mercerized than from the unmercerized membranes.

This rule is not suggested as a rigid law for the plastic behavior of all cellulose materials—it is merely an attempt to generalize the behavior of the samples investigated—but preliminary results indicate that it may be of general application, and it is interesting to note that a similar rule may be applied to the plastic flow of metals (11). It appears to be in agreement with the optical results of McNally and Sheppard (10) on cellulose nitrate and cellulose acetate films, and with the x-ray results of Trillat (19) on cellulose esters.

Although it is tentatively suggested that polar groups, as well as shape, may influence the selective orienting properties of cellulose, the present results are not conclusive either as to the shape and size of the membrane crystallite, or as to the exact cause of its orienting tendencies. It is tempting to assume that part of the orientation effects are due directly to cell distortion, or to the flattening of a honeycomb structure. Careful observation, however, indicates that it is necessary to invoke something beyond cell distortion; the orienting tendency of cellulose appears to be a fundamental property, present not only in native, but also in regenerated and cellulose derivatives where a cell structure cannot be assumed. As pointed out before, there is some evidence that bead-like strands of bacteria move as units during plastic flow, but the evidence is not conclusive. The unit may be considerably smaller, and it is difficult to predict at what crystallite dimensions the influence of shape or polar groups would begin to have an orienting effect. The major point which *the present results emphasize* in this connection is that, whatever the final concept of the membrane crystallite may be, this concept must take into consideration the fact *that the crystallite possesses a major orienting tendency with reference to the b-axis, and a minor or selective orienting tendency with reference to the (101) plane.*

The author wishes to express his gratitude to Professor G. L. Clark for his interest and support, and to Professor Harold Hibbert for furnishing the necessary membrane samples.

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THE INFLUENCE OF DENATURATION ON THE SPREADING OF PROTEINS ON A WATER SURFACE

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This paper describes observations on the effect of denaturation, by heat and by irradiation with ultra-violet light, on the spreading of aqueous solutions of ovalbumin and serum albumin on water. The term "denaturation" is somewhat loosely used to describe various changes in proteins, which lead to diminished solubility in water; thus besides the changes produced by heat and by ultra-violet light, Ramsden (15) and du Nouy (4) found that adsorption at the air-water surface produces insolubility of proteins and termed this also "denaturation." When proteins are spread on the surface of aqueous solutions they also usually become insoluble.

The numerous papers published in recent years on the spreading of proteins on a water surface (5, 6, 7, 8, 10, 11, 16) have led to the conclusion that a fully spread film of a protein at a water-air surface has the peptide chains of the protein molecules stretched out along the surface with the lyophilic groups towards the water. Serum albumin and ovalbumin show remarkable differences in their colloidal properties in bulk solution, and it was thought that a study of their power of spreading at a surface, before and after denaturation in bulk, would throw light on the nature of the denaturation process and show also whether there is an important difference in the processes of so-called "denaturation" by heat and by spreading out on a surface.

EXPERIMENTAL

Preparation of the protein solutions

Ovalbumin solutions were prepared from fresh hens' eggs by separating the yolk, diluting the white with distilled water, and filtering off the precipitated globulins; the filtrate was electrodialyzed in Pauli's apparatus (13) for several days, the voltage being gradually increased from 5 to 220 volts. After seven days' electrodialysis the conductivity had reached its minimum value of 6.5×10^{-6} mhos, with 2 per cent protein solutions.

Serum albumin was prepared from defibrinated horse serum, by freeing from globulins by adding ammonium sulfate to one-third saturation, filtering, again adding ammonium sulfate to two-thirds saturation, and electrodialyzing as with ovalbumin. The final conductivity was 4.5 × 10^{-6} mhos, at 2 per cent. The pH of the purified solutions was 4.80 for the ovalbumin and 4.85 for the serum albumin, measured with a quinhydrone electrode.

All solutions were kept in the ice chest at about 2°C., under a thin layer of a paraffin–toluene mixture to prevent infection. The concentration of the 2 per cent solutions was determined every few days by drying 2 cc. at 108°C. for twenty-four hours; the solutions for spreading were about one-hundredth of this concentration and were prepared from the stronger solutions by diluting with conductivity water.

Measurements of the surface pressure of the spread films

The apparatus of Adam and Jessop (2) was used. The films were frequently examined by the dark-ground illumination introduced by Zocher and Stiebel (19), with the simplifications used by Adam (1). The pH of the aqueous solutions, upon which the proteins were spread, was regulated by Walpole acetate buffers of $N/20$ or $N/300$ concentration in acetate; a brass trough was used, and the temperature regulated by an electrical heater below the trough.

The proteins were spread from aqueous solution, using Gorter's method (6, 7, 8), with but slight modifications. An Agla micrometer syringe, capable of being read to 0.0001 cc., was held horizontally close to the surface, and a measured quantity of the liquid, about 0.25 cc., expelled. It was found that if the height of the tip of the syringe was varied between 2 and 5 mm. above the water, the same results were obtained; if, however, it was brought so close to the surface that the issuing drops actually touched the water in the trough before being detached, the spreading was less complete. Every result quoted below is the mean of several measurements, which usually agreed within 1 per cent.

RESULTS

Figure 1, curves I to III, shows the surface pressure–area curves obtained with egg albumin on the buffer solutions of pH 4.8 (the isoelectric point) and 4.4. The areas were observed to increase with time slightly, owing to the spreading or unfolding of the molecule taking place slowly, up to about seven minutes. The values given are at about seven minutes after putting the material on the surface. The spreading was greater on the solution at the isoelectric point than on the more acid solution, in accordance with the findings of Gorter; it was also considerably greater on the more concentrated acid buffer than on the more dilute. Svedberg's values for the molecular weight, i.e., 34,500 for ovalbumin and 69,000 for serum albumin, were used (17, 18). No signs of inhomogeneity in the film could be detected on the two $N/20$ buffer solutions with the dark-ground illumination below 18 dynes at 4.8 and 15 dynes at 4.4 pH, at which pressures collapse commenced. The films showed slight signs of inhomogeneity at all pressures on the dilute buffer; considerable collapse occurred on this solution at 13 dynes.

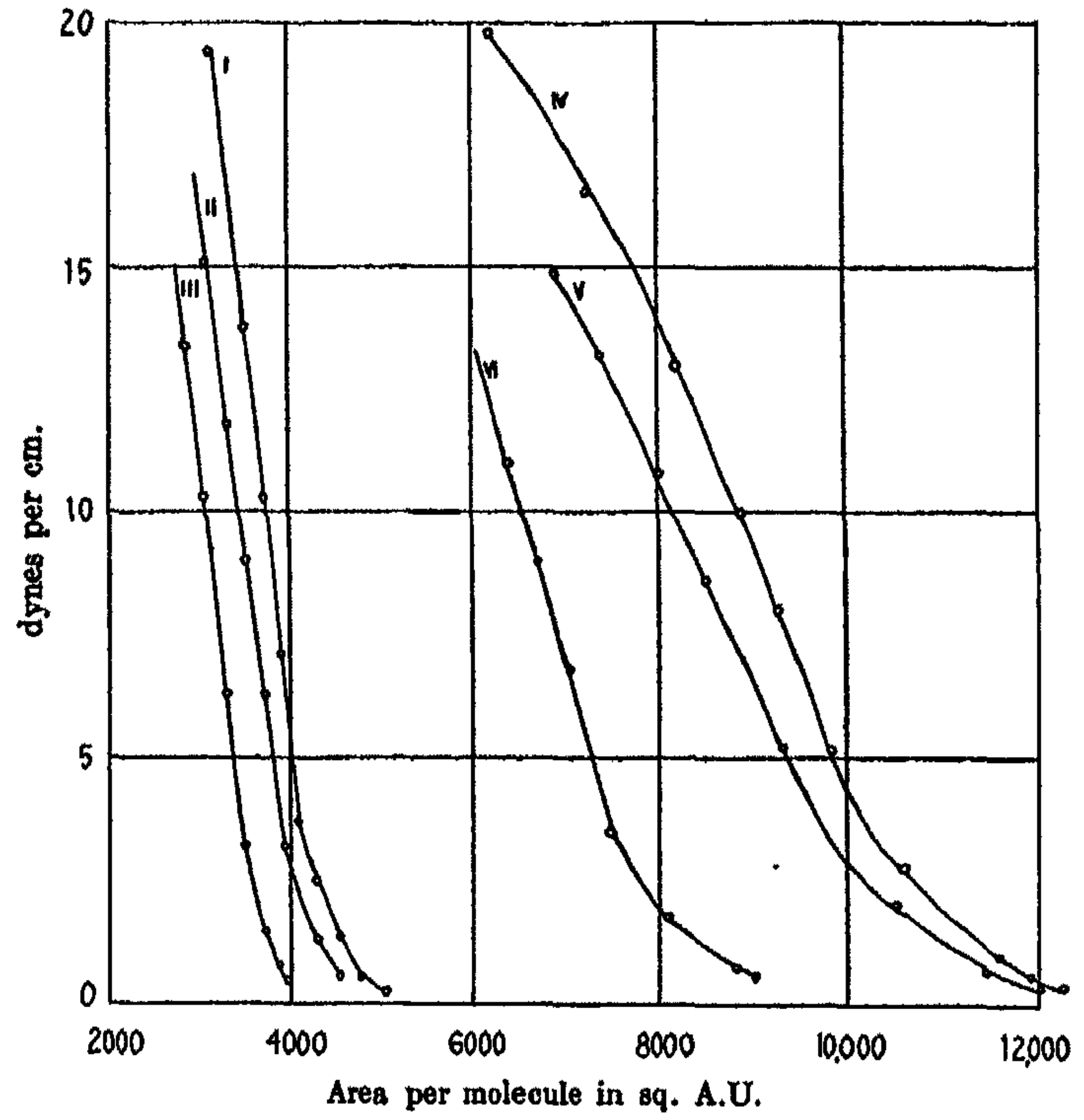

FIG. 1. Spreading of natural ovalbumin and serum albumin. Curve I, ovalbumin, pH 4.8, on $N/20$ acetate buffer, pH 4.8; curve II, ovalbumin, pH 4.4, on $N/20$ acetate buffer, pH 4.4; curve III, ovalbumin, pH 4.4, on $N/300$ acetate buffer, pH 4.4; curve IV, serum albumin, pH 4.8, on $N/20$ acetate buffer, pH 4.8; curve V, serum albumin, pH 4.4, on $N/20$ acetate buffer, pH 4.4; curve VI, serum albumin, pH 4.4, on $N/300$ acetate buffer, pH 4.4.

With serum albumin (curves IV to VI) very similar results were obtained; the velocity of spreading was somewhat less on the dilute acid buffer, and the curve refers to twelve minutes after the material was put on.

With the dark-ground illuminator, the films on the $N/20$ buffers were apparently homogeneous, and that on the dilute buffer slightly inhomogeneous; collapse occurred at 13 to 14 dynes in curve IV, at 11 to 12 dynes in curve V, and at 10 dynes in curve VI.

The films all became solid at about 3 dynes compression; this is the phenomenon described by Hughes and Rideal as "gelation" of the films.

The fully spread ovalbumin films tend to a limiting area of about 5000 sq. A.U. per molecule, or 0.88 sq. meter per milligram, in good agreement with Gorter's value of 0.9 sq. meter per milligram. This area is decidedly larger than the maximum obtained for crystallized egg albumin by Fossbinder and Lessig (5), 3750 sq. A.U. per molecule or 0.66 sq. meter per milligram. Svedberg has shown (17), however, that crystallized egg albumin contains a fraction of molecular weight 170,000, which cannot be removed even by repeated crystallization, but is precipitated on electro-

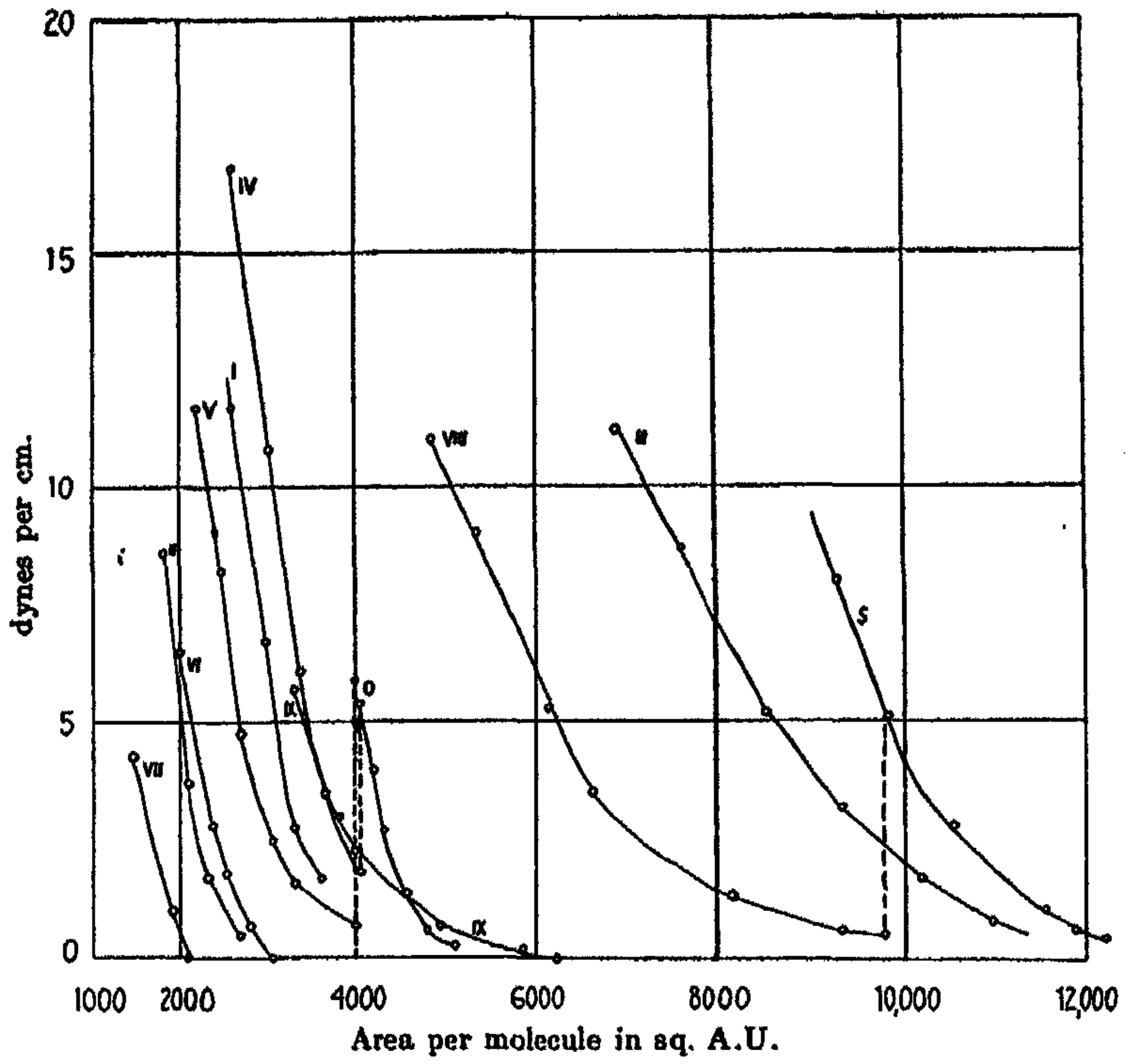

FIG. 2. Irradiation of proteins with ultra-violet light. Curve O, ovalbumin without irradiation; curve S, serum albumin without irradiation; curve I, ovalbumin, 15 minutes before spreading; curve II, ovalbumin, 70 minutes before spreading; curve III, serum albumin, 20 minutes before spreading; curve IV, ovalbumin, 3 minutes after spreading; curve V, ovalbumin, 6 minutes after spreading; curve VI, ovalbumin, 9 minutes after spreading; curve VII, ovalbumin, 20 minutes after spreading; curve VIII, serum albumin, 6 minutes after spreading; curve IX, serum albumin, 20 minutes after spreading.

dialysis. This would not have been present in the material used here, owing to the method of preparation. If it is assumed that the fraction of high molecular weight in crystallized egg albumin does not spread, while that of lower molecular weight spreads completely, then since Svedberg gives the average molecular weight of crystallized egg albumin as 43,000, it is easily calculated that Fossbinder and Lessig's results lead to an area per molecule for the fully spread constituent of lower molecular weight of 4950 sq. A.U., in excellent agreement with the present result and with Gorter's.

The limiting area per molecule for serum albumin is about 12,000 sq. A.U.; this value is larger than those given by Fossbinder and Lessig, but the films have been spread on solutions of very different pH.

The films give a nearly straight surface pressure-area curve above the pressure at which they become solid; the compressibility is about 70.5 sq. A.U. per dyne for egg albumin, or 1.41 per cent of the area at no compression; for serum albumin it is 250 sq. A.U. per dyne or 2.08 per cent. On decompressing the films once, there was a small amount of hysteresis, the area expanding to about 4 per cent less than before compression.

Serum albumin spreads to an area about 15 per cent larger, per gram, than ovalbumin, the area being 1.05 sq. meters per milligram.

Effects of denaturation

The dilute protein solutions (ca. 0.02 per cent) were adjusted to pH 4.4 by dilute hydrochloric acid, and heated in a quartz test tube for fifteen minutes at 100°C. The solutions were perfectly transparent after this treatment. Isoelectric solutions (pH 4.8) of the same concentration turned opaque when heated in this way; and on adding the same quantity of sulfosalicylic acid to the denatured solution and to the untreated solution, the same opacity was obtained.

On attempting to spread the heat-denatured solutions on $N/20$ or $N/300$ buffer, pH 4.4, no spreading could be obtained. No surface pressure greater than 0.3 dyne could be obtained until the area was diminished to less than one-eightieth of that at which this pressure was obtained with the natural egg albumin. The ultramicroscope showed large numbers of aggregates of different size and shape floating on the surface. Time did not promote spreading; even after twenty minutes no appreciable spreading had occurred. Incomplete denaturation, by heating for two or four minutes only, diminished the extent of spreading, but not so much as the longer heating. The spreading of both egg and serum albumin was prevented by denaturing in this way.

Denaturation by ultra-violet light was studied by irradiating the solutions before spreading in a rectangular quartz vessel of 3 mm. inside thickness at a distance of 12 cm. from a K.B.B. atmospheric quartz mercury vapor lamp, 220 v., 2 amps. The pH was adjusted to 4.4. The spreading power is diminished but not entirely destroyed. Curves I and II of figure 2, were taken on spreading the solutions irradiated for 15 and 70 minutes, respectively; after 70 minutes, the solution spread to about half the area of the natural egg albumin. Twenty minutes irradiation of the serum albumin solution diminished the area of spreading only by about 10 per cent. Inhomogeneity could be detected with the dark-ground illumination on all the films spread from irradiated solutions.

The effect of ultra-violet light was also studied by irradiating the films of natural protein after spreading. The same mercury vapor lamp was used, horizontally, about 12 cm. above the surface of the water. In order to diminish the amount of contamination accidentally reaching the surface during irradiation, the films were compressed to 5 dynes. Preliminary experiments showed that, qualitatively, the effect of irradiation was the same in the uncompressed as in the compressed state. The irradiation did not raise the temperature of the interior of the solution more than 2°C.; the rise in temperature of the surface was probably not much more than this.

Curves IV to VII show the effect of increasing times of irradiation for egg albumin; curves VIII and IX, for serum albumin. During irradiation the surface pressure fell to almost nothing. The films were seen to be very homogeneous after irradiation. Irradiation on solutions of pH 4.8 and 4.4 gave similar results.

The effect seemed to be rather greater with serum albumin than with egg albumin, the areas after irradiation for 20 minutes in the spread films being about 50 per cent of the original with egg albumin and 33 per cent with serum albumin.

DISCUSSION

It is evident that the different processes known as denaturation are not all the same. The spreading of the molecules out along a surface is almost certainly an unfolding of the molecule so as to be one amino acid thick in the fully spread form, the water-attracting groups, i.e., the —CO—NH— and any free COO^- or NH_3^+ groups, being in contact with the water and the hydrocarbon chains usually oriented away from the water. The protein does not easily dissolve in the water, once it has been spread or unfolded at a surface. According to du Nouy (4), a protein in aqueous solution accumulates at the surfaces until all the protein is at the surface and none remains in the interior. Thus the unfolding of the protein molecule during its transition from interior to surface appears to be a process which occurs spontaneously, whereas the reverse process, the coiling of the unfolded molecule and its passage back from surface to interior, does not occur easily. It is probable that, when in solution in water, the protein molecules are coiled up so that the hydrocarbon chains are buried in the interior, and the surface is covered by the water-attracting groups. Thus Ramsden's "denaturation" by shaking and adsorption at an air-water surface is probably an unfolding of the molecule.

By the action of heat, however, the transition from the coiled to the unfolded structure is practically prevented. This could arise either through an increase in the forces which bind the coiled molecule together, or by an increasing aggregation, i.e., several coiled molecules uniting. The first mechanism seems to agree best with electrochemical experience. According to Pauli (13, 14), the primary process of heat denaturation consists of an interaction between the free amino and carboxyl groups, leading to an amide-like linkage between these groups and consequently to the loss of the "zwitterion" structure. This would tend to diminish spreading for two reasons: first, because these groups would have less attraction for the water than the separate COO^- and NH_3^+ groups; second, because they would tend to bind the molecule together in the coiled-up form. Astbury (3) brings evidence that the side chain linkages between peptide chains in proteins are strengthened by denaturation; this would probably hinder the unfolding of the molecules.

Haurowitz (9) considered that denaturation consists of a breaking of the intramolecular attraction between positive and negative groups, with a loosening of the molecule by stretching the long peptide chains. The fact that the natural protein spread very much better than the denatured indicates that the internal structure of the protein molecule in solution is strengthened, not weakened, by denaturation.

The effect of irradiation seems to be slightly different from that of heat. The amount of irradiation given to the protein solutions (pH 4.4) in the quartz cell before spreading was sufficient to cause complete precipitation of solutions at the isoelectric point, yet, though the spreading was diminished, it was not entirely destroyed. It is interesting that irradiation of the spread films, i.e., of the completely uncoiled form of the molecules, causes some degree of coiling, evident through the collapse of the film. This may be because it is mainly the free COO^- and NH_3^+ groups which anchor the spread film to the surface and keep it spread. Further work has to be done for a complete elucidation of this effect.

The slight difference between the spreading of serum and egg albumin may be due to the greater number of water-attractive groups of serum albumin. Serum albumin, spreading to a 15 per cent larger area per gram than egg albumin, has about one hundred and three carboxyl and one hundred and twelve amino groups per molecule; egg albumin, thirty and thirty-six respectively (Pauli and Valko (13)). Also a comparatively small internal cohesion of the serum albumin molecule, as concluded from colloid chemical experience by Pauli (12, 13), might account for the greater ease of its unfolding.

SUMMARY

Egg albumin and serum albumin have been spread on aqueous buffer solutions at the isoelectric point and at pH 4.4. Serum albumin spreads to an about 15 per cent greater area, per gram, than egg albumin. The spreading is completely destroyed by previous denaturation of the solutions by heat, and partially destroyed by denaturation by irradiation; a fully spread film can be caused to collapse to a considerable extent by irradiation.

The bearing of these experiments on theories of denaturation is discussed. It is probable that denaturation both diminishes the attraction of the protein for water through the combination, within the molecule, of carboxyl and amino groups previously free; also the same combination probably tightens the internal structure of the protein molecule, making it more difficult to uncoil on the surface.

My heartiest thanks are due to Professor F. G. Donnan, F. R. S., for his generous hospitality and his interest and to Dr. N. K. Adam, F. R. S., for his very helpful criticism and advice.

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THE FORMATION OF LIESEGANG RINGS IN THE PRESENCE OF PRECIPITATES

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Much work has been done on the formation of periodic bands of precipitates of different substances in the presence of gels. It has been almost generally believed that gels are almost essential for such types of periodic precipitation, though the number of instances in which the formation of Liesegang rings is discernible even in the absence of gels has increased (4, 5, 6, 8) comparatively recently. It is the object of the present paper to report the formation of such periodic bands of precipitates, not in a gel but in the presence of certain other precipitates where the specific characteristics of gel-structure are absent and where the probability of the coexistence of sol and the precipitate of the same substance (1, 2, 3, 4), if not absent, would appear to play no prominent function. It is very difficult to explain the occurrence of such bands in the presence of these insoluble substances unless adequate experimental data are available, but it may be suggested that selective adsorption of some of the ionic species in the system by these precipitates may in all probability play a very important rôle in such a phenomenon.

EXPERIMENTAL

The calcium sulfate and the barium sulfate were powdered to a very fine state of subdivision. Into thoroughly cleaned test tubes known volumes of a solution of ferric chloride of known concentration were introduced and then 10 g. of the extremely fine powder of each of the precipitates was allowed to drop in. A further known volume of the solution of ferric chloride was next introduced into each of the test tubes. The exact volume of the solution to be added was found by trial, and such a volume was selected that when the 10 g. of powdered precipitate was placed in the solution, the mass of the precipitate would completely absorb the solution on standing. The precipitates in contact with the solution were allowed to stand for eight hours. The contents of the tubes were next centrifuged and kept overnight. It was then found that the mass of precipitate, after absorbing the solution completely, appeared to present some resemblance to a thickly set uniform gel of agar. It was, however, not transparent.

A known volume of the solution of potassium ferrocyanide of known concentration was then carefully added to the precipitate without causing any disturbance of the solid particles. The test tubes with their contents were then allowed to stand for days, and the changes were noted each day until the Prussian blue precipitate had reached the bottom of each tube.

As it has been brought out by the experiments of Lloyd and Moravek (7) that carrying out the reaction in a small space exerts a marked favorable influence on the formation of Liesegang rings, experiments were also performed in much the same way in tubes of narrow bore, having internal diameters of 0.5 and 0.25 cm. However, these experiments yielded no positive results.

It may be mentioned that 8 cc. of the ferric chloride solution was necessary for 10 g. of the calcium sulfate precipitate for complete absorption by the said precipitate; 4 cc. of the ferric chloride was added before and another 4 cc. after the introduction of the calcium sulfate into the test tube. In the case of barium sulfate, however, 6 cc. of the solution was necessary, of which 3 cc. was added before and 3 cc. after the introduction of the sulfate precipitate. The purpose in introducing some of the solution before the introduction of the precipitate was to minimize the possibility of the air bubbles being kept enclosed in the bodies of the solid precipitates. Care was always taken to ensure that no air bubbles could have a chance to remain thus enclosed.

Fig. 1. Liesegang rings obtained by using 10 g. of calcium sulfate, 8 cc. of 0.385 N ferric chloride, and 6 cc. of 1.15 N potassium ferrocyanide

RESULTS WITH CALCIUM SULFATE

The number of rings formed increased with the dilution of the ferric chloride solution, and the distance between the rings decreased as the concentration of the ferric chloride was increased. The concentration of the potassium ferrocyanide appeared to have no favorable influence on the formation of the rings (1.15 N solution was used in the experiments).

The first ring appeared after about forty hours; then another ring came in the course of a day.

The distance between these two rings was quite considerable. The thickness of the first ring was, however, greater than that of the second. The distance of the first ring from the surface of separation of the solid and the solution was about one-fourth the distance between the first and the second rings at favorable concentrations of ferric chloride.

After the appearance of the second ring the blue color proceeded downward, uniform in tint but weaker in shade. The progress continued for several days and then ceased. This position was maintained for about three days. At the end of that time there appeared a distinctly blue ring, much deeper in shade than the blue color which had just ceased moving, and uniformly thick, its lower edge coinciding with the edge of the blue tint which had ceased to move downward. The blue tint above the ring became lighter and lighter in shade; after a day a ring appeared above it making the intervening space colorless. Another ring appeared again above this second ring in the course of a day, and the intervening space again lost its color. In this way, a ring appeared every day until there were five successive rings. After the formation of the fifth ring in the series, no fresh rings appeared. The rings were stable and distinct for about a week, after which they began losing their distinctness. As soon as the rings began losing their distinctness, the blue color started travelling down from the lowermost ring, slowly and gradually, until it came to the bottom. This occurred in the course of another week. Even when the blue color had reached the bottom, the rings previously formed, though indistinct, were yet discernible and about a month more was required for them to lose their identity completely. It may be mentioned that the distance between the rings in the above series increased only slightly in the order of the sequence of appearance of the rings. It is also of interest to note that no periodicity in the precipitation was observed in the region below the above series of rings, through which the blue tint ultimately travelled down.

At very high concentrations of ferric chloride (above 1.5 *N*), two semicircular highly colored patches appeared just below the surface of separation of the liquid and the solid. No ring, however, was found to appear, even after keeping the system for about a week, but at the end of the week several periodic bands were observed in these highly colored spots in the form of arcs of circles.

At moderately high concentrations of ferric chloride (0.75–1.5 *N*), however, these two deeply colored patches also appeared but with increased areas, and a highly colored ring appeared 8 mm. below these two areas. In the course of about three days another ring appeared just above; this was succeeded in its upper region by three fully developed rings and three partly developed rings at equal distances apart, the last partly developed ring touching the lower borders of these spots. In the meantime, there appeared several periodic bands in the form of arcs of circles in each of the highly colored semicircular patches. The most favorable concentrations of ferric chloride for ring formation are in the range 0.3–0.6 *N*.

RESULTS WITH BARIUM SULFATE

In the case of barium sulfate, however, it was somewhat difficult to obtain the periodic bands. It appeared to be difficult as well to study the probability of the formation of the rings with reference to the concentration of the ferric chloride, the concentration of the potassium ferrocyanide having apparently no influence on the ring formation. In most concentrations no rings were obtained; if formed at all at some concentration, they were comparatively indistinct. The range of concentrations in which the ring formation was favored was also very narrow (0.15–0.25 *N*). It was only in this small range of concentration of the ferric chloride that comparatively distinct rings, though lighter in shade than those obtained in the body of the calcium sulfate precipitate, were obtained. In 0.2 *N* ferric chloride the most distinct rings were obtained, and three rings were discernible. The distances between the rings were approximately equal, but the thickness of the first ring was greater than that of the second and that of the second was greater than that of the third. The thickness of the rings was, however, considerably greater than that of those obtained in the body of calcium sulfate; the rate of travel of the blue color through the precipitate was also comparatively rapid.

SUMMARY

The formation of Liesegang rings of Prussian blue in the bodies of calcium sulfate and barium sulfate, moistened with ferric chloride solution, has been recorded.

The influence of the concentration of the ferric chloride on the characteristics of the rings has been studied.

My best thanks are due to Dr. P. Neogi for giving me facilities for carrying on this piece of work.

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NOTE ON THERMODYNAMIC EQUILIBRIUM IN THE GRAVITATIONAL FIELD

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I. THE FUNDAMENTAL GIBBSIAN EQUATIONS FOR THE CHARACTERISTIC FUNCTIONS OF A SUBPHASE

In his excellent treatise, E. A. Guggenheim (1) has recently given an exact (non-relativistic) account of thermodynamic equilibrium in gravitational fields, starting from differential equations of Gibbsian type for the characteristic functions of an infinitely thin homogeneous layer of matter of given gravitational potential. Thus for the energy, E^{α}, of such a layer, α, he writes

$$\mathrm{d}E^{\alpha} = T^{\alpha}\mathrm{d}S^{\alpha} - P^{\alpha}\mathrm{d}V^{\alpha} + \sum_{i} (\mu_i^{\alpha} + \bar{M}_i\varphi^{\alpha})\, \mathrm{d}n_i^{\alpha} \tag{1}$$

where T^{α}, S^{α}, P^{α}, V^{α}, and φ^{α} denote respectively temperature, entropy, pressure, volume, and gravitational potential of the layer, n_i^{α} the number of moles of the i^{th} component in the layer, $\bar{M}_i$ the molecular weight of the i^{th} component, and μ_i^{α} a function which is assumed to be completely determined by P^{α}, T^{α}, n_i^{α}.

It seems worth pointing out, for reasons stated below, that equation 1 can be generalized so as to take account of the fact that the energy of the layer in question can be varied without absorption of heat ($T^{\alpha}\mathrm{d}S^{\alpha}$), performance of volume work ($-P^{\alpha}\mathrm{d}V^{\alpha}$), or changes of composition ($(\mu_i^{\alpha} + \bar{M}_i\varphi^{\alpha})\mathrm{d}n_i^{\alpha}$), merely by a change of gravitational potential φ^{α}, as for instance through a shift of level in the earth's field. The contribution to E^{α} of an infinitesimal change in φ^{α} at constant S^{α}, V^{α}, n_i^{α} is evidently $M^{\alpha}\mathrm{d}\varphi^{\alpha}$ where M^{α} is the mass of the layer.

Equation 1 is accordingly replaced by

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + M\mathrm{d}\varphi + \sum_{i} \tau_i \mathrm{d}n_i \tag{2.1}$$

where for simplicity the superscript α is omitted and the sum $\mu_i + \bar{M}_i\varphi$ denoted by τ_i. Of the variables E, S, V, n_i, φ all but one are independent, so that if the number of components is k, the number of independent differentials in equation 2.1 is $k + 3$. The corresponding equations for the other characteristic functions, i.e., the heat content H, the Gibbs free energy F, and the Helmholtz free energy A, are of course

$$\mathrm{d}H = VdP + Td S + M\mathrm{d}\varphi + \sum_i \tau_i \mathrm{d}n_i \tag{2.2}$$

$$\mathrm{d}F = -S\mathrm{d}T + V\mathrm{d}P + M\mathrm{d}\varphi + \sum_i \tau_i \mathrm{d}n_i \tag{2.3}$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + M\mathrm{d}\varphi + \sum_i \tau_i \mathrm{d}n_i \tag{2.4}$$

For convenience the thin layer to which these equations apply may be called a "subphase."

The new equations (2) are of interest because (i) they further illustrate the point clearly made by Guggenheim (ref. 1, p. 154) that "the gravitational potential difference φ^α between two [sub-]phases, in contrast to the electric potential difference ψ^α is thermodynamically determinate, owing to the fact that its value is independent of the presence and nature of the phase there;" (ii) they show that the statement (ref. 1, p. 154) that "in all thermodynamic formulae the quantity φ^α occurs only in combinations of the form $(\mu_i^\alpha + M_i\varphi^\alpha)$" is generally true *only* for changes at constant φ^α; (iii) they are of the same form as the general thermodynamic equations for external electric and magnetic fields (2) and thus serve to emphasize certain important analogies. Equations 2 furthermore yield deductions of the laws of hydrostatic equilibrium and of sedimentation equilibrium which to the author seem more concise than previous ones and are accordingly given below. These deductions fall naturally into the stages indicated by the titles of the following paragraphs.

II. THERMAL AND CHEMICAL EQUILIBRIUM BETWEEN SUBPHASES

The general criteria for thermodynamic equilibrium in conjunction with the equations 2 lead in the usual manner to the familiar conditions

$$T^\alpha = T^\beta \tag{3}$$

$$\tau_i^\alpha = \tau_i^\beta \tag{4}$$

for thermal and chemical equilibrium, respectively, between any two subphases α and β.

III. THE GIBBS-DUHEM EQUATION FOR A SUBPHASE

The energy of a subphase like that of a bulk phase (in the absence of gravity) is clearly homogeneous of the first order in the capacity factors S, V, n_i. By Euler's theorem equation 2.1 therefore yields

$$E = TS - PV + \sum_i \tau_i n_i \tag{5}$$

which, on differentiation and comparison with equation 2.1 in the usual manner, gives

$$SdT - VdP - Md\varphi + \sum n_i d\tau_i = 0 \tag{6}$$

the analogue of the Gibbs-Duhem equation for a bulk phase. For the treatment of hydrostatic and sedimentation equilibrium it is convenient to write equation 6 in the form

$$dP = sdT - \rho d\varphi + \sum_i c_i d\tau_i \tag{7}$$

where s is the entropy per unit volume, c_i the volume concentration of the i^{th} component, and ρ the density of the subphase. Of the $k + 3$ intensive variables T, P, φ, τ_i in equations 6 and 7, any $k + 2$ are independent.

IV. HYDROSTATIC EQUILIBRIUM

If T, φ, τ_i are taken as the independent variables, it follows from equation 7 that for any subphase

$$\left(\frac{\partial P}{\partial \varphi}\right)_{T,\tau_i} = -\rho \tag{8}$$

Now by equations 3 and 4 all the (infinitely numerous) subphases of a fluid in thermal and chemical equilibrium have the same values of T and of the τ_i. But since any two adjacent subphases whatever differ infinitesimally in φ, it follows from equation 8 that any fluid in thermal and chemical equilibrium in a gravitational field is also in hydrostatic equilibrium, i.e., that

$$^*dP = -\rho d\varphi \tag{9}$$

where the operator d refers to the difference between two adjacent subphases. Any equation such as equation 9, in which d has this significance, is conveniently prefixed by an asterisk, to distinguish it from equations such as 1, 2, 6, 7 in which d refers to an infinitesimal change within a single subphase.

V. ACTIVITY COEFFICIENTS IN A SUBPHASE

For compactness in the expression for sedimentation equilibrium to be derived below it is expedient to introduce activity coefficients defined in a manner analogous to that for a bulk phase (ref. 1, p. 115), namely

$$\mu_i \equiv \mu_i^0(T, P) + RT \log N_i f_i \tag{10}$$

where μ_i^0 is a function only of T and P, N_i is the mole fraction of the i^{th} component in the subphase, and f_i is its activity coefficient, that is, a function of T, P, n_i so chosen as to be unity at infinite dilution. This definition evidently implies that μ_i is completely determined independently of φ by T, P, n_i alone, a fact readily proved from the equations 2, which herein reveal a decided advantage over the equations of type 1. From equation 2.3 it follows that

$$\left(\frac{\partial \tau_i}{\partial \varphi}\right)_{T,P,n_i} = \left(\frac{\partial M}{\partial n_i}\right)_{T,P,n'_i,\varphi} \qquad (11)$$

where the subscript n'_i indicates the constancy of all the n_i except a particular one with respect to which the differentiation is carried out. The introduction of the relations

$$\tau_i \equiv \mu_i + \bar{M}_i\varphi \qquad (12)$$

$$M = \sum_i n_i\bar{M}_i \qquad (13)$$

into equation 11 gives

$$\left(\frac{\partial \mu_i}{\partial \varphi}\right)_{T,P,n_i} = 0 \qquad (14)$$

$$\mu_i = \mu_i(T, P, n_i) \qquad (15)$$

VI. PARTIAL MOLAR VOLUMES AND PARTIAL MOLAR ENTROPIES IN A SUBPHASE

Besides the activity coefficients f_i it is expedient to introduce the partial molar volumes $\bar{V}_i$ and the partial molar entropies $\bar{S}_i$. That these quantities as well as V and S themselves are functions of T, P, n_i alone follows from equation 2.3 by proofs similar to the one given above for μ_i. Particularly useful for compact derivation of the law of sedimentation equilibrium are two equations readily deduced from equations 2.3, 12, and 10, namely

$$\left(\frac{\partial \mu_i^0}{\partial P}\right)_T = \bar{V}_i^0 \qquad (16)$$

$$\left(\frac{\partial \mu_i^0}{\partial T}\right)_P = -\bar{S}_i^0 \qquad (17)$$

in which $\bar{V}_i^0$ and $\bar{S}_i^0$ denote the values of $\bar{V}_i$ and $\bar{S}_i$ at infinite dilution.

VII. SEDIMENTATION EQUILIBRIUM

From equation 12 it follows that for any component of a subphase, say the j^{th},

$$d\mu_j + \bar{M}_j d\varphi - d\tau_j = 0 \qquad (18)$$

Differentiation of equation 10 and substitution of the result into equation 18 gives

$$\left(\frac{\partial \mu_j^0}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial \mu_j^0}{\partial P}\right)_T \mathrm{d}P + RT\mathrm{d} \log N_j f_j + R \log N_j f_j \,\mathrm{d}T \\ + \bar{M}_j \mathrm{d}\varphi - \mathrm{d}\tau_j = 0 \tag{19}$$

which, on introduction of equations 16 and 17 and elimination of dP by means of equation 7, becomes

$$RT\mathrm{d} \log N_j f_j - (\rho \bar{V}_j^0 - \bar{M}_j)\, \mathrm{d}\varphi + (s\bar{V}_j^0 - \bar{S}_j^0 + R \log N_j f_j)\, \mathrm{d}T \\ + \bar{V}_j^0 \sum_i c_i \mathrm{d}\tau_i - \mathrm{d}\tau_j = 0 \tag{20}$$

If T, φ, τ_i are taken to be the independent variables it follows that in any *subphase*

$$RT\left(\frac{\partial \log N_j f_j}{\partial \varphi}\right)_{T,\tau_i} = \rho \bar{V}_j^0 - \bar{M}_j \tag{21}$$

for each component. This equation in conjunction with equations 3 and 4 shows that in any *solution in thermal and chemical equilibrium in a gravitational field*

$$^{*}RT\mathrm{d} \log N_j f_j = (\rho \bar{V}_j^0 - \bar{M}_j)\, \mathrm{d}\varphi \tag{22}$$

for each component. Equation 22 is the exact law of sedimentation equilibrium in a form more compact than any hitherto given. It is readily shown to be identical with the expression given by Guggenheim (ref. 1, p. 157).

The integration of the sedimentation equation, neglecting compressibility, has been carried out by Guggenheim (ref. 1, pp. 157–8) for the binary ideal solution of any concentration and for the "extremely dilute" ideal solution of any number of components. The result for a third simple case of physical interest, that of the "extremely dilute" non-ideal solution of any number of components, seems worth giving; it is

$$\log \frac{N_j^\alpha f_j^\alpha}{N_j^\beta f_j^\beta} = \log \frac{c_j^\alpha f_j^\alpha}{c_j^\beta f_j^\beta} = (\rho_0 \bar{V}_j^0 - \bar{M}_j)\, \frac{\varphi^\alpha - \varphi^\beta}{RT} \tag{23}$$

where ρ_0 is the density of the pure solvent.

VIII. SUMMARY

The fundamental equations for the thermodynamics of the gravitational field are written in a form more general than hitherto by the inclusion of the gravitational potential φ as an independent variable. The theoretical interest of the resulting new equations is briefly pointed out, and their practical usefulness shown by deducing from them the known laws of hydrostatic equilibrium and sedimentation equilibrium. The latter law is expressed in a new and compact form involving the activity coefficient.

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A COMPARATIVE METHOD FOR MEASURING AQUEOUS VAPOR AND DISSOCIATION PRESSURES, WITH SOME OF ITS APPLICATIONS[1]

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The method here described is a comparative one because the aqueous pressure over an aqueous sulfuric acid solution, whose concentration can later be found, becomes equal at the same temperature to the aqueous pressure of the system under investigation. Since the variation of aqueous pressure with temperature of the two systems thus under comparison is, fortunately, very similar, refined temperature control is not a necessity. Measurements may therefore be made with ease up to temperatures well over 100°C., at which close control of temperature over lengthy periods has proved difficult to most workers. It is in part due to this difficulty that records of measurements of dissociation pressures of salt hydrate systems are scanty as well as notoriously discordant for temperatures much above room temperature, and we believe that this situation can be remedied by use of the method here described. It is essential to realize, however, that in measurements of dissociation pressures, there enters at the lower temperatures another little understood source of error which must be avoided, especially in dealing with systems of lower hydrates which of necessity exhibit very large surface areas when prepared by efflorescence from higher hydrates. The errors in question have been attributed to adsorbed water (23) and are here further discussed in the light of experimental results which we believe are little vitiated by the better recognized sources of error.

We shall show below the application of our procedure to the measurement of the aqueous pressures of saturated solutions and to the dissociation pressures of salt hydrate systems.

COMMENTS UPON CERTAIN OTHER METHODS

The first three methods mentioned below, because absolute rather than relative or comparative, require accurate temperature control, which is the more difficult the higher the temperature.

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[1] From a thesis presented by Edward M. Collins to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1933.

(*1*). The Bremer-Frowein tensimeter and its modifications (12, 34, 22, 6) are difficult to free from permanent gases, which may be but slowly released from solid phases (22).

(*2*). The isoteniscope (37) has the advantage that it can be freed from permanent gases by repeated trial until constant results are obtained, and thus it has been used successfully in many cases in which equilibrium is reached quickly (10).

(*3*). The gas current saturation method, although often successfully employed (22, 1, 2, 3, 35, 29), is cumbrous, requires much material, and is difficult in cases of slow equilibrium (1). It is not open to the objection suggested by Partington (28, 22).

(*4*). Those indirect methods which depend on equilibration with water through the liquid phase of salt hydrate systems in contact with this water dissolved in such liquids as ether (19), ethyl alcohol (11), isoamyl alcohol (27), nitrobenzene (32, 36), benzene or chloroform (23) are not as rapid as had been hoped, demand insolubility of the salts in the experimental liquid, and are obviously less suitable for higher temperatures.

(*5*). Lastly may be mentioned that indirect method which depends upon ascertaining by trial the concentration of an excess of aqueous sulfuric acid from or to which the system under investigation neither gains nor loses water through the vapor phase (25, 43, 21, 44). The method is commonly operated in the presence of air and is time-consuming, while the equilibrium concentration of acid cannot safely be judged by the rate of approach from either side; but refined temperature control has indeed proved unnecessary (43, 21).

OUTLINE OF METHOD HERE ADOPTED

The principle of our method is the same as of the method last mentioned, namely equilibration through the vapor phase with aqueous sulfuric acid. We allow the acid, however, automatically to alter its own concentration until its aqueous pressure matches that of the material under investigation, which, in the present work, is either a salt hydrate pair or a saturated solution. The acid, contained in an elongated weighing tube, which can be stoppered by the device of Richards (30), is stirred by mechanical rocking through about 20° of arc. In order to lessen the weight of water to be transferred in the process of equilibration, we use only about 0.2 g. of acid of known concentration, accurately weighed out. We furnish an abundant supply of the material that must govern the final pressure by using quantities of 10 to 20 g. We accelerate the transfer of water by removal of other gases. This is simply achieved by precooling, exhausting and sealing off an ordinary 2 x 15 cm. test tube which contains both the material and the acid weighing tube. Since our apparatus is sealed, we are no longer limited to pressures below one atmosphere. Because the essential portion of the apparatus is thus contained within a relatively small tube, we are able to run four determinations simultaneously in eight tubes placed in one cradle, each substance utilizing two test tubes, one with acid more, the other with acid less concentrated than the expected equilibrium concentration. Uniformity of temperature throughout each tube is ensured, especially above 50°C., by inclosing each in a short length of iron or copper pipe with capped ends. The desired temperature is maintained with sufficient steadiness in an ordinary Freas constant-temperature oven of one cubic foot capacity, the air of which is stirred by a fan driven by the same motor that rocks the cradle. In the normal case, we run the experiments overnight for convenience, and normally find in the morning that equilibrium has been reached from both sides. The minimum time necessary varies with circumstances from a couple of hours or less in simple cases to many days in difficult cases.

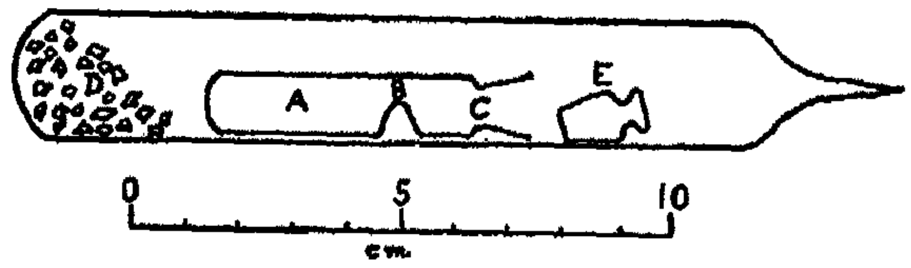

Fig. 1. Weighing tube within sealed test tube

EXPERIMENTAL DETAILS

Figure 1 shows the acid-containing weighing tube ABC confined within the same sealed test tube as the substance D. Tube ABC may be kept in position by means, for example, of a tuft of steel wool wedged between it and the test tube. The acid itself is present only in portion A which is separated from the mouth of the tube by the barrier B, formed by indenting the Pyrex glass while heated at this point. The ground glass stopper E is shown ready in position to be dropped home on erecting the tube. This process of stoppering is carried out at the temperature of the oven. After stoppering the acid tube, air is immediately admitted by breaking the sealed tip of the containing test tube, the apparatus is allowed to cool and finally cut open to release the acid tube for weighing. The final concentration of the acid is found by comparison of its final weight with its original weight and known concentration. A small correction due to the weight of the water vapor stoppered within the weighing tube is applied when necessary at higher temperatures. The dimensions of the apparatus are made obvious by the scale of centimeters on the diagram. Prior to evacuation, the test tube with its contents is cooled in a freezing mixture to minimize loss of water during evacuation, which may be carried by a

Hyvac pump below 0.2 mm. of mercury as measured by a simple MacLeod gauge.

When the substance D was a pair of salt hydrates, precaution was taken to effloresce the higher hydrate about halfway towards the composition of the lower hydrate so as to secure as large a number of active growth spots as possible. This precaution is well worth while, since Carpenter and Jette (6), who only "slightly effloresced" their higher hydrates, required much longer to reach equilibrium values than did Menzies (22) under similar conditions. The grain size of the hydrates used was not uniform but approximated 15 mesh.

When the vapor pressure of saturated solutions was desired, the portion D contained initially the highest hydrate moistened with its saturated solution. The attainment of identical final acid concentrations starting from stronger and weaker acid solutions respectively in a pair of tubes containing the same substance was in itself sufficient evidence that equilibrium between solid, solution, and vapor had been established.

Experiment showed that the rate of loss or gain of water from or by a salt hydrate pair was always, under our conditions, a slower process overall than the rate of transfer of water to or from the stirred acid. The active surface of salts used, therefore, governed the speed of the process of equilibration. Adequate stirring of the acid was secured by mechanically rocking the tubes about fifteen times per minute by means of an eccentric device upon a reducing gear.

CONTROL OF TEMPERATURE

In respect to the smallness of angle with which the temperature-pressure curves of other water vapor-yielding systems cut the curve of an aqueous sulfuric acid solution there are, naturally, differences according to the nature of these systems. But the angle is uniformly a small angle, and thus change of temperature influences the relative humidity of the two in a much smaller degree than it does their absolute aqueous pressures. Illustrating this in the case of dissociating cupric sulfate pentahydrate, the temperature error, at 25° and 50°C., sufficient to produce an error in the dissociation pressure measurement of 1 per cent is 0.2° and 0.2°C., respectively, for any absolute measurement and 2° and 1°C., respectively, for the present method. In general, for the systems studied by us at 50°C., the average temperature divergence to produce an error in pressure not greater than 1 per cent is 1° to 2°C.

By using a simple mechanical device to open momentarily the heating-current contact points of the automatic temperature regulator of our oven every half-minute, thus minimizing overshooting of temperature caused by adhering of these points, we were able to secure constancy of temperature at all temperatures used to within 0.5°C. The absolute measurement of temperature to 0.1°C. was made possible by comparisons from time to time with certificated standard thermometers after redetermination of their zero points. It will be understood that temperature precision is here of much less moment than it was in establishing the water pressures over aqueous sulfuric acid (8).

CHOICE OF SULFURIC ACID AS COMPARISON LIQUID

We contemplated and rejected the use of other substances. We learned (41) that sulfuric acid solutions not over 80 per cent lose by vaporization no sulfur below 220°C., while 89 per cent acid has a partial pressure ascribed to H_2SO_4 of only 0.5 mm. at 290°C. (40). We proved by gravimetric and volumetric methods that no measurable amount of either sulfate or acid hydrogen was lost from our weighing tubes at our highest experimental temperatures, either by evaporation or by action on the Pyrex glass. Furthermore, the Pyrex weighing tubes used for the acid remained constant in weight throughout.

Because we found that the values in the literature for the vapor pressures of aqueous sulfuric acid solutions at various temperatures were not concordant, these values were redetermined and have been reported elsewhere, as has also the preparation of the sulfuric acid solutions used in the present work (8).

PURITY OF SALTS USED

These salts were prepared by recrystallization of reagents of the highest purity (26). None contained more than 0.002 per cent of heavy metals as impurities. The possibly large influence of impurities upon the dissociation pressures of salt hydrates has seldom been recognized, and it is often forgotten; for example, 1 per cent of manganese sulfate in the mixed crystal lowers the dissociation pressure of cupric sulfate pentahydrate by 8.6 per cent at 20°C. (14). Our cupric sulfate was found to contain not more than 0.001 per cent of nitrates, chlorides, alkalis, or alkaline earths. The barium chloride and barium bromide contained not more than 0.02 per cent of strontium and calcium, and less than 0.1 per cent of the alkalis. The bromide contained less than 0.002 per cent of chloride. The strontium chloride and bromide were free from barium and calcium to the extent of 0.01 per cent, and from the alkalis to the extent of 0.05 per cent. The bromide contained less than 0.002 per cent chloride. The barium and strontium bromides were entirely free from bromate. The calcium chloride contained not over 0.002 per cent of barium and strontium, and less than 0.05 per cent of the alkalis.

ANOMALOUS RESULTS AND THEIR INTERPRETATION

In studies of the dissociation pressures of salt hydrates, it has been too often tacitly assumed that we are dealing from the start with nothing but two crystalline phases and one vapor phase. That this assumption is apparently allowable in certain cases was shown, for example, by Bolte (4), and in these cases he obtained in a reasonable time at constant temperature a pressure that was constant for all compositions of material intermediate in water content between those of the nearest two stoichiometrical hydrates. The two crystalline phases are presumably active in their control of aqueous pressure only at those points on a surface where they are in contact (18, 9),—the active spots. If merely vapor were present above such spots, all might be well from the phase rule standpoint, and early measurements yield the same pressure values as later ones. But if the surface is masked by a layer of non-vaporous water, the crystalline picture is blurred, and the simple phase rule prediction may be temporarily or more permanently unrealized according to the persistence of the layer. This layer has influence only at the active spots, but the mobility of its members may be much less than that of a two-dimensional gas, if one may use this method of expressing the energy of its binding. For this reason its influence upon the apparent dissociation pressure may be long-enduring. Whether its mode of attachment is physical or chemical is a purely academic question, as is the nature of attachment of a common ion from solution adsorbed preferentially upon a crystalline precipitate. One may recall in this connection the curious fact established by Menzies and Potter (24) in 1912 that dehydration of a hydrate may be more rapid and more thorough in the presence of increased pressures of water vapor. This has been confirmed recently in another instance by Topley and Smith (42).

Such considerations suggest an explanation of the difficulties and anomalous results encountered in the measurements of dissociation pressures, by Bolte (4, 5) for carnallite and for kainite; by Schumb (35), by Baxter and Cooper (1), and by Partington (28) for barium chloride dihydrate; by Carpenter and Jette (17) for nickel sulfate hexahydrate; and in many earlier cases. They may explain the high results of the last named workers for cupric sulfate trihydrate at 25° and 35°C., and likewise many other high results in the lower ranges of temperature to be found in the literature, as well as unnumbered disappointing results which, as suggested by Hackspill and Kieffer (13), have never been published because equivocal and discouraging to those who found them.

The question has already been discussed elsewhere by Menzies and Hitchcock (23), and we shall here briefly set down some of our conclusions substantiated by the present work. We find: (1) that the difficulty becomes less apparent the higher the temperature, as might be expected; (2) that material which has, for purposes of measurement, previously been in contact with a higher pressure of water vapor at a higher temperature is prone to yield too high pressure values for lower temperature measurements which immediately succeed them; (3) that, in certain cases, a genuine equilibrium pressure appears to present itself in experiments of customary duration, which falls in value only slowly with time. For example, samples of cupric sulfate trihydrate with the monohydrate, previously used at 100°C., reached "normal" pressure values only after five days in a subsequent experiment at 50°C., falling progressively in pressure at 50°C. from over 40 to 30.5 mm.; (4) that, with different hydrate pairs, the abnormality is the greater the lower the dissociation pressure for the same temperature; (5) that, if the material for investigation must be prepared by efflorescence, the anomaly is best avoided by preventing undue access of water vapor to the material prior to measurements.

TABLE 1

Dissociation pressures for the system $SrCl_2 \cdot 2H_2O \rightleftarrows SrCl_2 \cdot H_2O + H_2O$

t	INITIAL AND FINAL CONCENTRATION OF H_2SO_4	RELATIVE VAPOR PRESSURE	P
°C.	*per cent*		*mm.*
25	80 → 65.8	9.02	2.14
	65 → 66.3	8.45	2.01
50	66 → 64.0	13.2	12.2
	54 → 64.0	13.2	12.2
75	63 → 60.6	20.7	59.7
	55 → 60.7	20.5	59.3
90	59 → 58.4	25.9	136.1
	42 → 58.1	26.6	139.6
100	65 → 56.3	31.1	236.0
	45 → 56.2	31.3	237.7
110	61 → 54.4	36.1	388.2
	52 → 54.2	36.6	393.6
125	52 → 50.3	46.0	803.5
	43 → 50.5	45.6	794.3
130	50 → 49.4	48.2	975.0
	45 → 48.8	49.2	997.7

Hydrates which (in the presence of the next lower hydrate) have, if improperly treated, shown this anomaly in the present work are the following: cupric sulfate trihydrate and the dihydrates of barium chloride, barium bromide, and strontium chloride.

It is hoped to correlate these experimental findings in the light of better knowledge of crystal structure.

DETAILS OF ONE SERIES OF MEASUREMENTS

In table 1 we give details of our measurements upon a single system, namely $SrCl_2 \cdot 2H_2O \rightleftarrows SrCl_2 \cdot H_2O + H_2O$. In the second column are stated the initial and final concentrations of sulfuric acid in the two experi-

TABLE 2a

Aqueous vapor and dissociation pressures of cupric sulfate hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
$CuSO_4$, saturated solution							
Solid phase: $CuSO_4 \cdot 5H_2O$							
25	23.1	23.0	23.16 (38)	95	$550._8$	550.8	
		23.1				552.1	
30	30.9		30.93 (38)	95.88	$568._7$	(transition temperature)	
35	40.7						
40	53.3		53.39 (38)	Solid phase: $CuSO_4 \cdot 3H_2O$			
45	68.9			100	$656._1$	656.1	659.7 (38)
50	88.1					659.2	
55	$111._4$	111.4		105	$775._0$		
		111.4					
60	$140._3$		140.9 (38)	110	$911._4$	909.9 909.9	
65	$174._7$			115	106_7.	1067.	
70	$216._2$		215.5 (38)			1067.	
75	$265._5$			116.6	111_8.	(transition temperature)	
80	$323._3$		320.6 (38)				
85	$391._6$	390.8		Solid phase: $CuSO_4 \cdot H_2O$			
		391.7					
90	$466._5$	405.6	464.9 (38)	120	123_2.		
		466.7		125	143_9.	1435.	
						1439.	
$CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 \cdot 3H_2O + 2H_2O$							
25	7.8_2*	7.82	7.5 (44)	55	60.1_5		
		7.82	7.77 (22)	60	81.5_6		83.4 (6)
			7.78 (35)				80.8 ± 1.5 (23)
			7.8 (6)	65	$109._6$		
			7.92 (29)	70	$146._0$		
30	11.3_0	11.30		75	$192._9$		
		11.30		80	$252._8$		
35	16.1_4		16.3 (20)	85	$328._5$		
40	22.7_7			90	$424._6$*	424.6	432.7 (6)
45	31.8_1					424.6	
50	43.9_7	44.2	44.9 (6)	95	$544._5$		
		44.0		95.88	$568._7$	(transition temperature)	
$CuSO_4 \cdot 3H_2O \rightleftarrows CuSO_4 \cdot H_2O + 2H_2O$							
25	5.1_8*	5.09	5.6 (6)	70	$104._0$		
		5.20	4.7 (11)	75	$138._4$		
			4.5 (44)	80	$182._5$		182. (6)
30	7.5_6	7.60		85	$238._7$		
		7.60		90	$310._5$		
35	10.8_8	10.9	11.7 (6)	95	$400._7$		
		10.7	10.73 (20)	100	$513._8$	511.4	
40	15.5_0					516.8	
45	21.8_2		22.0 (6)	105	$654._0$		
50	30.4_0	30.3	30.3 (6)	110	$827._4$	837.5	
		30.8				831.8	
55	41.9_2			115	104_0.*	1023.	
60	57.2_7					1038.	
65	77.5_2		77.1 (6)	116.6	111_8.	(transition temperature)	

TABLE 2b

Aqueous vapor and dissociation pressures of barium chloride hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
$BaCl_2$, saturated solution							
Solid phase: $BaCl_2 \cdot 2H_2O$				100	$639._7$	639.7	
						639.7	
25	21.4		21.4 (39)	101.9	$684._1$	(transition temperature)	
30	28.6		28.6 (39)				
35	37.7		37.7 (39)				
40	49.3		49.3 (39)	Solid phase: $BaCl_2 \cdot H_2O$			
45	63.8		63.8 (39)				
50	81.9		81.7 (39)	105	$761._3$		
55	$103._9$			110	$901._6$	901.6	
60	$131._1$					901.6	
65	$163._5$			115	$106_4.$		
70	$202._8$			120	$129_3.$		
75	$249._5$	249.5		125	$146_0.$	1462.	
		248.9				1459.	
80	$304._4$			130	$169_0.$	1687.	
85	$369._7$					1694.	
90	$445._9$						
95	$535._8$	535.8					
		535.8					
$BaCl_2 \cdot 2H_2O \rightleftarrows BaCl_2 \cdot H_2O + H_2O$							
25	4.9_9	4.70	5.73 (1)	50	31.9_4	31.8	
		6.44	4.8 (11)			31.8	
			5.5 (35)	55	44.7_3		
			5.26 (28)	60	62.0_9		
			5.2 (12)	60.1			57.5 ± 1. (23)
			5.8 (44)	65	85.2_9		
30	7.4_1			70	$116._1$		
33.8	9.9_2		10.0 (15)	75	$156._7$*	156.7	
35	10.8_6*	10.0				156.7	
		11.8		80	$209._5$		
40	15.7_4		15.78 (1)	85	$277._7$		
45	22.5_4			90	$366._1$		
				95	$478._4$		
				100	$621._2$	620.9	
						620.9	
				101.9	$684._1$	(transition temperature)	
$BaCl_2 \cdot H_2O \rightleftarrows BaCl_2 + H_2O$							
50	1.3_1			90	30.5_8		
55	2.0_2			95	43.1_1		
60	3.0_9			100	60.3_9*	60.4	
61.5	3.5_5		3.1 (15)			58.6	
65	4.6_6			105	83.7_5		
66.5	5.2_8		5.4 (15)	110	$115._2$	115.3	
70	6.9_3					116.4	
74.5	9.8_3		10. (15)	115	$157._1$		
75	10.2_1			120	$212._7$		
80	14.8_5			125	$285._3$*	280.5	
85	21.3_7					285.8	
				130	$380._9$		

TABLE 2c

Aqueous vapor and dissociation pressures of barium bromide hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
$BaBr_2$, saturated solution							
Solid phase: $BaBr_2 \cdot 2H_2O$				80	$245._{6}$		
				85	$297._{9}$	299.9	
						299.2	
25	17.8	17.8		90	$358._{9}$	358.9	
		17.9				358.9	
30	23.6	23.7		95	$429._{0}$		
		23.6		100	$511._{7}$	507.0	
35	31.1	30.8				510.5	
		31.0		105	$605._{3}$	605.3	
40	40.3					605.3	
45	52.0	52.1		107.9	$664._{3}$	(transition temperature)	
		52.1					
50	66.3			Solid phase: $BaBr_2 \cdot H_2O$			
55	84.2						
60	$105._{8}$			110	$722._{6}$	722.8	
65	$132._{1}$	131.5				727.8	
		132.4		115	$856._{7}$		
70	$163._{6}$			120	$979._{6}$		
75	$201._{1}$			125	$115_{1}.$	1148.	
						1151.	
$BaBr_2 \cdot 2H_2O \rightleftarrows BaBr_2 \cdot H_2O + H_2O$							
25	3.7_{3}	2.71		70	85.9_{6}		
		4.58		75	$115._{9}$	116.9	
30	5.5_{3}					117.8	
35	8.1_{0}	7.82		80	$154._{3}$		
		9.02		85	$205._{1}$	205.1	
40	11.7_{3}					205.1	
43.3	14.5		10.0 (15)	90	$270._{0}$		
45	16.7_{3}			95	$352._{6}$		
50	23.7_{6}*	23.4		100	$457._{6}$	460.3	
		23.6				465.6	
55	33.2_{3}			105	$588._{8}$*	580.8	
60	46.0_{8}					582.1	
65	63.2_{1}	63.2		107.9	$664._{3}$	(transition temperature	
		63.8					
$BaBr_2 \cdot H_2O \rightleftarrows BaBr_2 + H_2O$							
50	0.7_{7}			95	$10._{7}$		
55	1.0_{8}			100	$13._{8}$		
60	1.4_{6}			105	$17._{7}$		
65	1.9_{9}			110	$22._{6}$*	22.5	
70	2.6_{9}			112.8	$25._{7}$		10.0 (15)
75	3.6_{1}			115	$28._{4}$		
80	4.7_{9}			120	$35._{3}$		
85	6.3_{0}			125	$44._{7}$*	44.7	
90	8.2_{5}			130	$55._{5}$		

TABLE 2d

Aqueous vapor and dissociation pressures of strontium chloride hydrate systems

t in °C.	P calcd.	P obsd.	P (found by others)	t in °C.	P calcd.	P obsd.	P (found by others)
$SrCl_2$, saturated solution							
Solid phase: $SrCl_2 \cdot 6H_2O$				70	$127._8$		
				75	$157._6$	157.8	
25	17.0					158.1	
30	22.0	22.0		80	$193._9$		
		22.0		85	$235._8$		
35	28.4	28.4		90	$285._4$		
		28.4		95	$344._3$		
40	36.1			100	$414._0$	414.0	
45	45.3					413.0	
50	56.2	56.2		105	$494._1$		
		56.4		110	$584._9$	583.4	
55	69.3					583.4	
60	84.5	84.7 84.5		115	$687._4$	688.7 688.7	
61.34	88.4	transition temp. detd. by Richards		120	$797._8$		
				125	$922._6$	918.3	
61.6	89.7	trans. temp. from intersection of curves				922.6	
				130	$104_7.$	1047.	
						1047.	
Solid phase: $SrCl_2 \cdot 2H_2O$							
65	$103._0$	103.0 103.0					
$SrCl_2 \cdot 6H_2O \rightleftarrows SrCl_2 \cdot 2H_2O + 4H_2O$							
25	8.3_5*	8.32	8.37 (2)	45	32.7_0		
		8.37	7.5 (12)	50	44.8_1	44.2	
			8.4 (5)			45.0	
			8.52 (35)	55	60.7_9		
			6.35 (15)	60	81.7_5*	82.0	
30	11.9_5					81.5	
35	16.8_9	16.8		61.34	88.3_7	Richards trans. temp.	
		17.1		61.6	89.7_4	trans. temp. from intersection of curves	
40	23.6_2						
$SrCl_2 \cdot 2H_2O \rightleftarrows SrCl_2 \cdot H_2O + H_2O$							
25	1.9_0	2.14		85	$105._9$		
		2.01		90	$139._5$	136.1	
30	2.8_2					139.6	
35	4.1_5		2.09 (15)	95	$182._4$		
40	5.9_9			100	$236._9$*	236.0	
45	8.5_5					237.7	
50	12.2_0*	12.2		105	$305._1$		
		12.2		110	$390._7$	388.2	
55	17.0_4					393.6	
60	23.6_5			115	$496._8$		
65	32.4_9			120	$628._3$		
70	44.2_4			125	$790._1$	803.5	
75	59.7_2	59.7				794.3	
		59.3		130	$987._2$	975.0	
						997.7	

TABLE 2e

Aqueous vapor and dissociation pressures of strontium bromide hydrate systems

t in °C.	P calcd.	P obsd.	P (found by others)	t in °C.	P calcd.	P obsd.	P (found by others)
$SrBr_2$, saturated solution							
Solid phase: $SrBr_2 \cdot 6H_2O$				84.5	$125._9$	125.9	
25	14.0	14.0				125.6	
		14.0		85	$105._7$		
				85.5	$123._3$	123.0	
30	17.9					123.6	
35	22.8	22.8		88.0	$118._3$	(transition temperature)	
		23.1					
40	28.8						
45	35.9			Solid phase: $SrBr_2 \cdot H_2O$			
50	44.5	44.6					
		44.4		90	$128._5$	128.5	
						130.3	
55	54.6			95	$155._6$	153.5	
60	66.6					155.6	
65	80.0	80.0		100	$187._1$	185.4	
		80.0				189.7	
				105	$224._3$		
70	94.7			110	$268._6$	266.1	
75	$111._3$	110.7				263.0	
		111.4		115	$319._0$		
80	$127._6$	127.9		120	$378._1$		
		127.4		125	$447._7$	453.9	
						450.8	
$SrBr_2 \cdot 6H_2O \rightleftarrows SrBr_2 \cdot H_2O + 5H_2O$							
25	2.1_5*	2.14		70	43.7_1		
		2.17					
30	3.1_5			75	58.2_3	56.6	
						58.8	
35	4.5_4	4.62		80	76.8_5		
		5.00					
40	6.4_7			85	$100._6$		
45	9.1_2			85.5	$103._5$*	103.8	
						103.8	
50	12.7_3	12.5	12.0 (15)	86.5	$109._1$	108.9	
		12.8				108.9	
55	17.5_4			88.0	$118._3$	(transition temperature)	
60	24.0_3						
65	32.5_5						

ments which were made at each temperature. One of these initial concentrations (tabulated above) was higher, the other (tabulated below) lower than the final concentration. In the third column are stated the relative aqueous pressures of acids of these final concentrations, taken from the work already published (8). In the fourth column under P is stated the actual aqueous pressure in millimeters of mercury at 0°C. and standard gravity.

TABLE 2f

Aqueous vapor and dissociation pressures of calcium chloride hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
$CaCl_2$, saturated solution							
Solid phase: $CaCl_2 \cdot 6H_2O$				Solid phase: $CaCl_2 \cdot 2H_2O$			
25	6.7_3	6.73	6.7 (33)	50	15.4	15.4	15.5 (33)
		6.92	6.97 (16)			15.4	15.5 (16)
29	7.1_0	7.24	6.9 (33)	55	19.8		
		7.02	7.33 (16)	60	25.3		
30	7.0_3	7.24	6.7 (33)	65	32.1		
		7.03	6.88 (16)	70	40.2		
30	(transition temperature)			75	51.3	49.4	54.0 (33)
Solid phase: $CaCl_2 \cdot 4\alpha H_2O$						49.4	51.3 (16)
				80	62.0		
				85	76.0		
35	8.6_5	8.65	8.6 (33)	90	92.9		
		9.02	8.63 (16)	95	$112._4$		
40	10.5	10.6	10.4 (33)	100	$135._3$	135.2	145. (33)
		10.4	10.53 (16)			135.2	138. (16)
45	11.7	11.7	11.7 (33)	105	$161._7$		
		11.7	11.9 (16)	110	$192._8$	192.8	
45.4	11.6_8	(transition temperature)				192.8	
				115	$226._6$		
				120	$265._3$		
				125	$309._7$	309.7	308. (16)
						309.7	
$CaCl_2 \cdot 4\alpha H_2O \rightleftarrows CaCl_2 \cdot 2H_2O + 2H_2O$							
25	2.5_6*	2.58	3.4 (33)	40	7.9_6	7.93	8.5 (33)
		2.56				8.19	
30	3.7_9	3.66	4.6 (33)	45	11.3_5*	11.3	11.0 (33)
		3.61				11.5	
35	5.5_3	5.47	6.3 (33)	45.4	11.6_8	(transition temperature)	
		5.66					

INTERPOLATION, SMOOTHING, AND TABULATION OF RESULTS

In order to obtain values for temperatures other than those observed and to smooth the observed values we used two methods (A and B).

Method A. For dissociation pressures of the salt hydrate systems an equation of the form

$$\log_{10} P = A - B/T \qquad (N)$$

fits the observations sufficiently well over our temperature ranges. In selecting constants for such equations, smaller weight was given to lower temperature observations which were less reliable for the reasons advanced above. The pressure values yielded for 5°C. intervals by the equations are shown under "*P* calcd." in the second columns of tables 2a to 2f, where the two starred pressures are those used in defining the straight line; these are followed in the third columns by our observed values, two for each temperature studied, in the order stated above; and in the fourth columns by values observed by other investigators. In table 3 are shown the values of the constants *A* and *B* of the above equation for the hydrates studied, and also the latent heat of vaporization, *L*, per mole of water as derived from these equations with the customary simplifying assumptions.

Method B. For saturated salt solutions it is not usually possible to represent the facts by an equation of the type *N*. This is at once apparent when one learns that the curves representing the experimental results plotted with log *P* as ordinate and $1/T$ as abscissa sometimes exhibit a maximum. This has been observed by three earlier workers (39, 10, 33) and was found by us in two cases, those of saturated solutions of $CaCl_2 \cdot 6H_2O$ and of $SrBr_2 \cdot 6H_2O$. When no maximum appears, the curvature nevertheless often changes more rapidly as a transition temperature is approached. The reason for this may be appreciated on recalling that the slope of such a curve is proportional to the work of removing liquid water from the solution and converting it to vapor. In the case of a saturated salt solution, removal of water necessitates concomitant deposition of solid salt, a process in which energy may enter the system, so that the work for vaporization, considered as a whole, may legitimately become zero or change sign.

TABLE 3

Constants for the type N equations and the latent heats of vaporization per mole of water

SYSTEM	*A*	*B*	*L* CALCULATED
$CuSO_4 \cdot 5$—$3H_2O$	10.5844	2888.93	13.2_9
$CuSO_4 \cdot 3$—$1H_2O$	10.6446	2960.15	13.5_6
$BaCl_2 \cdot 2$—$1H_2O$	11.1212	3107.24	14.2_9
$BaCl_2 \cdot 1$—$0H_2O$	12.5305	4010.70	18.4_5
$BaBr_2 \cdot 2$—$1H_2O$	10.9623	3097.51	14.1_7
$BaBr_2 \cdot 1$—$0H_2O$	9.2600	3029.47	13.9_4
$SrCl_2 \cdot 6$—$2H_2O$	10.3525	2811.35	12.9_3
$SrCl_2 \cdot 2$—$1H_2O$	10.7065	3108.73	14.3_0
$SrBr_2 \cdot 6$—$1H_2O$	10.3020	2971.73	13.6_7
$CaCl_2 \cdot 4\alpha$—$2H_2O$	10.6918	3065.43	14.1_0

For this reason we were obliged to use graphical interpolation and smoothing. Instead of interpolating directly from the smoothed curves of log P versus $1/T$ a more sensitive method was used. In this method the pressures at the observed temperatures are calculated on the temporary assumption that log P is a linear function of $1/T$. This assumption not being true, there was a difference between the logs of the observed pressures and those so calculated. These differences were plotted as a function of

TABLE 4

Heats of vaporization per gram of water from the saturated solutions

t in °C.	H_2O	$CuSO_4 \cdot 5H_2O$	$BaCl_2 \cdot 2H_2O$	$BaBr_2 \cdot 2H_2O$	$SrCl_2 \cdot 6H_2O$	$SrBr_2 \cdot 6H_2O$	$CaCl_2 \cdot 6H_2O$
25	583	557	583	552	521	486	249
28.5	581						0
30	580						−81
							$CaCl_2 \cdot 4\alpha H_2O$
35	577						449
45	572						246
							$CaCl_2 \cdot 2H_2O$
50	569	553	561	550	489	467	575
60	564				476		
					$SrCl_2 \cdot 2H_2O$		
65	561				545		
75	555	540	540	550	546	379	571
82.3	550					0	
87	548					−261	
						$SrBr_2 \cdot H_2O$	
90	546					529	
95	543	488					
		$CuSO_4 \cdot 3H_2O$					
100	540	507	540	521	540	548	570
			$BaCl_2 \cdot H_2O$				
105	537		543	506			
				$BaBr_2 \cdot H_2O$			
110	533			513			
115	530	502					
		$CuSO_4 \cdot H_2O$					
120	526	517					
125	523	515	522	515	453	614	515

the temperature, and by the aid of the smooth curve connecting them the pressures were calculated for intervals of 5°C.

To obtain for the saturated solutions approximate values for Q, the heat of vaporization per gram of water, we made use of the relation already discussed in the case of sulfuric acid (8). The values of Q at various temperatures as arrived at in this way are set down in table 4, which shows the changes which take place in Q in the vicinity of a transition point. Q for water is given for comparison.

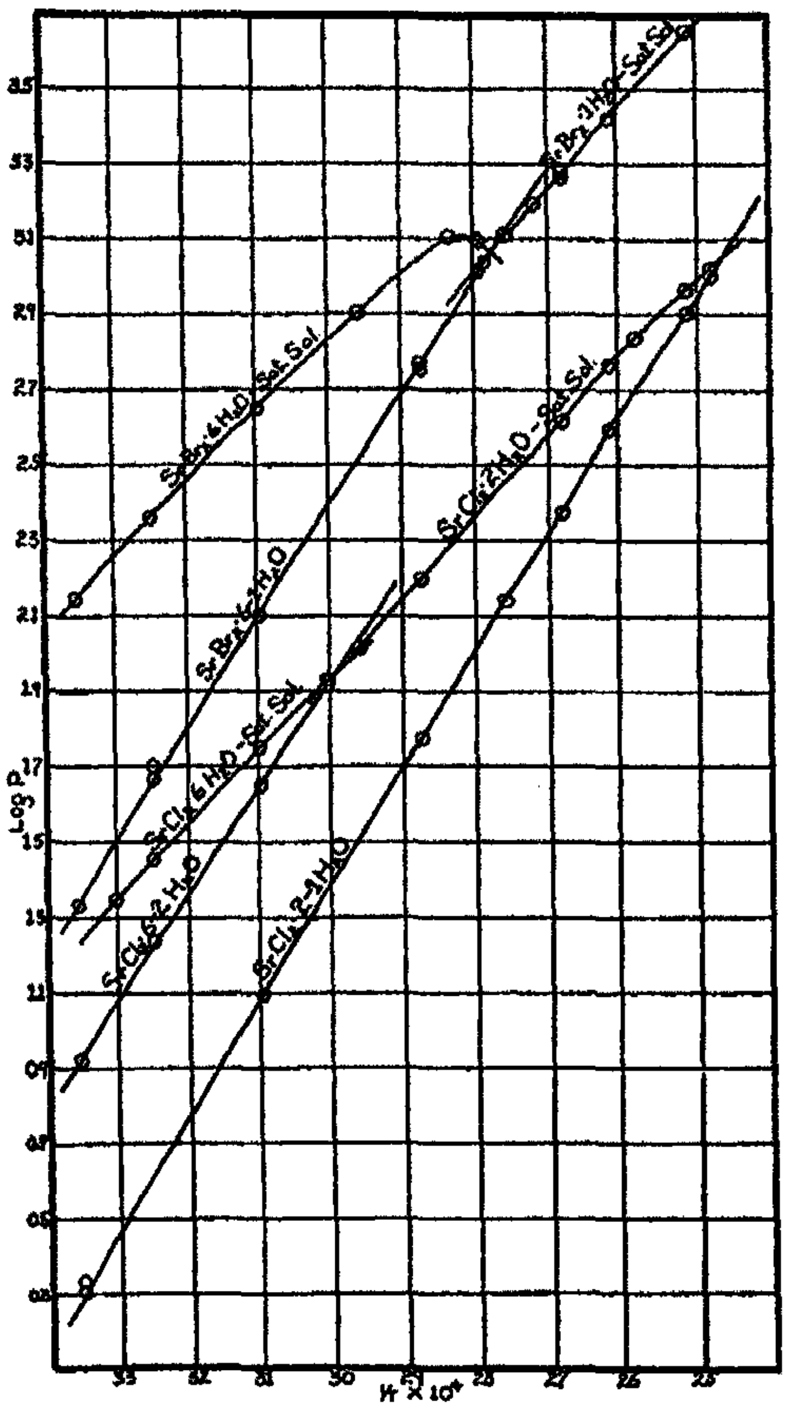

FIG. 2. Aqueous vapor and dissociation pressures in the systems strontium bromide–water and strontium chloride–water. (For the strontium bromide–water system subtract 1.0 from the log P scale.)

Because of the interest of their dissimilarity, graphs with log P as ordinates and $1/T$ as abscissas are exhibited in figure 2 for both aqueous pressures of saturated solutions and for dissociation pressures of the solid hydrates in the two systems strontium chloride and strontium bromide with water.

DISCUSSION OF ERROR

Sufficient data have been presented here and elsewhere (8) to enable one to make stepwise an estimate of a minimum probable error for an individual reported value of pressure, but it is more practical to compare the actual results of a number of duplicate experiments. When this is done, and the improvement due to smoothing taken into account, it is seen that errors in the tabulated smoothed values of pressures should, unless at low pressures, seldom exceed by 1 per cent the percentage errors of the published (16) vapor pressures of water which were taken as standard. We are encouraged to believe that serious systematic error is absent because of our essential agreement with the best results of a few others who have used different methods with due precaution.

REMARKS ON THE INDIVIDUAL SYSTEMS AND THEIR TRANSITION TEMPERATURES

Cupric sulfate. Our observations are not sufficiently numerous to indicate a transition in the pentahydrate at 56°C., as reported by Cohen (7). The values quoted in table 2a for Wilson's observations are the values of aqueous pressure corresponding to his stated equilibrium concentration of sulfuric acid as converted by the table published by Collins (8), and not from Wilson's similar table (45). We determined the transition temperature of pentahydrate to trihydrate by the heat effect, using a method similar to that of Richards and Yngve (31), and measuring temperature by a platinum resistance thermometer. Sharp arrests were obtained both on heating and on cooling at 95.88 ± 0.02°C. This is in agreement with the point of intersection at 95.9 ± 0.1°C. of the dissociation pressure curve of the pentahydrate with the vapor pressure curve of the saturated solution. International Critical Tables give 95.7 ± 0.2°C. The transition temperature between tri- and monohydrate is defined as 116.6 ± 0.2°C. by the point of intersection of our curve for the dissociation pressure of the trihydrate with the vapor pressure curve of the saturated solution.

Barium chloride. The transition temperature between the di- and the monohydrate was directly determined from the heat effect as above described, and found to be at 101.94 ± 0.05°C., in agreement with the intersection of the appropriate aqueous vapor curves at 101.9 ± 0.1°C. For the dissociation pressure of the monohydrate values of 2.5 (11), 2.4 (25), 2.9 (28), and 1.1 mm. (34) have been reported for 25°C. These values are presumably all high, for the reasons outlined above. Extrapolation of our rectilinear relation yields only 0.12 mm.

Barium bromide. Direct determination by the heat effect of the transition temperature between di- and monohydrate yielded 107.91 ± 0.05°C., while the appropriate aqueous pressure curves cut at 108.0 ± 0.1°C. The values given for the dissociation pressures of the monohydrate are tentative, since equilibrium was attained from only one direction.

Strontium chloride. The transition temperatures at 61.6°C. and 132.5°C. found, the latter by extrapolation, from the intersection of the appropriate aqueous pressure curves are in only fair agreement with the values of Richards and Yngve (31) at 61.34°C. and of Menzies (unpublished work on solubility) at 135.6°C., respectively.

Strontium bromide. There has been uncertainty in the literature as to the existence of a dihydrate. Richards and Yngve believed that the transition which, as a preliminary result, they set at 88.62°C. was from hexahydrate to, possibly, dihydrate. In dehydration experiments we found no evidence for a dihydrate. Repeating their determination of the transition point, we obtained 88.0 ± 0.1°C., and found by analysis that the product of the transition was the monohydrate. Of a series of samples which we dehydrated so as to obtain products of gross analysis corresponding to 4.5, 3.5, 2.5, 1.8, 1.3 and 0.6 H_2O with $SrBr_2$, all gave identical dissociation pressures except the last, whose pressure was lower. Since our work was completed, the same conclusion as to the absence of a dihydrate has been reached by others (15).

Calcium chloride. The transition temperatures as tabulated were arrived at from curve intersections, and are in good agreement with the values given in International Critical Tables.

SUMMARY

An isopiestic method has been described for measuring aqueous vapor and dissociation pressures by equilibration with aqueous sulfuric acid solutions.

Because the aqueous pressures of the reference solution vary with temperature in a manner very similar to that of the substance under investigation, the need for close constancy of long-continued temperature control is much relaxed in stringency, and this makes for experimental simplicity especially at temperatures above 100°C.

Experiments are conducted in common test tubes which are sealed, thus offering no greater difficulty for pressures above one atmosphere than below.

To illustrate the unusual breadth of range in temperature and pressure thus made easily accessible, six salt hydrate systems were examined and reported upon for temperatures up to 130°C. These include, in anhydrous and various hydrated forms, the chlorides of barium, strontium, and calcium, the bromides of barium and strontium, and cupric sulfate. For each salt pressure equilibrium values have been tabulated for the various univariant and many of the invariant systems formed with water.

Heats of vaporization of water from the several hydrates and from their saturated solutions have been evaluated.

Causes for difficulty of attaining true equilibrium values in such measurements have been discussed.

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A NEW ELECTROPHORESIS CELL FOR MICROSCOPIC OBSERVATIONS[1,2]

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PART I. DESCRIPTION, THEORY, AND THEORETICAL ADVANTAGES OF THE NEW CELL

Recent electrophoretic studies have involved the use of closed type cells, of either rectangular or circular cross section. The theory and use of such cells have recently been reviewed by Abramson (1). In both of these types the liquid returns along the axis of the cells, the velocity of the liquid being a parabolic function of the depth. The actual electrophoretic velocity can be obtained from observations at certain depths. However, at these depths the velocity gradient is large; the observed velocity changes rapidly with depth, and inaccuracy results.

The new cell described in this paper consists of two tubes in parallel between the electrodes, the dimensions of the tubes having a relation such that return flow takes place only through the tube of larger radius; there is no movement of the liquid along the axis of the tube of smaller radius, hence the velocities observed at the one-half depth in this tube are the actual electrophoretic velocities. At this depth the velocity gradient is zero, so that a slight inaccuracy in determining the depth of observation produces no appreciable change in the observed velocity of the particles.

DESCRIPTION OF APPARATUS

Diagrams of the apparatus are shown in figure 1. The essential parts of the apparatus are two fused quartz tubes, T_1 and T_2, used in parallel, two end tubes having stopcocks for filling the apparatus, and electrodes.

The dimensions of these two quartz tubes should have the relation

$$L_2/L_1 = A^2(A^2 - 2)$$

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[1] The data in this paper are taken from a thesis submitted by Margaret E. Smith to the Faculty of the Pennsylvania State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

[2] Authorized on July 27, 1935 for publication as Paper No. 698 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

where $A = R_2/R_1$, and L_2, L_1, R_2, and R_1 are the lengths and radii of tubes T_2 and T_1, respectively. The development of this equation is given in the section concerned with the theory of the cell.[3]

The procedure followed to obtain tubes of the correct dimensions was as follows: Tube 1 was ordered according to certain specifications,[4] viz., a capillary tube of good optical quality fused quartz, outer diameter approximately 3 mm., bore 0.5 – 0.7 mm., three sides of the tube to be ground off giving two parallel planes and one at right angles to these, thus allowing for observation, and for illumination either from the side or from underneath as desired. A diagram of the cross section of the tube is also shown in figure 1. The dimensions permissible for the cross section of this tube are limited by the working distance of the optical equipment to be used.

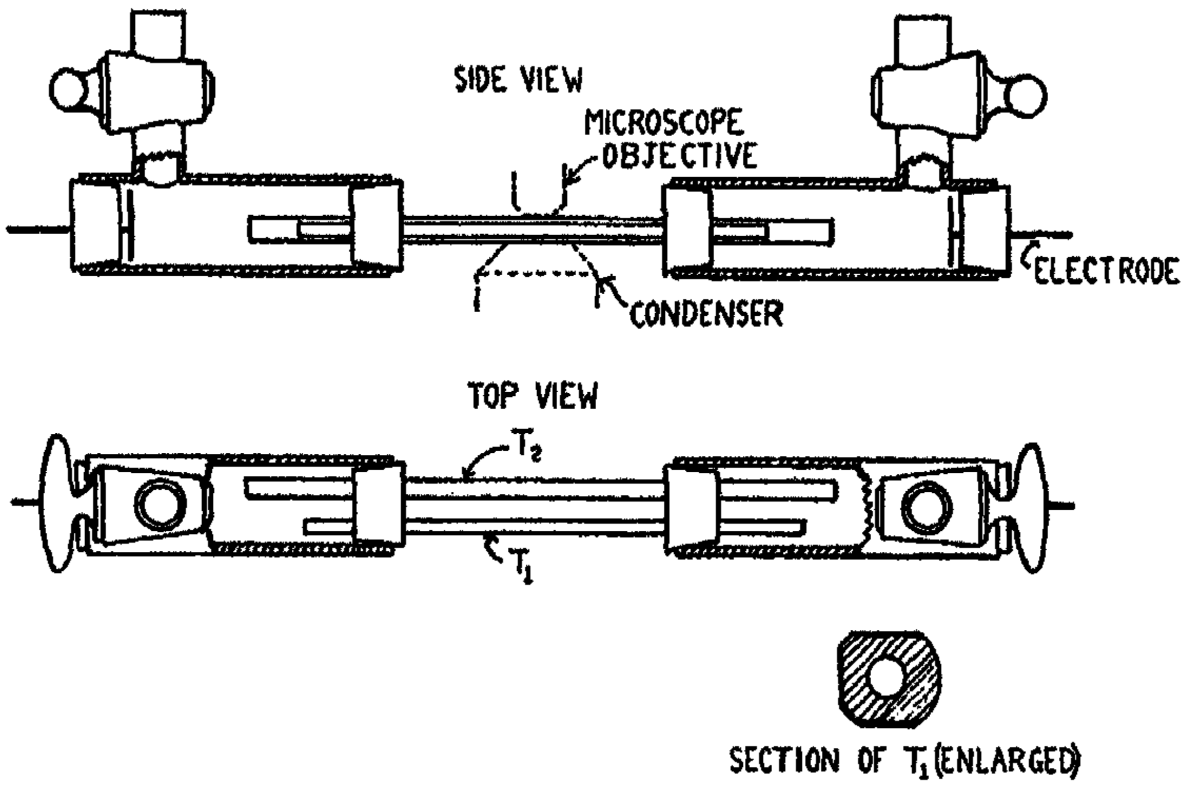

Fig. 1. Diagrams of the new double-tube cell for determination of electrophoretic mobilities

The bore of tube 1 was carefully determined by calculation from the length and weight of a column of mercury placed in the tube. Then a length of tubing was ordered from the stock supply of fused quartz tubing, with the specification that its bore should be uniform, and within the range of 1.5 to 1.6 times that of tube 1. The bore of this tube was determined in the same manner as described for tube 1, and the desired length cut off for tube 2.

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[3] The authors are indebted to Dr. Turner L. Smith of the Carnegie Institute of Technology, Pittsburgh, Pennsylvania, for the suggestion of the new cell and development of the theory concerning it.

[4] The quartz tubes were obtained from the Thermal Syndicate, Ltd., Brooklyn, New York.

Thus, if T_1 has a length of 10 cm., a radius of 0.3 mm., and T_2 has a radius of 0.48 mm., the length of T_2 is given by

$$L_2 = 10 \times 1.6^2(1.6^2 - 2)$$

or $L_2 = 14.34$ cm.

It is essential that tubes 1 and 2 be of the same material, since development of the theory of the cell assumes like surface conditions in the two tubes. Quartz was selected for these tubes, since (a) an optically good plane surface can be obtained through grinding and polishing of the quartz, and (b) the indices of refraction of quartz and water are more alike than those of glass and water, hence there should be less distortion of the images.

The quartz tubes were then inserted into two-hole rubber stoppers, making sure that the two tubes were far enough apart so that the larger tube would not interfere with the use of the objective and condenser on the microscope, and sealed into the stoppers with deKhotinsky cement.

The end tubes were of Pyrex glass tubing, with Pyrex glass stopcocks added for filling. The exact dimensions used are not important; in this case the length was approximately 12 cm. and the bore 1.8 cm.

The electrodes used were circular platinum disks, with wires attached leading through the rubber stoppers for connecting to the source of potential. In case solutions are used in which polarization occurs readily, nonpolarizable electrodes should be used.

OPERATION OF CELL

Operation of the cell involves the same technic as in the operation of other cells for microscopic observation of electrophoretic movement, except that the microscope is focused on the one-half depth in the tube of smaller radius. Hence the procedure is discussed here only in brief.

An apparatus resting on three leveling screws was built for holding the cell; this gave a simple means of adjustment for getting the plane of the cell parallel to the surface of the condenser. After the cell is filled with suspension and placed in position the electrodes are connected to the source of potential. A double-throw switch allows for frequent reversal of the current, thus preventing polarization. A milliammeter may be connected in series with the cell if desired.

The mobility of the particles (velocity per unit potential gradient) can be determined if the potential gradient is known. Since the radii of tubes T_1 and T_2 are much less than the radii of the end tubes, for most work the fall of potential through the end tubes can be neglected. Then the potential gradient through the tube where observation is made is given by E/L_1, where E is the total fall in potential between the electrodes, measured with a voltmeter in parallel with the cell, and L_1 is the length of T_1.

If a greater degree of accuracy is warranted, the potential gradient can be calculated more exactly from the dimensions of the apparatus. The use of this method in reference to electrophoretic cells is discussed by Northrop (3). Measurement of the current allows for another method of calculating the potential gradient; this method is discussed by Abramson (1).

For cleaning the apparatus, the rubber stoppers are removed from the end tubes. The two quartz tubes are left sealed in the two-hole stoppers. These tubes can be filled with water, alcohol, ether, or cleaning solution as desired with the aid of a hypodermic syringe; also, if desired, a small wire (insulated, thus preventing scratching of the surface) can be passed through the tubes. The end tubes and the electrodes are also cleaned. Thorough rinsing of the apparatus is very important, since small traces of electrolytes markedly affect electrophoretic potentials.

THEORY OF THE CELL

1. General theory of electrosmotic flow in tubes

The theory of electrophoresis cells assumes that the liquid is electrically neutral except for a charged layer lying very close to the wall of the cell. The electric field which is applied causes motion in this layer; this is defined as electrosmosis. Owing to the viscosity of the fluid, the motion of this layer induces a motion of the entire fluid in the cell. This motion is assumed to be both steady and nonturbulent.

The theory of tubular electrophoresis cells may be derived in the following manner. Consider the portion of the liquid inside a cylinder coaxial with the tube but of smaller radius. Electrosmotic movement of the liquid results in a difference in pressure at the ends of the tubes; the resultant force acting on the ends of the cylindrical portion of the fluid is just balanced by the shearing stress on the cylindrical surface, caused by the viscosity and thus proportional to the rate of change of velocity with the radius. This balance is expressed by the equation

$$2\pi r L\eta \frac{\mathrm{d}v_W}{\mathrm{d}r} = \pi r^2 P$$

which gives on integration

$$v_W = \frac{P}{4\eta L} r^2 + C \tag{1}$$

in which v_W denotes the velocity of the liquid, P the difference in hydrostatic pressure at the ends of the tube of length L, η the coefficient of viscosity of the liquid, and r the radius of the tube of flow being considered. This equation is the fundamental equation for flow of liquids in tubes; its development is found in treatises concerned with hydrodynamics of liquids (see Lamb (2)).

In the case being considered, the constant C can be evaluated from the condition that the velocity of the liquid at the wall of the tube is the electrosmotic velocity; that is, when $r = R$, $v_W = V_eE/L$, where R denotes the radius of the tube, V_e the electrosmotic mobility of the liquid, E the applied electromotive force, and L, as above, is the length of the tube. Hence equation 1 becomes

$$v_W = \frac{P}{4\eta L}(r^2 - R^2) + \frac{V_eE}{L} \tag{2}$$

The total volume, W, of liquid transported per unit time across any section is given by

$$W = \int_0^R v_W \cdot 2\pi r \, dr$$

Substituting in this the value of v_W given in equation 2, and integrating, we obtain

$$W = \pi R^2\left(\frac{V_eE}{L} - \frac{PR^2}{8\eta L}\right) \tag{3}$$

Equations 2 and 3 are the general equations for the velocity of electrosmotic flow of liquids and the volume of liquid transported by electrosmosis in cylindrical tubes.

2. *Theory of electrophoresis in a single closed tube*

The observed velocity, $V_{\text{obsd.}}$, of a particle at any depth in the tube will be the sum of the actual electrophoretic velocity, U, and the velocity of the liquid, i.e.,

$$V_{\text{obsd.}} = U + v_W \tag{4}$$

In a single closed tube, the total volume of liquid transported in one direction is zero. When $W = 0$, from equations 2 and 3 we obtain the equation for the velocity of the liquid in a closed tube

$$v_W = \frac{P}{4\eta L}\left(r^2 - \frac{R^2}{2}\right) \tag{5}$$

The depths at which there is no movement of the liquid are found by setting $v_W = 0$ in equation 5; this gives

$$r = \pm\frac{R}{2}\sqrt{2}$$

Focusing at these depths, the observed velocity is the actual electrophoretic velocity of the particles.

Actual electrophoretic velocities can also be obtained in another manner, thus,

$$\int_0^R V_{\text{obsd.}}\cdot 2\pi r\,\mathrm{d}r = \int_0^R U\cdot 2\pi r\,\mathrm{d}r + \int_0^R v_W\cdot 2\pi r\,\mathrm{d}r \qquad (6)$$

In a closed tube the total volume of liquid transported, represented by the last term in the preceding equation, is zero; hence equation 6 becomes

$$U = \frac{2}{R^2}\int_0^R V_{\text{obsd.}}\cdot r\,\mathrm{d}r \qquad (7)$$

Therefore, by taking readings at various depths in the cell, an approximation of the actual electrophoretic velocity can be obtained.

By substituting $r = 0$ and $r = R$ in turn in equation 5, it appears that the velocity of the liquid at the axis of the tube is equal in magnitude but opposite in direction to the velocity of the liquid at the wall of the tube, i.e., to the electrosmotic velocity, V_eE/L. Hence by use of equation 4 we obtain

$$V_eE/L = U - V'_{\text{obsd.}} \qquad (8)$$

where $V'_{\text{obsd.}}$ is the observed particle velocity in the single tube cell at depth $r = 0$. Thus the electrosmotic velocity can be calculated if the observed particle velocity at the one-half depth and the electrophoretic velocity are known.

3. Theory of cell consisting of two tubes in parallel

Consider two tubes of different radii in parallel between two electrodes. Let T_1 denote the tube of smaller radius, and T_2 that of larger radius. The general equations 2 and 3 for the velocity and volume of liquid transported apply; subscripts will be used to refer to the dimensions of these two tubes, as L_1 for the length of T_1, R_1 its radius, etc. The actual electrosmotic mobility, V_e, will be the same in both tubes, since the tubes are of the same material; also, the applied E.M.F. and the difference in pressure, denoted by E and P, respectively, will be the same in both tubes.

The total volume of liquid transported in one direction in the two tubes is zero; hence from equation 3 we obtain

$$W = \frac{\pi R_1^2}{L_1}\left(V_eE - \frac{PR_1^2}{8\eta}\right) + \frac{\pi R_2^2}{L_2}\left(V_eE - \frac{PR_2^2}{8\eta}\right) = 0 \qquad (9)$$

We wish to determine conditions such that there will be no movement of liquid along the axis of the smaller tube. The velocity at this depth can be obtained by setting $r = 0$ in equation 2. This gives

$$v_W \text{ along axis of } T_1 = -\frac{PR_1^2}{4\eta L_1} + \frac{V_e E}{L_1} \tag{10}$$

When this velocity = 0,

$$V_e E = \frac{PR_1^2}{4\eta} \tag{11}$$

This value substituted in equation 9 gives on simplification

$$R_1^4 L_2 + 2R_2^2 R_1^2 L_1 - R_2^4 L_1 = 0$$

Solving this for L_2,

$$L_2 = \frac{L_1(R_2^4 - 2R_1^2 R_2^2)}{R_1^4} \tag{12}$$

Let the ratio of the radii, R_2/R_1, be denoted by A. Then equation 12 can be written in the form,

$$L_2/L_1 = A^2(A^2 - 2) \tag{13}$$

If tubes are used whose dimensions satisfy the relations given in equation 13, there will be no movement of liquid along the axis of the smaller tube; velocities observed at this depth will be the actual electrophoretic velocities of the particles.

THEORETICAL ADVANTAGES OF THE NEW CELL

According to the development of the theory as given, velocity of liquid in tubes due to electrosmosis is a parabolic function of the depth; this is evident from the general equation 2, which is of the type $v_W = Ar^2 + B$, the constants A and B being dependent on conditions in the tubes used.

Equation 5 gives the equation for velocity of liquid in a single closed tube. This is a parabola, with the velocity at the maximum equal in magnitude but opposite in direction to the electrosmotic velocity of the liquid. Curves for cylindrical tube type cells are given by Abramson (1). At depths given by

$$r = \pm \frac{R}{2}\sqrt{2}$$

at which actual electrophoretic velocities are obtained, the velocity gradient (change in velocity with depth) is large; hence inaccurate results are obtained if a slight error in focusing is made.

The same condition is present at the levels used for observation in a single cell of rectangular cross section; in such a cell velocities are obtained at approximately the one-fifth and four-fifths depths, at which depths velocity changes rapidly with depth.

For the new cell the condition was stipulated that there should be no movement of the liquid at the axis of the tube of smaller radius. The velocity of the liquid in this tube expressed as a function of the radius can be obtained from equations 2 and 11; this is

$$v_W = Pr_1^2/4\eta L_1$$

This corresponds to a parabola with the maximum at the points where $r = 0$, and $v_W = 0$. It is evident that the velocity gradient, dv_W/dr_1, is also zero at this point.

The observed velocity of the particles is the algebraic sum of the electrophoretic velocity and the velocity of the liquid. Assuming that the electrophoretic velocity is constant, it is evident that the $V_{\text{obsd.}}$–depth curve is a parabola of the same general form as the v_W–depth curve; the coördinates of the maximum for this curve in the new cell are $r = 0$ and $V_{\text{obsd.}} = U$, and the velocity gradient at this point is zero.

Theoretical advantages of the new cell in comparison with a single tube cell are dependent on the fact that electrophoretic velocities are determined at the maximum of the velocity observed–depth curve. They may be listed as follows: (a) The proper depth for observation is readily found; since observations are made at the depth where the particle velocity is greatest, a few readings above and below this depth aid in checking the correct level. (b) A slight error in focusing does not result in appreciable errors in velocities, since change in velocity with depth is small at points near the correct level. (c) Depth of field of view is not as important a factor as in the case of a single closed tube, in which particles at a slightly different level have noticeably different velocities. (d) Rotational effects on particles are at a minimum, since the velocity gradient near the level of observation is small. This particular advantage suggests the use of a cell of this type for studies on larger particles where the effect of change in velocity with depth is a factor which must be considered.

SUMMARY

1. A new electrophoresis cell for microscopical observations of particle velocities is described; this consists of two tubes in parallel between the electrodes. By extension of the general theory of electrosmotic flow of liquid in tubes, it is shown that the flow of liquid at the one-half depth in the tube of smaller radius can be eliminated if the dimensions of the two tubes have a definite relation to each other. Hence, the observed particle velocities at this depth are the actual electrophoretic velocities, from which the mobilities can be calculated.

2. In this new cell electrophoretic velocities are given at the maximum of the parabolic curve expressing velocity as a function of depth. Advantages resulting thereby are: (a) Difficulty in focusing is alleviated, since

the observed velocity is a maximum at the correct level. (b) Slight errors in focusing, or errors due to depth of field of view of the microscope, are less important than in a single tube cell, since the velocity gradient is small near the correct level of observation. (c) Rotational effects of the liquid are less in the case of the new cell, since change of velocity with depth is at a minimum at the depth of observation.

PART II. EXPERIMENTAL COMPARISON OF THE NEW CELL AND A CYLINDRICAL TUBE CELL

As a means of confirming the theory and construction of the new cell, the electrophoretic mobility of quartz particles in distilled water was determined by three different methods, as follows: (a) In the new cell, actual electrophoretic mobilities being determined from observations at the one-half depth in the tube of smaller radius. (b) In a single-tube cell, actual mobilities being obtained from observations at depths where theoretically there should be no movement of the liquid. (c) In a single-tube cell, observing at various depths, and obtaining an approximate value for the electrophoretic mobility.

EXPERIMENTAL PROCEDURE AND RESULTS

General technic

Pieces of quartz tubing (the same material as used in the quartz tubes of the new electrophoresis cell) were cleaned with cleaning solution, thoroughly rinsed with distilled water, then with triply distilled water, dried, and ground in an agate mortar. A suspension of this powder was made in triply distilled water; this was allowed to settle for about four hours, after which the upper portion was siphoned off and used for the experiments. The quartz particles in this portion of the suspension were therefore small enough to stay suspended for some time.

Observation was made in T_1 (see description of the new cell given in Part I), used either as a single-tube cell or in parallel with T_2. The cell was carefully cleaned before using, and thoroughly rinsed, including two rinsings with triply distilled water previous to filling with the suspension. The optical combination consisted of a 10x ocular, a 21x (8 mm. 0.50) objective, and a cardioid condenser giving dark-field illumination. Observations of the velocities were made and mobilities calculated, the potential gradient being given with sufficient accuracy by E/L_1, where E is the applied E.M.F. and L_1 is the length of T_1. Experiments were carried out at room temperature and corrected to a temperature of 25°C. on the assumption that electrophoretic velocity varies inversely as the viscosity of the medium, i.e., $U\eta$ = constant. This would appear probable for suspensions of quartz particles, at least for the small range of temperature (25–29°C.) concerned in the experiments.

Series I

Six experiments were carried out using the new cell. Each experiment consisted of one hundred observations on a suspension of quartz particles prepared as previously described; the current was reversed in order to prevent polarization after each set of five readings, the microscope refocused after twenty readings, and the cell refilled with fresh suspension after sixty readings. The mobilities were calculated, and the arithmetic mean (A.M.) and standard deviation (S.D.) of the values determined; these values were then corrected for a temperature of 25°C.

TABLE 1

Electrophoretic mobilities of quartz particles in distilled water at 25°C. as determined at depths where there was no movement of the liquid in the new cell, and in a single-tube cell

EXPT. NO.	A.M.[*] AND S.D.[†] OF MOBILITIES IN μ/SEC./VOLT/CM.			
	Series I—New cell		Series II—Single-tube cell	
	A.M.	S.D.	A.M.	S.D.
1	3.55	0.24	2.84	0.60
2	2.93	0.31	2.76	0.63
3	3.07	0.21	3.56	0.42
4	3.14	0.14	3.00	0.42
5	2.68	0.24	2.83	0.25
6	3.39	0.22	2.73	0.22
Sum..........	18.76		17.72	
A.M..........	3.13		2.95	

[*] A.M. = arithmetic mean.

[†] S.D. = standard deviation.

Series II

This series consisted of six experiments, using T_1 as a single-tube cell. The technic followed was the same as in series I, velocities being observed at the depth where there was no movement of the liquid, i.e., where

$$r = \pm \frac{R}{2} \sqrt{2}$$

In the first two experiments of the series, half of the observations were made at the upper level, and half at the lower. In experiments 3, 4, 5, and 6, values were obtained at the upper level only.

Experimental results of series I and II are given in table 1.

Series III

Each of the three experiments in this series consisted of observations taken at levels differing by 50 μ throughout the depth of the cell, from ten to forty observations being taken at each level. From these observations the arithmetic mean of mobilities for each level was calculated. The mobilities at different levels plotted against depth resulted in curves of parabolic form; the mean mobilities of the maxima of these curves, obtained where $r = 0$, were 6.53, 6.24, and 5.61 μ per second per volt per centimeter, respectively, giving a mean mobility for the three experiments of approximately 6.1 μ per second per volt per centimeter. At the walls of the tubes the particles moved in the opposite direction, the mean mobilities for the three experiments giving values of −2.66 and −3.10 μ per second per volt per centimeter at depths of $+R$ and $-R$ respectively.

TABLE 2

Electrophoretic mobilities of quartz particles in distilled water at 25°C., as determined in a single-tube cell from observations obtained at various levels in the cell

EXPT. NO.	MOBILITY IN μ/SEC./VOLT/CM.
1	2.37
2	2.16
3	2.13
Sum	6.66
A.M.	2.22

Electrophoretic velocity is given by equation 7. A rough approximation of this velocity is given by

$$U = \frac{2}{R^2} \sum_{r=0}^{r=R} V_{\text{obsd.}} \cdot r \, dr$$

This approximation is readily seen to be inaccurate unless observations are taken at a large number of levels, since it gives no weight to the value of the velocity at the axis of the tube, where $r = 0$, and gives undue emphasis to the value at the wall of the tube, where $r = R$. A better method of approximation consists in the use of the average of the mobilities observed at depths differing by dr. Values of mobilities so calculated for the three experiments in this series are given in table 2.

DISCUSSION OF RESULTS

Examination of the data in table 1 indicates that practically the same values of mobilities are given in the two cells. The value of the arithmetic mean of the mean mobilities for the six series of experiments of series I is 3.13 μ per second per volt per centimeter with a standard deviation of ± 0.31 μ per second per volt per centimeter, and for the six experiments of series II, 2.95 ± 0.31 μ per second per volt per centimeter; hence there is no significant difference in the mobilities, as found in the two cells, greater than that which might be expected from the amount of variation in the experiments comprising a series. The mobility of quartz particles in triply distilled water at 25°C. as obtained by these two methods is therefore approximately 3.0 μ per second per volt per centimeter.

The electrosmotic velocity of the liquid is equal to the difference between the electrophoretic velocity of the particles and the maximum observed velocity of the particles in the single tube (see equation 8); therefore the electrosmotic velocity of the liquid in the present case is $3.0 - 6.1$ or -3.1 μ per second per volt per centimeter. With consideration of the relatively high experimental error inherent in experiments of the type concerned, these results seem to substantiate the theory that the electrophoretic mobility of the particles is equal in magnitude to the electrophoretic mobility of the liquid.

Comparison of mobilities given in table 2 with those given in table 1 shows that mobilities as obtained in the single-tube cell by means of observations taken at various levels in the cell are not equal, within the experimental error, to those obtained in the new cell or in the single-tube cell at depths of $\pm R\sqrt{2}/2$.

A plausible explanation of the different results obtained with the third method would seem to be that values not conforming to the theoretical values are obtained near the walls of the tube. Evidence in direct support of this is disclosed by examination of the data obtained in the three series of experiments. Since the electrosmotic mobility and the electrophoretic mobility appear to be equal in magnitude but opposite in direction, we should expect that there would be no movement of the particles at the wall of the tube. Experimentally, however, the particles at the walls were observed to move in the opposite direction from those at the axis of the tube. On the basis that the velocities should have been zero at the walls of the tube, the experimental values there determined were neglected, and the curves drawn to meet the axis, giving $V_{\text{obsd.}} = 0$ at distances $r = +R$ and $-R$, respectively. By interpolation of the values obtained at distances of 50 μ from the walls, and use of the values as obtained experimentally at the other depths, approximation of mobilities by the method previously employed gave values of 2.87, 2.93, and 3.03 μ per second per volt per centimeter, respectively, for the three experiments. These values are in the range of mobilities as obtained by the other two methods. This method of calculation of mobilities is not to be recommended for general use, however; it depends on the assumption that the electrophoretic mobility of the particles is equal to the electrosmotic mobility of the liquid, a condition which would be expected to occur only in cases where the wall of the tube and the particles are of the same material, and has not been found to occur in all of these cases. Moreover, the method of interpolation does not give accurate results, since it is not known how far the influence of the wall extends. Another objection to the method lies in the large number of observations which must be made to obtain an approximation of the desired accuracy.

The advantages of the new cell in comparison with the single-tube cell, in both cases observations being made at the depths where theoretically there is no movement of the liquid, are apparent from a consideration of the values of standard deviations obtained in the experiments of series I and II; these are given in columns 3 and 5 of table 1. Standard deviation is an index of variance, i.e., it indicates how closely the values obtained are grouped about the arithmetic mean. The standard deviations found for the first two experiments in series II, in which values were observed at both the upper and lower levels in the single-tube cell, are much greater than the values of standard deviations obtained with the new cell. These high values probably came from failure to focus on the correct levels; it is difficult to find the correct levels such that readings at the upper and lower depths agree. It is also difficult to obtain readings at the lower level, therefore readings in the other four experiments of the series were taken at the upper level only. In all cases the microscope was refocused after each set of twenty readings. The values of standard deviations in experiments 3 and 4 of series II are also higher than those for the new cell, probably owing to the readings having been obtained at slightly different levels. In the last two experiments of this series standard deviations are not greater than with the new cell, indicating that observations were made at approximately the same level throughout the experiment; however, since these observations were made only at the upper level, it is difficult to be sure that the correct level was used. The uniformity of the values of standard deviations obtained in the experiments with the new cell (series I) make its advantages apparent. The correct level for observation is obtained readily; moreover, small differences in levels of observation do not introduce large errors in the observed values. For results of a certain degree of accuracy a smaller number of observations is justifiable with the new cell than with a single tube cell.

CONCLUSIONS

1. Values of electrophoretic mobilities of finely ground quartz particles in triply distilled water obtained in the new double-tube cell agreed within the experimental error with values as determined in a single cylindrical tube, in both cases observations being made at depths where theoretically there should be no movement of the liquid.

2. Values of electrosmotic mobilities obtained with a single cylindrical tube from observations made at various levels in the cell did not agree with values as obtained by the other two methods. Experimental evidence suggests that erroneous values are obtained in the walls of the tube.

3. The approximate electrophoretic mobility of quartz particles in triply distilled water as obtained by the two methods which agreed within experimental error was 3.0 μ per second per volt per centimeter.

4. The value of electrosmotic mobility of water in quartz tubes as obtained from these experiments was approximately -3.1 μ per second per volt per centimeter.

5. Consistency of experimental results with the new double-tube cell indicates the advantages of the new cell.

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SILICA FLUFF

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A form of hydrated silica is obtained by drying at a low temperature the silicic acid resulting from the action of silicon tetrafluoride upon water. This product possesses unusual properties, and has been called silica fluff to distinguish it from all other forms of silica. The reaction is formulated as follows:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4$$

When silicic acid precipitates from water solution it is a transparent gel, growing gradually translucent and opaque when filtered and dried. If left for some weeks drying in the open air it assumes the above-mentioned white fluffy character. No apparent change takes place in the material after a month's drying, and it maintains its composition over a period of years as definitely as does quartz itself.

This light, fluffy, white powder is composed of aggregates of tiny flakes of irregular outline, containing inclusions of air bubbles of uniform size that give color phenomena with polarized light, as if the substance were composed of doubly refracting globular crystals. These tiny air inclusions cannot be observed except with a 600 diameter magnification, or larger.

The specific gravity of the material is 1.018, as determined by obtaining the volume of kerosene displaced by a given weight of silica fluff, using an oil pump to remove the air from the pores of the material. The specific gravity of orthosilicic acid is 1.57, and for the meta acid 2.2, while the specific gravity of anhydrous silicon dioxide varies from 2.3 to 2.6. It is apparent, therefore, that the low specific gravity of silica fluff, a lower hydrated form of silica than metasilicic acid, is due to the air inclusions in the flakes which cannot be dislocated by a vacuum pump.

Weighed in air, under as nearly the same degree of packing as possible, the apparent specific gravities of a number of light materials in comparison with silica fluff are given in table 1. It is seen that even ground cork and air-floated carbon black are more than twice as heavy as silica fluff. Numerous attempts have been made to duplicate this material, but no other product has been quite so light or with as high air adsorption as the material which the author made at the Johns Hopkins University in 1919–20. The long time required for drying, as well as the high humidity during the drying, may account for these unusual properties.

Silica fluff has an index of refraction of 1.45. The flakes are from 0.01 to 0.3 mm. in diameter and from 0.003 to 0.008 mm. in thickness. The diameter of the air bubbles is 1.0 to 1.5 microns.

TABLE I

Apparent specific gravity of silica fluff compared with that of other light materials

MATERIAL	SPECIFIC GRAVITY
Silica fluff	0.0248
Ground cork	0.0621
Carbon black (high color gas carbon)	0.0635
Swedish soft wood flour	0.1543
Silica black, Grade A	0.2201
Merck's precipitated silica	0.2265
Lycopodium powder	0.3624
Powdered silica	0.9199

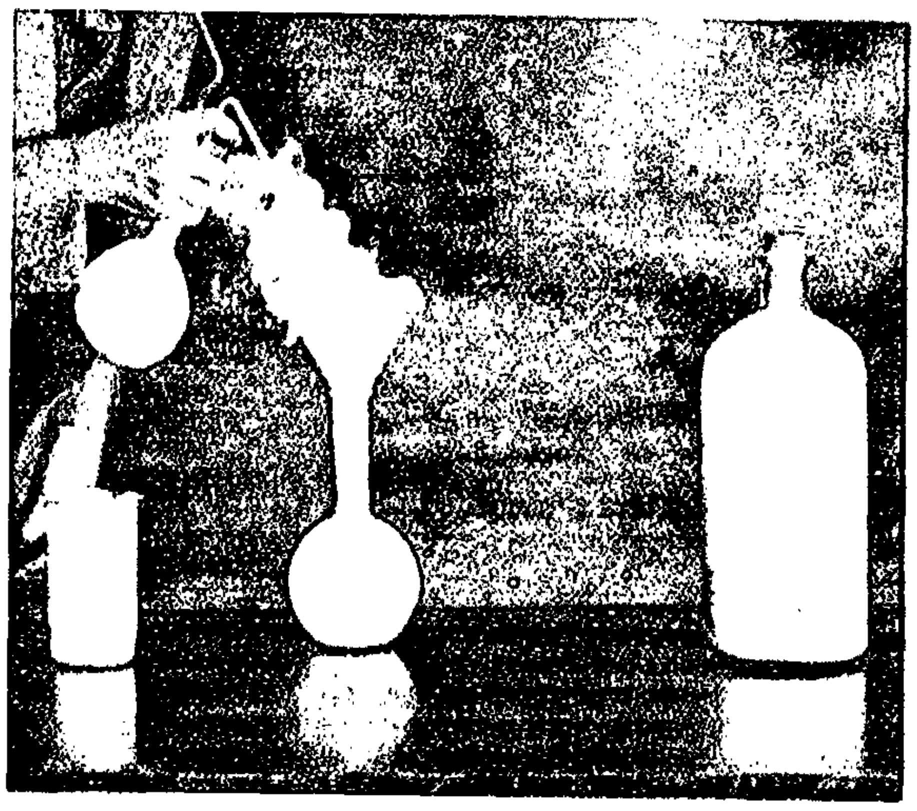


FIG. 1. Silica fluff

On account of its high air adsorption silica fluff behaves like a liquid, flopping and splashing from side to side in the bottle, and can be poured through a narrow-stem funnel or blown through a wash bottle like a liquid, as is shown in figure 1.

No elements were found to be present in silica fluff other than silicon, hydrogen, and oxygen, but the last two are not in the ratio to form water. Its composition is given in table 2. From the percentage composition obtained by experiment its empirical formula is calculated to be $H_6Si_{12}O_{27}$ or $(SiO_2)_{12} \cdot 3H_2O$. A survey of the literature brings out the fact that Victor Lenher (5) reported silicic acid desiccated over concentrated sulfuric acid for two months with a water content of 6.75 per cent. G. Tschermak (8) obtained a similar product, also desiccated over sulfuric acid, with a water content of 6.7 per cent. Bernhard Neumann (7) investigated the dehydration of silicic acid from 200° to 1000°C., starting with a product having a water content of 6.6 per cent.

TABLE 2

Analysis of silica fluff

LOT	H_2O AT 120°C.	H_2O AT BRIGHT CHERRY RED HEAT (800 – 850°C.)	TOTAL H_2O	SiO_2 BY H_2F_2
	per cent	*per cent*	*per cent*	*per cent*
1	0.48	6.60	7.08	92.92
2	0.43	6.76	7.19	92.80
Average.......	0.455	6.68	7.135	92.865

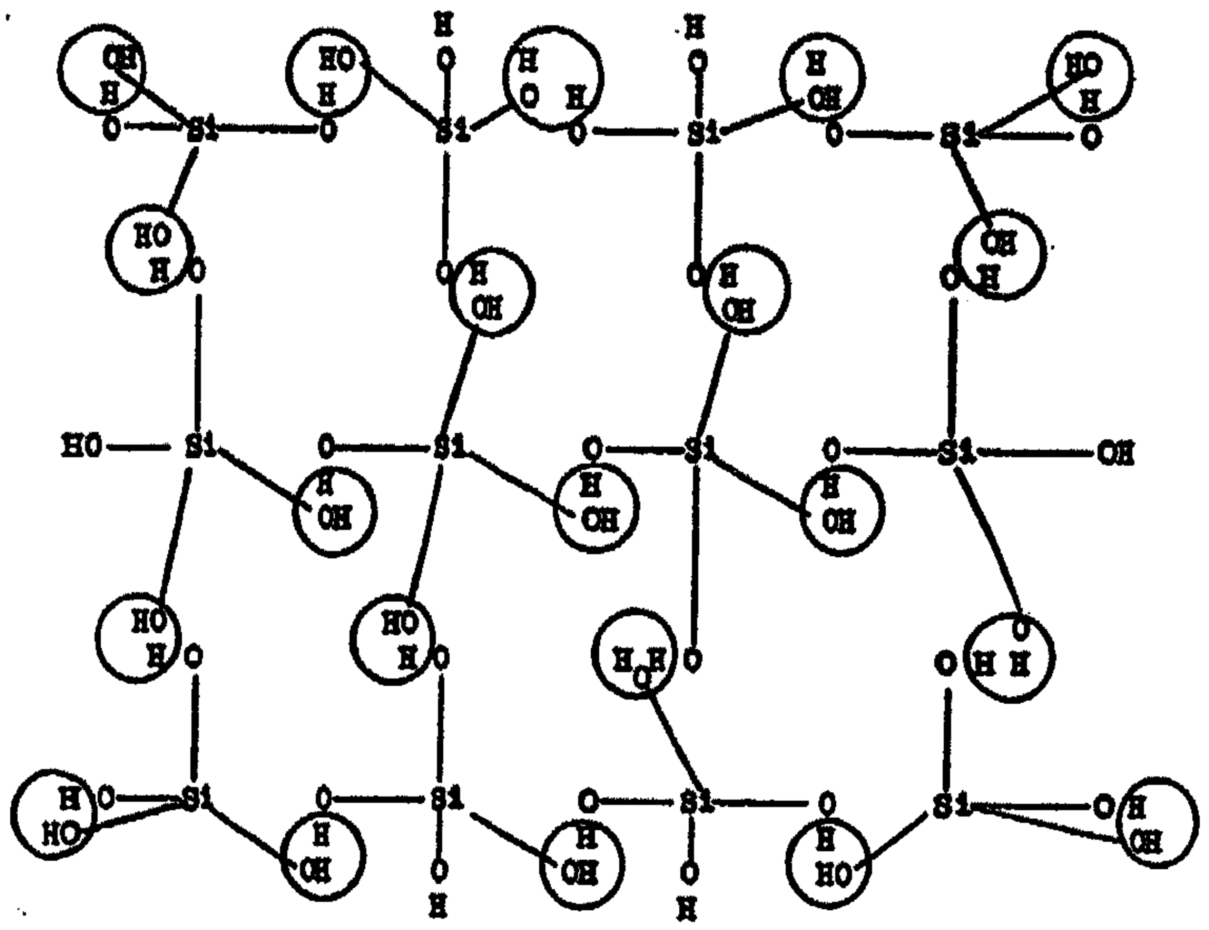
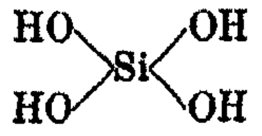


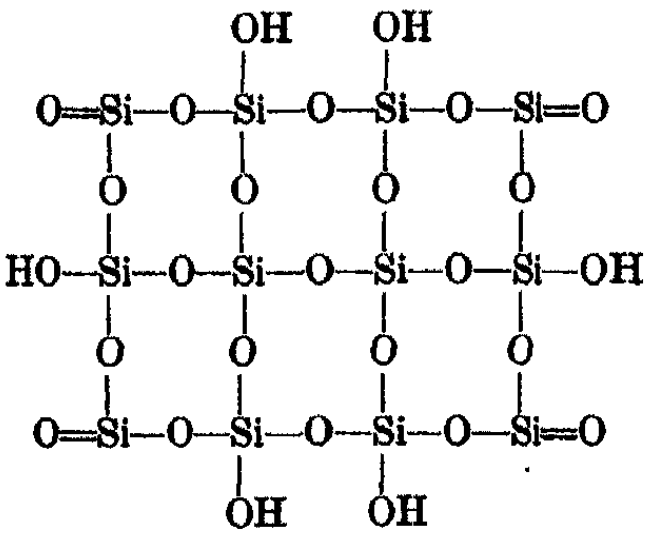
Fig. 2. The condensation of twelve molecules of orthosilicic acid, by elimination of twenty-one molecules of water, to yield silica fluff

The above-mentioned analyses, together with those obtained in this laboratory, furnished the basis for the following speculation regarding the structure of the molecule of this very stable and remarkable form of silica or silicic acid.

Apparently there are three molecules of water in the compound. On the basis that dihydrated silicon dioxide is orthosilicic acid, in which the water is incorporated in four hydroxyl groups as seen in the graphic formula



the author was led to place twelve such molecules in juxtaposition and to eliminate twenty-one molecules of water where the hydroxyl groups are in proximity to each other (see figure 2), yielding a molecule which exactly fits the analysis, and is represented by the following graphic formula for silica fluff.



A compound with this formula calls for a molecular weight of 774.77, of which 6.98 per cent is water, whereas the average water content obtained experimentally is 7.13 per cent.

If we consider that some of the water obtained at 120°C. existed free, the hydroxyl groups in the formula exactly represent the water obtained when the material was ignited.

Assuming that dehydrated silicic acids possess structures of this type it is easy to understand how various degrees of hydration can be had, and consequently how dehydration may take place so gradually that no noticeable break in the curve appears. If we assume, for example, that the four corner silicon atoms in the graphic formula hold eight hydroxyl groups instead of four oxygen atoms, the water content will amount to 14.89 per cent.

Many workers in this field, for example, O. Mugge (6), H. Chatelier (3),

J. Bruckmoser (1), G. Tschermak (9), H. Kantsky (4), and others, have expressed varied opinions about the composition of silicic acids and the nature of the water which they contain.

It is a well-known fact that diatomite, more often called diatomaceous earth or kieselguhr, is almost wholly siliceous (85 to 92 per cent silica). This material has resulted from the accumulation of the remains of unicellular organisms called diatoms, whose living structure must have contained silica in some soluble form.

Now upon the decomposition and dehydration of this siliceous material it might be expected that a product would result, similar in properties to silica fluff, especially in its relation to combined water.

To test this theory, the water contents of various diatomaceous earths are given in table 3. All but one of these values are taken from analyses reported by Calvert (2). The percentages in the table are based upon the total weight of the diatomaceous earth samples and not upon the silica present in them. When these percentages are recalculated on the silica content alone, excluding the sample from Herkimer, N. Y. (which obviously contains adsorbed water), the average per cent of water in the silica of twelve different samples of diatomaceous earth becomes 7.15, which is almost identical with the water normally present in silica fluff, whose molecular structure is postulated in the graphic formula shown.

TABLE 3

Water content of diatomaceous earths

SOURCE	WATER CONTENT	SOURCE	WATER CONTENT
	per cent		*per cent*
Herkimer, N. Y.	12.12	Monterey, Calif.	4.89
Richmond, Va.	8.37	Toome, Ireland	7.35
Wilmont Wharf, Va.	3.40	Algiers	9.14
Pope's Creek, Md.	3.47	Algiers	3.50
Ellensburg, Wash.	5.98	Algiers	7.40
Fossil Hill, Nev.	5.99	Storey County, Nev.	6.07
Lompoc, Calif.	5.00		
Average of all values			6.36

This fact would seem to be more than an accidental coincidence. The combined water in diatomaceous earth cannot be present in the form of definite hydrates, for no sharp break in the dehydration curve has ever been reported. It would not be surprising, however, if the silica and combined water in diatomaceous earth exist in some such way as that postulated for silica fluff.

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ADSORPTION OF RADON BY GLASS

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During the course of certain radiochemical experiments it was noticed that radon which was kept for several days in Pyrex bulbs was in part strongly adsorbed on the glass (1). The bulbs were thin walled, and had volumes of approximately 0.1 cc. The pressure of the impurities which accompanied the radon was never greater than a few millimeters, and was probably in most cases less than 1 millimeter. The bulbs were blown from clean tubing, but were not subjected to any chemical cleaning after being made. The sealed bulbs containing the radon were introduced into a horizontal tube which was attached by 20 cm. of 2-mm. capillary tubing to a 100-cc. vessel. After the system had been evacuated (to a pressure of less than 10^{-4} mm.), it was cut off from the vacuum line, and the 100-cc. vessel was immersed in liquid air. The fragile bulb containing the radon was then shattered by a magnetically-operated, glass-enclosed plunger. The distribution of the fluorescent glow indicated that the greater part of the radon distilled over almost instantaneously. After fifteen or twenty minutes the side tube was sealed off from the 100-cc. vessel, which was still immersed in liquid air. Six or eight hours later the side tube was examined in the dark. If the glass showed any fluorescence, the amount of radon was determined (usually twenty or thirty hours after breaking the bulb) with a γ-ray electroscope. It is noteworthy that in every case where radon remained in the tube, the fluorescent glow was visible only on the fragments of the bulb. Even after forty hours there

TABLE 1

Evidence for the slow irreversible adsorption of radon on glass

INITIAL AMOUNT OF RADON IN MILLICURIES	TIME DURING WHICH THE RADON WAS SEALED IN THE BULB	PER CENT OF THE RADON WHICH REMAINED ON THE WALLS OF THE BULB
mc.	*hours*	*per cent*
156.5	17.5	<1
188.5	37	11
119.7	49	19
102.5	68	16

was no visible evidence that any of the radon had diffused into the containing tube. Table 1 summarizes the available quantitative evidence.

Although it is not precluded that the observed differences in the percentage adsorption may be due to possible differences in the surface of the bulbs or in the impurities of the radon, these data suggest that the percentage adsorption depends upon the time of contact. It is possible that the adsorption may be the result of "pitting" of the glass by α-particle bombardment. In this case the adsorption would be proportional to the intensity of the α-particle bombardment on the glass. These results make it obvious that certain precautions must be taken in the transfer or measurement of radon used in radiochemical experiments; particularly is it undesirable to leave radon in a small tube longer than necessary for the gamma-ray measurement before transferring it.

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NEW BOOKS

Origins and Development of Applied Chemistry. By J. R. PARTINGTON. 25 x 15 cm.; xii + 597 pp. London: Longmans, Green and Co., 1935. Price: 45s. net.

Dr. Partington's book arrived as the reviewer was leaving for the United States, and the "Origins" became his constant companion in America. The reviewer had full opportunity for reading the work most thoroughly. Dr. Partington's book, by its encyclopaedic knowledge, seems at first perhaps a little frightening, but as the study of the book proceeds so one's admiration for it grows. This is not just a reference book. It is much more than that, and a careful reading through the whole work as it stands would fully repay the time and energy devoted to it.

No single reviewer can really do justice to the "Origins," in view of its tremendous scope and the comprehensive nature of its information. The writer has therefore judged the book solely from its plant chemical content, with which he is familiar. Students of the history of plant chemistry will find a great deal of information on the plant materials of Egypt, Babylonia and Assyria, Crete, Troy and Cyprus, Asia Minor, Persia, Phoenicia, and Palestine. The information contained on these lines has taught the reviewer to appreciate not only the extent but also the soundness of Dr. Partington's knowledge. A survey of the plant materials contained in this book revealed nothing that is not mentioned in it, and some of the most difficult points on the history of plant chemistry have been dealt with in a manner that commands only admiration. To take one example (p. 169), the case of kyphi, the incense of the Egyptians: this is a most difficult topic, and Professor Partington has threaded through it with care and remarkable lucidity. Kyphi has been the object of many lengthy discussions, and Dr. Partington has managed to convey all that is known about it without leaving that peculiar feeling of uncertainty one has after the study of this subject in other works. Those who know the difficulties must appreciate Dr. Partington's attitude, and those who are blessedly ignorant of them do not realize through what a maze they have been so successfully conveyed,—a most remarkable achievement. Attention must also be drawn to the helpful indexes, especially the subject index, which contains many references to plants and plant materials.

Viewed from any aspect, there is no doubt that Dr. Partington's "Origins" will become one of the classics on the history of chemistry.

M. NIERENSTEIN.

Electron Emission and Adsorption Phenomena. By J. H. DE BOER. The Cambridge series of physical chemistry. Translated from the manuscript by Mrs. H. E. Teves-Acly. 398 pp.; 150 figs. The Macmillan Co., The University Press at Cambridge, England, 1935.

The author deals with the nature of surface forces as revealed by the study of electron emission from metals and dielectrics and by the knowledge of adsorption of substances on such surfaces. He hopes to obtain information on the subject of adsorption on surfaces by studying their electron emission, and, vice versa, he expects to learn concerning the nature of electron emission by a study of adsorption phenomena on surfaces. From the nature of these topics it is at once seen that the book is of interest to individuals who are concerned with the nature of catalysis. Since this latter phenomenon is of the greatest importance to chemists, the book should appeal to a large circle of readers. The subject-matter of the volume does not include the phenomena of catalysis however. Indeed the word "catalysis" is not found in the index! It is merely the reviewer's opinion that the studies portrayed here should be of interest to physical chemists who wish to elucidate the problems of catalysis. The methods of research employed and discussed by the author may well find extended application and lead to a richer and more precise knowledge of surface chemistry. The content of this interesting book is divided into fifteen chapters and can be discussed in the briefest manner by mentioning the various topics: electron emission from metals; the nature of adsorption forces; the adsorption of cesium on tungsten surfaces and other electropositive metals on metal surfaces; photoelectric emission after adsorption of electropositive metals on metal surfaces; double layers formed by the adsorption of gases; the adsorption of light by matter in the gaseous and in the adsorbed state; the selective photoelectric effect; alkali-metal atoms adsorbed within the lattice of the alkali halides and their photoelectric properties; electronic conduction in the lattices of the alkali halides and other lattices; photoelectric cathodes with thick intermediate layers of a dielectric and metal particles; thermionic emission of cathodes with a dielectric; oxide-covered cathodes; emission of electrons into intermediate layers of dielectrics and into blocking layers. The author makes abundant use of energy diagrams in his discussion. To the chemist with modern training this method of treatment should be very satisfactory.

Geo. Glockler.

The Structure of Crystals. Supplement for 1930–34 to the second edition. By Ralph W. G. Wyckoff. American Chemical Society Monograph No. 19A. 240 pp.; 75 figs. New York: Reinhold Publishing Corporation, 1935.

The present volume supplements the second edition of the author's well-known treatise and covers the work for the last four years on structure determination of crystals by x-ray methods. The eleven chapters are numbered to correspond to those in the second edition, and an appendix gives the complete literature of the subject. The same chronological arrangement is maintained as is found in the second edition. This bibliography covers sixty-one pages. It is evident that the book is indispensable to the worker in the field of crystal structure determination, but any one interested in the general field of atomic and molecular structure and the solid state will by necessity have to refer to this treatise-supplement. The figures shown are excellent in execution and an invaluable help in understanding the intricate patterns of the more complex crystals. The book represents an enormous amount of the most painstaking effort, and the author is to be congratulated on the result of his labors.

Geo. Glockler.

Body Water—The Exchange of Fluids in Man. By John P. Peters. 14.5 x 23 cm.; 5 figs.; viii + 405 pp. Springfield, Illinois, and Baltimore, Maryland: Charles C. Thomas. Price: $4.00.

There has been great need for such a comprehensive discussion of the rôle of water in the vital processes of the human organism. Professor Peters is excellently qualified to bring together the many papers which have been published in this field and to discuss them critically, inasmuch as he has himself actively worked in this field for many years.

This volume contains much more than its title would indicate. In addition to considering the composition of the various body fluids, it is a rather complete survey of the physiology of the absorption, secretion, and excretion of many substances such as carbohydrates, nitrogen-containing compounds, fats, salts, etc., within the body, all considered in the light of the direction of water flow which takes place either through interstitial spaces or across membranes.

The maintenance of equilibria between various fluids and tissues by means of the Gibbs-Donnan phenomena, osmotic pressure, "colloid osmotic pressure," tissue tension, etc., are adequately discussed from the standpoint of both theory and application, and the effect of these forces in causing fluid flow, ultrafiltration, and absorption is emphasized. Both normal and pathological physiology are considered.

Every chapter contains applications of physicochemical principles to physiological processes, so that the book would serve admirably as reference and source material for courses in physical chemistry designed to emphasize physiological and medical aspects.

The reviewer was particularly desirous of seeing how the question of "bound water" would be treated. To his surprise it was rather summarily dismissed without any particular discussion, the author believing that bound water does not exist as a measurable entity. Similarly the imbibition pressure of colloids is spoken of (p. 53) as if it were of no particular significance.

In a discussion of the exchange of fluids between blood cells and serum the author considers (pp. 120-3) that the "potassium salts of hemoglobin" are largely "undissociated." This view is decidedly at variance with those of certain physical chemists who have assumed a stoichiometrical compound formation between proteins and acids and bases, with a subsequent complete ionization of the "salt." It is difficult for the reviewer to see how a potassium-protein "salt" can be completely or nearly completely unionized, whereas adsorption of potassium on the protein micelles would account for such behavior.

The chapter headings are as follows: (1) Chemical forces which control exchanges of fluid and solutes; (2) The nature and movements of interstitial fluid and lymph; (3) Exchanges between blood and interstitial fluids; (4) Serous fluids and transudates; (5) Exchanges between blood cells and serum; (6) Exchanges between tissue cells and interstitial fluids; (7) Water of oxidation and the losses of water and solutes through skin and respiratory passages; (8) Alimentary exchanges; (9) The general nature of renal activity; (10) Renal excretion of filtrable organic solutes; (11) Renal excretion of water and inorganic salts; (12) Nervous and hormonal control of urine excretion.

The author lists complete titles and journal citations to 875 references in the author index and also indicates the specific pages in the text where the reference is considered. A short but adequate subject index closes the volume. The volume should be carefully read by all students of physiological processes.

ROSS AIKEN GORTNER.

Monographien aus dem Gesamtgebiete der Mikrochemie. Farbmessungen, Theoretische Grundlagen und Anwendungen. By E. HASCHEK and MAX HAITINGER. 85 pp.; 6 figs.; 14 tables. Wien and Leipzig: Emil Haim and Company, 1936.

Although the sensation of color is entirely subjective, it is possible to measure the qualities responsible for the sensation in a more or less exact way. In doing so the description of color becomes independent of subjective impressions and external conditions. The quantitative measurement of color has been codified by international agreement some years ago. Based on the color theory of Young-Helmholtz, which distinguishes between hue, saturation, and brightness as the characteristics of color, the authors derive the quantitative expression of these magnitudes. The monograph is of interest not only to chemists and physicists but to anyone interested in the quantitative description of color. Contrary to the authors, the reviewer is of the opinion that in the characterization of a certain object the quantitative description of color is of secondary significance only, since the color is a function of the state of subdivision of the object. It seems, therefore, an exaggeration to state (p. 57): "Der Farbpunkt spielt eine ähnliche Rolle wie der Schmelzpunkt oder Siedepunkt."

I. M. KOLTHOFF.

Structure and Properties of Matter. By HERMAN T. BRISCOE. 420 pp. New York: McGraw-Hill Book Company, 1935.

The author states that his object is to present to students of chemistry a readily understandable account of the newer discoveries in the physical sciences which have brought about the great advances since 1900 in our knowledge of the nature of matter. The book is addressed not to specialists but to those having sufficient training,—presumably this might mean Senior or possibly Junior Chemists, or graduate students in chemistry not majoring in physical chemistry.

The reviewer is quite in sympathy with the desirability of such a course, and believes that the author has furnished a very acceptable text for the purpose in mind. Among other subjects he treats the electron, the proton, the nucleus, radioactivity, crystal structure, radiation as introductory to Bohr theory, valence, and quantum mechanics.

Some of the minor defects can easily be remedied in a future edition, such as revision of the list of isotopes on page 115, the substitution of the modern values of atomic weights in the actinium series (page 67), and the use of the older assumption that there are free electrons in the nucleus. Probably geophysicists and cosmic physicists would not agree that any extensive formation of new nuclei has occurred on our planet, though this is an interesting field for speculation.

While some of the material presented may be included in other courses in general and physical chemistry, the present book meets a real need for the advanced undergraduate in chemistry who does not intend to specialize in some phase of atomistics.

S. C. LIND.

Die Bierhefe als Heil-, Nähr-, und Futtermittel. By JULIUS SCHÜLEIN. (Technische Fortschrittsberichte. Fortschritte der chem. Technologie in Einzeldarstellungen. Herausgegeben von Prof. Dr. B. Rassow, Leipzig.) 22 x 15 cm.; vi and 194 pp. Dresden und Leipzig: Theodor Steinkopff, 1935. Price: geheftet, 9RM; gebunden, 10RM.

This book deals with brewer's yeast as an aid to nutrition and pharmacology. The therapeutic value of yeast is taken to depend largely on its vitamin content, and much of the book is devoted to an account of the vitamins so far as they occur in yeast or can be invoked therein by irradiation. The author includes much of the most recent work, but shows a lamentable lack of first-hand acquaintance with the English literature on the subject. No reference appears to be made to the important work of the International Committee on Vitamin Standards. A detailed account, supported by references to the medical literature, is given of the application of yeast and yeast preparations to the cure of a large number of diseases.

The value of yeast as a nutrient also depends in a large measure on its vitamin content, but in addition the protein, salts, and other constituents are in themselves of great nutritive value. Dried yeast is advocated as as addition to the normal diet of human beings on the ground, no doubt valid in many districts, that at the present time the ordinary diet of large numbers of people does not contain sufficient of the various vitamins to ensure complete health and resistance to disease.

In the field of animal nutrition yeast may also play an important part, and striking results are quoted with respect to the increased milk production of cows fed on a diet containing irradiated yeast.

The author has brought together in this work an imposing mass of material showing in how many ways yeast can be usefully employed dietetically, and although it is obvious that he is putting forward the best possible case for the use of yeast, there seems to be no doubt that there is a large nutritional field in which yeast may be usefully employed.

A. HARDEN.

The Structure of Metallic Coatings. A General Discussion held by the Faraday Society. 25 x 16 cm.; 247 pp.; 77 plates. London: Gurney and Jackson, 1935. Price: 21/- net.

This volume has been reprinted from the Transactions of the Faraday Society and is divided into the two main sections "Electron Diffraction Methods" and "The Structure of Metallic Coatings," each followed by discussion on the individual papers. Professor Desch contributes an introductory paper, and various aspects of the electron diffraction method of examining surface structure are discussed by G. P. Thomson, G. I. Finch, W. E. Laschkarew, H. G. Hopkins, and others. The most interesting paper in part I is certainly that of Finch and collaborators; in this the problems of electron diffraction and surface structure are dealt with very thoroughly. A very interesting point concerns the appearance of "extra" rings not normally associated with the particular solid. Finch has shown that they are due to the entry of gas into the crystal lattice. The hope of many, that electron diffraction would play an important part in the solution of problems of gas absorption in metals, appears likely to be fulfilled in the near future.

The second part of the discussion is perhaps not quite so well arranged as it might be; the papers dealing with x-ray work would have fitted better into the physical scheme of part I. The papers in this section are too numerous to receive detailed individual attention. A considerable section deals with the properties and structure of electrodeposited layers. Andrade deals with the crystallization of thin metal films, Ornstein with optical research on evaporated metal layers. Both the authors represented in this volume and their publishers are to be congratulated on the particularly fine set of plates collected here.

J. T. RANDALL.

The Eruption of Mt. Pelee, 1929–32. By FRANK A. PERRET. Publication No. 458 of the Carnegie Institution of Washington, 1935. 9 x 11.5 in.; 126 pp.; 71 figs., 3 diagrams and a chart of *nuée ardenté* activity; 2 appendices.

The investigation here reported was *lived* on the mountain itself, day and night. Excursion, observation, photography, and intermittent sleep were the author's lot.

The report opens with a brief discussion of terminology, and a history of Mt. Pelee, which has erupted before. The main part of the book is in two parts,—first a narrative of the eruption of 1929 to 1932, and then an analytical study of the volcanic activity. Chemical studies include only an analysis of water in the first appendix, but the lack is not so serious because the lavas are surprisingly similar to those of the 1902 eruption, well studied by Lacroix. The emphasis here is on the physical aspects.

Volcanic flows differ in their physical condition: first, the Mauna Loa type of swiftly moving, luminous, coherent liquid; second, the Etna type, more viscous, consolidating at the surface into discrete blocks; and third, the Pelean type with its autoexplosive liquid, self-expelled in the form of a completely subdivided mass of still active particles isolated from one another by vapor films—the whole mass flowing down any slope with incredible speed because it is frictionless. The particles of liquid lava contain vapors in solution and give them off so rapidly that they are cushioned from each other, and the great avalanches rush down the mountain slopes in utter silence! These are the *nuées ardentées* named in reference to the clouds which rise, but the name does not adequately express the great source of energy in the avalanche at the base of the cloud.

The data are microphonic, seismologic, and astronomic, in addition to the narrative of major events and a few notes on the temperatures. The observed speeds of flow of the *nuées ardentées* ranged from 10 to 33 meters per second. There are some electrical charges from the clouds, and "flashing arcs" are described as possibly light reflected from a *sound* wave-front.

One physicochemical hypothesis is presented by the author with the frank remark that it may be "outrageous,"—namely, that at depths some igneous magma may be in a vapor phase because of excess heat. The latest statement of expert opinion on this is by Fenner (in *Economic Geology*, volume 30, pp. 929–930, 1935) and is unfavorable to the idea, showing also that high pressures may develop from dissolved gases without having the magma itself become gaseous.

The general reader will find interest in the section (pp. 8 to 12) on the diagnosis and prediction of volcanic eruption, and in the many excellent photographs.

FRANK F. GROUT.

Das Kristallzeichnen auf Grundlage der stereographischen Projektion. By H. TERTSCH. 23 x 15 cm.; iv and 38 pp.; 34 figs. Wien: Julius Springer, 1935. Price: 3.60 RM.

The orthodox methods of drawing crystals from a stereographic projection are described with special emphasis on their application to the study of habit. Successive sections deal with the drawing of a plan on the plane of projection and with representation in parallel perspective on an arbitrary plane, the true habit being obtained by the use of measured central distances. A further section describes the drawing of twin crystals. The writing is clear and concise, but a few of the more complicated figures might have been reproduced with advantage on a larger scale.

F. C. PHILLIPS.

Wasserstoff-Ionenkonzentration (pH). By H. JÖRGENSEN, with an introduction by S. P. L. Sörensen. 15 x 22 cm.; 264 pp. Dresden: Theodor Steinkopff. Price: paper, 15 RM; bound, 16 RM.

In recent years there have appeared both in the English and in the German languages, a number of excellent books dealing with the determination and applications of hydrogen-ion concentrations; the author of the book under review has nevertheless written another, apparently at the request of the publishers to fill a gap in their series of scientific monographs. Nearly half of the book, 114 out of 246 pages of text, is devoted to a consideration of the fundamental principles involved in the determination of pH, and the theoretical aspects of electrode potentials, buffer solutions, and electrolytic equilibria are discussed in a concise but adequate manner. The treatment of acids and bases is particularly interesting, since the author adopts throughout the modern viewpoint which regards acids as yielding and bases as accepting protons, respectively.

The next section of the book, 52 pages in length, consists of a review of the methods of measuring pH; the author does not intend this to be complete, for the reader is referred to other treatises for further practical details. Nevertheless the methods of using the hydrogen and quinhydrone electrodes are described in sufficient detail, but the account of the glass electrode is little more than an indication of how it can be used. Colorimetric methods for determining pH, which either do or do not involve the use of buffer solutions, are described, although the simple "drop-ratio" method of Gillespie is not mentioned.

The last portion of the text, entitled "Technischer Teil," occupies some seventy pages, and in it are described sixty-two examples of the importance of measurements of hydrogen-ion concentrations in industry: amongst these are references to fermentation, baking, sugar, paper, leather, organotherapy, agriculture, milk, confectionery, textiles, and dyeing. A ten-page appendix on the subject of pH in acid-alkali titrations then follows, and it is here that the newer concept of acids and bases is particularly useful. The book is completed by a list of over two hundred and forty references, arranged in alphabetical order according to the names of the authors, and there is also a good subject index. It is not surprising to find a relatively large number of references to Danish and Scandinavian literature, since the author is working in Copenhagen, but English, American, and German journals are well represented in the list. The book can be recommended as giving an excellent survey of the subject of hydrogen-ion concentrations; its viewpoint is up to date and it is written in a clear and simple style.

S. GLASSTONE.

Journal of the Institute of Metals. Volume LVI (Proceedings), No. 1, 1935. 306 pp.; 31 plates. Cloth. Edited by G. Shaw Scott, M.Sc., F.C.I.S. London: The Institute of Metals, 36 Victoria Street, Westminster, S.W.1. Price: £1. 11s. 6d.

The latest volume of the *Journal of the Institute of Metals*, Volume LVI, No. 1, 1935, constitutes a complete record of the two most recent meetings of the scientific society that is responsible for the publication of this useful book. The respective gatherings were the Spring Meeting and the May Meeting, both held in London. At the latter Professor W. L. Bragg, F.R.S., delivered the twenty-fifth annual May Lecture, his subject being "Atomic Arrangement in Metals and Alloys." This discourse—in which an account of the theory of atomic arrangement in the crystalline structure of an alloy is given—is reproduced in full, and constitutes a valuable addition to scientific knowledge. It brings up-to-date the work that has been done on this subject since Professor Bragg's father, Sir William Bragg, F.R.S., delivered a previous May Lecture—in 1916—on "X-rays and Crystalline Structure, with Special Reference to Certain Metals."

A dozen papers dealing with many aspects of metallurgical work make up the bulk of the present volume, these papers having been presented at the March Meeting of the Institute of Metals. Two specially interesting groups are those dealing with fatigue in metals due either to atmospheric action or to corrosion. Another group is devoted to the constitution or properties of tin alloys. "Unsoundness in Aluminium Sand Castings" and "The Mechanical Properties of Some Wrought Magnesium Alloys" are the titles of two other papers of considerable industrial importance. All these and other papers, which are very fully illustrated—for the most part by photomicrographs—are reproduced *in extenso*, together with a record of the discussions which took place when they were presented and written communications upon them that have been subsequently made.

As the March Meeting was also the Annual General Meeting it is appropriate that in the present volume there should appear the Report of Council on the work of the Institute for the past year, the report showing that the work of the Institute has been fully maintained.

Metallurgical Abstracts (General and Non-ferrous). Volume I (New Series) 1934. 780 pp. Cloth. Edited by G. Shaw Scott., M.Sc., F.C.I.S. London: The Institute of Metals, 36 Victoria Street, Westminster, S.W.1. Subscription price: £4, inclusive of two "Proceedings" volumes.

Metallurgical Abstracts, published under this title since January 1931 and issued as a supplement to *The Monthly Journal of the Institute of Metals*, has appeared hitherto as part of the *Journal* series. The present issue of *Metallurgical Abstracts* is the first volume of a new series; it appears in a distinctive binding and is complete with its own index containing many thousands of entries.

The extent of the publication can be gauged from the fact that the abstracts are gleaned from over one thousand of the world's scientific and technical publications by a staff of fifty-eight abstractors and reviewers whose names form an impressive list on the opening page of the new volume.

The subjects dealt with are grouped under twenty-four main headings and range from "Properties of Metals" to "Industrial Uses and Applications." It is difficult to overrate the value of these abstracts to the busy man who desires to keep in close and regular touch with important technical developments in various parts of the world.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 4: Stickstoff. Lieferung 2. 26 x 18 cm.; pp. x + 283–506. Berlin: Verlag Chemie, 1935. Price: (abroad) 26.25 marks.

The second issue of the volume on nitrogen deals entirely with its compounds with hydrogen and the greater part is devoted to ammonia, including its manufacture. The discussion of synthetic ammonia includes the Haber, Claude, Casale, Fauser, and other processes. The text has been submitted in some cases to the technical interests, who are not likely to have disclosed much of value. The physical and chemical properties of ammonia are very fully dealt with and there are numerous tables and diagrams in the text. The literature references are brought to May, 1935, and in the section dealing with the manufacture of ammonia are less satisfactory than usual, reference to English publications being surprisingly incomplete.

J. R. PARTINGTON.

Eisen- und Stahllegierungen. Patentsammlung. 1 Ergänzungsheft. By A. GRÜTZNER. Zugleich Anhang zur Metallurgie des Eisens in Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 26 x 18 cm.; 425 pp. Berlin: Verlag Chemie, 1935. Price: unbound, 44 marks; bound, 48 marks.

This volume is a supplement to that published by the same author and in the same series in 1932, and forms an independent supplement to Gmelin's *Handbuch.* It includes patents in Austria, England, France, Germany, Switzerland and the United States of America for the period from March 1932 to the end of 1934. It gives in three columns the composition, the properties and applications, and the patent references. The alloys are classified according to composition. Although the first part included patents from 1880 to 1932, it was a hundred pages smaller than this supplement, so that some idea may be gained of progress in recent years in this field of metallurgy. The work is likely to prove very useful in technical libraries.

J. R. PARTINGTON.

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THE JOURNAL OF PHYSICAL CHEMISTRY

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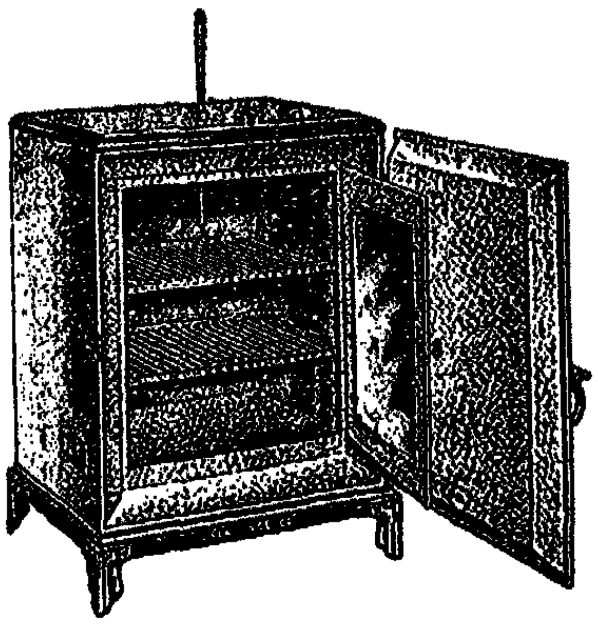

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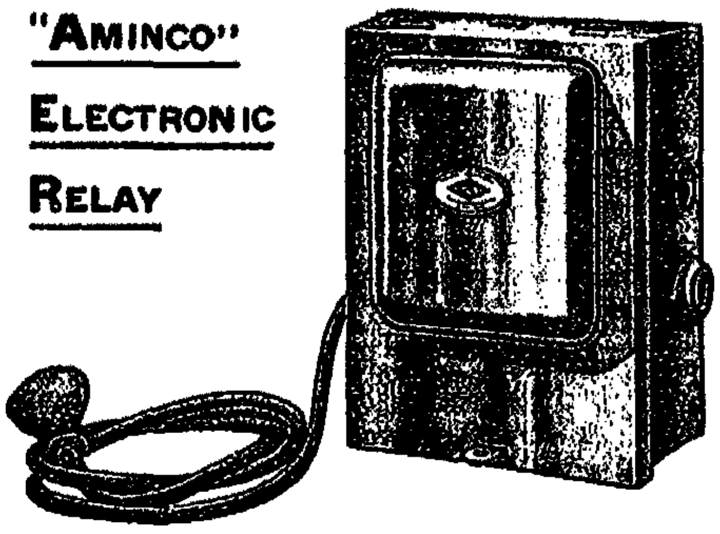

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THE HEAT CAPACITY OF SATURATED SODIUM SULFATE SOLUTION

KENNETH A. KOBE AND CLARENCE H. ANDERSON

Department of Chemical Engineering, University of Washington, Seattle, Washington

Received October 17, 1935

The heat capacity of saturated sodium sulfate solution is of importance in the problem of recovery of the anhydrous salt from its aqueous solution. No data are reported in the literature for the saturated solution. In fact, data for heat capacities of practically all saturated solutions in contact with the salt are not in the literature.

APPARATUS

Heating element. A piece of Pyrex tubing, inside diameter 3 mm., is drawn out to give a thin-walled center section 1 meter long and 1 mm. in diameter. A 20-gauge copper wire is soldered to one end of a piece of 28-gauge constantan wire 1 meter long. The constantan wire is threaded through the tubing and the end soldered to another 20-gauge copper lead wire. The fine glass tubing is wound into a spiral approximately 35 mm. in diameter and with 3 mm. between the turns. The ends of the heavy tubing containing the copper leads are brought up at right angles to the plane of the spiral. The copper leads are connected to the lower ends of binding posts in a suitable cork stopper.

Calorimeter arrangement. A 200-cc. wide-mouth Dewar flask is used. In the cork containing the heating element are a 100°C. calibrated thermometer graduated in tenths and a glass drill stirring rod driven by a motor stirrer. The heating element is placed in a circuit with suitable variable resistances, calibrated ammeter, and voltmeter across the heating element to check constantly the resistance of the heating element.

Water equivalent. A constant current of 1 ampere is passed through the heating element immersed in 100 g. of water in the calorimeter. The range of temperature is 25° to 95°C. At each 10°C. interval the current is shut off and the rate of cooling determined. The room temperature is maintained constant.

HEAT CAPACITY, 32.4°C. TO 102.8°C.

Above the transition temperature of sodium sulfate decahydrate (32.4°C.) the solubility curve is inverted. A saturated solution of the salt is prepared at 34.5°C. and 100 ml. of it is pipetted into the calorimeter. One gram of excess anhydrous salt is added to insure crystallization of salt from the solution as the temperature rises. Data are taken over the range 35° to 95°C., with cooling curves at 10°C. intervals, as in the determination of the water equivalent. One additional correction must be made in the calculations to account for the heat content of the anhydrous sodium sulfate precipitated from the solution as the temperature rises. The average amount of this salt (+1 g.) is determined by a graphical integration of the solubility curve. The heat content is then calculated for each temperature interval, using the heat capacity from the International Critical Tables (5).

TABLE 1

Heat capacity of saturated sodium sulfate solution

TEMPERATURE	RUN			AVERAGE	GRADUATED VALUE, *C*	CALCULATED VALUE, *C*, BY EQUATION 1	ERROR
	13	14	15				
°*C.*							*per cent*
32.5					0.7946	0.7959	+0.16
35–45	0.793	0.793	0.795	0.794	0.7934	0.7933	−0.01
45–55	0.789	0.790	0.790	0.790	0.7902	0.7893	−0.11
55–65	0.785	0.787	0.785	0.786	0.7854	0.7846	−0.10
65–75	0.779	0.780	0.778	0.779	0.7799	0.7793	−0.08
75–85	0.775	0.775	0.774	0.775	0.7742	0.7734	−0.10
85–95	0.763	0.768	0.767	0.7675	0.7672	0.7668	−0.05
100					0.7563	0.7596	+0.44
102.8					0.7528	0.7575	+0.62

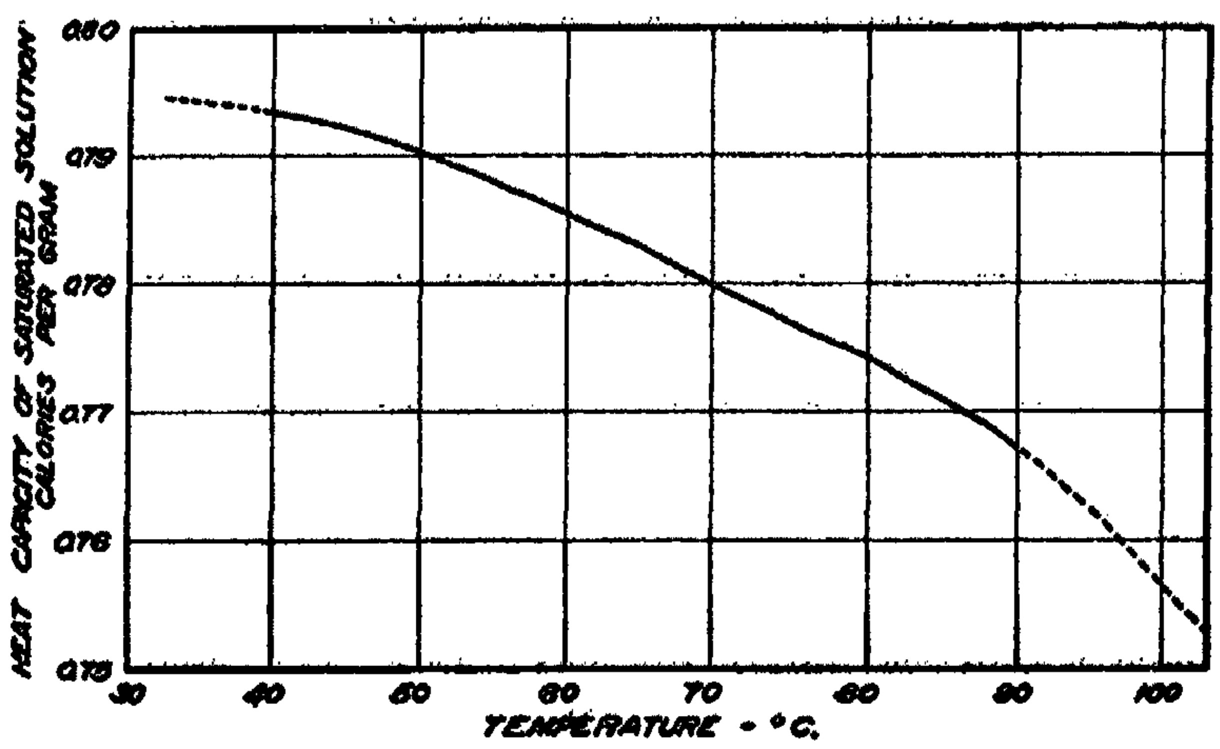

FIG. 1. Heat capacity of saturated sodium sulfate solution

The data are tabulated in table 1. From the average of values for the heat capacity a graduated value is determined by the method of Eggers (3). This method also gives a means of extrapolation which is used to give the heat capacity curve over the ranges 32.4° to 40°C. and 90° to 102.8°C. The graduated curve for heat capacity is shown in figure 1. This curve may be expressed by equation 1, where t = °C.

$$C = 0.803 - 1.14 \times 10^{-4}t - 3.2 \times 10^{-6}t^2 \qquad (1)$$

The agreement between the values calculated by equation 1 and the graduated values is shown in table 1.

The mean heat capacity over the range 32.4° to 102.8°C. determined by graphical integration is 0.7796 cal. per gram. This value is very close to the 0.781 cal. per gram reported by Pagliani (8), who determined the heat capacity of 1 mole of sodium sulfate in 18 moles of water over the range 24° to 100°C. This system has an excess of the decahydrate up to 31°C., is unsaturated between 31° and 74°C., and has an excess of the anhydrous salt above 74°C.

MEAN HEAT CAPACITY, 20°C. TO 32.4°C.

Below 32.4°C. the saturated solution is in equilibrium with the decahydrate, for which the solubility curve rises steeply. Fifty milliliters of a solution saturated at 20°C. are pipetted into the calorimeter. Calculation shows 91.5 g. of sodium sulfate decahydrate will dissolve in this to give a solution saturated at 32.4°C. The decahydrate is added to the solution in four portions over equal parts of the temperature range. Room temperature is raised at the same rate as the temperature of the calorimeter to eliminate radiation and emergent stem correction. Corrections must be made for the excess decahydrate crystals present in the solution. Data are not available for the heat capacity of sodium sulfate decahydrate; Kopp's rule (4) may be used over this small range without great error.

The mean heat capacity may be calculated per gram of initial solution or per gram of average solution. The average weight of solution is found by graphical integration of the solubility curve over the range 20° to 32.4°C. The average weight must be corrected for the amount of unhydrated sodium sulfate in the decahydrate, as the hydrate readily effloresces.

From the data the mean heat capacities calculated are: 5.51 calories per gram of solution (average) and 7.92 calories per gram of solution (initial).

HEAT OF TRANSITION

Two values for the heat of transition are found in the literature. Cohen (2) found 16,509 cal. per gram-mole, and Leenhardt and Boutaric (7) found 18,400 cal. per gram-mole. The method used by both workers started with the salt in solution and measured the heat of crystallization, which may be lower than the heat of transition as all of the heat of the crystal may not be given up immediately. The method used in this work was to measure directly the heat of transition.

Sodium sulfate decahydrate crystals are introduced into either nitrobenzene or toluene as the heat transfer liquid. The liquid is heated to 32.4°C., the decahydrate crystals added, and heat applied. As heat is applied, the temperature rises slowly until the transition is complete, then rises rapidly. By plotting temperature against time the intersection of the two lines gives the end of the transition. Correction is made for the heat necessary to bring the crystals from room temperature to the transition temperature. The heat capacity data for nitrobenzene as given in International Critical Tables (6) do not agree with those of Parks and Todd (9), whose data are used. The results are given in table 2.

TABLE 2

Heat of transition of $Na_2SO_4 \cdot 10H_2O$

RUN	HEAT OF TRANSITION IN CAL. PER GRAM-MOLE	MEDIUM
9	18,800	Nitrobenzene
12	18,900	Nitrobenzene
13	18,900	Nitrobenzene
14	18,600	Toluene
15	18,600	Toluene
16	18,400	Toluene
17	18,700	Toluene
Average..................	18,700	

The heat of transition may also be calculated from the vapor pressure data for the decahydrate crystals and the saturated solution by using the Clausius-Clapeyron equation. The value found by this calculation is 19,000 cal. per gram-mole.

Data, calculations, and corrections applied are too detailed to be given here, but may be found in the original report of the work (1).

SUMMARY

1. The heat capacity of saturated sodium sulfate solution from 32.4° to 102.8°C. may be represented by the equation

$$C = 0.803 - 1.14 \times 10^{-4}t - 3.2 \times 10^{-6}t^2$$

The mean heat capacity over this range is 0.780 cal. per gram.

2. The mean heat capacity of saturated sodium sulfate solution from 20° to 32.4°C. is: 5.51 cal. per gram of solution (average) and 7.92 cal. per gram of solution (initial).

3. The heat of transition of sodium sulfate decahydrate is 18,700 cal. per gram-mole.

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THE THERMAL DISSOCIATION OF CALCIUM CARBONATE

J. C. SOUTHARD AND P. H. ROYSTER

Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

Received December 12, 1935

The thermal dissociation of calcium carbonate is a chemical reaction of considerable technical importance, not only in the case of the calcination of agricultural limestone as such, but in a number of fertilizer-production projects, such as the fixation of nitrogen as calcium cyanamide, and in the several proposed potash-volatilization processes. The experiments reported here were undertaken at this laboratory in connection with the development of a blast furnace method of producing potash from silicate rocks.

Several investigators (7, 10, 12) have shown that calcium carbonate dissociates into calcium oxide and carbon dioxide without the formation of an intermediate basic oxide and without solid solution of the resultant calcium oxide in the undissociated calcium carbonate. The atmospheric dissociation temperature has not hitherto been determined, however, with much accuracy. Among the more careful and recent measurements this temperature is given by Johnston (5) as 898°C., by Smyth and Adams (9) as 897°C., by Andrussow (1) as 882°C., and by Tamaru, Siomi, and Adati (10) as 882°C. While these observers differ by as much as 16°C. in their determination of the dissociation temperature, the heat of reaction at atmospheric pressure, as calculated from the pressure-temperature equation of these several investigators, varies about 1 per cent from a mean. The respective variations in temperature and slope of the $\log p$ curve suggest that the discrepancies were due largely to errors in temperature measurement.

In Andrussow's apparatus, the thermocouple was enclosed in the reaction chamber in an effort to measure the actual temperature of the dissociating carbonate. Andrussow, however, does not refer to the calibration of his couple or of his millivoltmeter. Tamaru, Siomi, and Adati used a calibrated thermocouple. Since they employed the Nernst quartz-fiber balance method, however, they were unable to place the couple inside the reaction chamber. It seems probable that this external couple was not at the temperature of the reacting carbonate, since the vessel and couple were inserted into the furnace to a depth of only three and one-half times the diameter of the enclosing quartz tube, and since neither baffles nor other thermal protecting devices were used to minimize the thermal disturbance due to the circulation of room temperature air through the heated parts of the apparatus. Johnston discovered that his couple gave erroneous temperatures and attempted to correct for it.

DESCRIPTION OF APPARATUS

In the apparatus used in the present investigation, an improved type of reaction chamber, thermal environment, and temperature control was developed. Figure 1 shows a section of the central portion of the furnace. This furnace was 10 in. in outside diameter and 22 in. long, and was lined with 4½ in. of insulating fire brick. A central alundum tube (A), outside diameter 4 cm., was wound with a nichrome heating coil which served as the main heating resistance. A hollow nichrome block (B), 2.5 cm. in outside diameter and 12 cm. long, capped with a cover plate (D) carried a nichrome wire auxiliary heating resistance (4). A base metal thermocouple (3) was imbedded in a hole in block B and was in metallic contact with it. The E.M.F. in this couple was opposed by a constant external E.M.F.; a Leeds and Northrup high sensitivity galvanometer was used as a null instrument; light reflected from the galvanometer mirror actuated a photocell which controlled, by a relay, the current through the auxiliary heater (11). This device held the block at 900°C. for more than thirty hours with a maximum variation of 0.04°C. from its mean temperature.

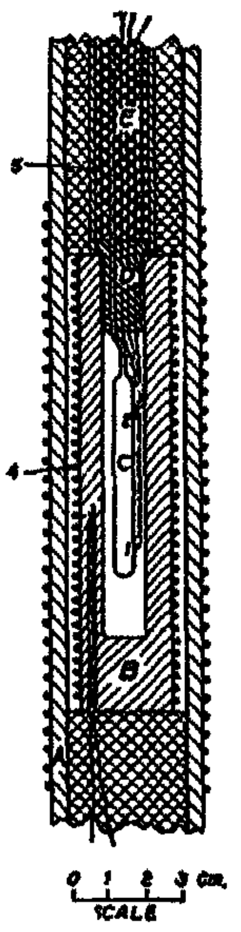

FIG. 1. The reaction tube

It was found necessary to provide a third heating coil, the stem heater labelled 5 in figure 1, in order to prevent a cold spot appearing at block D due to upward radiation. A thin-walled platinum reaction chamber (C), 50 mm. long and 5.0 mm. in outside diameter, was located within block D and was connected with the external pressure-measuring system by a 1-mm. bore platinum tube E. All connections in this part of the apparatus were gold-soldered.

The principal thermocouple (platinum–10 per cent rhodium–platinum) was gold-soldered to the reaction chamber at a lower point (indicated by the numeral 1 in figure 1). This couple had been calibrated at the Bureau of Standards. On the basis of this calibration the melting point of gold was found in our apparatus prior to the installation of the reaction tube to be 1062.9°C. (1063°C. melting point of gold, 1927 International Temperature Scale). A second 10 per cent rhodium–platinum wire was gold-soldered to platinum chamber C at an upper point (point 2), and in connection with the rhodium–platinum wire at point 1 served as a difference couple. Hand regulation of the current in the stem heater 5 prevented a temperature difference between points 1 and 2 of more than 0.05°C. Pressure within chamber C was read on a mercury manometer having an internal diameter of 10 mm. This manometer tube was mounted in front of a mirrored glass scale which had been calibrated at the Bureau of Standards. Pressure readings were reduced to 0°C., and a gravity correction of 0.44 mm. per atmosphere applied. These readings were probably accurate to 0.1 mm. of mercury. Before admitting mercury to the manometer, the reaction chamber containing the carbonate sample was heated to 300°C., pumped down by a mercury diffusion pump, and outgassed overnight at a pressure of 10^{-5} mm. of mercury as read on a McLeod gauge.

TABLE 1

Dissociation pressure of calcium carbonate

TEMPERATURE IN °C.	PRESSURE IN CM. OF MERCURY (OBSERVED)	PRESSURE IN CM. OF MERCURY (CALCULATED)	DIFFERENCE: OBSERVED MINUS CALCULATED
900.3	82.60	82.68	−0.08
877.8	59.87	59.83	+0.04
854.6	42.23	42.23	0.00
774.8	10.93	11.21	−0.28

RESULTS

The carbonate sample was taken from an optically clear crystal of calcite from Minnesota. Analysis showed the crystal to contain 0.011 per cent of magnesium oxide. A sample weighing 0.773 g., crushed to about 100 mesh, was placed in chamber C, filling it approximately half full. The sample was subjected to thermal dissociation, the carbon dioxide evolved was measured in a buret, and the composition of the solid phase used in these measurements was found to be approximately 80 per cent calcium oxide and 20 per cent calcium carbonate, as calculated from the measured carbon dioxide removed. In the case of each equilibrium pressure shown in the table, the temperature was maintained constant from one to two days. In each case equilibrium was approached from both sides.

The pressure–temperature relation recorded in table 1 may be represented by the equation

$$\log_{10} p_{\text{cm.}} = \frac{-9140}{T} + 0.382 \log_{10} T - 0.668 \times 10^{-3} T + 9.3171 \qquad (1)$$

The linear relation

$$\Delta C_p = 0.76 - 0.00061T \qquad (2)$$

was assumed to represent ΔC_p for the dissociation reaction (2, 3, 4, 6, 8) in the temperature range (900–1200° K). The coefficients of the third and fourth terms in equation 1 were taken from equation 2. The second and fifth terms of equation 1 were adopted to give agreement with the observations as indicated in the table.

Calculated from equation 1, the atmospheric dissociation temperature is 894.4°C. and should be correct to better than 0.3°C. This temperature is 12°C. higher than the 882°C. obtained independently by Andrussow and by Tamaru, Siomi, and Adati. It is 2.6°C. lower than the 897°C. obtained by Smyth and Adams, which may be within their probable error. From equation 1

$$\Delta H^0_{1167.6} = 38{,}550 \text{ cal.}$$

SUMMARY

1. A furnace was constructed containing a reaction chamber which was maintained isothermal within 0.04° at 900°C. for more than thirty hours.

2. The temperature at which the dissociation pressure of calcium carbonate equals one atmosphere was found to be 894.4°C.

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THE CREEPING OF SATURATED SALT SOLUTIONS

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INTRODUCTION

Two studies of creeping have been recorded. E. R. Washburn (4) tried various solutions and solid surfaces and noted the general nature of the phenomenon. He observed that creeping is found not only in aqueous solutions of electrolytes, but also in non-aqueous solutions (e.g, sulfur in carbon bisulfide), and occurs not only on glass, but also on porcelain and metals. J. G. F. Druce (1), in common with Washburn, found quantitative results practically impossible because of the large number of variables, but submitted a list of substances "in descending order of creeping:" ammonium chloride, zinc sulfate, barium chloride, potassium nitrate, manganous sulfate, sodium chloride. Druce does not describe his experiments. Washburn seems to have worked with solutions evaporating in dishes. The latter offers as an explanation of the phenomenon the formation of capillaries by the deposited crystals, up which the solution may rise with the subsequent deposition of more crystals and the formation of new capillaries. It is difficult to picture how the capillaries are formed originally, for the protrusion of the crystals beyond the limits of the solution seems much like raising oneself by one's bootstraps. The present authors find that creeping does not *start* by the formation of capillaries, although these undoubtedly contribute largely to the maintenance of vertical creeping. The prime factor in the production of creeping is the ability of the *solid solute to wet preferentially the solid surface over which the creeping takes place.*

EXPERIMENTS

To obtain a quantitative estimate of the height to which a creeping solution will climb, glass rods, thoroughly washed and repeatedly rinsed with distilled water, were suspended with the lower end of each rod under the surface of a saturated solution of either ammonium chloride, potassium chloride, sodium chloride, or potassium iodide. The apparatus was placed under a bell jar to insure as far as possible uniform conditions of evaporation. Concentrated sulfuric acid served as a drying agent. Table 1 shows the numerical results obtained.

In agreement with the results of Druce, ammonium chloride is the "best" creeper. However, the numbers listed are rough averages. Three rods were suspended in each solution and the average height to which the solute climbed was recorded. In spite of every care to insure nearly uniform conditions, results could not be checked by subsequent experiment, except in the case of potassium chloride. In fact, the three rods suspended simultaneously in the same solution would be covered to heights differing by an inch or more. This shows that a control of the usual macroscopic variables is insufficient to secure concordant results. Doubtless such practically uncontrollable factors as local concentration and temperature conditions in the immediate neighborhood of a deposited crystal have a great influence upon the rate and character of succeeding deposits there.

It was evident that creeping was of two sorts. Along the rod itself and closely adherent to it was a layer of very fine crystals. Once creeping had commenced, the upper edge of this crystal mass was added to fairly regularly. At intervals this process was halted temporarily and more crystals would grow outside the first layer. The first layer was regular and even; the second and succeeding layers grew in localized regions and irregularly. Dome-shaped, pyramidal, or cauliflower-like growths appeared, and not infrequently "hair crystals" (2, 3). Ammonium chloride was particularly prolific in this respect. The distinction between the two sorts of creeping was even more evident when studied microscopically.

TABLE I

Creeping on glass rods

SOLUTE	HEIGHT IN INCHES AFTER		
	18 hours	24 hours	90 hours
KI	1.3	1.9	2.5
NaCl	0.0	0.6	1.5
KCl	3.0	3.0	3.0
NH_4Cl	2.5	3.0	3.6
NH_4Cl*	2.0	2.5	3.3
KCl	3.0	3.0	3.0

* This solution contained 1 per cent gelatin.

Very frequently deposition of crystals took place in the bulk of the solution continuously for some time (e.g., eighteen hours in the case of sodium chloride) before creeping commenced. Invariably, as far as the eye could detect, crystallization began on the surface of the rod well *below* the surface of the solution before creeping was visible. According to Washburn's explanation of creeping, the rod, which was certainly clean and wet with the solution, should have allowed creeping immediately, and there should have been no necessity for the presence of crystals well beneath the surface to initiate the process.

When drops of the solutions were evaporated upon glass slides, the deposited crystals were found over an area far larger than that of the original drop. That they found their way out over the slide by a mechanism identical with that by which they crept up rods or the sides of beakers was evident. This arrangement made possible microscopic observation of the process using magnification up to 500 times. Invariably creeping was preceded by crystallization in the interior, and began at those points where the crystals approached and thrust against the edge of the drop.

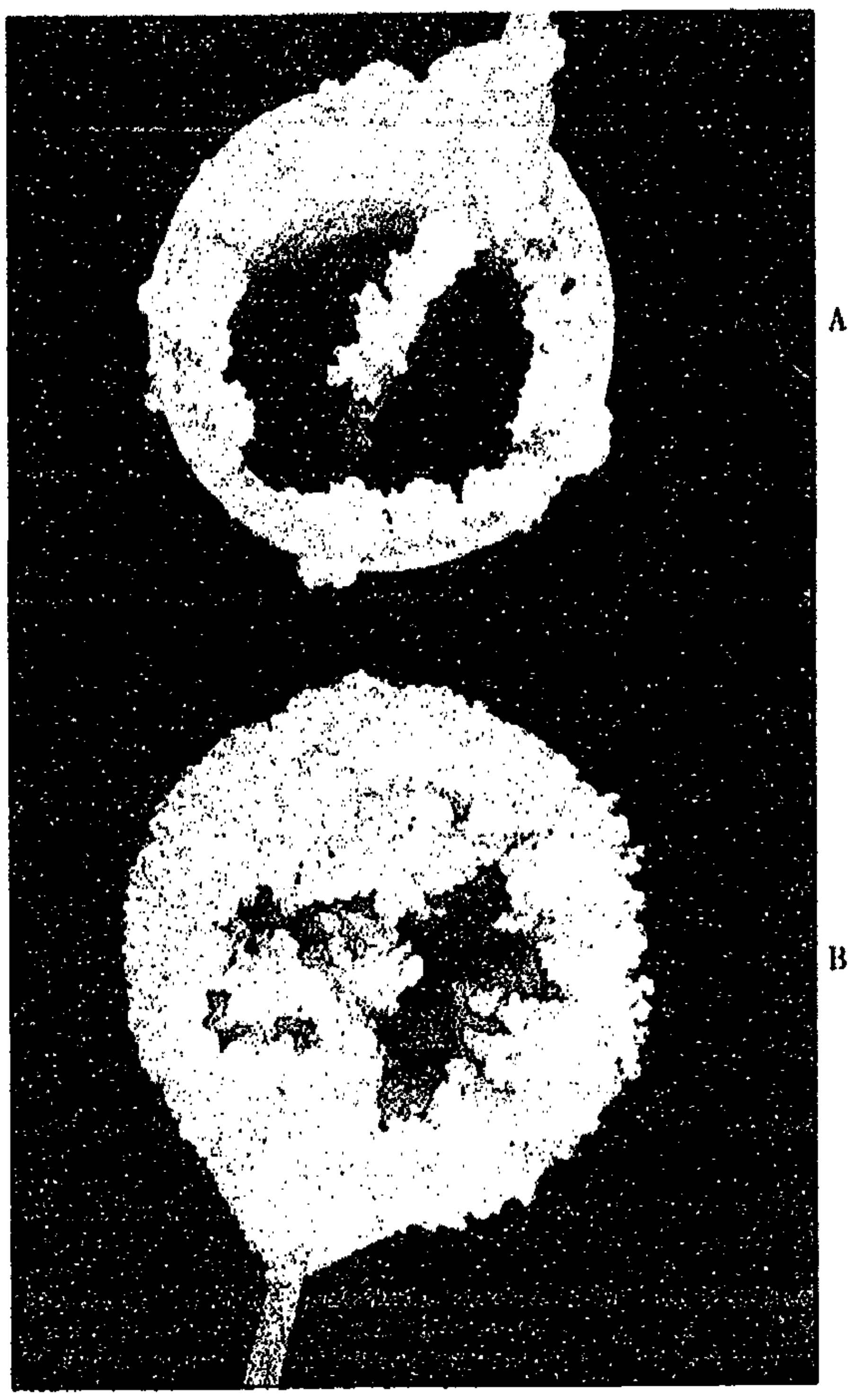

FIG. 1. Beakers containing ammonium chloride solution which was allowed to evaporate freely: (a) evaporation in progress; (b) after reaching dryness

Note in figure 2a how the uppermost crystal of potassium chloride appears to be pushing or stretching the edge of the drop.

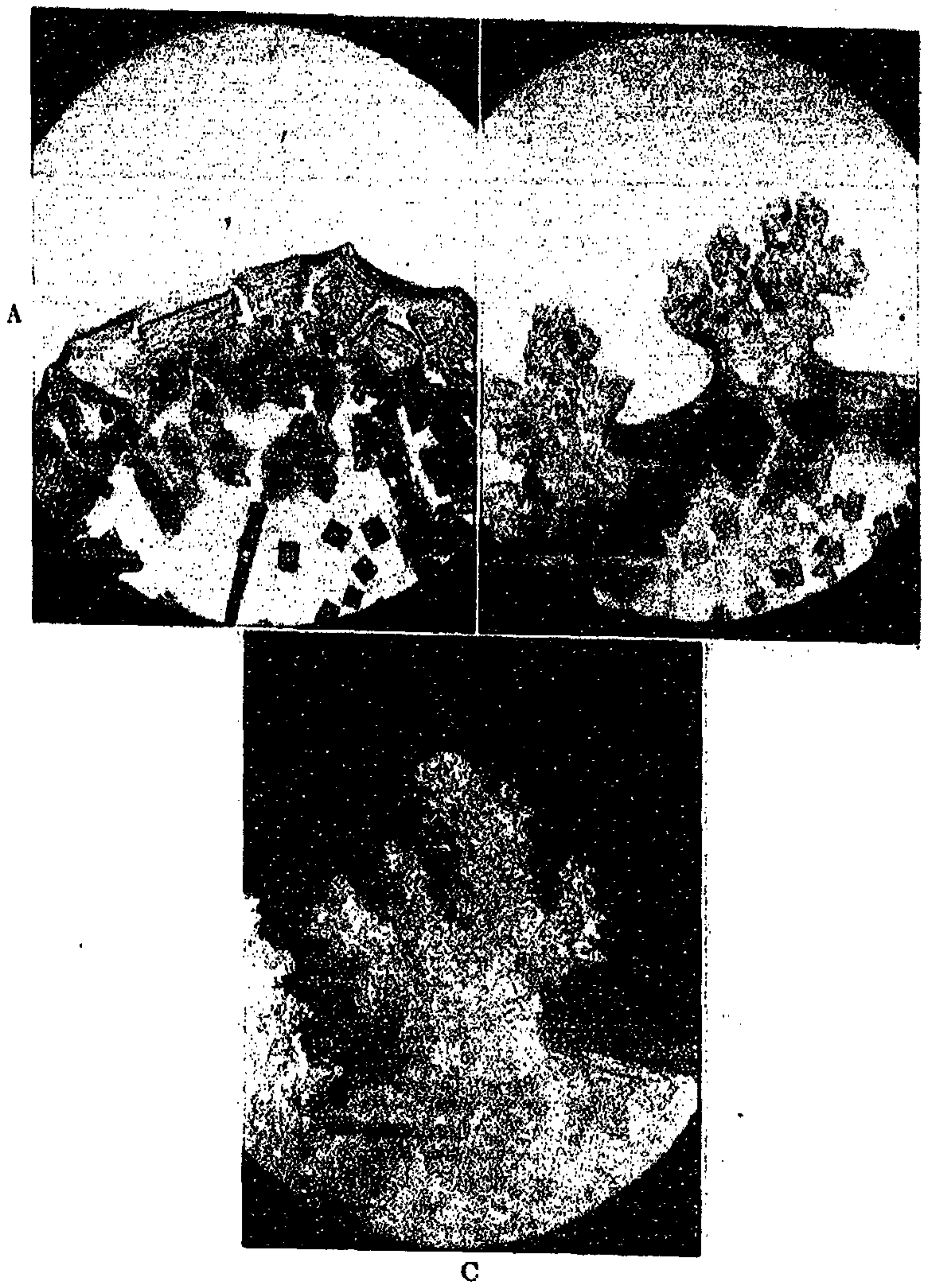

FIG. 2. Photomicrographs, taken at intervals of a few seconds, of the beginning and progress of creeping in a drop of potassium chloride solution. 2a and 2b were taken with bright field illumination; 2c with dark field.

In many drops, especially of solutions of ammonium chloride and the alkali halides, another curious thing took place. The advance of creeping was regular and fairly rapid until suddenly there occurred a "flooding." The advancing mass[1] of crystals was very suddenly broken up and inundated by a relatively large quantity of solution. In about half the cases of flooding the very outermost ring of material is unaffected, remaining fixed in position during the whole process until creeping begins again. In other cases the outer edge is also loosened and is *swept back towards the center of the drop.* After flooding occurs, creeping ceases until the loosened mass becomes compact again through settling and the deposition of further crystalline material. Flooding is invariably localized. Regular creeping occurs at other points of the periphery even while flooding is proceeding at certain points. The crystal mass loosened by flooding and subsequently reconsolidated is noticeably thicker that the unflooded portions. Each successive flooding produces a new thickening, and it is possible to look

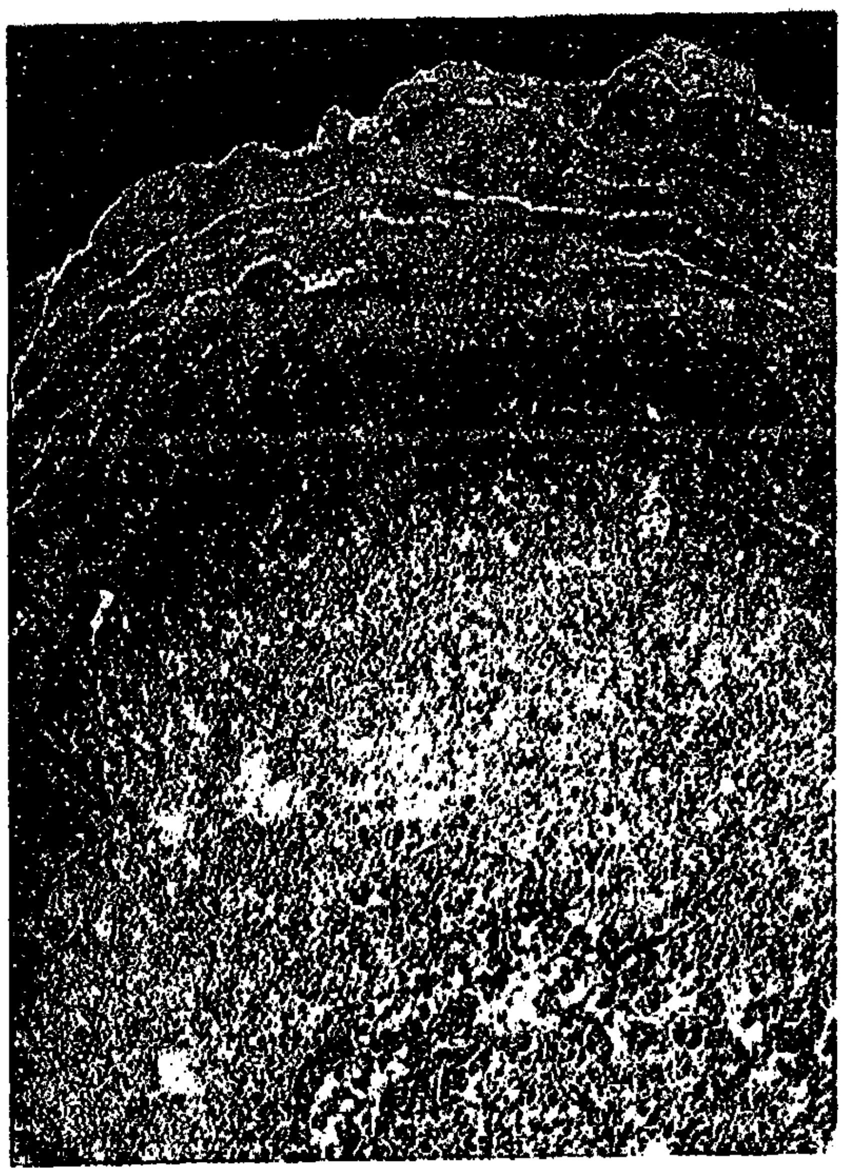

FIG. 3. Illustrating the traces of the periodic flooding phenomenon

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[1] Of course the crystals themselves do not move while creeping is going on. The outer edge of the deposited material advances because new crystals grow beyond the limits of those already there.

at a dried drop and tell how many floodings occurred during the creeping (cf. figure 3). A similar appearance was observed in the material which had climbed the glass rods in the previous experiments.

Negative results were obtained when a definite rhythm was sought in the floodings. Although a certain tendency towards a definite time interval between floodings could be traced in a given region of a given drop, the interval bore no simple relation to those observed even in other portions of the same drop. Some drops went to complete dryness without observable flooding at all.

MECHANISM OF CREEPING

The hypothesis which seems to the authors most fruitful in explaining the phenomena connected with creeping is as follows. A drop of solution, becoming supersaturated by evaporation, will deposit crystals wherever there are nuclei. Since these are not necessarily at the edge of the drop, crystals often appear first in the interior. No crystals will form outside the drop, for the reason that no solution and so no solute exists beyond the drop.[2] This applies with equal force to the possibility of crystallization beyond the visible limits of the solution in the common case of creeping up the wall of a dish. The notion that crystallization can occur there and so form capillaries up which the solution may climb appears highly improbable.

The small crystals first formed in the interior of the drop may be and frequently are drawn by the action of surface forces to the three-phase line where solution, glass, and air meet. It often happens that crystals are formed near this line, because the convex surface of the drop nearby promotes evaporation and so local supersaturation, which favors crystallization. The crystals now have the opportunity, if the interfacial tensions are of the proper magnitude, of wetting the glass preferentially, i.e., of coming into intimate or optical contact with it, no solution or solvent intervening. The solution touches and wets the glass all around but not under the crystal. The crystal will grow most rapidly in the direction away from the drop, because crystallization is most rapid in the thin film of

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[2] It is true that aqueous solutions "wet" glass, but the angle of contact is almost never zero in practice, and is certainly not so when a drop will maintain its shape and not spread to form a film of uniform thickness. The possibility of a monomolecular film, or even a very thin polymolecular film, over the slide beyond the limits of the drop is not entirely precluded, but the film, if it exists, contains a wholly negligible amount of solute for two reasons: (1) in aqueous electrolytic solutions the solute is negatively adsorbed to the surface, and the film would be, in a manner of speaking, all surface; (2) spreading to such a thin film probably occurs by evaporation and subsequent recondensation at favorable points, a procedure which is impossible for the solute (cf. N. K. Adam, The Physics and Chemistry of Surfaces, Oxford University Press, 1930).

solution covering the outer edge of the crystal. The growth of the crystal in this direction carries the solution along with it. The crystal grows outwards, covered by a layer of solution which extends beyond the advancing edge and there acts as a mother liquor for the growth of the crystal already formed and for the formation of new ones if nuclei appear. The layer is constantly replenished from the body of the drop.

Such a growth on a horizontal slide where what small effect gravity has would assist the spreading, might conceivably continue steadily until all the solvent had evaporated, and this does happen in the absence of flooding. Not infrequently the area originally occupied by the drop is almost bare of deposited crystals at the end, practically the entire mass of solution having followed the creeping crystals.

It may be noted in the various illustrations that the creeping mass is very compact and that there are certainly no obvious capillaries. It is highly probable that there are no capillary spaces *beneath* the outer crystals. The solution is advancing *over* them, not through or under them.

If some fault in the mass permits the liquid to penetrate it and reach the slide, thus getting *under* the crystals, there is a sudden and violent alteration of surface energy relations. The mass is broken up as far as it can be loosened by the shock. The advanced edge of the solution experiences a force tending to make it assume more or less the position it originally occupied. The tiny individual crystals become separated and tend to be pulled back to the main body of the drop. This is evidence that if the crystals were not in intimate contact with the slide, creeping would not take place.

The fact that flooding is sometimes absent shows that it is not an essential part of creeping but is caused by fortuitous circumstances, say the existence of a very minute speck of impurity on the slide which prevents the crystal from making optical contact.

It often happens that little knobs and other growths appear in the crept material on the slide just as they do in material which creeps on rods. They are especially frequent in the thicker regions where flooding has occurred. They represent the "efflorescent" creeping, i.e., creeping upon previously deposited crystals. Both solution and solute will be able to wet such a surface readily. In spite of this it is usually true that the major portion of the material is to be found in the smooth "mural" creeping (creeping directly along the wall), and only a small part in the knobs. This is due in large part to the relative *smoothness* of the surfaces. Freshly grown crystal surfaces, being nearly plane, can come into intimate contact with smooth surfaces far more readily than with rough. The glass plate or rod is smooth, while the mass of small crystals, oriented more or less at random, is rough. In following the rough surfaces such growths as do occur may proceed in any direction, even vertically. In the process of flooding and subsequent reconsolidation it is readily conceivable that some droplets of solution may become trapped and have no outlet for depositing crystals except upwards.

Drops were allowed to dry simultaneously upon (i) a polished slide, (ii) a slide etched by hydrofluoric acid, and (iii) a slide ground upon a fine stone. In every case creeping was definitely less pronounced upon the rough than upon the smooth surface. This may seem surprising, because liquids will spread farther upon rough than upon smooth surfaces because of the capillary attraction of the pits and grooves. That creeping occurs less readily upon surfaces which are more easily wet by the solution itself is good evidence that it is the ability of the *solid solute* to advance by wetting the surface that is the primary factor.[3] In support of these experiments it was found that the addition of wetting agents such as gelatin and gardinol caused the liquid drop to be flatter but had no effect upon the extent of creeping, as judged by the relation between the area of the drop and the area covered by creeping.[4]

The effect of gravity was ascertained to be negligible by allowing drops to dry upon slanting slides or even hanging from the bottom. No significant effect was observed. Surface effects take precedence entirely. Washburn (4) remarks that after crystallization has proceeded up to the rim of a dish and has started down the outside the advance is accelerated, because the solution "siphons" out and gravity helps instead of hindering. This has not been the experience of the authors in the relatively few cases in which they studied creeping out of beakers. If a glass rod be allowed to rest against the side of the beaker, creeping seems to proceed just about as readily *up* the rod above the rim as over the rim and *down* the beaker (cf. figure 1).

The following observation affords direct evidence that the solid solute wets the slide. If a drop of solution is allowed to dry, and the slide is examined from *beneath,* it will be noticed that there is a distinct difference between the outer edge of the crept crystals and the remainder of the deposited solute. Let the slide be held in such a position that it reflects the light from a patch of sky or a frosted bulb. If there are no crystals on the slide, light will be reflected uniformly from both surfaces of the slide.

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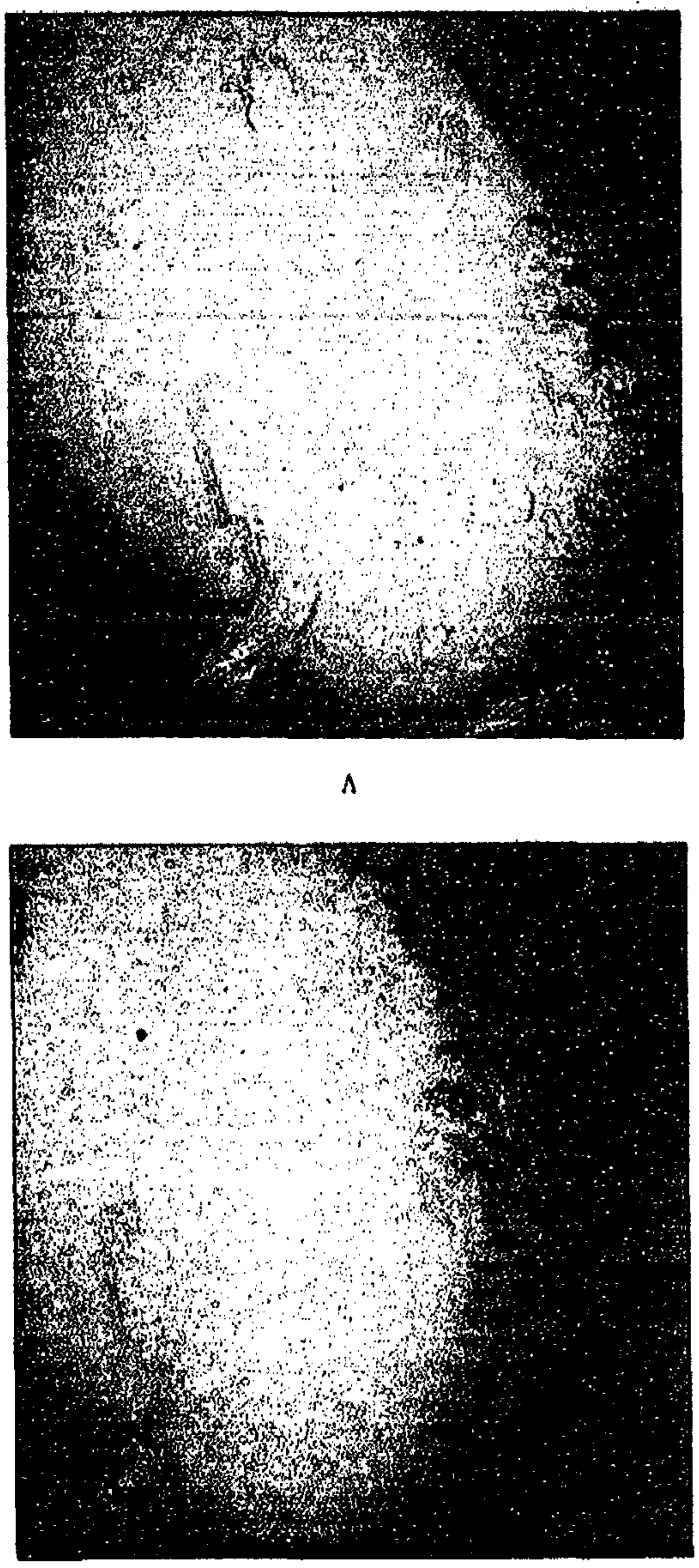
[3] Washburn (4) notes that sulfur in carbon bisulfide creeps readily over metallic copper "in spite of" the fact that a deposit of sulfide of copper immediately forms. This is merely an extreme case in which the solute "wets" the supporting surface chemically.

[4] Quantitative results are hard to obtain. Ratios such as that mentioned were measured for fifty drops nearly identical in magnitude and conditions of evaporation. They varied from 2.78 to 11.61, with a mean of 6.12 and a mean deviation of 1.72. All conclusions recorded in this paper have been drawn from a large number of experiments in order to obtain a reliable average. Quantitative conclusions drawn from a single experiment are entirely untrustworthy.



A

B

Fig. 4. Showing that the outer rim of crystals which have crept on a slide is in very intimate contact with the slide

If the air beyond the farther surface is displaced by a crystal or any other medium of large refractive index, the amount of light reflected is cut down considerably. Hence those portions of the farther surface with which the crystals are in *optical contact* will appear relatively dark. It is always the *outer rim* of crept material which gives this effect, as shown in figure 4a.[5] Figure 4b shows the same slide in the same position, but after the crystals had been rubbed off as well as possible with the ball of the thumb. It is typical that the outer rim of crystals should resist removal by rubbing, another indication of the extremely intimate contact of these crystals with the slide. They must be *scraped* off with the finger nail. The closely adherent crystals are evidently those which appeared dark in the first picture. It is clear that the outer rim of crystals has a close hold upon the slide and pulls the liquid with it as it grows.

FACTORS INFLUENCING CREEPING

Among the factors governing the extent of creeping, crystal habit is one of the most important. Ammonium chloride is typically dendritic and creeps rapidly. On the contrary, potassium nitrate forms rod-like crystals and so grows preferentially in one direction. Hence ammonium chloride usually creeps to form a roughly circular mass conforming to the shape of the drop, while potassium nitrate forms a few directed masses.[6] Further, the formation of a relatively simple structure of few units similarly directed offers less opportunity for flaws leading to flooding. Ammonium chloride floods habitually, potassium nitrate only exceptionally. The alkali halides, which are cubic like ammonium chloride but not usually dendritic, do not creep as readily as ammonium chloride.

The nature and structure of the supporting surface is obviously important. Smooth surfaces are better for creeping than are rough. It is also evidently necessary that the solution wet the surface or it would not advance in front of the crystals. It was found that ammonium chloride solutions crept decreasingly well on the following surfaces: glass, stearic acid, vaseline, paraffin, sulfur. This is about the order in which these surfaces are wetted by water.

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[5] This photograph was obtained as follows. Light from a frosted Mazda bulb was reflected by means of an inclined glass plate down upon a slide bearing on its under surface the crystals formed during the evaporation of a drop of potassium nitrate solution. The light reflected from the slide passed back through the glass plate into the camera vertically above the slide. Superposed upon the image of the bulb can be seen the dark regions where the crystals are in optical contact. The other crystals can be seen faintly by scattered illumination.

[6] It may be of interest to note that observation of the deposited potassium nitrate between crossed Nicols shows that the major portion of the material in one of the directed masses has the optical axis similarly directed, although the thickness varies from point to point and observation with ordinary light shows a number of separate crystals.

Even if the supporting surface can be wetted by both solute and solution, creeping may not occur. If the free surface energy of the crystal–solid interface is greater than the combined free surface energies of the solution–solid interface and the solution–crystal interface, the crystalline solute cannot wet the solid surface preferentially and creeping cannot commence.

The above applies to creeping directly along the wall,—"mural" creeping. It is possible, however, for creeping solutes to cross a barrier of, say, sulfur, as follows. By "efflorescent" creeping the solute builds up a wall of material at the edge of the barrier. Such walls have been observed to grow to heights of over 2 mm. on slides. By a continuation of efflorescent creeping parallel to, but not in actual contact with, the supporting surface, the solute advances almost indefinitely. If the barrier is narrow and other circumstances are right, mural creeping may recommence on the other side of the barrier. Narrow barriers actually do not prevent creeping.

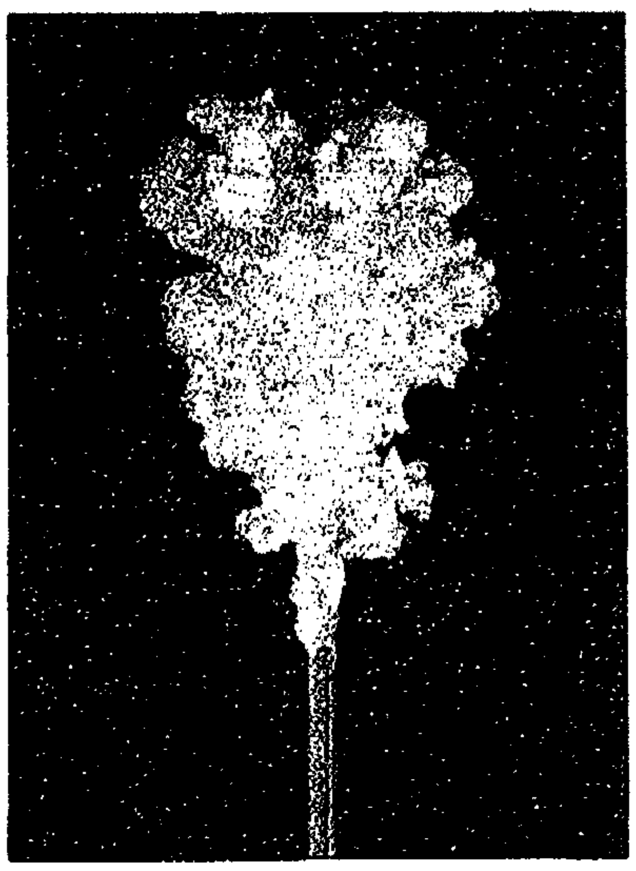

FIG. 5a. Knob of ammonium chloride crystals formed on the end of a glass capillary of about 1 mm. outside diameter

When the solute is creeping upwards along a beaker wall the formation and maintenance of capillaries must be important. It is probable that strictly mural creeping must be supplemented by floodings which loosen the mass a little, permitting the formation of capillaries. A somewhat violent flooding might seriously damage the layer of crystals at a particular point and induce efflorescent creeping there. In figure 1 are two beakers of ammonium chloride solution, one just approaching dryness and the other dry. Note the localized growths, particularly on the stirring rod

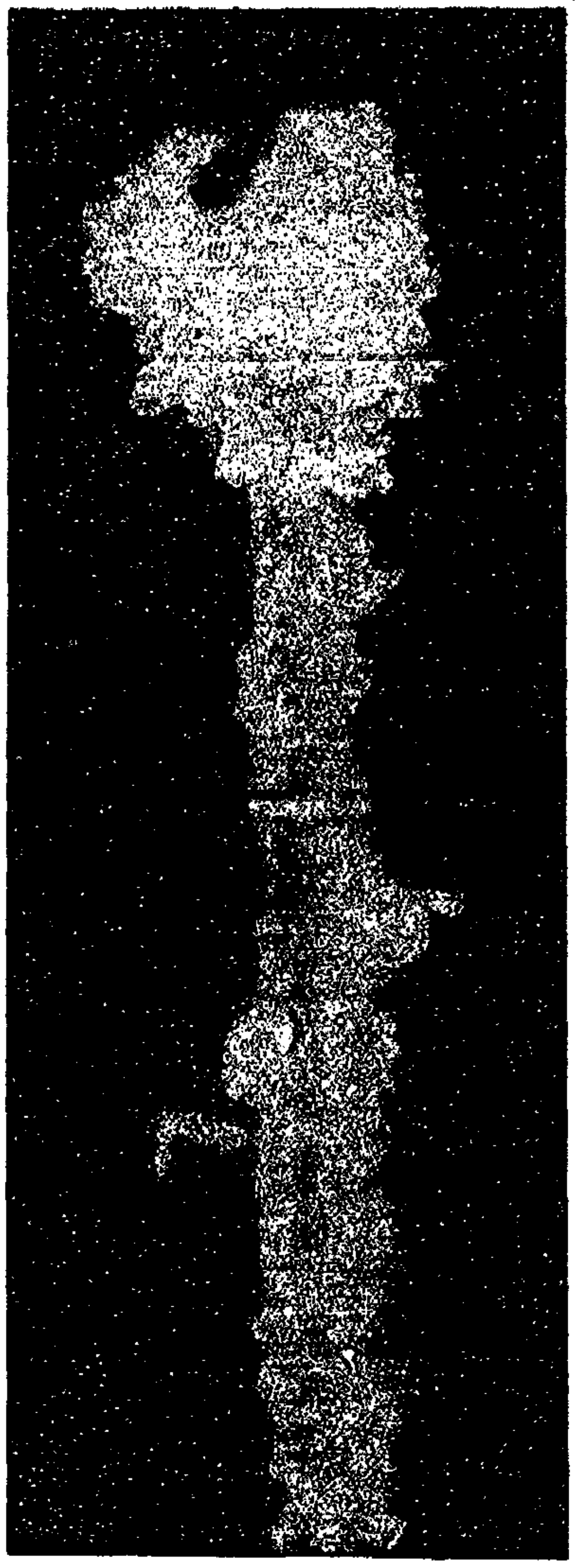

FIG. 5b. Potassium nitrate crystals grown on the end of a glass capillary of about 1 mm. outside diameter. Note the sheath of crystalline material along the outside of the tube and the numerous and complicated growths of "hair crystals."

in the first beaker, and the consolidated mass of growths in the other. The capillaries serve to keep the advancing edge supplied with solution and they fail to do this if they become either too wide or clogged, as Washburn has pointed out.

EFFLORESCENT STRUCTURES

The crystalline structures formed by efflorescent creeping are interesting and worthy of study. If a very fine glass capillary is allowed to stand in a saturated solution of ammonium chloride or potassium nitrate to such a depth that the solution will rise to the top of it, crystals are deposited there. In some cases knobs of material are formed (figure 5) and practically no creeping *down* the outside of the tube occurs. Once a spherical mass of potassium nitrate crystals over $\frac{3}{4}''$ in diameter was obtained. In other cases creeping down the tube also takes place, and in both cases hair crystals are frequently formed (figures 5 and 6). The formation of hair crystals without the use of collodion or silica gel is being studied.

FIG. 6. "Hair crystals" of potassium chloride. Note the resemblance to figure 5a. The hair crystal is hollow and has grown a knob on top

SUMMARY

The previous work of Washburn and of Druce has been extended, and a few roughly quantitative results obtained. The hypothesis advanced by them as to the mechanism of creeping has been extended to explain the formation of the capillaries they assume. Creeping is supposed to occur when the *solute* is capable of displacing the solution from, and spreading over, the supporting surface. Creeping is commonly accompanied by "flooding," a process which loosens the compact mass and permits capillaries to form. The solution rises *through* the capillaries and *over* the outermost edge of deposited material, which has been shown to be in optical contact with the surface.

The effect of the nature of the supporting surface, of the crystal habit of the solute, and of the various free surface energies involved has been discussed.

Certain curious crystal formations have been noted.

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ISOELECTRIC POINT OF GLYCININ[1]

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INTRODUCTION

There are two different points of view with regard to the relationship between the minimum physical properties and the isoelectric point of a protein. Loeb (4), who studied gelatin, concluded that at the isoelectric point the physical properties of a protein are all at a minimum. Michaelis (5) developed a theory according to which the solubility of an amphoteric substance is directly proportional to the ionization, so that at the isoelectric point the solubility must be at a minimum. An entirely different opinion concerning the relationship between the isoelectric point and the minimum physical properties of gelatin is held by Johlin (2). He reported that there is no definite relationship between the minimum physical properties and the isoelectric point of gelatin, as pointed out by Loeb and Michaelis. Very recently, however, Pedersen (7) found that the pH at the minimum solubility of certain blood proteins (helix, hemocyanin) coincides with their isoelectric points.

No record, hitherto, can be found in the literature concerning the isoelectric point of glycinin. It is the purpose of this investigation to determine the isoelectric point of glycinin, i.e., the point at which the negative and positive charges carried by the glycinin particles are equal; and, furthermore, to study the relationship that exists between the isoelectric point and the minimum of certain physical properties such as viscosity, solubility, and conductivity.

EXPERIMENTAL

Materials

The glycinin used in this study was prepared by the modified Osborne and Clapp method (6). It was twice purified by dissolving in 10 per cent

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[1] This is one of two papers constructed from a dissertation presented by Libin Tsi Cheng to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1934.

[2] Chief Research Biochemist, Department of Physiological Chemistry, the Science Society of China, Nanking, China.

sodium chloride solution, filtering, dialyzing, and finally treating with methyl alcohol and ether.

Method of procedure

The isoelectric point of glycinin was found by means of electrophoresis. The pH values at which the glycinin solution showed minimum physical properties were also measured.

(*a*) *pH measurements.* The pH values reported in this paper were all measured by means of the hydrogen electrode at 25°C. (±0.1°). In some cases these values were checked with measurements made with the quinhydrone electrode at the same temperature.

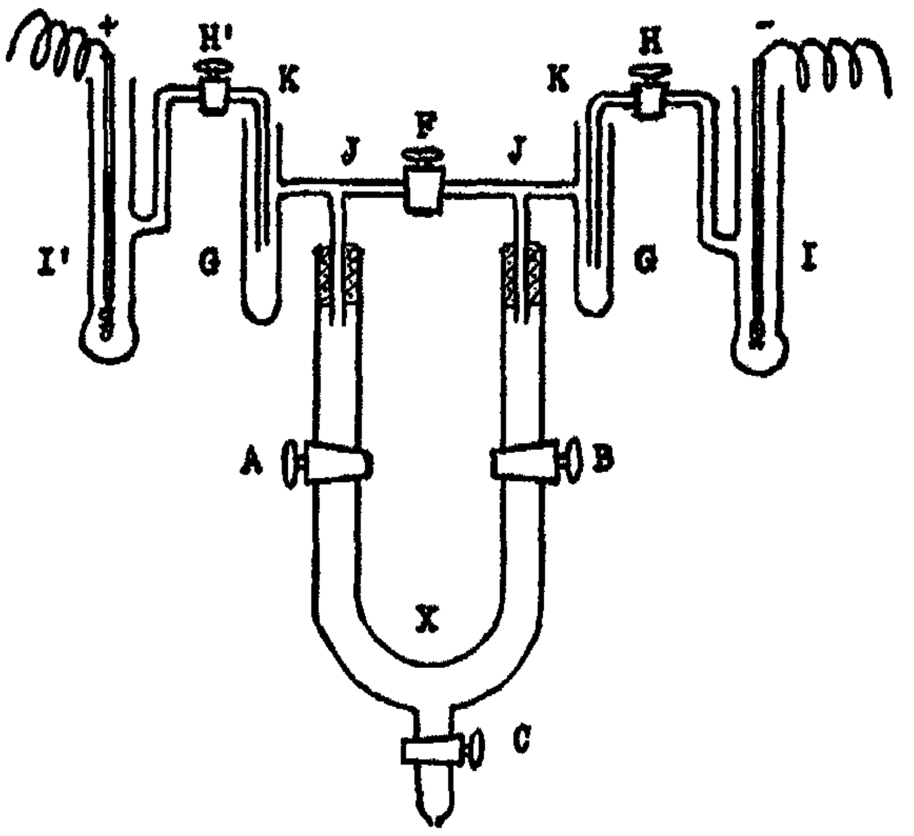

Fig. 1. The apparatus

(*b*) *Electrophoresis.* The apparatus and method of Sherman, Thomas, and Caldwell (8), slightly modified by the authors, was used in this study. A sketch of the apparatus is shown in figure 1. The procedure employed is described as follows: A 0.5-g. sample of glycinin was dissolved in 50 ml. of 1 per cent sodium chloride solution in a 125-ml. Erlenmeyer flask. The mixture was shaken for 20 minutes and then filtered. More 1 per cent sodium chloride solution was added to bring the volume of the filtrate to 50 ml. Fifteen milliliters of the protein solution thus prepared was taken for each determination and was drained into a large Pyrex test tube to which was added 15 ml. of buffer mixture of definite pH. Potassium phthalate–sodium hydroxide buffer mixtures of various pH were prepared according to Clark (1). This resulting solution was thoroughly mixed and its pH measured. Twenty-five milliliters of the protein–buffer mixture was then pipetted into the U-tube (figure 1); this quantity just filled the bend, x, and the stopcocks, A and B. After all the bubbles were excluded, the stopcocks A and B were closed. The two arms above the stopcocks were washed with distilled water and filled with buffer solution of the same pH as was used in preparing the protein–buffer mixture. The leveling bridges (J) and the connecting flasks (G) were then inserted. Buffer solution of the same pH was used to fill the entire bridge. This was accomplished by opening the stopcock, F, adding the buffer solution to one end, and letting it flow through the bridge to the other end. The electrode vessels (I and I′) and their bridges (K) were also filled with the same buffer solution and inserted in the connecting flasks (G). Solid copper sulfate and a copper electrode were placed in vessel I, and solid potassium biphthalate and a platinum electrode were placed in vessel I′. When the whole apparatus was assembled as shown in figure 1, the stopcocks H, H′, and F were opened in order to adjust the level in the whole system. A 110-volt direct current was turned on while the stopcocks, H, H′, and F were still open and the stopcocks A and B closed. The stopcocks H and H′ were then loosely closed, so that a film of the buffer solution surrounded them, thus conducting the current. The stopcock F was then closed as tightly as possible. Stopcocks A and B were then opened simultaneously. The electrophoresis was continued for twenty-four hours in each determination and at 20°C. (±1°). At the end of twenty-four hours the stopcocks A and B were both closed simultaneously, the current broken, and the other parts disconnected. The solution present in each arm of the U-tube was then poured carefully into two large test tubes. The arms were rinsed thoroughly with distilled water. The solution in the bend of the U-tube was emptied through stopcock C with stopcocks A and B open. The pH of the latter solution was determined again. Five milliliters of the solution from each arm of the U-tube was used to determine the nitrogen content by the Koch-McMeekin-Kjeldahl method (3).

(*c*) *Solubility measurements.* In order to determine the solubility of glycinin, 10 ml. of a 1 per cent solution of glycinin prepared by dissolving 1 g. of glycinin in 100 ml. of 1 per cent sodium chloride solution was mixed with 10 ml. of a buffer mixture of desired pH. The mixture was shaken for five minutes and then centrifuged for ten minutes. The clear liquid part was decanted into a dry test tube. Five milliliters of this clear liquid was taken for total nitrogen determination by the Koch-McMeekin-Kjeldahl method (3). A Duboscq colorimeter was used in determining the nitrogen content of the solution. The solubility is expressed in terms of the per cent nitrogen in solution (table 2).

(*d*) *Viscosity determinations.* Ten milliliters of the 1 per cent protein solution was mixed with 10 ml. of buffer mixture. After shaking for ten

TABLE 1

Electrophoresis of glycinin

pH OF PROTEIN SOLUTION BEFORE ELECTROPHORESIS	N IN MG. PER 500 ML. IN CATHODIC SOLUTION	N IN MG. PER 500 ML. IN ANODIC SOLUTION
4.25	15.0	2.3
4.43	6.4	6.0
4.63	6.2	5.8
4.83	5.7	5.5
4.94	3.7	3.4
5.02*	2.2	2.3
5.11	3.6	3.8
5.23	5.5	5.6
5.42	5.2	6.3
5.63	6.0	6.6
5.83	6.4	8.8
6.05	6.5	9.0
6.28	2.0	10.5

* Isoelectric point = pH 5.02.

TABLE 2

Solubility of glycinin

pH	DUBOSCQ COLORIMETER READING OF UNKNOWN*	N IN MG. PER 50 ML.
3.25	12.0	5.00
3.45	13.4	4.48
3.65	14.4	4.17
3.85	15.4	3.90
4.05	16.4	3.66
4.23	17.4	3.45
4.43	18.4	3.21
4.63	20.5	2.93
4.83	21.4	2.81
5.02	23.1	2.60
5.42	22.4	2.68
5.63	15.0	4.00

* The standard reading in each instance was 20.

TABLE 3

Viscosity of glycinin

pH	TIME OF FLOW* IN SECONDS	pH	TIME OF FLOW IN SECONDS
3.6	85.0	4.6	83.0
3.9	84.5	4.8	80.0
4.0	84.0	5.0	79.8
4.2	83.8	5.2	82.1
4.4	81.0	5.4	88.0

* All determinations were checked several times, using two different Ostwald viscosity pipets at 25°C. (±0.1°).

minutes, the time of flow of this solution was determined by means of an Ostwald viscosity pipet at 25°C. The pH was also determined in each case at the same temperature.

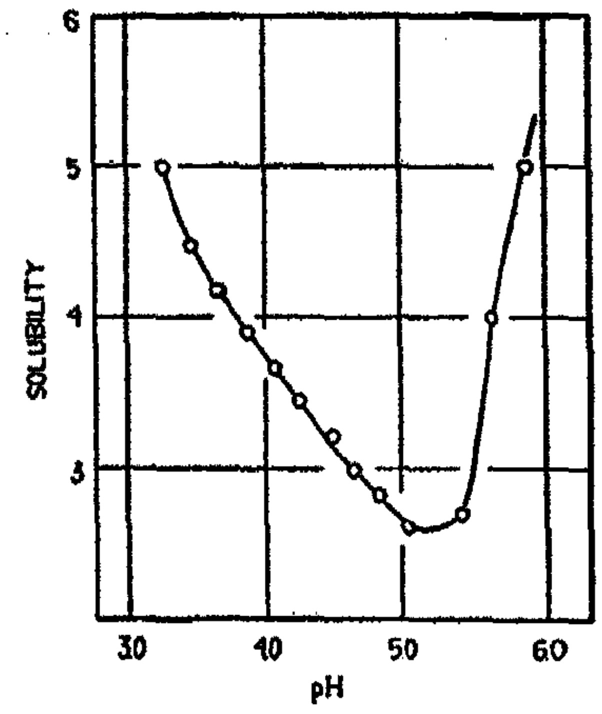

Fig. 2. Solubility of glycinin at different pH values

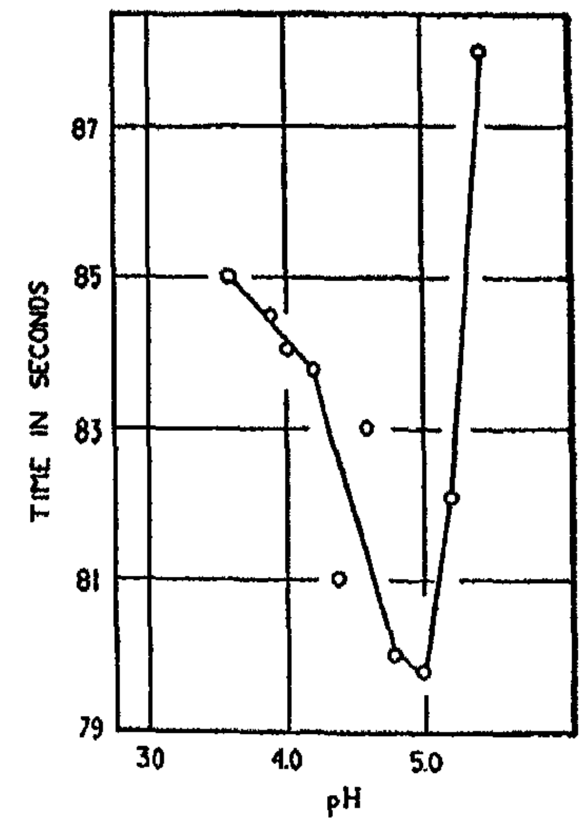

Fig. 3. Viscosity of glycinin at different pH values

(e) *Conductivity measurements.* In making the conductivity measurements the resistance of the mixtures of 10 ml. of 1 per cent glycinin solution and 10 ml. of each buffer mixture was measured in the usual way. The resistance of each buffer solution employed was also determined in order to obtain by difference the conductivity due to protein.

TABLE 4

Conductivity of glycinin

pH	R BUFFER ALONE	R' BUFFER-PROTEIN	D (R' − R)	ΔD	$\left(\frac{1}{\Delta D}\right)$ ΔC	$\frac{\Delta C}{\Delta pH}$
	ohms	*ohms*	*ohms*			
4.2	591.1	1113.0	521.9			
				12.9	0 07751	0.03875
4.4	562.0	1071.0	509.0			
				30.0	0.03333	0.01666
4.6	531.0	1010.0	479.0			
				31.5	0.03174	0.01587
4.8	492.0	939.5	447.5			
				30.5	0.03277	0.01688
5.0	460.3	877.0	417.0			
				32.1	0.03115	0.01557
5.2	425.0	809.9	384.9			
				27.4	0.03650	0.01825
5.4	396.5	754.0	357.5			
				22.1	0.04524	0.02262
5.6	371.9	707.3	335.4			
				16.1	0.06211	0.03105
5.8	356.7	676.0	319.3			
				15.3	0.06536	0.03218
6.0	346.2	649.0	304 0			

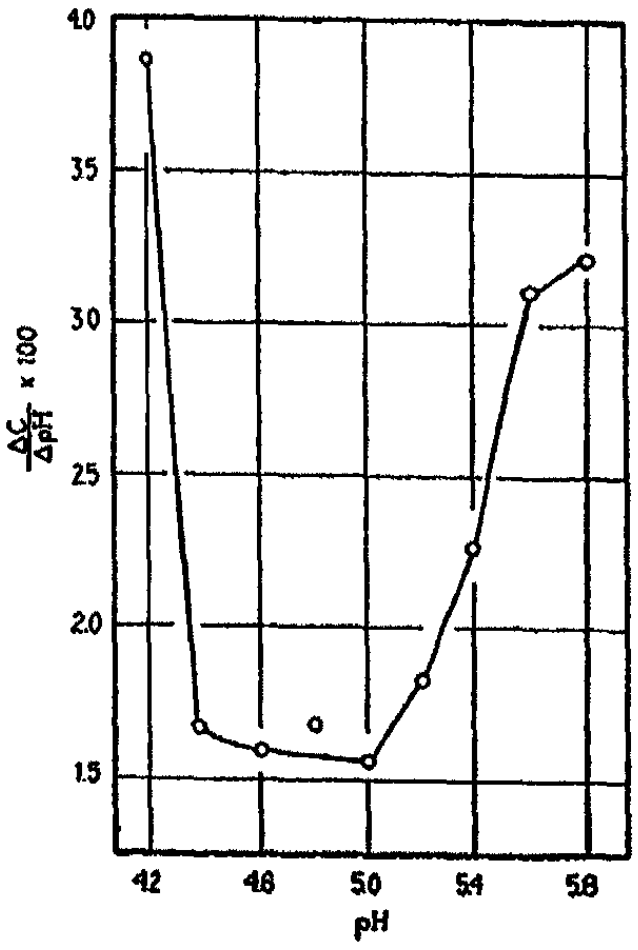

FIG. 4. Change in conductivity of glycinin with change in pH

RESULTS

The data given in table 1 show clearly that the migration of the glycinin particles is at a minimum near a pH value of 5.02.

The minimum solubility occurs near a pH value of 5.02 (see table 2). The curve shown in figure 2 was obtained by plotting the pH as abscissa and the solubility expressed in milligrams per 50 ml. of solution as ordinate.

The data in regard to the viscosity of glycinin (table 3) show that the minimum time of flow occurred at a pH of 5.0. The curve obtained by plotting the time of flow in seconds against pH is shown in figure 3. The pH at which the protein shows a minimum time of flow is the same as the pH at which the protein shows its minimum viscosity. Therefore the minimum viscosity of the glycinin solution is near a pH value of 5.0.

The results of the conductivity measurements are given in table 4. R represents the resistance of the buffer solution alone, while R' is the resistance of the buffer-protein mixture. The resistance due to the protein is indicated by D. The term ΔD is the change in resistance due to a change in pH of 0.2; ΔC, the change of conductivity; and ΔpH the corresponding change of pH. The ratio, $\Delta C/\Delta$pH, represents the change in conductivity with respect to an accompanying change in pH.

According to the data in table 4 the value of the ratio $\Delta C/\Delta$pH reaches a minimum when the pH is 5.00.

CONCLUSION AND DISCUSSION

It is clearly shown in the foregoing data that the isoelectric point of glycinin is near a pH value of 5.02 as determined by electrophoresis. Accordingly, the minimum physical properties, i.e., solubility, viscosity, and the ratio, $\Delta C/\Delta$pH, of the glycinin solution all occur at a pH of 5.0. The difference of pH in the isoelectric point as determined by electrophoresis and the pH of minimum physical properties is only 0.02. Thus, the data presented in this paper evidently confirm Loeb's statement (4), namely, that protein solutions show minimum physical properties at their isoelectric point. The difference of 0.02 in pH is no doubt within the limits of experimental error.

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THE APPARENT VOLUMES AND APPARENT COMPRESSIBILITIES OF SOLUTES IN SOLUTION. III

UNSATURATED AND SUPERSATURATED SOLUTIONS OF CALCIUM NITRATE

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The study of the effect of concentration on the apparent properties is, in the case of most electrolytes, limited to a relatively small range of concentration. Since there is no reason (5, 8) to expect the variation of solution properties to exhibit a discontinuity at the saturated state, one means of increasing the range of concentration is to consider the supersaturated state along with the unsaturated state. It was with this object in view that the present series of measurements of calcium nitrate solutions were undertaken. Highly supersaturated solutions of this salt, it will be recalled, are quite stable.

PURIFICATION OF MATERIALS

Water was doubly distilled, once from dilute alkaline permanganate, and once from dilute sulfuric acid through block-tin condensers.

Calcium nitrate was made by dissolving 1 kg. of technical calcium carbonate in an excess of C.P. nitric acid. After filtration to remove insoluble matter, the solution was made basic by adding pure calcium oxide in slight excess and again filtered to remove the insoluble magnesium hydroxide and most of the slightly soluble strontium and barium hydroxides. Further purification of the salt was accomplished by bringing about the crystallization of the tetrahydrate from a slightly acid solution, the crystals of which were collected and finally drained in the centrifuge. Two crops of the crystals, each roughly one-third of the material, were collected and the residual mother liquor discarded. The first crop gave negative tests for strontium, barium, and iron, and was used in making the first stock solution (No. 23). The second crop contained traces of strontium, barium, and iron. This portion of the salt was ultimately combined with solutions prepared from stock solution No. 23, and the crystallization process was repeated. The material obtained at this stage gave no further evidence of impurity and was used in making up stock solutions No. 20, No. 22, and No. 19. The calcium nitrate in the solutions prepared from these stock solutions was again recovered by recrystallizing as the tetrahydrate and used to prepare stock solutions Nos. 18 and 21.

PREPARATION AND ANALYSIS OF SOLUTIONS

All of the solutions which were investigated were prepared by diluting or concentrating stock solutions. The solutions more dilute than the stock solutions were made by diluting weighed portions of the stock solution with water, the composition being obtained from the ratio of the weights before and after dilution. The supersaturated solutions were prepared by evaporating weighed amounts of the stock solutions in weighing flasks on the hot plate at about 70°C. During this operation the flasks were kept covered to prevent entrance of dust. When the solutions had evaporated to the desired composition, the flasks were stoppered, cooled, and weighed. Suitable counterpoises were used in all weighings and vacuum corrections were applied.

The analysis of four of these stock solutions was carried out by the following method, which is a modification of that described by Ewing (1). Enough solution to yield about 1 g. of anhydride was weighed in weighing bottles and evaporated in an electric oven at 110°C. overnight. The samples were then seeded with a minute particle of the anhydride and dehydrated to the anhydride by gradually raising the temperature to 170°C. Constant weight was usually attained in twenty-four hours, the samples being cooled in a desiccator over phosphorus pentoxide before weighing. In all cases triplicate determinations were made and vacuum corrections applied.

That this method of analysis is trustworthy and precise was shown by two sets of experiments which were carried out solely as checks. In one case, stock solution No. 20 was analyzed by the conventional oxalate method as well as by the dehydration method described above, giving the following values for the per cent of calcium nitrate:

Analytical method	*Mean of 3 analyses*	*Average deviation*
Oxalate → CaO	53.65	0.10
Dehydration	53.40	0.02

In a second series of experiments, a solution was prepared by melting crystals of the tetrahydrate which had been dried in a vacuum desiccator over 60 per cent sulfuric acid (2). Analysis of this stock solution (No. 25) by the dehydration method gave 69.47 for the per cent of calcium nitrate, with an average deviation of 0.01. This mean figure is practically that (69.50 per cent) calculated from the formula of the tetrahydrate.

Toward the end of the work, when the high concentration region had been thoroughly investigated, three of the stock solutions were analyzed from density measurements. In order to have a sufficiently sensitive means of determining the composition of these solutions from their density values, the following procedure was adopted. Using the data obtained from the four stock solutions analyzed by the dehydration method, a large scale plot of the ϕ (apparent molal volume) values against the corresponding density values was constructed. From this plot the ϕ values of the three new stock solutions could be read directly. With the ϕ value known, the composition of the solutions could then be calculated from the equation:

$$\text{Per cent Ca(NO}_3\text{)}_2\text{ in the solution} = \frac{100M(v_w - v_s)}{Mv_w - \phi}$$

where

M = molecular weight of calcium nitrate,

v_w = specific volume of water $= \frac{1}{d_w}$, and

v_s = specific volume of solution $= \frac{1}{d_s}$

This equation is a direct consequence of the definition of ϕ.

DETERMINATION OF DENSITIES AND COMPRESSIBILITY COEFFICIENTS

Three different sizes of pyknometers were employed for the determination of the densities of the calcium nitrate solutions. For all of the unsaturated solutions except Nos. 1, 2 and 4, the 100-ml. pyknometers described by Scott, Obenhaus, and Wilson (9) were used. In the case of the three exceptions just noted, the densities were determined with a 500-ml. pyknometer. Because of the difficulty of handling large amounts of the very viscous supersaturated solutions, a small 25-ml. pyknometer was employed in the density measurements of these solutions. Both the large and small pyknometers were of the same design as the 100-ml. pyknometers. It may be remarked here that, although the uncertainty in the density values is greater the smaller the volume of the pyknometer, the estimated uncertainty in the apparent molal properties turns out to be approximately constant for all concentrations.

The filling of the pyknometers with unsaturated solutions was carried out in the usual way. With supersaturated solutions the following procedure was found necessary. The solution was first warmed to about 70°C. in order to reduce the viscosity, and then drawn by suction into a pipet having a capillary stem. The solution in the pipet was then discharged slowly into the pyknometer by application of air pressure.

The apparatus and the procedure for the determination of the compressibility coefficients of the solutions have been described fully in previous papers (9, 10). It is interesting to observe that the glass piezometer has shown practically no change over a period of more than a year of constant use. Thus, the value of the compression of the piezometer filled with mercury was redetermined and found to be 0.151 g. in place of 0.150 g., the former figure. Using this new value, the results of several new experiments yield for the compressibility coefficient of water 41.78×10^{-6}, a value which is essentially the same as the earlier value, 41.80×10^{-6}. In all calculations of the compressibility coefficients 4.00×10^{-6} has been accepted, as before, for the coefficient for mercury. In filling the piezometer with the supersaturated solutions, the method described above for filling the pyknometer was used. Since with the more concentrated solutions a greater period of time was required for the attainment of pressure equilibrium, a general practice was made in all measurements of taking the pressure reading 30 minutes after the initial application instead of after the customary 15 minutes.

EXPERIMENTAL RESULTS

The results of the experiments are summarized in table 1. The origin of each solution and the method whereby its composition was determined are indicated by the symbols in parentheses following the solution number. In this code "an" and "dens" signify that the solution was a stock solution and that the composition was determined by the dehydration or density procedure, respectively. Further, if the solution was prepared by concentration or dilution of a stock solution, say No. 23, this fact is shown by the symbols "c23" or "d23." All density values recorded in the table are the results of a single measurement. A majority of the compressibility coefficients are the mean values of duplicate measurements, the average deviations of which from the mean are given in the last column. The subscript digits in the last decimal place of some of the values indicate that the uncertainty may be as much as 3 or 4 units in that place.

DISCUSSION OF RESULTS

From the data given in table 1, values of ϕ (apparent molal volume), $\bar{B}$ (apparent molal compressibility), and f $\left[=\left(\frac{\partial\phi}{\partial c}\right)_p \frac{dc}{dp}\right]$ have been calculated by methods already described (10, 11) and are listed in table 2.

The relationships between the two apparent properties, ϕ and $(\bar{B} + f)$, of calcium nitrate and the square root of the concentration of this electrolyte are portrayed in figure 1. The solid dots in this graph represent the values given in table 2 and the open circles represent ϕ–$c^{\frac{1}{2}}$ values at 18°C., which were calculated from data tabulated in the International Critical Tables. It should be noted perhaps that the quantities used in constructing the $(\bar{B} + f)$–$c^{\frac{1}{2}}$ plot are for solutions under a pressure of 200 metric atmospheres. The other two plots both portray solution data at atmospheric pressure. Attention is also called to the fact that at the top of the graph a supplementary scale is marked which, corresponding to the bottom scale, shows the number of moles of water (n_w) per mole of solute in the more concentrated solutions.

With regard to the general nature of the ϕ–$c^{\frac{1}{2}}$ relationship, a question which has been the subject of numerous studies in recent years, two distinct views are held at present. According to Masson's empirical rule (6)

TABLE 1

Results of measurements on calcium nitrate solutions

SOLUTION NO.	WEIGHT PER CENT	DENSITY AT 35°C.	$\beta \times 10^6$ AT 35°C.	AVERAGE DEVIATION
	0.00	0.994059	41.78	<0.01
1 (d21)	0.5282_0	0.99792_5		
2 (d21)	1.209_9	1.00291_7		
3 (d22)	4.114_7	1.0244_1		
4 (d21)	4.807_2	1.02966_0		
5 (d23)	7.337	1.0490_7		
6 (d22)	13.99_7	1.1027_4	36.40	0.02
7 (d10)	18.07_0	1.1376_2		
8 (d14)	19.90_8	1.1539_0		
9 (d23)	21.18_4	1.1656_7	33.51	
10 (d18)	23.54_8	1.1870_0		
11 (d19)	25.62_6	1.2066_3		
12 (d19)	26.63_2	1.2162_9		
13 (d18)	27.45_1	1.2241_4		
14 (d18)	28.57_1	1.2351_0		
15 (d23)	32.62_8	1.2763_7	29.31	0.04
16 (d18)	39.63_9	1.3510_8		
17 (d23)	47.01_0	1.4363_2	24.20	<0.01
18 (dens)	52.39	1.5028_9		
19 (an)	53.25	1.5138_2		
20 (an)	53.40	1.5160_0		
21 (dens)	53.44	1.5164_1		
22 (dens)	53.72	1.5200_6		
23 (an)	54.80	1.5339_1	21.70	0.01
24 (c23)	65.18	1.6772	18.83	0.04
25 (an)	69.47	1.7418		
26 (c20)	72.82	1.7941	16.78	
27 (c22)	75.23	1.8351		
28 (c22)	75.51	1.8392	16.06	

the ϕ–$c^{\frac{1}{2}}$ relationship for strong electrolytes is linear, the rate of change of ϕ with $c^{\frac{1}{2}}$ being markedly different for electrolytes of the same valence type. Theoretically also, as Redlich and Rosenfeld (7) have shown, this relationship in extremely dilute solutions should be linear, but the slope in this case is established by the valence type of the electrolyte. With these two conclusions in mind it is interesting to examine the ϕ–$c^{\frac{1}{2}}$ plot in figure 1. Since it is obvious that the plotted points do not fall on a straight line, it must be concluded that solutions of calcium nitrate do not conform to Masson's rule. A similar, direct test of the theoretical deduction of Redlich and Rosenfeld is not possible, because our measurements do not extend into the region of extremely dilute solutions. It is worth noting, however, that the actual rate of variation of ϕ with $c^{\frac{1}{2}}$ in dilute solution is very much smaller than the theoretical value which is indicated in the graph. Furthermore, if, as is quite possible, the actual slope should approach the theoretical slope as the concentration approaches zero, the complete ϕ–$c^{\frac{1}{2}}$ relationship would necessarily have a point of inflection in the region of dilute solution, a fact which would be indicative of a definite alteration in the structure of the solution state.

TABLE 2

Apparent molal properties of calcium nitrate solutions

SOLUTION NO.	c	c_{30°	ϕ	ϕ_{30°	$-\bar{B} \times 10^4$	$f \times 10^4$
	moles/liter	*moles/liter*	*ml.*	*ml.*		
1	0.0321209_0		44.1_4			
2	0.073944_5		44.6_4			
3	0.2568_6		46.2			
4	0.301632_0		46.3_6			
5	0.4690_4		47.1			
6	0.9405_4	0.9474_9	48.82	49.5_6	36.8_0	1.01
7	1.2527		49.8_0			
8	1.3995		50.2_0			
9	1.5048	1.5149	50.3_6	51.0_3	33.9_2	
10	1.7033		51.1_3			
11	1.884_4		51.5_6			
12	1.973_9		51.8_3			
13	2.047_8		52.0_6			
14	2.150_4		52.3_9			
15	2.537_9	2.552_4	53.1_6	53.7_0	26.9_3	1.99
16	3.263_8		55.0_3			
17	4.114_6	4.134_6	56.9_6	57.3_4	18.9_3	2.09
19	4.912_5		58.6_3			
20	4.933_3		58.6_4			
23	5.122_4	5.145_0	59.0_6	59.3_5	14.53	2.09
24	6.661_8	6.687_0	61.9_2	62.0_9	8.58	2.07
25	7.373_7		63.0_7			
26	7.961	7.988	63.9_9	64.0_8	4.66	2.02
27	8.413		64.5_2			
28	8.463	8.490	64.6_2	64.6_9	3.39	1.99

We have made two attempts to find a function which would represent the experimental data. The first possibility to be investigated was that ϕ is linearly dependent on c^x, where x has some other value than one-half, a relationship which Masson found to be valid for weak electrolytes and non-electrolytes. The most satisfactory function of this kind may be written as follows:

$$\phi = 44.32 + 4.687c^{0.70} \quad (1)$$

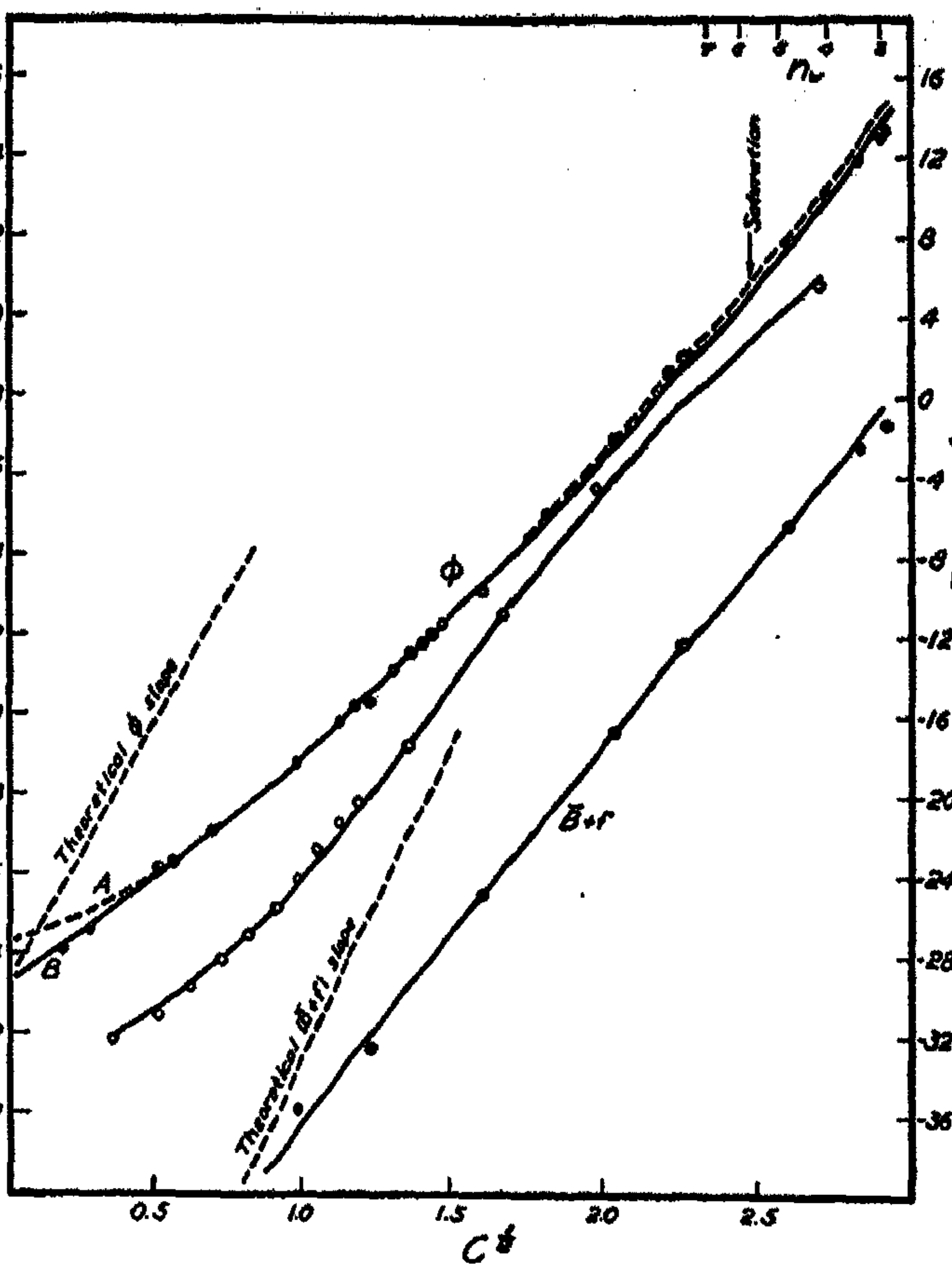

FIG. 1. Plots of apparent molal properties of calcium nitrate against the square root of the concentration. The two upper plots depict the apparent molal volume ϕ (left-hand ordinate) and the lower plot, the apparent molal compressibility $[\bar{B} + f]$ (right-hand ordinate).

Line A in figure 1 represents the values of ϕ, calculated from this equation, plotted against $c^{1/2}$. Although equation 1 appears to be reasonably satisfactory for a limited concentration range, it is by no means adequate for the entire concentration range covered by the experiments.

A second and more promising function is expressed by the following equation, the constants of which were determined by the method of least squares:

$$\phi = 43.35 + 4.782c^{\frac{1}{2}} + 0.908c \qquad (2)$$

Line B in the figure represents the variation of the calculated values of ϕ with changes in $c^{\frac{1}{2}}$. It may be noted that the average deviation between the calculated and experimental values of ϕ is slightly less than 0.1 ml., a quite satisfactory figure. A still better "fit" could be obtained if the data of the most uncertain solutions, those made from the first stock solution (No. 23), were neglected in the calculation of the constants of the equation.

Concerning the $(\bar{B} + f)$-$c^{\frac{1}{2}}$ plot in figure 1 only a few comments can be made. Because of the relatively large uncertainty in the plotted $(\bar{B} + f)$ values as well as the limited number of points available, no decision can be made as to the nature of the relationship between $(\bar{B} + f)$ and concentration. One possibility is that $(\bar{B} + f)$ is linearly dependent on $c^{\frac{1}{2}}$, the relationship indicated by the straight line drawn in the graph. The theoretical slope of this square-root relationship, as derived by Gucker (4) from considerations similar to those underlying the Redlich-Rosenfeld theory, is indicated in the graph. A second possible relationship is one analogous to equation 2, for if $(\bar{B} + f)$ values are plotted against the corresponding ϕ_{200} values, the plotted points, with the exception of those for the two most dilute solutions, fall closely on a straight line. The slope of this line $\frac{\partial(\bar{B} + f)}{\partial\phi_{200}}$ has the value 2.3×10^{-4}.

In concluding this discussion of the apparent properties of calcium nitrate in solution, it will be of interest to examine them further along lines which were developed in previous studies of the apparent properties of alkali halides in solution. First, it may be recalled that the maximum conceivable value of the apparent molal volume ϕ_m is reached, according to definition, when

$$\phi_m = \frac{1000}{c_m} \qquad (3)$$

On the assumption that equation 2 is valid up to this limit of the solution state, the maximum value ϕ_m has been computed to be 73.5 ml. As was found to be the case with the alkali halides, this figure is a trifle larger than the molecular volume of the anhydrous salt, measurements of which range from 67.5 ml. to 73.4 ml. The maximum value of $(\bar{B} + f)$ corresponding to ϕ_m, assuming that these two quantities are linearly related, turns out to be 18.0×10^{-4}. The hypothetical value of the compressibility coefficient of the solute in this state is therefore $18.0 \times 10^{-4}/73.5 = 24.5 \times 10^{-6}$. This figure, by analogy with the corresponding quantities found with the alkali halides, must be much greater than the compressibility coefficient of the solid anhydrous salt, the value of which has never been determined.

Another estimate of the compressibility coefficient, β_s, of the solid salt can be made, provided the relationship between $(\bar{B} + f)$ and ϕ_{200} is linear. Using the empirical rule, which was found to be valid for solutions of the alkali halides and which is expressed by equation 8 of paper No. I (10), β_s is calculated to be 12.4×10^{-6}. This estimate must be looked upon as somewhat too large. It is, for instance, approximately ten times greater than the compressibility coefficient of calcium carbonate. The failure to get a more reasonable value for β_s is due doubtless to the inapplicability of equation 8, mentioned above, rather than to a mistake in assuming a linear relationship between $(\bar{B} + f)$ and ϕ_{200}.

Finally, it may be noted that, although calcium nitrate in the solid state is known (3) in the forms of the di-, tri-, and tetra-hydrates, there is no definite evidence in the plots in figure 1 that these hydrates exist in the solution state. The fact that the ϕ and $(\bar{B} + f)$ values of the most concentrated solutions are low could be the consequence of a change in the solution state at a concentration corresponding to $Ca(NO_3)_2 \cdot 4H_2O$, the hydrate stable at 35°C., but, because of the difficulty of working with the very viscous solutions, it is equally probable that the low values are due to errors in the measurements.

For the sake of completeness we may record the fact that the density at 35°C. of the crystalline tetrahydrate was found to be 1.896, which is essentially the same as the values (1.78 to 1.90) reported in the literature. Using this figure, the ϕ value is calculated to be 52.0 ml., which is 11.1 ml. lower than the ϕ value of the supercooled hydrate (solution No. 25). An attempt to determine the compressibility coefficient of the hydrated salt with our present piezometer was unsuccessful.

SUMMARY

Measurements of the densities and compressibility coefficients of both unsaturated and supersaturated solutions of calcium nitrate have been made at 35°C.

The effect of concentration on the apparent molal volume and compressibility of the solute is discussed. It is found that neither the empirical relationship of Masson nor the theoretical relationship of Redlich and Rosenfeld is applicable to these solutions.

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HIDE SUBSTANCE WITH HYDROGEN CHLORIDE AND AMMONIA

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INTRODUCTION

In a study of the two-component system hide substance–hydrogen chloride, using the method of Bancroft and Barnett (1), Beek (2) reports that a compound is formed in which the combining weight of hide protein for hydrogen chloride is 332. The complete phase diagram was not obtained, but the compound was reported to have a dissociation pressure equivalent to 30 mm. of mercury at room temperature. Using the same method, Tsai and Hsiao (3) found that at 35°C., hydrogen chloride combines with hide protein to the extent of 26.4 mg. of HCl per gram of hide substance, to give the latter a combining weight of 1380. The dissociation pressure of this compound they reported as being equivalent to 1.41 mm. of mercury at 35°C. In the present work, complete phase rule data, obtained by the method of Bancroft and Barnett, are given for the two-component systems hide substance–hydrogen chloride and hide substance–ammonia. In neither case is there found to be any evidence of compound formation.

MATERIALS

The hide substance used was American Standard Hide Powder, obtained from the Standard Manufacturing Company of Ridgway, Pa., and was used without further treatment other than drying. The hydrogen chloride was generated by the action of C.P. sulfuric acid on crystalline ammonium chloride. It was dried by passing through two 4-in. columns of sulfuric acid before being added to the system. The ammonia gas was taken directly from a cylinder of anhydrous ammonia, obtained from the Matheson Company, North Bergen, N. J. The gas was passed through a 12-in. column of soda lime before being admitted to the reaction flask. The mercury was vacuum distilled before using.

METHOD

A weighed amount of hide powder was placed in a calibrated flask, which communicated with the gas supply through one arm of a mercury manometer connected directly to the reaction flask. After evacuation of the system, gas was added to the flask a few cubic centimeters at a time,

TABLE 1

Adsorption of hydrogen chloride by hide powder at low pressures

$dp/dv = 0.96$

HCl PRESENT AT 25°C. AND 760 MM. Hg	EQUILIBRIUM PRESSURE	HCl ADSORBED BY 5.0 G. OF HIDE POWDER	x/m IN MG. HCl PER GRAM OF HIDE POWDER
cc.	*mm.* Hg	*cc.*	*mg.*
9.6	0.012	9.6	2.86
29.9	0.04	29.9	8.90
60.8	0.10	60.7	18.1
76.7	0.15	76.6	22.8
98.5	0.36	98.1	29.2
124.4	0.48	123.9	36.9
165.0	1.20	163.7	48.8
203.5	2.20	201.2	60.0

TABLE 2

Adsorption of hydrogen chloride by hide powder

$dp/dv = 1.24$

HCl PRESENT AT 25°C. AND 760 MM. Hg	EQUILIBRIUM PRESSURE	HCl ADSORBED BY 5.0 G. OF HIDE POWDER	x/m IN MG. HCl PER GRAM OF HIDE POWDER
cc.	*mm.* Hg	*cc.*	*mg.*
177.2	1.5	176	52
295.3	7.8	289	86
312.7	9.5	305	91
349.3	11.5	340	102
374.6	15.6	362	108
400.7	19.5	385	115
459	34.8	431	128
554	68.2	499	149
709	150	588	175
819	208	651	194
942	300	700	209
1302	586	829	247
1371	649	848	253
1461	725	877	261
1298	555	850	253
1200	463	826	246
1074	343	798	238
934	224	754	225
793	122	695	207
693	70	637	190
573	32	547	163
401	9	394	117

waiting until the pressure reached a constant value before making further additions. The free gas remaining in the system at equilibrium was calculated from the existing pressure and the previous calibration. Subtraction of this calculated value from the total amount of gas added gave the volume of gas taken up by the sample. By plotting the equilibrium pressure against the corresponding amounts of gas taken up by the sample, the phase diagram for the system gas–hide substance may be obtained. All pressure readings were made at 25°C.

Table 1 contains the data obtained for the system hydrogen chloride-hide substance, at low pressures. Table 2 contains the data for the same system over a greater range of pressure. Table 3 summarizes the data for the system ammonia-hide substance. The dp/dv values given in the tables were obtained from the calibrations, and represent the change of pressure in the system, in millimeters of mercury per cubic centimeter of gas, measured at 25°C. and 760 mm. of mercury.

TABLE 3

Adsorption of ammonia by hide powder

$dp/dv = 1.82$

NH_3 PRESENT AT 25°C. AND 760 MM. Hg	EQUILIBRIUM PRESSURE	NH_3 ADSORBED BY 5.0 G. OF HIDE POWDER	x/m IN MG. NH_3 PER GRAM OF HIDE POWDER
cc.	*mm.* Hg	*cc.*	*mg.*
136	40	114	15.9
214.5	91	165	22.9
273	138	197	27.4
398.5	263	254	35.3
434	295	272	37.9
469	345	279	38.8
548	423	315	43.8
658	560	350	48.7
805	732	404	56.4
908	856	437	60.7
810	718	415	57.5
756	646	401	55.6
688	557	382	53.2
561	394	344	47.8
429	255	289	40.2
255.4	102.5	199	27.6
85.7	18.5	75.5	10.5
36.2	5.5	33.2	4.6

DISCUSSION

The phase rule, $P + V = C + 2$, where P represents the number of phases, V the number of degrees of freedom, and C the number of components, tells us that when a system of two components exists in three phases at constant temperature, the number of variables or degrees of freedom is zero. At constant temperature the pressure must remain constant as long as three phases exist. On the phase diagram, the simultaneous existence of three phases is represented by a "flat," showing constant pressure, parallel to the axis of composition. The length of the flat, as measured on the composition axis, gives the ratio of the two components in the compound. When two components exist in but two phases at constant temperature, the number of degrees of freedom will be one, and the pressure will vary simultaneously with the composition. In this case a plot of the equilibrium data will result in a smooth curve. Phase diagrams constructed from the data of tables 1, 2, and 3 are of this type, showing that an adsorption complex rather than a true compound is formed.

An important factor to be considered in the construction of the phase diagram between hide substance and gases is that of equilibrium and the rate of its attainment. The disagreement of results in the present work with the results of Tsai and Hsiao and with the results of Beek is undoubtedly due to this factor. Tsai and Hsiao report that the equilibrium between hydrogen chloride and hide substance is established in one to two days. In the early course of this investigation it became apparent that a period of time considerably longer than one to two days was necessary for the system to arrive at the true equilibrium value. A period of twenty to twenty-five days was found in most cases necessary before readings that checked within the experimental error of the method were obtained. What has just been said applies in particular to the case where one proceeds from a lower to a higher pressure. In the reverse case, the hysteresis curves, obtained by proceeding from a higher to a lower pressure by removal of gas, represent values nearer the true equilibrium values, since check readings were usually obtained in fifteen to eighteen days after extraction. Since the pressure will decrease after addition of gas and increase after removal of gas, the conclusion is reached that the true equilibrium values lie between the two curves and are more nearly represented by the hysteresis or "down" curve than by the "up" curve. The experimental point at a pressure of 300 mm. and an x/m value of 209 may be used in support of this argument. This point is the value obtained after standing approximately twenty-five days. At this time it became necessary for the system to remain without further addition of gas for an additional period of time extending from July 14, 1933 to September 8, 1933, or approximately eight weeks. At the end of this time the pressure had fallen to a value of 287 mm. and the x/m value increased correspondingly to a value of 216. These values lie between the "up" and "down" curves.

The compound reported by Beek, whose vapor pressure was in the region of 30 mm. of mercury, had an equivalent weight of 332. This corresponds to 110 mg. of HCl per gram of hide substance. An examination of the present work shows that the up curve gives an x/m value of 125 at 30 mm. of mercury, and the down curve, which probably represents a truer equilibrium value, gives an x/m value of 160 at the same pressure. Thus one must conclude that Beek's system had not reached equilibrium.

SUMMARY

Complete phase rule data, obtained by the method of Bancroft and Barnett, are given for the two-component systems hide substance–hydrogen chloride and hide substance–ammonia. An interpretation of these results indicates that adsorption complexes rather than definite chemical compounds are formed.

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AN HYPOTHESIS CONCERNING BACTERIOPHAGY

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A number of explanations have been advanced to account for bacteriophage and its action on bacteria. No evidence yet presented validates any one of these. D'Herelle considers phage to be animate, Wollman and Wollman (9) see a connection between it and the heredity of the organism, and Bronfenbrenner (2) believes it to be a stimulant of bacterial metabolism.

It is the purpose of this paper to propose and consider another hypothesis. It is suggested that phage may be a suspension of extremely small crystals of one or more of the compounds contained in the homologous bacteria. Bacteriophagy, then, would be the seeding of these amorphous compounds by the phage particle and their subsequent crystallization.

Evidence has been presented by a number of workers to show that phage is particulate; the size of the particles for various phages has been measured. That phage acts as an antigen indicates it is a protein, and Schlesinger's (8) analysis of a phage, in which he found 13 per cent nitrogen, confirms this. A number of proteins have been crystallized, so the hypothesis meets no difficulty here. Since proteins are hard to crystallize, it would be expected that spontaneous formation of crystals would be rare and that seeding would be highly specific; that is, only the appropriate crystal would start the amorphous compound crystallizing. Both of these conditions are in accord with the character of bacteriophage. A particular phage will attack only its homologous bacteria and closely related species. Furthermore, the spontaneous appearance of phage has been reported once or twice, although this has been generally ascribed to contamination. Plantureux (7) claimed to have prepared phage by what was essentially a crystallization method. He added graded amounts of calcium chloride solution to cultures of bacteria.

When bacteria are attacked by phage a number of cells simply disappear, while others swell until they burst. This is readily explained by the crystallization hypothesis. If the cell wall were damaged during crystallization, the contents of the cell would be discharged at once into the medium; if the cell wall retained its strength, swelling would follow. Consider the interior of a cell in which crystallization had taken place. Synthesis would cease and, under the influence of the intracellular enzymes, chemical equilibrium would be restored. This would result in an increase in the number of molecules within the cell and water would be imbibed until the cell burst. In either case, the destruction of the cell would cause a dispersion of more crystalline material. Andrewes and Elford (1) have shown that if lysis is inhibited by sodium citrate, there is no increase in the amount of phage.

If bacteriophagy is crystallization caused by a seeding crystal, it should be sensitive to protective substances and to high viscosity. Bronfenbrenner and Hetler (3) have shown that the presence of 4 to 5 per cent agar in the medium inhibits bacteriophagy; Colvin (4) and Evans (6) have demonstrated that serum, ascitic fluid, saliva, pus, and urine have the same effect. D'Herelle (5) reported inactivation with glycerol.

The granular appearance of bacteria subject to bacteriophagy is perhaps an indication of crystallization.

D'Herelle (5) found bacteriophage to become more resistant to the action of deleterious physical and chemical agents during the first few days following its separation from susceptible bacteria. He interpreted this to mean that the smaller, less well fed parasites were the more resistant. On the basis of the present argument, it would be explained as the tendency of the larger crystals (which would grow at the expense of smaller ones) to keep their crystal structure longest under adverse conditions. The same applies to the gradual inactivation phage undergoes on standing.

If bacteriophage is the crystalline form of cell constituents, it should not have antigenicity independent of the homologous bacteria. Results of various investigators seem to show that it is an independent antigen. However, the procedures followed may not be decisive. If the bacterial antibodies are removed from the test serum by treating it with the whole bacteria, and the resulting serum gives a precipitation reaction with purified phage, the possibility remains that a compound within the cell was concerned, the antibodies for which would not have been removed. The antibodies should be removed with a suspension of disintegrated bacteria; if precipitation were still obtained from the phage-serum mixture, the hypothesis would be invalidated.

Inactivation of phage by serum should not be considered as evidence against the crystallization hypothesis; a crystal could be so coated as to be ineffective by traces of agglutinin which could not be removed from the serum.

My thanks are due to Dr. R. E. Buchanan and Dr. E. I. Fulmer for their careful consideration of this hypothesis.

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SPECIFIC HEATS AND RELATED PROPERTIES OF THE BINARY SYSTEM METHYL ALCOHOL–TOLUENE

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Departure of the behavior of binary liquid solutions from ideality has provoked a number of attempts to correlate measurements of physical constants with the state, and change of state, of molecular aggregation within the solution. The conclusions that may be drawn from a study of one type of constant, however, are often but partially sustained by, or wholly inconsistent with, those deduced from studies of some other constants. It is at present rather generally presumed that mutual solution of two or more liquids may be accompanied by dissociation of complex groups of molecules present in either or all of the component liquids into simpler units, and by aggregation of unlike molecules as a result of compound formation or the so-called process of solvation. Inconsistencies in the application of this view are attributed to variation in the sequence and degree in which the association, dissociation, and solvation occur as a result of the different thermodynamic conditions in which measurements of different constants are performed. The vagueness of such assumptions emphasizes the qualitative nature of our knowledge about these processes.

Various investigators have examined diverse phases of the problem of solution (2, 3, 4, 5, 6, 7, 10, 18). In this laboratory property-composition data are being accumulated for binary systems of low molecular weight alcohols with low molecular weight hydrocarbons of the aromatic series and with six-carbon cycloparaffins, and for ternary systems of the above combinations with water as the third component (11, 14, 15, 16). It is hoped that an extensive study of such systems will reveal more of the mechanism of solution than is at present known, and that results of such studies may afford generalizations more widely applicable than those in vogue.

During the course of these investigations interest in the pertinence of heats of mixing to the problems of solution has arisen. Knowledge of the specific heats of solutions is a prerequisite of the determinations of heats of mixing, and a study of the literature reveals but very few data on the specific heats of solutions of organic liquids. The purpose of the present work was to devise a convenient and efficient technique for determining the specific heats of liquid mixtures and for measuring the heat changes attending the solution of the liquids, and to study these and other properties of the system methyl alcohol–toluene.

MATERIALS

Methyl alcohol. The methyl alcohol used was a synthetically prepared product of a degree of purity originally greater than 99.5 per cent. This alcohol was desiccated over lime and carefully fractionated in an all-glass still. The relative density of the purified product was $d_{4°}^{25°} = 0.78672$, and the refractive index was $n_{D}^{25°} = 1.32659$.

Toluene. The best grade of toluene obtainable from the Eastman Kodak Company was treated repeatedly with freshly cut sodium and fractionated. No change in density was observed. A sample showed only a faint yellow coloration after standing over concentrated sulfuric acid for several hours. The relative density of the material was $d_{4°}^{25°} = 0.86229$ and its refractive index $n_{D}^{25°} = 1.49365$. Toluene obtained from the Mallinckrodt Chemical Company was used for supplementary determinations of the thermal quantities after it had been treated with concentrated sulfuric acid, then sodium, and finally fractionated.

EXPERIMENTAL

Apparatus and procedure

Specific heats of solutions of methyl alcohol and toluene through the concentration range were measured adiabatically at 25°C. and 35°C. by a method involving the use of a Dewar flask in a hand-controlled air bath as a calorimeter. Heat was supplied to the liquids by a heating coil of nichrome wire of measured resistance, which was connected to two 6-volt storage batteries and a silver coulometer in series. The magnitude of the current passed was calculated from the weight of silver deposited in the coulometer and the length of time of deposition, the latter being measured with a stopwatch. The temperature rise was measured on a Beckmann thermometer which passed through a stopper fitting tightly in the Dewar flask. A series of five copper–constantan thermocouples indicated when any difference of temperature existed between the liquid in the flask and the air of the bath, and the bath was heated or cooled to restore equality of temperature. The heat supplied for each determination was calculated from Joule's law. All solutions for these and other measurements were prepared with weight pipets. The heat capacity of the calorimeter, which was found to be 20.86 cal. per degree at 25°C. and 21.41 at 35°C., was determined by using toluene and methyl alcohol as "standard" liquids in the calorimeter. The values are the averages of groups of determinations in which the average deviation from the mean is less than 0.7 per cent. The values used for the specific heats of methyl alcohol and toluene are those of Bose (1) and of

Williams and Daniels (17), respectively. The specific heats of methyl alcohol and toluene recalculated on the basis of the determined heat capacity of the calorimeter are 0.610 and 0.392 at 25°C. and 0.613 and 0.402 at 35°C.

The calorimeter was a Dewar flask of approximately 200-cc. capacity fitted with a cork stopper coated with water glass and equipped with a Beckmann thermometer graduated in 0.005°, a vertical glass stirrer, five thermocouples, and a nichrome heating coil. The series of thermal junctions was connected to a critically damped wall galvanometer whose deflections were observed with the customary arrangement of telescope and scale. The thermocouples were used only to indicate if a difference of temperature existed inside and outside the calorimeter. The resistance of the heating coil, which was found to be 7.730 ohms at 25°C., was measured potentiometrically by balancing the *IR* drop across the coil against the *IR* drop across a Bureau of Standards 10-ohm resistance. The temperature coefficient of the resistance of the heating coil exerted a negligible effect on the quantities measured at 35°C.

The air bath was a wooden cabinet 3 x 3 x 2 feet in dimensions, equipped with a window to permit observation of the interior, a large fan for circulating the air, and heating and cooling units which permitted rapid adjustment of the temperature of the interior to any desired value. A long metal shaft, attached eccentrically to a pulley above, passed through the roof of the cabinet and operated the stirrer in the calorimeter. The Beckmann thermometer in the calorimeter was read through the window of the cabinet by means of the telescope on a cathetometer.

The silver coulometer consisted of two electrodes of sheet silver, approximately 13 x 10 x 1 mm. in dimensions, supported by silver wires welded to them. These electrodes were suspended in a 1-l. beaker filled with an electrolyte, prepared according to the method of Wartenburg and Schutza (12) and stirred by a rotary stirrer. The cathode was weighed, before and after each deposition, after it had been thoroughly washed with distilled water, dried in an electric oven at 125°C. for ten to fifteen minutes, and allowed to cool twenty minutes. The electrodes were interchanged after six depositions had been made on one of them. The silver coulometer proved to be convenient and reliable for measurements of current strength. A good quality stop-watch graduated in tenths of a second was used to measure the lengths of time that current passed in the circuit.

Heat changes of mixing were measured for the concentration range at 25°C. and 35°C., using the same calorimeter as for the measurements of specific heats. A small flask, also equipped with thermocouples, was suspended in the cabinet in such a manner that a weighed amount of one liquid could be delivered directly into the calorimeter to be mixed with a weighed amount of the other liquid. The entire system was closed and in temperature equilibrium before mixing. Temperature changes occurred within one minute, and it was found unnecessary to maintain adiabaticity during such a short time interval. It was necessary, however, to determine the heat capacity of the calorimeter for this short interval of temperature change. The value 16.9 cal. per degree was used for calculations at 25°C. and 17.6 at 35°C.

The densities of the series of solutions were determined at 25°C. and 35°C., using pycnometers of the type designed by Wade and Merriman (13). Volume changes were calculated from the measured densities.

TABLE 1

Specific heats

WEIGHT PER CENT ALCOHOL	WEIGHT OF SOLUTION	CATHODE WEIGHTS	TEMPERATURE RISE	TIME IN SECONDS	SPECIFIC HEAT
		$T = 25°C.$			
10.17	84.440	0.2910	3.920	540	0.453
18.71	83.743	0.2974	3.996	540	0.474
28.37	83.025	0.2971	3.856	540	0.503
37.43	82.678	0.3065	4.083	540	0.518
52.27	81.452	0.3208	4.021	600	0.547
60.77	80.944	0.3310	4.058	600	0.564
70.94	79.991	0.3174	4.095	540	0.581
80.34	79.493	0.3028	3.873	510	0.600
89.55	79.041	0.3337	3.985	600	0.607
		$T = 35°C.$			
9.17	85.030	0.3145	4.181	588	0.447
18.73	83.791	0.3063	3.913	576	0.479
28.09	83.273	0.3149	4.104	564	0.503
37.96	82.236	0.3124	4.044	552	0.525
47.66	81.608	0.3128	4.086	540	0.541
57.63	81.675	0.3034	3.833	528	0.560
68.21	80.555	0.3068	3.970	516	0.577
78.47	79.627	0.3048	3.951	504	0.597
89.25	78.231	0.3081	4.126	492	0.610

Refractive indices of the solutions were measured with reference to the D line of sodium at 25°C. and 35°C. with a Bausch and Lomb immersion type refractometer.

RESULTS

Some of the values obtained for the specific heats of the methyl alcohol-toluene solutions at 25°C. and 35°C. are given in table 1. The first column to the table, from left to right, expresses the weight per cent of alcohol in the solutions; the second, the weight of solution used in the determination;

the third, the weight of silver deposited in the cathode of the silver coulometer; the fourth, the temperature rise observed on the Beckmann thermometer; the fifth, the time in seconds during which the determination was performed; and the sixth, the calculated specific heat of the solution.

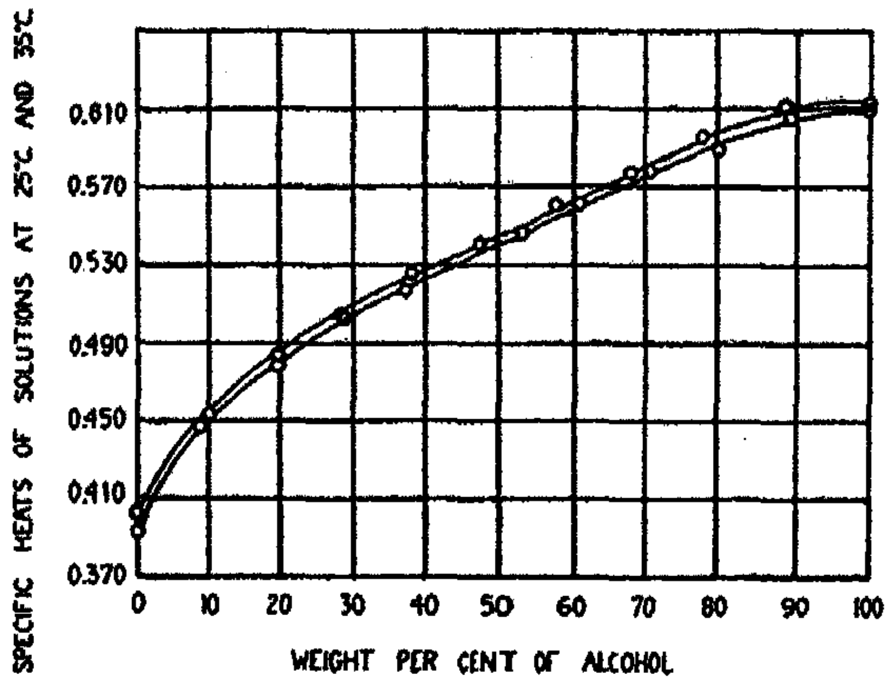

FIG. 1

TABLE 2

Changes in specific heat and partial molal specific heats

WEIGHT PER CENT ALCOHOL	C_p AT 25°C. FROM GRAPH	CALCULATED C_p AT 25°C.	CHANGE OF C_p AT 25°C. PER CENT OF CALCULATED C_p	C_p AT 35°C. FROM GRAPH	CALCULATED C_p AT 35°C.	CHANGE OF C_p AT 35°C. PER CENT OF CALCULATED C_p	MOLAL C_p AT 25°C.	MOLAL C_p AT 35°C.	$\bar{C}_p$ ALCOHOL AT 25°C.	$\bar{C}_p$ TOLUENE AT 25°C.	$\bar{C}_p$ ALCOHOL AT 35°C.	$\bar{C}_p$ TOLUENE AT 35°C.
00.0	0.392	0.392		0.402	0.402		36.1	37.0				
10.0	0.448	0.414	+8.2	0.454	0.423	+7.3	34.7	35.2	31.1	36.3	29.8	37.3
20.0	0.481	0.436	+10.3	0.486	0.444	+9.5	32.2	32.6	28.7	36.7	27.6	37.6
30.0	0.504	0.457	+10.3	0.510	0.465	+9.7	29.7	30.1	25.1	37.8	25.0	38.4
40.0	0.524	0.479	+9.4	0.528	0.486	+8.6	27.6	27.8	22.8	39.0	22.9	39.6
50.0	0.541	0.501	+8.0	0.545	0.508	+7.3	25.7	25.9	21.4	40.1	21.7	40.5
60.0	0.559	0.523	+6.9	0.562	0.529	+6.2	24.2	24.4	20.5	41.2	20.5	42.0
70.0	0.576	0.545	+5.7	0.580	0.550	+5.5	22.9	23.1	20.4	41.5	20.4	42.2
80.0	0.592	0.566	+4.6	0.597	0.571	+4.6	21.8	22.0	20.3	41.7	20.3	42.2
90.0	0.604	0.588	+2.7	0.610	0.592	+3.0	20.7	20.9	20.1	43.0	20.1	43.2
100.0	0.610	0.610		0.613	0.613		19.5	19.6				

Duplicate determinations on solutions of the same concentration in all but a few cases vary less than 0.5 per cent.

Figure 1 is a graphical representation of the data shown in table 1. The upper curve shows the values obtained at 35°C. and the lower those at 25°C.

In table 2 the first column is the weight per cent of alcohol in the solutions; the second, the specific heat of the solution at 25°C. read from an enlarged graph like figure 1; the third, the specific heat of the solution calculated from a linear relationship; and the fourth, the deviation of the specific heat from the linear relationship expressed in per cent of the calculated specific heat (the + preceding the values indicates a positive devia-

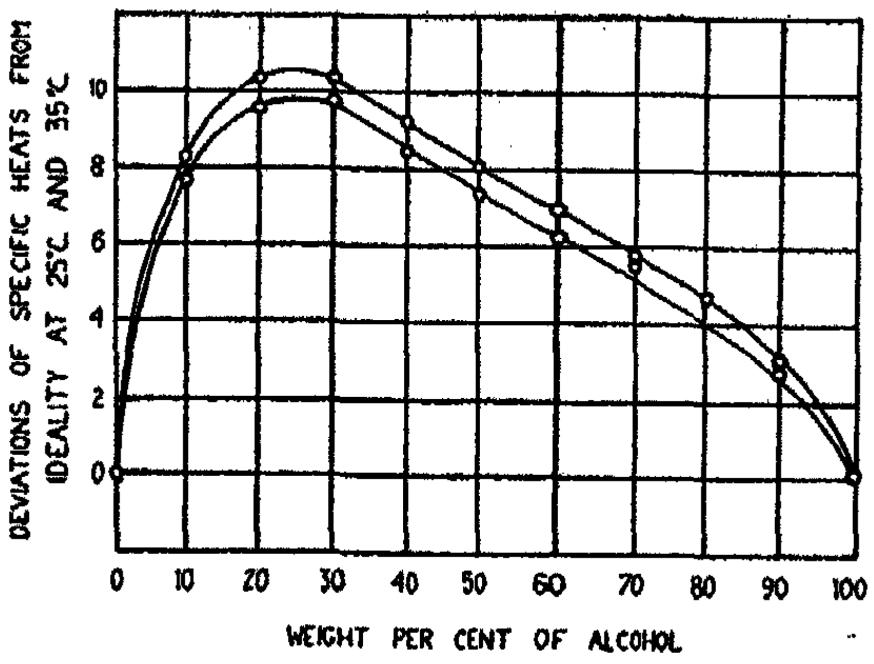

FIG. 2

TABLE 3

Heats of mixing

WEIGHT PER CENT ALCOHOL	WEIGHT OF MIXTURE	C_p OF MIXTURE	TEMPERATURE CHANGE	HEAT OF MIXING IN CAL. PER GRAM
		$T = 25°C.$		
10.38	86.067	0.450	−3.028	−2.343
19.62	84.592	0.480	−3.882	−2.639
29.80	85.299	0.504	−3.833	−2.692
38.82	81.922	0.521	−3.412	−2.482
48.28	80.930	0.538	−2.909	−2.174
57.64	81.214	0.554	−2.404	−1.832
68.07	80.395	0.573	−1.852	−1.450
78.56	78.999	0.590	−1.303	−1.047
88.68	79.046	0.602	−0.712	−0.581
		$T = 35°C.$		
10.10	85.223	0.455	−3.721	−2.462
18.86	84.023	0.483	−3.983	−2.758
37.74	82.032	0.523	−3.702	−2.731
57.74	81.150	0.559	−2.504	−1.943
78.61	79.337	0.595	−1.285	−1.050

tion). The fifth, sixth, and seventh columns give the same values for 35°C. In the eighth and ninth columns are listed the molal specific heats of the solutions at 25°C. and 35°C., calculated by dividing the observed specific heat at each concentration by the sum of the number of moles of each constituent, assuming 1 g. of solution in all cases. In the last four columns are shown the partial molal specific heats, $\bar{C}_p$, of alcohol and toluene at 25°C. and 35°C., obtained by a graphical method described by Lewis and Randall (8).

In figure 2 the deviations of specific heats from ideality are plotted against the weight per cent of alcohol in the solutions at 25°C. and 35°C., the upper curve being for 35°C.

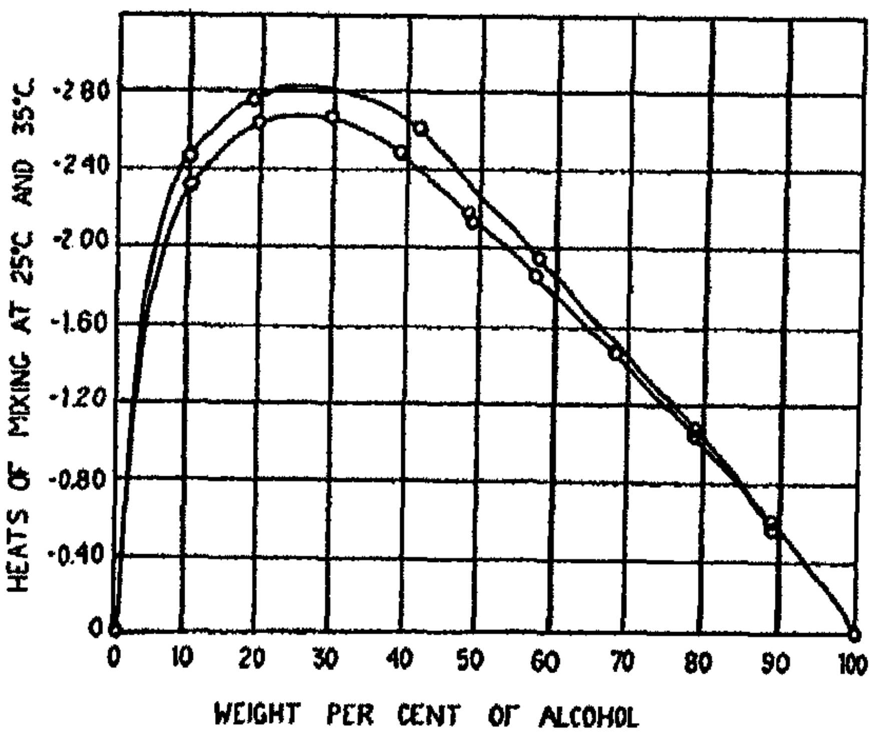

FIG. 3

Heats of mixing expressed in calories per gram of solution are tabulated in table 3, and are plotted against weight per cent of alcohol in figure 3. The upper curve represents the values at 35°C. The specific heats of the solutions used in the calculations were obtained from the graphs of the specific heats versus composition at the two temperatures.

In table 4 are found the observed densities and the volume contractions which attend mixing of the liquids at 25°C. and 35°C., together with the refractive indices and per cent deviations of refractive indices from a linear relationship for both temperatures. Volume changes are expressed in per cent of the volumes which the solutions would have had, had there been no change on mixing. Volume changes are plotted against concentration of alcohol in the solutions at both temperatures in figure 4. In these curves the greater deviations are observed at 25°C.

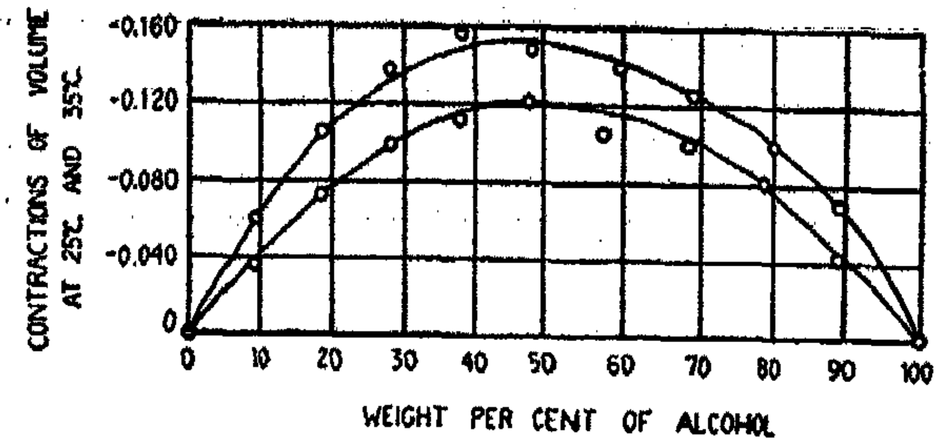

Fig. 4

TABLE 4

Changes in volume and refractive indices

WEIGHT PER CENT ALCOHOL	OBSERVED DENSITY	VOLUME CHANGE IN PER CENT	WEIGHT PER CENT ALCOHOL	OBSERVED REFRACTIVE INDEX	CHANGE IN REFRACTIVE INDEX IN PER CENT
T = 25°C.			T = 25°C.		
00.00	0.86229	000	00.00	1.49365	000
9.17	0.85528	−0.060	9.68	1.47622	−0.085
18.67	0.84799	−0.105	18.46	1.45903	−0.259
28.09	0.84081	−0.139	29.20	1.44120	−0.254
37.94	0.83330	−0.159	38.87	1.42523	−0.244
48.41	0.82519	−0.148	48.41	1.40873	−0.286
59.73	0.81666	−0.139	59.73	1.39045	−0.245
68.92	0.80977	−0.126	68.92	1.37544	−0.221
80.00	0.80156	−0.100	80.00	1.35756	−0.180
89.42	0.79463	−0.069	89.42	1.34289	−0.103
100.0	0.78672	000	100.0	1.32659	000
T = 35°C.			T = 35°C.		
00.00	0.85294	000	00.00	1.48839	000
9.17	0.84571	−0.036	9.17	1.47110	−0.151
18.67	0.83833	−0.072	18.67	1.45416	−0.242
28.09	0.83116	−0.106	28.09	1.43824	−0.280
37.94	0.82354	−0.112	37.94	1.42222	−0.273
47.66	0.81617	−0.122	47.66	1.40527	−0.333
57.54	0.80862	−0.105	57.54	1.38952	−0.308
67.97	0.80087	−0.097	67.97	1.37249	−0.310
78.47	0.79313	−0.081	78.47	1.35533	−0.300
89.25	0.78518	−0.042	89.25	1.33907	−0.192
100.0	0.77738	000	100.0	1.3240	000

DISCUSSION

If the heat added to solutions of methyl alcohol and toluene were utilized only for raising the temperature of the solutions, specific heat would be a straight-line function of composition, with the line terminating in the specific heats of the pure components. The specific heats of the solutions, however, are greater than those calculated from additivity for all concentrations, as is shown by figure 1. Figure 2 emphasizes the extent of the deviations and shows the concentrations at which the deviations are most pronounced. Toluene is regarded as a normal liquid and methyl alcohol as strongly associated. The heating of solutions of the two liquids during specific heat determinations probably causes partial dissociation of the methyl alcohol, and this most markedly in the solutions of low alcoholic content. It appears that the presence of toluene enhances this dissociation by a dilution effect. The large heat capacities of the solutions of low alcohol concentrations are due, in a measure at least, to the absorption of heat involved in the process of dissociation of the alcohol aggregates. The plotted data indicate that the changes of specific heat from ideality are greater at 35°C. than at 25°C., which would suggest that a greater dissociation occurs at the higher temperature.

The partial molal heat capacities, $\bar{C}_{p_2}$ (values listed in table 2), are greater for all values calculated than the molal heat capacities of the pure liquids. Williams and Daniels (18) attribute such behavior to the formation of a compound of the components, or to the fact that heat capacity is increased by an increase in the number of molecules even though the total weight remains unchanged. It would seem that the latter effect is predominant in the system under consideration in view of the large negative heats of mixing, which furnish evidence that compound formation is unlikely. The difference between the partial molal heat capacity in solution and the molal heat capacity of the pure alcohol is greatest in the mixtures of low alcohol content, which would indicate a greater number of molecules and hence greater positive deviations from ideality for the heat capacities of the mixtures in that region of concentration.

The view that dissociation of the alcohol is aided by the dilution with toluene is supported by a consideration of the heat changes which attend solution of the liquids. At all concentrations, and at both 25°C. and 35°C., heat is absorbed on mixing, and the greatest absorptions are in the solutions of high concentrations of toluene, and these are greatest at 35°C. Evidence, in the case both of heat capacity deviations and of heats of mixing, indicates that more dissociation occurs at the higher temperature and at the lower concentrations of alcohol. It would be expected, however, that measurements at successively higher temperatures would ultimately show smaller and smaller deviations and smaller heat changes as the alcohol became more and more dissociated.

Large negative heats of mixing indicate the absence of compound formation or solvation in that these processes are usually associated with an evolution of heat. However, it is possible that such processes occur to a small extent, or with small evolution of heat, or conceivably, with a negative heat of formation. Under these conditions their thermal effects would be obscured by the heat absorption of dissociation.

It would be expected that an increase in the number of molecules in a solution, by virtue of dissociation, would be accompanied by an increase in volume, but in the case of the present system apparent dissociation of the alcohol is accompanied by a contraction in volume, and the largest contractions are found in approximately the same concentration areas as are the greatest deviations of specific heats and the greatest absorptions of heat on mixing. The evidence adduced from the thermal quantities indicates that dissociation is increased at the higher temperature, but volume contractions are found to be decreased. If a combination of alcohol and toluene molecules occurs in the manner suggested in connection with heats of mixing, the volume contractions might be reconciled. Such a combination, however, would be assumed to be quite unstable, and undoubtedly would be broken up when the temperature of the solutions was raised during determinations of heat capacities.

Washburn and Lightbody (15) observed that mixtures of ethyl alcohol with both benzene and toluene display both contractions and expansions of volume on mixing, and that methyl alcohol and benzene show both expansion and contraction. They postulated that a change from volume expansion to volume contraction is due to a shifting of the equilibrium among simple, complex, and compound molecules with changing concentration (9), but why methyl alcohol and toluene should be unique among these four systems in showing a contraction throughout the concentration range it is difficult to say, especially in view of the fact that the similarity of the liquids would lead to the expectation that the mixtures would behave similarly. Measurements of volume changes at other temperatures should be of help in answering this problem.

Refractive indices vary slightly from a straight-line function of composition, and the refractive indices of the mixtures are lower than the values obtained from calculations on the basis of an ideal solution. A decrease of refractive index is contrary to what would be expected if the only molecular change occurring in the solutions is one of dissociation of the alcohol. The supposed increased number of molecules together with a contraction in volume should produce an increase in the refractive indices. Here, as in the case of volume changes, a union of alcohol and toluene molecules may be the governing factor in causing the decrease in refractive indices. It would seem, however, that influences other than relative numbers of molecules are in effect, because the maximum deviations of refractive indices occur in solutions of greater alcohol content than do the greatest contractions in volume. Some changes in the chemical nature of the molecules, not yet understood, must be responsible for the situations observed. As yet it is possible to make only qualitative interpretations of the type of data presented here, but more complete knowledge of this and similar systems should furnish evidence for roughly quantitative predictions.

SUMMARY

A rapid and efficient technique for measuring specific heats of solutions of organic liquids has been developed. The apparatus used, with slight modification, is readily applicable to the determination of heat changes attending solution of the liquids in each other.

Specific heats and heats of mixing of methyl alcohol–toluene solutions have been determined at 25°C. and 35°C. for the entire range of concentration. The heat capacities observed for the solutions are greater than those calculated from additivity for all concentrations. Mixing of the liquids is accompanied by an absorption of heat in all cases. Both effects are most pronounced in concentrations of low alcohol content.

The changes in volume resulting from mutual solution of the liquids, and the refractive indices of the solution, have been measured throughout the concentration range at 25°C. and 35°C. Solution of the liquids is accompanied by a contraction in volume; refractive indices are lower than those calculated on the basis of additivity.

The thermal effects observed are accounted for by assuming that methyl alcohol, which in the pure state is associated, undergoes dissociation into simpler molecular aggregates during mixing of the liquids and during subsequent heating in the determinations of the heat capacities of the solutions. A union of the constituent molecules has been assumed to explain the observed changes of volume and refractive index.

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MIXTURES OF COLLOIDAL ELECTROLYTES WITH UNI-UNIVALENT SALTS

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Owing to the dearth of information as to the effect of mixtures of colloidal electrolytes and uni-univalent salts upon each other, the following data are instructive. One of the more interesting results of the study of colloidal electrolytes (1, 4, 5, 7, 9) is that the ionic strength principle does not apply to ionic micelles unless they are treated as uni-univalent electrolytes. Although ionic micelles are highly charged colloidal particles, their charges are spaced so far apart that they are effectively independent. In this respect, they are sharply differentiated from ordinary polyvalent ions in which the charges are coincident. The present data illustrate this in graphical form, both for freezing point lowering and for conductivity.

MODE OF CALCULATION

For comparison with the observed data for mixtures, it is customary to make use of various simple additive rules (2, 8, 10, 11). We have used three. First (method 1) is the "classical" mixture rule, where the molar conductivity, both observed and calculated, refers to the specific conductivity multiplied by the number of cubic centimeters containing one gram-equivalent of the common ion. For example, for mixtures of potassium laurate with potassium chloride

$$\mu_{\text{total K}^+} = \mu_{\text{KCl}_{\text{total}}} \times N_{\text{KCl}}/N_{\text{total}} + \mu_{\text{KL}_{\text{total}}} \times N_{\text{KL}}/N_{\text{total}}$$

where $\mu_{\text{KCl}_{\text{total}}}$ is the conductivity of a solution of potassium chloride alone of the same concentration of potassium ion as the total concentration in the mixture; whereas N_{KCl} is the actual equivalent weight normality (molality or gram-equivalents per 1000 grams of water) of the potassium chloride present. The assumption is that each salt contributes toward the total conductivity in proportion to its actual concentration and to its conductivity in a solution of the same total concentration as that of the mixture.

The second basis of comparison (method 2) is likewise only a first approximation to the truth, for it assumes that each salt present is exhibiting the same conductivity in the mixture which it would have if the other salt were absent.

$$\mu_{\text{sum}} = N_{\text{KCl}} \times \mu_{\text{KCl}_N} + N_{\text{KL}} \times \mu_{\text{KL}_N}$$

This is compared with the observed conductivity of the mixture; that is, the observed specific conductivity multiplied by that volume which contains the stated number of equivalents of each of the two salts.

It should be noted that for solutions containing much soap, the values of weight normality and volume normality may differ by as much as 30 per cent, owing to the fact that soap solutions, in spite of the large weight of soap present, differ comparatively little in density from water. For this reason, application of the "classical" mixture rule to specific conductivities (method 3), that is, to equal volumes of solutions of the same total weight normality in common ion, leads again to a distinctly different result from the first method of comparison. All three provide some basis for examining the mutual effect of the constituents of the mixture. Data for pure substances were taken from International Critical Tables, published papers, or measured *ad hoc*.

Freezing points of mixtures were compared by two methods of calculation. The first (method 4) corresponds to the second of those above mentioned, that is, simple addition of the freezing points exhibited by each salt at a weight normality equal to that which it possessed in the mixture.

$$\theta_{\text{mixture}} = \theta_1 + \theta_2$$

Lastly (method 5), they were compared through the osmotic coefficient of the mixture

$$g_m = g_{1_m} \times m_1/m + g_{2_m} \times m_2/m$$

where g_{1_m} is the osmotic coefficient of one constituent at the total molality of the mixture. Bjerrum's osmotic coefficient $g = 1 - j = \theta/\nu\lambda m$, where $\nu\lambda$ is the molal lowering at infinite dilution, obtained by diluting the mixture without changing the ratio between the two constituents. Thus

$$\nu = (\nu_1 m_1 + \nu_2 m_2)/(m_1 + m_2)$$

where $m = m_1 + m_2$ and $\lambda = 1.858°$.

All conductivity data refer to 25.00° ± 0.01°C., measured with the usual precautions in water of conductivity 0.5 to 1.0 $\times$ 10^{-6} in an oil thermostat. Freezing point measurements were by the Beckmann method with undercooling 0.3° to 0.5°. The best available materials were employed and all instruments were standardized.

The partial specific volumes of soaps above the concentration exhibiting minimum conductivity lie between 0.973 and 0.982 for lauryl- and myristylsulfonic acids, and 0.945 to 0.935 for the *n*-undecylsulfonic acid; that for potassium laurate as found by Bury and Parry (3) lies between 0.912 and 0.917, but whereas the latter fell sharply in lower concentrations, the partial specific volumes of the straight chain sulfonic acids are slightly greater in more dilute solution.

CONDUCTIVITY RESULTS

Figure 1 exhibits the first two methods of comparison of mixtures of 0.955 N_w potassium laurate with potassium chloride up to 1.235 N_w. It is observed that the conductivity of the mixture by both methods of comparison is definitely less than the calculated value. The same result follows from comparison of specific conductivities.

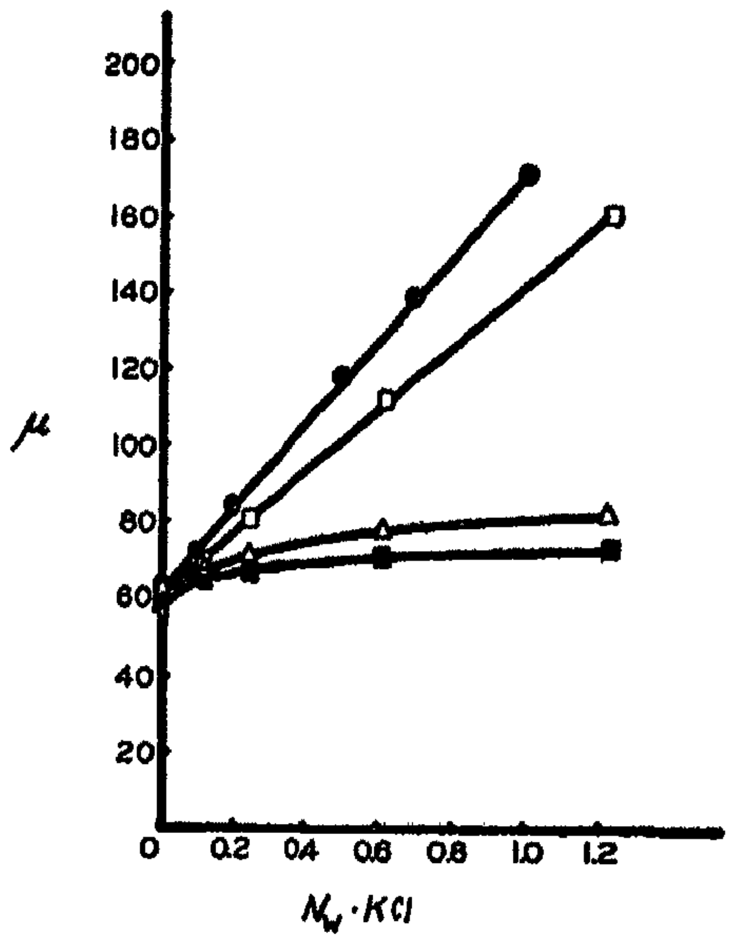

FIG. 1. Molar conductivity of 0.955 $N_w(m)$ potassium laurate containing potassium chloride. ■, observed, referred to 1 mole of total K; △, sum of constituents (method 2); □, observed, referred to total K in 1000 g. of water; ●, sum of constituents (method 1).

In contrast to this, figure 2, for mixtures of 0.1 N_w undecylsulfonic acid with hydrochloric acid up to 1 N_w, shows fairly close agreement between calculated and observed values, the latter being generally even higher. Similarly, if, according to the third method of calculation, observed conductivity is plotted against total molality (N_w) for true mixtures and separate constituents, the curve of observed values in every case lies slightly but definitely higher even than the calculated values. This may be largely attributed to increased formation of ionic micelle.

A mixture, 0.1016 N_w with respect to laurylsulfonic acid and also with respect to hydrochloric acid, calculated by the first method, gave an equivalent conductivity with respect to total acid of 53.67 mhos as compared with the calculated value 54.6.

From the foregoing it may be concluded that the conductivity of the mixtures of soaps with electrolytes does not depart very much from simple additive rules.

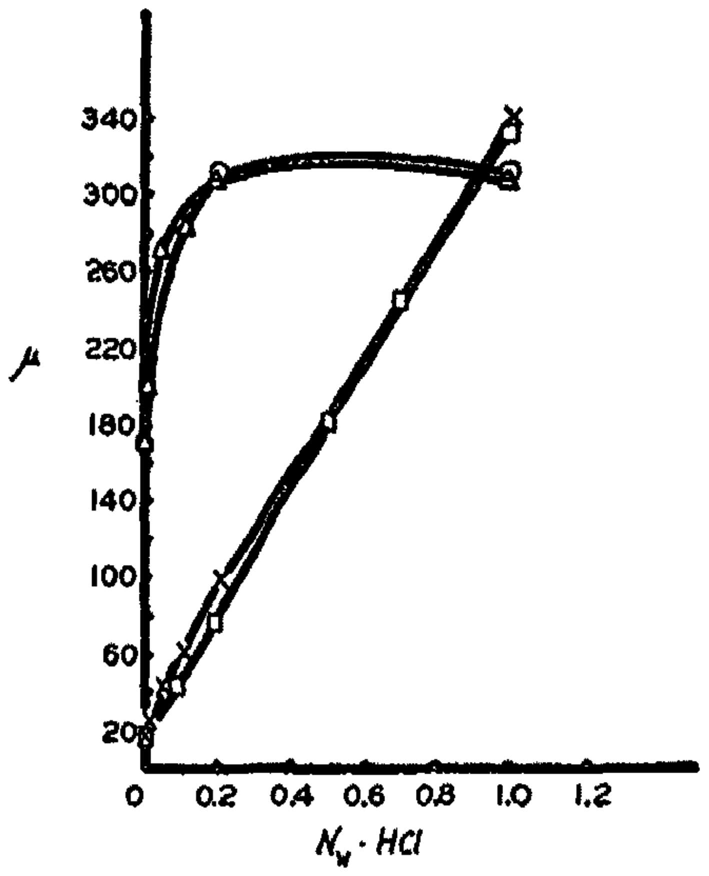

FIG. 2. Molar conductivity of 0.1 N_w undecylsulfonic acid containing hydrochloric acid. △, observed, referred to 1 mole of total H; ○, sum of constituents (method 2); ×, observed, referred to total acid in 1000 g. of water; □, sum of constituents (method 1).

FREEZING POINT RESULTS

Figure 3 exhibits the data for mixtures of 0.1 N_w undecylsulfonic acid with addition of hydrochloric acid up to 1 N_w. It will be seen that well within the error of experiment the total lowering is the sum of the constituents.

Figure 4 shows that the osmotic coefficient of the mixture is definitely even greater than that calculated from the constituents, for a mixture—0.1016 N_w laurylsulfonic acid containing 0.1016 N_w hydrochloric acid—exhibited a freezing point lowering of 0.440°, as compared with 0.420° for the sum of the constituents and an osmotic coefficient of 0.583 as com-

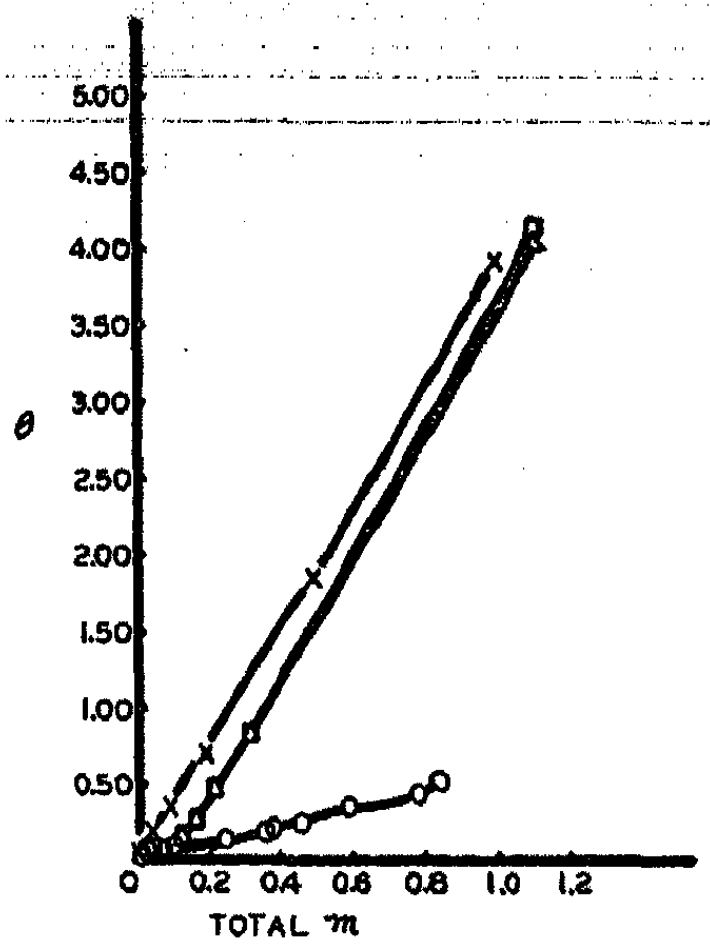

FIG. 3. Freezing point lowering (θ) of 0.1 N_w undecylsulfonic acid containing hydrochloric acid. □, observed values; △, calculated values (method 4); ×, International Critical Tables values for hydrochloric acid alone; ○, Miss Betz' values for $C_{11}H_{23}SO_3H$ alone.

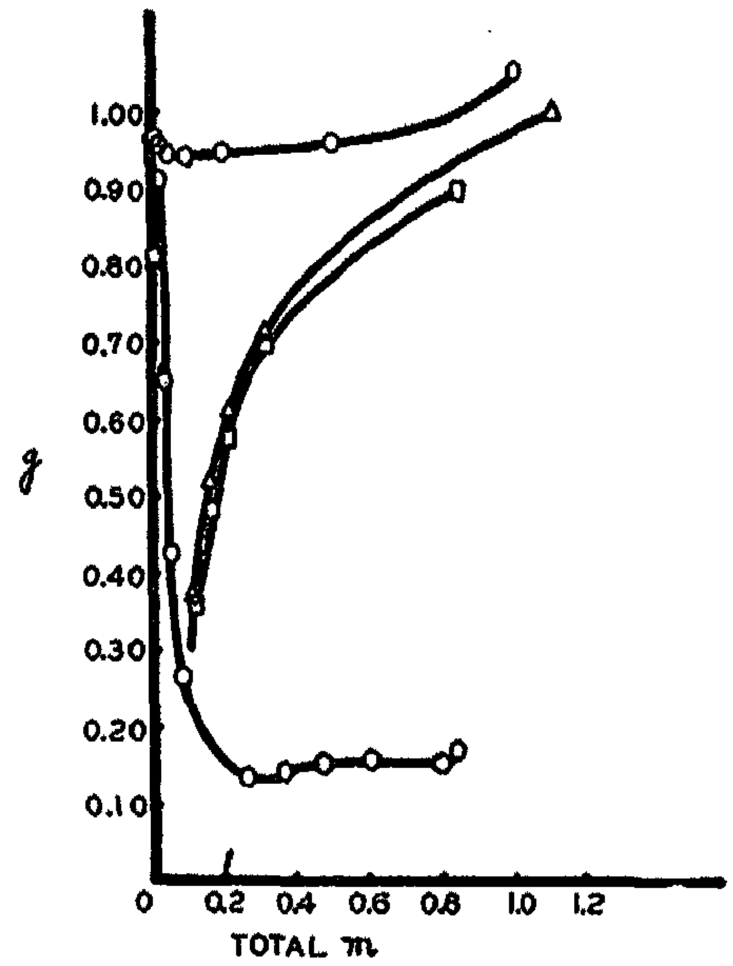

FIG. 4 Osmotic coefficients (g) of 0.1 N_w undecylsulfonic acid containing hydrochloric acid. △, observed values; □, calculated values (method 5); ○, International Critical Tables values for hydrochloric acid alone; ●, Miss Betz' values for $C_{11}H_{23}SO_3H$ alone.

pared with predicted 0.551. Thus again the observed values are higher than those calculated from the constituents. This result applies equally to ordinary soaps. Quick (6), for example, found the following dew point lowerings at 18°C.: 1 N_w potassium laurate, 0.22°; 1 N_w potassium chloride, 0.50°; mixture 1 N_w with respect to each, 0.77°, as compared with the sum of the constituents, only 0.72°. In these strong soap solutions, the increased lowering is presumably due to hydration of the soap.

It is evident that presence of ionic micelle does not exert any great effect toward suppression of conductivity or freezing point lowering as had been assumed by a number of writers.[1]

Sodium salts of dibasic organic acids carry upon the anion charges which are far apart. The following mixtures were studied, concentration being expressed in molality, *m*; the values of freezing point lowering in brackets are for the respective constituents, and the sum of these:—0.1 sodium chloride, 0.1 sodium oxalate (0.348°, 0.445°, 0.793°), 0.787°; 0.2 sodium chloride, 0.1 sodium oxalate (0.685°, 0.445°, 1.130°), 1.130°; 0.1 sodium chloride, 0.1 sodium succinate (0.348°, 0.532°, 0.880°), 0.885°; 0.2 sodium chloride, 0.1 sodium succinate (0.685°, 0.532°, 1.217°), 1.233°; 0.5 sodium chloride, 0.486 sodium succinate (1.675°, 2.545°, 4.220°), 4.305°; 0.1 sodium chloride, 0.1 sodium tartrate (0.348°, 0.476°, 0.824°), 0.803°; 0.2 sodium chloride, 0.1 sodium tartrate (0.685°, 0.476°, 1.161°), 1.141°; 0.5 sodium chloride, 0.5 sodium tartrate (1.675°, 2.002°, 3.677°), 3.626°; 0.230 sodium chloride, 0.115 sodium phthalate (0.775°, 0.731°, 1.506°), 1.475°; 0.5 sodium chloride, 0.247 sodium phthalate (1.675°, 1.561°, 3.236°), 3.510°; 0.270 sodium chloride, 0.137 sodium isophthalate (0.925°, 1.400°, 2.325°), 2.450°; 0.5 sodium chloride, 0.266 sodium isophthalate (1.675°, 2.814°, 4.489°), 4.464°; 0.230 sodium chloride, 0.113 sodium terephthalate (0.775°, 0.780°, 1.555°), 1.633°; 0.450 sodium chloride, 0.2315 sodium terephthalate (1.510°, 1.980°, 3.490°), 3.475°.

In every case it is seen that the observed lowering is, within experimental error, equal to that of the sum of the lowerings caused by the two constittuents independently. For the tartrates, succinates, and *o*-phthalates, osmotic coefficients could be calculated and were likewise within a few per cent of those observed.

SUMMARY

Mixtures of ordinary electrolytes with ordinary alkali soaps or with hydrogen soaps, like mixtures of sodium chloride with sodium salts of organic acids, exhibit conductivities and freezing point lowerings in sub-

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[1] G. W. Fuller in this laboratory has found that the electrometric titration curves of these hydrogen soaps show the normal form and position for a moderately strong univalent acid. A similar observation on gum arabic was made by Thomas and Murray (J. Phys. Chem. **32**, 696 (1928)).

stantial agreement with the simple additive mixture rules. In all these cases, the charges on the polyvalent ion or micelle are spaced so far apart as to be effectively independent. Hence the ionic strength of colloidal electrolytes resembles that for a uni-univalent electrolyte.

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SIMPLE KINETIC THEORY OF IONIC EXCHANGE. I[1]

Ions of Equal Valency

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INTRODUCTION

Many colloidal systems, particularly the aluminosilicates, the proteins, soaps, hydrous oxides, and numerous metallic colloids, exhibit the phenomenon of exchange adsorption or ionic exchange. Negatively charged colloidal particles are known to possess cation exchange (base exchange), whereas positive particles have anion exchange. Amphoteric colloids may comprise both types of reactions.

The present status of exchange adsorption is one of confusion. A great mass of experimental data is at hand, and over a dozen equations have been proposed. These are either wholly empirical or represent in the main questionable applications of the law of mass action. The constants of the equations have but little physical significance. No attempts have been made to advance a theory which links the exchange isotherms with other fundamental properties of colloidal systems such as electric potential and stability.

The purpose of the present study is to deduce on theoretical grounds an exchange adsorption isotherm. A very simple *ionic exchange model* will be depicted, and on the basis of kinetic concepts an equation will be formulated with the aid of statistical methods. Special emphasis will be laid on a rational interpretation of the constants. No claim is made that the model proposed and the equation deduced are valid for all ionic exchange systems known, but it is hoped that they will furnish a platform from which the great mass of empirical data may be viewed more intelligently than has been hitherto possible.

QUALITATIVE ASPECTS

Let us consider the special case of a large muscovite crystal. Upon being ground to colloidal dimensions the crystal breaks up, preferably along the basal cleavage planes. According to Pauling (4) these surfaces consist of layers of negative oxygen ions which form a rigid framework.

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Between the planes are located the potassium ions which, as a result of grinding, become exposed and appear in exchangeable form (figure 1). They behave as adsorbed ions, although previous to the mechanical treatment they were an integral part of the crystal. If the colloidal plates thus obtained are put into a solution of sodium chloride, ionic exchange takes place and a part of the potassium ions on the crystals is replaced by sodium ions. How shall such a surface reaction be pictured? It is important to remember that the potassium ions on the exposed oxygen layers are not at rest. Owing to heat motion and on account of the random bombardment by water molecules, the potassium ions oscillate irregularly. At times they may be at a considerable distance (several Ångström units) from the wall, but are pulled back by the electrically charged oxygen ions. In the solution, the sodium ions wander at random as a necessary consequence of Brownian movement. Now, if it so happens that by chance a migrating sodium ion slips between the wall and an oscillating potassium ion which has momentarily moved away from the surface, an exchange reaction will occur. The positive sodium ion is electrically attracted by the negative wall, and the potassium ion is left in the solution or even

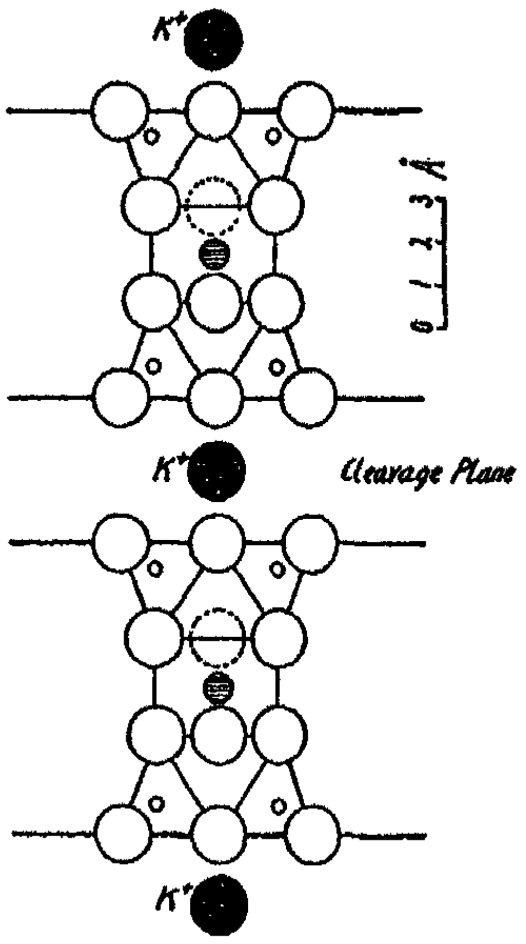
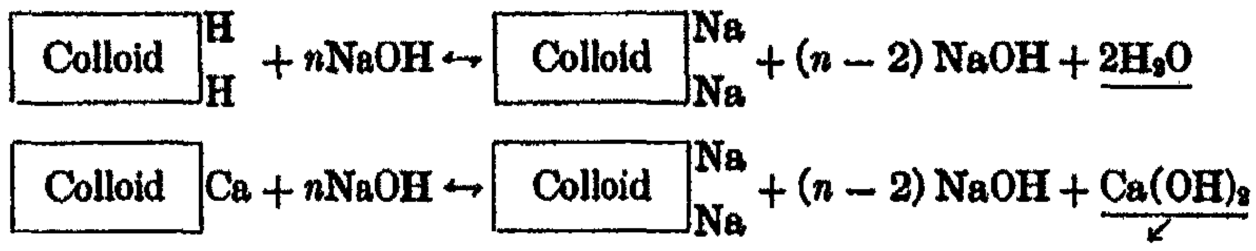


FIG. 1. Structure of muscovite according to Pauling (4). The large black circles are K ions; the large white circles are O and OH ions; the shaded small circles are Al ions in octahedra portions; and the small white circles are Al or Si ions within tetrahedra.

pushed into it by the electrical repulsion forces of the sodium ion. The chloride anion in the liquid does not participate in the reaction.

It should be emphasized that the mechanism proposed does not include the adsorption of cations or anions without an equivalent release of corresponding surface ions. Of course, weak electrolytes may be adsorbed as a molecular entity, but this case falls into the category of Langmuir's adsorption of molecules. In particular, the adsorption of OH ions, which is frequently reported in the literature, can be explained as mere anion exchange or a cation exchange involving hydrogen ions or polyvalent cations, according to the schemes:



$$\boxed{\text{Colloid}}\begin{matrix}\text{H}\\\text{H}\end{matrix} + n\text{NaOH} \leftrightarrows \boxed{\text{Colloid}}\begin{matrix}\text{Na}\\\text{Na}\end{matrix} + (n-2)\,\text{NaOH} + \underline{2\text{H}_2\text{O}}$$

$$\boxed{\text{Colloid}}\text{Ca} + n\text{NaOH} \leftrightarrows \boxed{\text{Colloid}}\begin{matrix}\text{Na}\\\text{Na}\end{matrix} + (n-2)\,\text{NaOH} + \underset{\swarrow}{\underline{\text{Ca(OH)}_2}}$$

In both cases OH ions may disappear from the solution, but not by means of straight adsorption. The subsequent increase in dispersion of the particles follows from the fact that Na-colloids have higher potentials than either H- or Ca-colloids (2).

For systems which do not contain bases (K, Ca, etc.) in the crystal lattice, for instance kaolinite, pyrophyllite, and many organic compounds, we believe that the OH ion of the crystal is the seat of exchange, or, more specifically, the H ion of the exposed OH ion will be replaced upon addition of an electrolyte.

QUANTITATIVE FORMULATION OF EXCHANGE ADSORPTION

We shall abandon the specific case of muscovite and work with the general case of a (planar) surface which contains a definite number of attraction spots per unit area. The ions, atoms, or molecules—or more generally the "particles"—which are initially adsorbed are called "black" or *b*. Those which are added to the system to function as exchanging particles are called "white" or *w*. Additional black particles which wander about like the white ones may also be introduced (corresponding to the special case of K-mica + NaCl + KCl). To simplify the mathematical treatment all particles are considered to possess the same mass and, if ions, the same electric charge but not necessarily the same size. The particles do not influence each other, and the principle of equipartition of energy is supposed to hold.

Terminology

Every adsorbed black particle oscillates within a given space called the oscillation cell, the average volume of which is v_b. The oscillation cell is a very small fraction of the total volume (V) of the system. There are z_b attraction spots and consequently z_b adsorbed black particles on the entire surface. It shall be postulated that exchange occurs whenever a white particle enters an oscillation cell in such a way that it slips between the wall and the vibrating black particle or, more generally speaking, that it comes closer to the attraction spot. The number of white particles in V is N_w and the corresponding number of wandering black particles is N_b. The total number of b in V is therefore $N_b + z_b$. The average number of migrating w and b particles in one exchange cell (not counting the adsorbed ions) is

$$\mu = \frac{v_b}{V}(N_w + N_b)$$

which is the sum of:

$$\text{average number of } w \text{ in } v_b \text{ is } \frac{v_b}{V} N_w = \mu_w$$

$$\text{average number of } b \text{ in } v_b \text{ is } \frac{v_b}{V} N_b = \mu_b$$

The justification for using a simple statistical distribution instead of the Maxwell-Boltzmann principle lies in the nature of the exchange model suggested. Unlike the free surfaces operated with by Langmuir, Hückel, and others, the electric fields of the surface are "neutralized" by the adsorbed ions. Using the classical valence picture of the chemist, we assume that the attraction forces are localized in a straight line extending from the attraction spot on the wall to the center of the adsorbed ion. In other words, as long as the migrating ion does not come between the wall and the exchange ion—though it may be inside of the oscillation space—it is not under the influence of forces which differ from those in the bulk of the liquid. Furthermore, the adsorbed ions never evaporate, even in absence of migrating particles, otherwise the axiom of electroneutrality would be violated.

Distribution considerations

At any given instant some oscillation cells have no migration particles at all, some have one, others two, or three, or more. Again, those cells having one particle may have either a white one or a black one. The latter case would contribute nothing to the exchange process, since the replacement of a black particle by another black particle could not be detected experimentally. Cells with several particles may have all white, or all black, or mixtures of the two colors. The probabilities of these possible cases must be ascertained.

Let us designate the probability that a specific cell has none of the white particles by W_0, that it has one white particle by W_1, and in general, n particles of type w by W_n. Similarly for the migrating black particles we have $B_0, B_1, \ldots\ldots B_n$.

W_0B_0 is the probability that a given cell contains no migrating particles at all; W_1B_0 is the probability that it has a white particle, and W_0B_1 is the value for a wandering black particle. If two particles enter a specific cell the following cases exist:

Possibilities	*Probabilities*
$w\ w$	W_2B_0
$w\ b$	W_1B_1
$b\ b$	W_0B_2

For n particles we obtain the series:

$$W_nB_0 + W_{n-1}B_1 + W_{n-2}\,B_2 + \ldots\ldots\ W_0B_n = 1$$

According to definition only such cells will produce exchange as happen to have a white particle on the left of the oscillating b (figure 2); in other words, only a fraction of the cells with wandering w's will actually show exchange. Designating the fractions by $\alpha_n, \beta_n, \ldots\ldots$, one obtains for the probability of exchange for n particles in a cell:

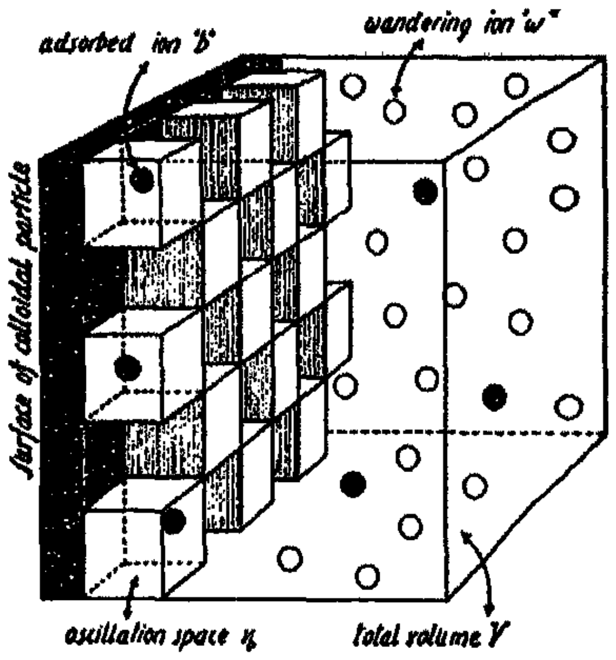


FIG. 2. Schematic representation of the surface of a plate of colloidal dimensions showing adsorbed ions (black) and their oscillation spaces

$$P_n = \alpha_nW_nB_0 + \beta_nW_{n-1}B_1 + \ldots\ldots\ \Omega_nW_0B_n$$

The index n takes the successive values 0, 1, 2, 3, ... The total exchange probability, P, is the sum of these individual probabilities. For the sake of illustration the initial members of the final series shall be given:

$$P = \Sigma P_n = (\alpha_0W_0B_0) + (\alpha_1W_1B_0 + \beta_1W_0B_1) + (\alpha_2W_2B_0 + \beta_2W_1B_1 + \gamma_2W_0B_2) + \ldots\ldots \quad (1)$$

Application of the Poisson series

The actual values of W_n and B_n in terms of v_b, V, N_w, and N_b are found with the aid of Smoluchowski's equations (5), also known as Poisson series:

$$W_{n(v_b)} = \frac{(\mu_w)^n}{n!} e^{-\mu_w} \quad \text{and} \quad B_{n(v_b)} = \frac{(\mu_b)^n}{n!} e^{-\mu_b} \tag{2, 3}$$

These equations yield the probability that n white or n black wandering particles are in a selected oscillation cell v_b.

Inserting equations 2 and 3 into formula 1 furnishes:

$$e^{-\frac{v_b}{V}(N_w+N_b)}\left[\alpha_0 + \frac{v_b}{V}(\alpha_1 N_w + \beta_1 N_b) + \left(\frac{v_b}{V}\right)^2\left(\alpha_2 N_w^2 + \beta_2 N_w N_b + \gamma N_b^2\right) + \cdots\right] \tag{4}$$

In order to simplify the above expression, we shall conduct the experiments in such a way that V is very great in comparison to v_b, that is, use dilute sols only. The magnitudes of $\left(\frac{v_b}{V}\right)^n$ for $n > 1$ become very small in comparison to $\frac{v_b}{V}$, and the members with the higher terms of n in $\left(\frac{v_b}{V}\right)$ can be neglected. Since α_0 and β_1 are zero by definition, expression 4 reduces to:

$$\alpha_1 \frac{v_b}{V} N_w e^{-\frac{v_b}{V}(N_w+N_b)} \tag{5}$$

which is the probability of exchange for one cell under the experimental restrictions specified. For z_b cells the most probable number that will contribute to exchange is z_b times the above value.

The amount of exchange in the time Δt is a function of the velocity u of the particles. The rate of adsorption of white particles is evidently

$$\frac{\Delta w}{\Delta t} = z_b \alpha_1 \frac{v_b}{V} N_w e^{-\frac{v_b}{V}(N_w+N_b)} f(u) \tag{6}$$

which is also the rate of release of adsorbed black particles.

Equilibrium aspects

Equation 6 describes but one phase of the exchange phenomenon, namely, the release of black particles by white ones. The latter, which become adsorbed, may in turn be replaced by wandering black particles. The derivation of the equation of this reversed process is similar to the one just given, except that some of the symbols are to be changed: v_b

becomes v_w, the oscillation space of the adsorbed white particle, and z_b is changed to z_w, which represents the number of white particles adsorbed. The final equation corresponding to formula 6 is of the form

$$\frac{\Delta b}{\Delta t} = z_w \alpha_1 \frac{v_w}{V} N_b e^{-\frac{v_w}{V}(N_w + N_b)} f(u) \tag{7}$$

$\Delta b/\Delta t$ represents the rate of adsorption of black particles, which is also the rate of release of white particles. Equilibrium exists when

$$\frac{\Delta w}{\Delta t} = \frac{\Delta b}{\Delta t}$$

or

$$\frac{z_b}{z_w} \frac{N_w}{N_b} = \frac{v_w}{v_b} e^{\left(\frac{v_b - v_w}{V}\right)(N_w + N_b)} \tag{8}$$

Equation 8 is of a more general type than is required for the common base-exchange experiments. As a rule no wandering b particles are added to the migrating white particles. Furthermore, we shall express the equilibrium conditions in terms of white particles adsorbed (w_a) as a function of the white particles added (N_{w_0}). The following substitutions result:

N_w becomes $N_{w_0} - w_a$
z_b becomes $z_{b_0} - w_a$
z_w and N_b become w_a

Introducing these magnitudes into equation 8 leads to

$$\frac{(z_b - w_a)(N_{w_0} - w_a)}{w_a^2} = \frac{v_w}{v_b} e^{\left(\frac{v_b - v_w}{V}\right) N_{w_0}} \tag{9}$$

Inasmuch as v_b and v_w, and particularly $v_b - v_w$, are very small in comparison to V, the exponential term closely approaches 1; hence,

$$w_a^2 \left(1 - \frac{v_w}{v_b}\right) - w_a (z_{b_0} + N_{w_0}) + z_b N_{w_0} = 0 \tag{10}$$

For ordinary cation-exchange experiments we may write

$$w^2 \left(1 - \frac{v_w}{v_b}\right) - w(s + N) + sN = 0 \tag{11}$$

$$w \doteq \frac{+(s + N) \pm \sqrt{(s + N)^2 - 4sN\left(1 - \frac{v_w}{v_b}\right)}}{2\left(1 - \frac{v_w}{v_b}\right)} \tag{11}$$

where N = amount of electrolyte added initially (number of ions),
w = number of cations adsorbed or released at equilibrium,
s = saturation capacity, and
v_w, v_b = oscillation spaces of the adsorbed ions.

The equation has been deduced for a platy colloidal particle, but it applies to spheres as well; nor is it restricted to colloidal dimensions or to crystallites.

The most general equation embracing the case in which both white and black particles are added has the form:

$$w = \frac{\left[s + N_w + N_b\left(1 - \frac{v_w}{v_b}\right)\right] \pm \sqrt{\left[s + N_w + N_b\left(1 - \frac{v_w}{v_b}\right)\right]^2 - 4sN_w\left(1 - \frac{v_w}{v_b}\right)}}{2\left(1 - \frac{v_w}{v_b}\right)} \qquad (11a)$$

The symbols have the following meaning:

N_w = number of white particles added initially (electrolyte ion w),
N_b = number of black particles added initially (electrolyte ion b), and
w = number of white particles (electrolyte ion w) adsorbed or black particles (electrolyte ion b) released at equilibrium.

Equation 11a becomes of importance in studies on competition adsorption or competition exchange. Two kinds of particles, w and b, compete for a place on the surface. If N_b is zero, equation 11a goes over into equation 11. Figure 3 shows what types of curves can be expected in competition exchange. The uppermost curve depicts the conditions for $N_b = 0$, that is, no wandering black particles are added. If one introduces black particles equal to twice or ten times the saturation capacity ($N_b = 2S$, $10S$), the adsorption of white particles becomes greatly repressed. This is most pronounced in low concentrations of the electrolyte ion w. The slope becomes less marked and the curves tend to approach straight lines. On the other hand, if equal numbers of white and black particles ($N_w = N_b$) are added, the slope of the curve becomes accentuated at low concentrations, whereas at higher concentrations the curve tends to run parallel to the abscissa, but never reaching the 50 per cent mark.

It is not likely that the natural colloidal systems are of such simple type that they correspond directly to the conditions which were specified for the ionic exchange model. A certain selection of the experimental results becomes necessary. Data obtained for very high electrolyte concentrations will have to be omitted in order to conform to the restrictions mentioned in the derivation of the equation. On the other hand, systems of high dilution are apt to show disturbances due to hydrolysis effects, i.e., ionic exchange with hydrogen ions of water. Intermediate ranges of electrolyte concentrations appear to be most suitable to test the validity of the equation.

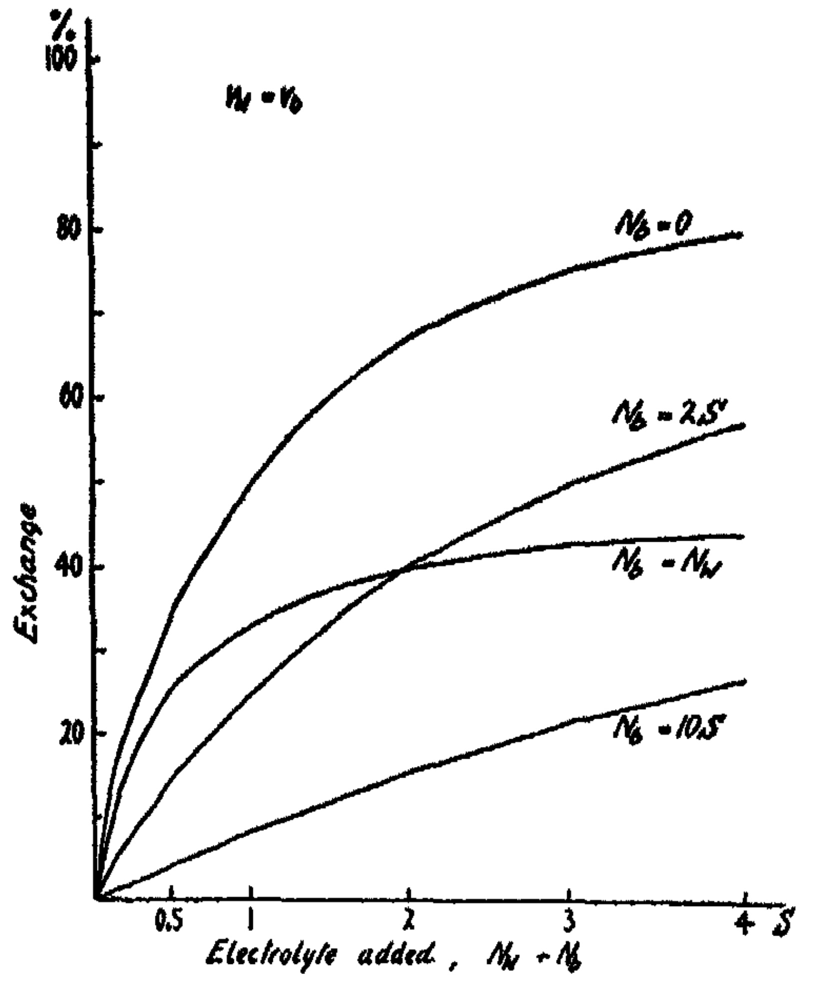


FIG. 3. Theoretical curves showing competition adsorption for a system of the type

$$\underset{(S)}{\text{K-colloid}} + \underset{(N_w)}{NH_4Cl} + \underset{(N_b)}{KCl}$$

The number of cations added is expressed in terms of saturation capacities (S). The intensity of exchange adsorption is given as per cent exchange in terms of saturation capacities. Activities are neglected.

Results with colloidal Putnam clay particles[2] *(analyses by J. E. Gieseking)*

The most careful and extensive work on ionic exchange has been carried out with aluminosilicates, and among these the permutites, zeolites, and natural soil colloids have been most extensively investigated. Cation-exchange experiments with purified Putnam clay were conducted according to methods previously described (1). In all experiments 7.5 g. of colloidal clay carrying 4.50 milliequivalents (M.E.) of adsorbed ions was treated

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[2] The author is indebted to the National Research Council for a Grant-in-Aid.

with various amounts of chlorides, and the number of ions released was determined in the supernatant liquid. In every case the total volume of the system was 500 cc., and the temperature was kept constant at 28° ±0.5°C. The exchange values expressed in terms of saturation capacities (4.50 M.E. = 100 per cent) are given in table 1 and also in figures 4, 5, and 6. The lines drawn were calculated with the aid of equation 11.

Upon inspection of the curves it must be concluded that the equation developed is able to describe very satisfactorily the position and trend of the curves over a considerable range of electrolyte concentration. In some instances the fitting is almost perfect; in others, systematic deviations seem to occur. They are especially noticeable in exchange reactions which involve hydrogen ions.

TABLE 1

Ionic exchange experiments with Putnam clay

Analyses by J. E. Gieseking

SYSTEM	IONIC EXCHANGE PERCENTAGES FOR THE FOLLOWING INITIAL ELECTROLYTE CONCENTRATIONS $1 S = 4.50$ M.E.				AVERAGE VALUE FOR $\frac{v_y}{v_x}$
	0.5 *S*	1.0 *S*	2.0 *S*	4.0 *S*	
NH_4-clay + LiCl	20.6*	29.9	44.4	54.7	5.16
NH_4-clay + NaCl	20.6	32.0	45.1	54.9	4.56
NH_4-clay + KCl	32.8	51.3	66.8	75.2	1.10
NH_4-clay + RbCl	41.1	62.6	80.2	90.0	0.354
NH_4-clay + CsCl	51.3	68.8	85.3	90.0	0.268
NH_4-clay + HCl	50.4	84.9	90.9	90.9	(0.03)
Ca-clay + $MgCl_2$	32.1	47.5	63.3	76.7	1.23
Ca-clay + $BaCl_2$	35.1	52.9	67.0	80.8	0.855
Mg-clay + $BaCl_2$	28.7	50.3	71.0	83.6	0.800
H-clay + LiCl	4.5	6.6	9.0	13.0	207
H-clay + NaCl	3.5	6.2	9.8	13.5	197
H-clay + KCl	8.6	14.5	22.0	34.2	(31.4)
H-clay + RbCl	19.0	28.2	41.2	62.2	5.53
H-clay + CsCl	25.2	39.7	60.2	82.9	

* The first result indicates the following: There are 4.50 M.E. (1 *S*) adsorbed NH_4 (7.5 g. NH_4-clay) in 500 cc. volume and 1/2 *S* or 2.25 M.E. LiCl have been added. At equilibrium 0.927 M.E. NH_4 or 20.6 per cent have been released from the surface. The figure under "4 *S*" means that 4 × 4.50 = 18.00 M.E. LiCl have been added and 2.462 M.E. NH_4 or 54.7 per cent have been exchanged.

Influence of the structure of the colloids and the properties of the ions

Numerous exchange data published by various investigators have been tested as to the applicability of the equation, and the results lead to the following conclusions.

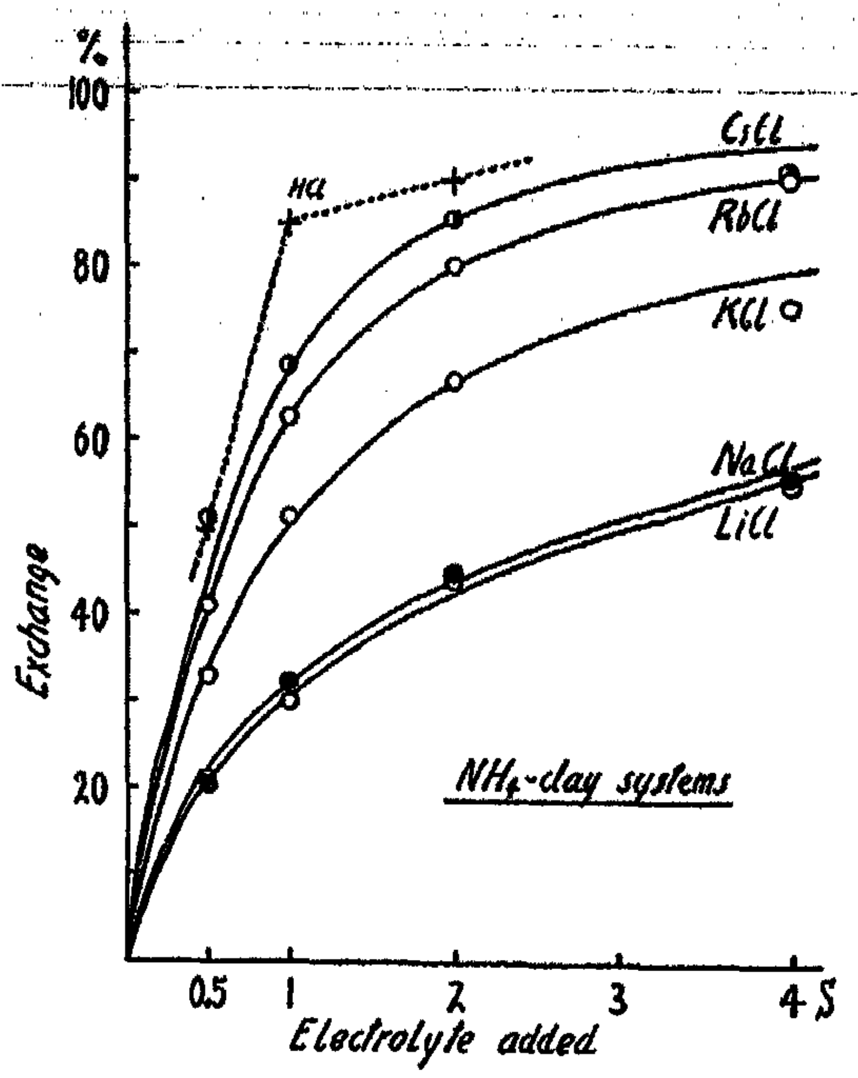

FIG. 4. Exchange isotherms for colloidal Putnam clay. Monovalent cations. Data are from table 1

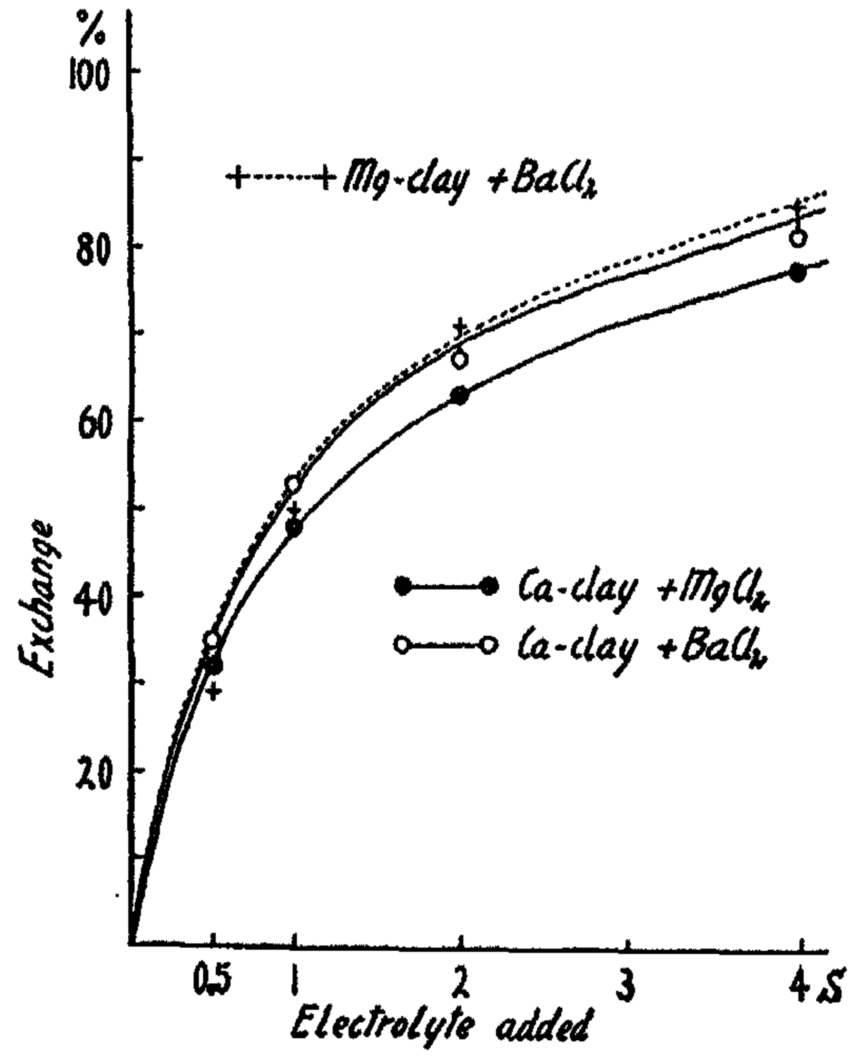

FIG. 5. Exchange isotherm for colloidal Putnam clay. Divalent ions. Data are from table 1

First, the *structure* of the colloidal particles appears to be an important factor. The equation yields good values for soil colloids and for bentonitic clays (data of Vanselow (6)), all of which have platy structures and seem to exchange on the outer surfaces only. Equation 11 is less satisfactory for permutites and certain zeolites. These systems are characterized by an abundance of ultramicroscopic pores and channels in which the exchangeable ions are seated. The ions are so close together that they interfere with each other, and by virtue of this fact the porous bodies fall outside of the realm of the equation.

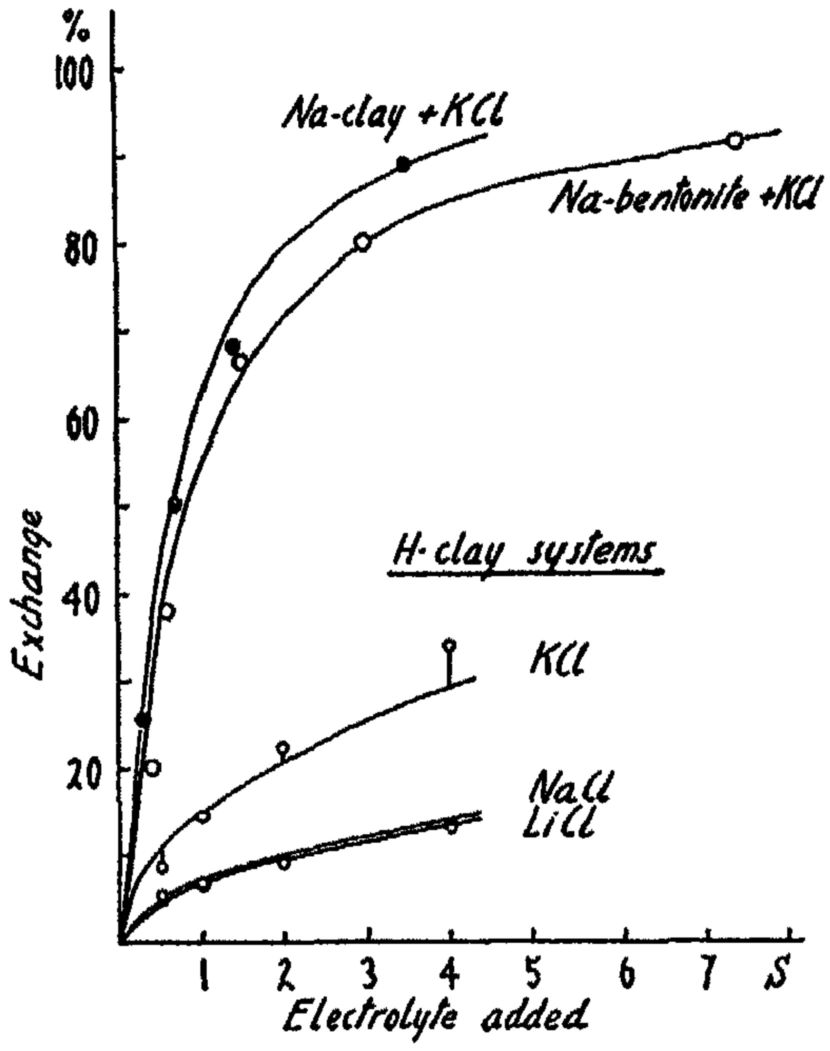

FIG. 6. Exchange isotherms for H-Putnam clay (table 1) and Na-clays and Na-bentonite. The two latter series are taken from Marshall (3)

Secondly, the *nature of the exchanging ions* has to be taken into consideration. If the ions differ greatly in their properties discrepancies occur. This is the case, for example, with the hydrogen ion as contrasted with the large size monovalent rare gas type ions (potassium, cesium), or barium versus magnesium. These can be explained as follows. The derivation of equation 11 rests on the assumption that the magnitude of the oscillation space is independent of the concentration of the wandering ions. However, according to Debye, the thickness of the ionic atmosphere of the electric double layer—which is related to the oscillation distance of the adsorbed ions—varies as the square root of the electrolyte concentration. If the exchanging ions have similar properties, for example, size, then the ratio v_w/v_b is not affected by the number of migrating particles; however, in any other case the rates of change of v_w and v_b with salt concentration may differ materially from each other and the quotient v_w/v_b may vary with the electrolyte concentration; in other words, the constant ceases to be a constant. Refinements in the present mode of approach may ultimately overcome these difficulties.

Consequences of the base-exchange equation

Several investigators claim that ionic exchange involving ions of equal valency is not affected by dilution except for minor effects due to hydrolyses and changes in activities. Equation 11 agrees with this contention, inasmuch as it does not contain the magnitude V, that is, the total volume of the system.

Of particular interest is the behavior of the lyotropic series. According to figure 4 the adsorption series is of the form:

LiCl $\leqq$ NaCl $<$ KCl $<$ RbCl $<$ CsCl $<$ HCl (exchange with NH_4-clay)

and, as previously shown (1), the release series follows the reverse order: namely,

Li-clay $\gtrsim$ Na-clay $>$ NH_4-clay $>$ Rb-clay $>$ Cs-clay $>$ H-clay (exchange with KCl)

Equation 11 predicts the latter series from the former as demonstrated in the following example. The system NH_4-clay + LiCl yields the constant $k = v_{Li}/v_{NH_4}$, and consequently the ratio

$$\frac{1}{k} = k' = \frac{v_{NH_4}}{v_{Li}}$$

gives the desired constant for the reverse process, namely, Li-clay + NH_4Cl. This conclusion rests on the fact that the base-exchange equilibrium in many cases is a true one (for details compare Vanselow's hysteresis effect).

With the aid of equation 11 it is also possible to obtain information on exchange reactions which are difficult to study for analytical reasons, for instance the system Rb-clay + CsCl. If one determines $k_1 = v_{Rb}/v_{NH_4}$ from the system NH_4-clay + RbCl and similarly $k_2 = v_{Cs}/v_{NH_4}$ from NH_4-clay + CsCl, the value

$$\frac{k_2}{k_1} = k_3 = \frac{v_{Cs}}{v_{Rb}}$$

furnishes the constant which is required to calculate the reaction Rb-clay + CsCl.

The average oscillation space v must be considered as a characteristic property of an adsorbed ion for a given colloidal particle. The common saying that "the ion b is better adsorbed than the ion w" simply means that b has a smaller oscillation volume than w, which implies that b is more strongly attracted by the surface.

Certain anions form undissociated compounds with the released ions, as illustrated by the reaction:

$$\text{H-clay} + CH_3COO^- + Na^+ \rightleftarrows \text{Na-clay} + CH_3COOH$$

In such cases the equality $N_b = w_e$ no longer holds, and the equation given in the form of No. 11 cannot be applied.

Comparison with other adsorption equations

Equation 11 is of the same nature as the thermodynamic equation of Vanselow (6), except that his undetermined constant k has now a specific meaning, namely, the ratio of the oscillation spaces of the adsorbed ions. The solid solution or mixed crystal theory is unable to offer an explanation why the equation fails for certain systems such as permutites, zeolites, and H-colloids. The new equation possesses several advantages over the widely used Freundlich-Wiegner isotherm, because the constants have a distinct physical significance and the exchange is shown to reach a maximum. Moreover the Freundlich type of formulation does not include cases like K-colloid + NaCl + KCl. On the other hand the parabolic formula is somewhat more flexible because it contains an additional constant.

For ions of similar exchange intensities, such as NH_4 and K, the oscillation volumes assume equal magnitudes, $v_w = v_b$, and equation 11 reduces to

$$w = \frac{sN}{s + N}$$

which is identical in form with the Vageler-Langmuir exchange isotherm.

EXCHANGE ADSORPTION AND ELECTRIC POTENTIAL

v_w and v_b designate the oscillation spaces of the adsorbed ions in the absence of wandering ions. The cubic root of the ratio v_w/v_b is equal to the quotient of the average oscillation distances, that is,

$$\sqrt[3]{\frac{v_w}{v_b}} = \frac{\vartheta_w}{\vartheta_b}$$

The magnitudes ϑ_w and ϑ_b correspond to the thickness of the Helmholtz electric double layer of particles coated with w- or b-type ions. On the basis of the diffuse double layer concept, ϑ is a measure of the distance from the wall to the electrical center of gravity.

The arrangement illustrated in figure 2 can be viewed from the standpoint of an electric plate condenser in which the negative plate is given by the rigid wall of negative oxygen ions and the positive plate by the average position of the cation coat (figure 7). The electric intensity between the plates is $4\pi\sigma/D$ and the potential difference is

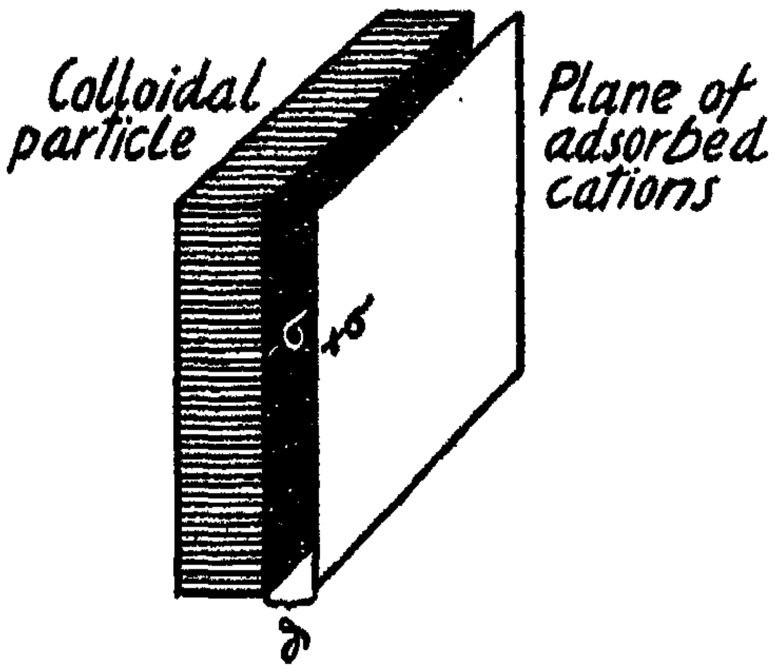

FIG. 7. Schematic presentation of a colloidal particle acting as an electric plate condenser. The black inner layer represents the wall composed of oxygen or hydroxide ions. The white outer layer represents a geometrical surface through the center of the average positions of the adsorbed ions.

$$P = \int_{\text{inner layer}}^{\text{outer layer}} \frac{4\pi\sigma}{D\mathrm{d}}\,\vartheta$$

σ is the charge of the plates, which is equal to the saturation capacity of one particle, and D the dielectric constant. Thus we obtain ϑ_w for a colloidal particle with only ions of the w-type in the outer layer:

$$\vartheta_w = \frac{P_w D}{4\pi\sigma}\,;\ \vartheta_b = \frac{P_t D}{4\pi\sigma}$$

and ϑ_b for a b-colloid. We arrive at the interesting equality

$$\frac{\vartheta_w}{\vartheta_b} = \frac{P_w}{P_b} = \sqrt[3]{\frac{v_w}{v_b}}$$

which shows that the ionic exchange constant is equal to the cube of the ratio of the potentials. The same relationship applies to large spherical particles. In tables 2 and 3 are listed the experimental ratios based on measurements of potentials (2) of pure Ca-, Mg-, Li-, Na-, and other clays, and the base exchange constants from table 1. The agreement is satisfactory as far as the order of magnitude is concerned, and it is noteworthy that the position of the ions within the lyotropic series is strictly consistent in both sets of data. Numerous causes for the discrepancies could be cited; the major one is to be sought in the type of potentials actually measured. These are so-called zeta potentials, based on migration velocities of colloidal particles in electric fields, rather than the simple Helmholtz potentials. Furthermore it might be possible that the values of the dielectric constants do not cancel but depend on the nature of the ion in the outer layer.

TABLE 2

Correlation between ionic exchange constants and electric potentials (divalent ions)

SYSTEM	$\sqrt[3]{v_w}:\sqrt[3]{v_b}$*	$P_w:P_b$†
Ca-clay + $MgCl_2$	1.07	1.03
Ca-clay + $BaCl_2$	0.95	0.97
Mg-clay + $BaCl_2$	0.93	0.94

* From table 1.

† From reference 2.

TABLE 3

Correlation between ionic exchange constants and electric potential (monovalent ions)

P_b for NH_4-clay = 56.0 millivolts

ION	Li	Na	K	NH_4	Rb	Cs	H
$\sqrt[3]{v_w}:\sqrt[3]{v_{NH_4}}$*	1.73	1.66	1.03	1	0.71	0.65	0.31
$P_w:P_{NH_4}$†	1.05	1.03	1.01	1	0.98	0.96	0.86

* From table 1.

† From reference 2.

CONCLUSIONS

It appears that the ionic exchange mechanism proposed and the equation deduced permit a quantitative understanding of the most essential facts of exchange adsorption and its relation to problems of colloid stability (2). In some instances the agreement between theory and experiment is not so close as one might wish. Undoubtedly in the future the interaction of neighboring ions on and near the surface will have to be taken into consideration. Furthermore, the interpretation of electric potential measurements of colloidal particles needs elucidation.

SUMMARY

1. A simple model of the mechanism of ionic exchange has been proposed.

2. With the aid of the model an exchange adsorption isotherm has been theoretically deduced. The equation could be verified for colloidal clay systems over a considerable range of concentration.

3. Certain systems are but poorly governed by the equation. This particular behavior is explained on the basis of structural peculiarities of the colloidal particles and extreme variations of the properties of the participating ions.

4. The third root of the base exchange constant is shown to be equal to the ratio of the electric potentials of the double layers. This relationship directly connects ionic exchange with problems of colloid stability.

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THE REDUCTION OF SOME ADSORBED OXIDATION-REDUCTION INDICATORS

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Although many oxidation processes in biological systems apparently take place at surfaces or in their presence, the study of oxidation–reduction reactions at phase boundaries in liquids does not seem to have been examined in simple systems. Furthermore, the analysis of the effects of an adsorbed substance capable of undergoing a reversible oxidation and reduction on the ζ-potential (electrokinetic potential) of inert and ionogenic surfaces may provide a new method of approach to the surface chemistry of oxidations and reductions. For these reasons we have investigated the effect of reductants on adsorbed methylene blue, litmus, and phenosafranine. It has been found that these dyestuffs can be reduced and reoxidized reversibly in the adsorbed state.

METHYLENE BLUE

Filter paper[1] was dipped into methylene blue solutions (about 0.5 per cent or more dilute) and the excess methylene blue washed off in running tap water, leaving the paper stained blue. If a piece of this blue paper is suspended in a stream of hydrogen in water or in phosphate buffer in the presence of platinized asbestos, reduction of the adsorbed methylene blue by the gaseous hydrogen does not occur to any appreciable extent.[2] The presence simultaneously of relatively large amounts of methylene white in solution complicates this result, because of the equilibrium set up between dissolved methylene white and adsorbed methylene blue. This was first observed by Doctor I. Korr in a preliminary experiment. Although hydrogen gas in the presence of large quantities of catalyst does not reduce adsorbed methylene blue, this can be readily brought about by addition of sodium hydrosulfite, cysteine, or thiourea. The thiourea, however, is efficacious only in acid solution. On addition of sodium hydrosulfite,

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[1] Schleicher and Schüll No. 1. Also dye which has been adsorbed by blotting paper, adsorbent cotton, cotton toweling, porcelain, and hairs of a cleaning brush can be reversibly reduced.

[2] This confirms a personal communication to one of us (H. A. A.) from Professor L. Michaelis.

the slightly tinted solution of methylene blue becomes colorless, the filter paper itself then bleaching more slowly and in a spotty fashion but finally becoming white. If the white filter paper is now removed from the solution and the excess of reductant washed off, the paper remains white for some time unless the washing is prolonged. Most of the adsorbed methylene blue still remains on the filter paper in the form of methylene white, for addition of quinone or potassium ferricyanide restores the blue color to almost its original intensity. The adsorbed blue dye can now be reduced again and reoxidized several times. Cysteine does not reduce the adsorbed dye as quickly as hydrosulfite. Even with a 5 per cent solution of cysteine (Eastman Kodak) slight heating is needed for the reduction reaction to go to completion within a reasonably short time. With dilute solutions at room temperature the reduction may take hours. The autooxidation of adsorbed methylene white seems to take place readily in the air but rather slowly. As mentioned previously, traces of hydrosulfite or of cysteine adsorbed onto the filter paper inhibit the autoöxidation of methylene white for a period quite sufficient to test the effects of other oxidants. Methylene white is known to be adsorbed by various surfaces. This can be demonstrated by dipping filter paper into a solution of methylene blue reduced by hydrosulfite or cysteine. After moderate washing in running water, little or no color appears. Addition of an oxidant however, reveals at once that a large quantity of methylene white has been adsorbed.

LITMUS

Litmus paper is rendered colorless by hydrosulfite in both acid and neutral solutions. Autoöxidation is slow. The white paper can be washed in running water and then reoxidized to the red or blue dye depending on the pH.

PHENOSAFRANINE

This dye is readily adsorbed by filter paper and can be reversibly oxidized and reduced in the adsorbed state.

DISCUSSION

The bonds responsible for the adsorption of the dyestuffs here investigated do not appear to affect appreciably those groups involved in the oxidation-reduction process. A parallel instance is that observed for the ionization of adsorbed protein. Since the electric mobilities of protein-covered quartz particles do not differ very much from the dissolved protein, the free amino and carboxyl groups are not primarily involved in the adsorption reaction. It is of some interest to see a similar phenomenon occur with smaller molecules.

A surface having selective adsorption for one form of the constituents of a reversible oxidation-reduction system could shift the oxidation-reduction potential of the system. Adsorption reactions of this type have apparently been investigated only with pH indicators. Thus Deutsch has shown that indicators like bromothymol blue, malachite green, and many others have the undissociated form of the dyestuff selectively adsorbed if adsorption occurs at a pH near the value of p*k* of the indicator. In this instance the pH of the solution does not change appreciably, for the color change occurs in well-buffered solutions. Since adsorbed methylene blue is not readily reduced by hydrogen gas-platinized asbestos, and since an electrode would indicate that the solution was very near the potential of the hydrogen electrode, it is evident that the electrometric measurement gives no indication of the potential at the surface (where adsorption occurs), even though the electrode potential has reached "equilibrium." In heterogeneous systems the attainment of "equilibrium" in solution does not necessarily indicate the reduction intensity at the surface. This should be borne in mind in connection with discussions involving the reduction intensity in living systems.

THE ADSORPTION OF THE HEAVIER RARE GASES BY MERCURY[1]

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Since the nature of the van der Waals forces was revealed as a consequence of the atomic zero point vibrations of the electrons, the adsorption as caused by such attraction fields of solid or liquid surfaces also became accessible to advanced theoretical treatment. The theory due to London (12) at first was applied to the simplest example, that of spherical symmetrical atoms and molecules which may be regarded as spheres. Introducing certain further simplifying assumptions, London calculated the heats of adsorption by charcoal.

Owing to a numerical error, the values so obtained seemed at first to be in excellent agreement with the experimental results. The correctly calculated values, however, are only one-tenth, or, if repelling forces are disregarded, nearly one-fifth of the observed amounts. Thus, although the right order of magnitude is attained, there exists a discrepancy, the reason for which must be sought in the nature of the experimental conditions rather than in the theory.

As London has already pointed out, an increase of the attraction beyond that due to entirely plane surfaces is to be expected, owing to the porous structure of the crystalline adsorbent. Experimentally, it would seem possible to avoid these irregularities by using single crystals as the adsorbent. This method, however, has the disadvantage of so limiting the surface that it would be difficult to obtain measurable adsorption.

Measurement of the surface tension of liquid adsorbents may be a better procedure, for on this basis surface densities of the adsorbed gas atoms may be derived by the Gibbs thermodynamic equation. Though at first sight this method appears to be rather indirect, its advantage over the mere observation of adsorbed quantities is that it does not require a special measurement of the adsorbing surface area. The heats of adsorption are then derived from the determination of different isotherms.

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[1] The measurements were carried out in collaboration with K. Neugebauer in the Technische Hochschule, Berlin; see also the dissertation of H. Binne, Technische Hochschule, Berlin, 1932.

Liquid mercury was used as the adsorbent in our experiments. This material proved to be well suited for checking the adsorption theory. Although in the earlier stage of our knowledge of the metallic state the application of London's theory to metals was objectionable, now, on the basis of Bloch's (2) ideas,[2] it is justified by the new dispersion theory of metals advocated by Kronig (9).

The experimental equipment was that previously used for the study of the adsorption of some polar and non-polar compounds by mercury (5) and was very similar to that of the capillary electrometer. In order to measure the surface tension, σ, the height of a mercury column necessary to press a mercury droplet through a small hole was determined. This opening, about 0.1 mm. in diameter, consisted of a stainless steel nozzle such as is employed for the purpose of manufacturing artificial silk. It was sealed to the bottom of a vertical glass tube communicating with the container of the mercury, which was purified by vacuum distillation and lifted pneumatically to the desired level. The observations made by means of a cathetometer were in error by less than 0.05 mm., that is to say, they corresponded to the formula

$$p = \sigma(1/r_1 + 1/r_2)$$

by less than 0.1 dyne per centimeter. In order to eliminate the uncertainty in the effective value of the curvatures, $1/r_1 + 1/r_2$, of the hole, the value 480.00 dynes per centimeter for the surface tension of mercury at room temperature (20°C.), as determined by Bircumshaw (1), was taken as a standard for calibration.[3] Owing to the smallness of the radii, corrections for the influence of gravity could be neglected.

The accuracy of ±0.05 dyne per centimeter thus obtained was, however, not sufficient to indicate any decrease of the surface tension by the action of argon at room temperature, even at a pressure of 100 mm. of mercury.

To continue the investigation, therefore, the heavier rare gases, krypton and xenon, were brought into contact with the metal. In these cases also the observable effects at room temperature were rather small, although well-defined values of the decrease in surface tension could be measured on cooling the system. Particular care was taken to keep the temperatures constant. Here of course the freezing point of mercury determined the lowest temperature.

The experimental results are given in the first and second columns of table 1. The corresponding figure (figure 1) shows the decrease in the surface tension, $\sigma_0 - \sigma = F$, as plotted against the gas pressure, p.

[2] We are indebted to Dr. Felix Bloch of Stanford University for his kind suggestions.

[3] With the value recently obtained by Bradley (3) our results had to be increased by 4 per cent.

In the range of lower pressures, the isotherms are approximately straight lines converging towards the zero point. Under these conditions $dF/dp = F/p$, so that the Gibbs relation, $dF/dp = \Gamma RT/p$, yields the simple "two-dimensional" osmotic equation of state: $F = \Gamma RT$, where Γ denotes the number of adsorbed moles per unit area.

TABLE 1

Isotherms for adsorption of rare gases by mercury

a. Krypton

p	F	Γ	p	F	Γ
T = 235°K.			T = 253°K.		
mm. Hg	*dynes per cm.*	10^{-11} *cm.*^{2}	*mm.* Hg	*dynes per cm.*	10^{-11} *cm.*^{2}
93	0.35	1.1	60	0.20	0.6
198	0.85	2.5	160	0.50	1.6
263	1.10	3.4	221	0.75	2.2
320	1.30	4.0	339	1.15	3.4

b. Xenon

p	F	Γ	p	F	Γ
T = 237°K.			T = 253°K.		
mm. Hg	*dynes per cm.*	10^{-11} *cm.*^{2}	*mm.* Hg	*dynes per cm.*	10^{-11} *cm.*^{2}
50	1.65	5.0	59	1.20	3.5
89	2.85	8.5	130	2.60	7.5
198	6.05	18.0	234	4.40	12.0
331	9.10	25.0	295	5.50	15.5
Vapor density		8.65	Vapor density		11.50
Liquid density		43.50	Liquid density		52.50
T = 273°K.			T = 293°K.		
69	0.80	2.0	40	0.35	1.0
93	1.10	3.0	91	0.70	2.0
146	1.75	4.5	149	1.20	3.0
227	2.75	7.5	205	1.60	4.0
278	3.35	9.0	280	2.00	5.5
Vapor density		18.3	355	2.80	7.0
Liquid density		47.7			

At higher pressures, the 237°K. and the 253°K. isotherm of xenon incline distinctly toward the p-axis. This curving, familiar from the Langmuir type of adsorption isotherms, in the case of mobile adatoms[4] indicates a

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[4] The word "adatom," as introduced by F. A. Becker, is here used to designate the adsorbed particles according to Langmuir (10).

predominance of the virial term which arises from the repulsion of the adatoms over that due to the mutual attraction (θ). Let us suppose that the simple van der Waals equation holds true for the gaseous state (constants a and b) as well as for the adsorbed state (constants α and β). The

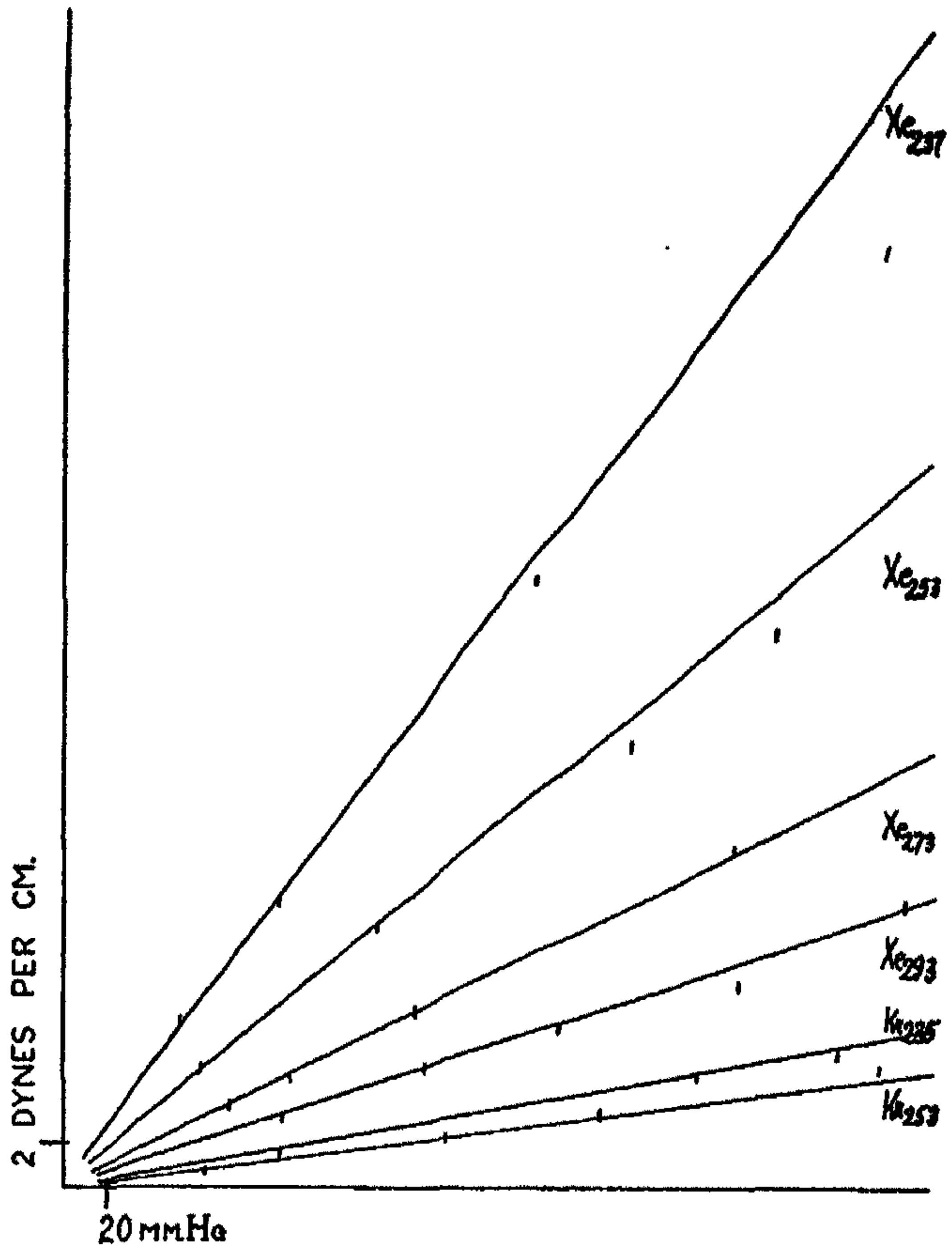

FIG. 1. The decrease of the surface tension, F, is plotted against the gas pressure. The observations are represented by vertical lines, the length of which corresponds to the possible error. The drawn straight lines are the initial tangents of the isotherms corresponding to the ideal two-dimensional gas law $F = \Gamma RT$.

critical temperature of the adsorbed state may then be estimated by means of the equation

$$T_{k_{\mathrm{ads}}} = \frac{\alpha \cdot b}{a \cdot \beta} \cdot T_{k_{\mathrm{vol}}}$$

Since, according to Volmer (19), β is equal to twice the cross section of the adatoms, b/β is given by $8/3r$ if r denotes the radius of the atom. The amounts of a and α on the other hand, as determined by the virial coefficients of the attracting forces, may be calculated from the inverse seventh-power law as derived by London (12). Thus, the ratio a/α is found to be the same as b/β. Hence, in the case of xenon the critical temperatures should be equal, namely, 289.6°K. This deduction, however, fails to agree with the experiments.

The surface densities (number of atoms per unit area) of the liquid state and the coexisting vapor of xenon in bulk, as calculated from the measurements of Patterson, Cripps, and Gray (14), may be compared with the surface densities of the adatoms corresponding to the Gibbs equation as given in the third column of table 1. The values, although exceeding the vapor densities of 253°K. and 237°K., do not reach those of the liquid state.

It must be concluded, therefore, that the critical temperature of the adsorbed state lies below the range here observed. This behavior obviously corresponds to a very general rule (17): condensation phenomena in adsorbed layers occur only at temperatures far below the critical point of the masses in bulk.

In the case here studied, this may be due to the fact that the assumption of a free two-dimensional mobility is not quite justified, owing to distinct elementary spaces of adsorption. It was necessary to assume a semicrystalline structure of the mercury, as was suggested for the interior of the liquid by Debye and Menke (8) and observed by Bresler (4) for the reflection of electron beams from the surface of liquid mercury. There is, furthermore, reason to believe that an increase in β beyond the value employed above could be brought about in the electric field of the metallic surface by the polarization, which reinforces the mutual repulsion of the adatoms by induced dipole moments.

For the purpose of further tests, the heats of adsorption on A, on the basis of the experimental results, were calculated for the different isotherms according to the formula (7),

$$A = RT^2\left(\frac{\partial \ln p}{\partial T}\right)_v$$

which corresponds to the statement that the "dividing surface" coincides with the surface of the adsorbent. The values thus obtained are given in table 2.

The simplest method of checking these results, and one requiring a minimum of hypothesis, could be established by the knowledge of the binding energy, U, of the diatomic compounds between mercury and the rare gases. The existence of such molecules caused by polarization forces was suggested by Oldenberg (13) in order to account for his spectroscopical observations. The heat of adsorption then may be calculated with satisfactory approximation, taking into consideration the attraction exerted only by the next neighbors of the adatom. This quantity, of course, depends on the type of arrangement of the atoms of the adsorbent. For hexagonal, spherical, close packing, corresponding to the work of Stranski and Kaischew (18), the inverse seventh-power law of attraction yields $A = 4.35\ U$, as an average value of different possible surfaces (see table 3, A_d).

However, as the interpretation of the spectroscopic data is rather problematical, especially in the case of xenon, the complete requirement of the London theory has to be applied, representing the heat of adsorption by the equation:

TABLE 2

Heats of adsorption

GAS	TEMPERATURE	HEAT OF ADSORPTION
	°K.	cal.
Krypton	239	2700
Xenon	245	3450
	263	3350
	283	3400

TABLE 3

Certain physical constants of the rare gases and mercury

ELEMENT	R_a	R_b	R_c	α	I	A_a	A_b	A_c	A_d	A_0	L
	cm.^{-8}	cm.^{-8}	cm.^{-8}	$\times 10^{-24}$	kg-cal.	cal.	cal.	cal.	cal.	cal.	cal.
Neon..........	1.55	1.20	1.60	0.42	514	850	1200	800			(500)
Argon..........	1.85	1.47	1.95	1.70	375	2300	3250	2100	2700		1500
Krypton.......	1.95	1.57	1.98	2.35	332	2750	3900	2700	3700	3000	2300
Xenon.........	2.10	1.72	2.20	3.85	285	3750	5200	3500		3700	3100
Mercury.......	1.60			11.2	240						

$$A = \frac{\pi}{4} N \frac{\alpha\alpha'}{D^3} \frac{I \cdot I'}{I + I'}$$

where I and I' denote the ionization potentials, α and α' the atomic polarizabilities, N the number of mercury atoms per cubic centimeter, and D the distance of the adsorbate and the adsorbent, as given by the sum of the radii of the noble gas and the mercury atoms. Since this quantity enters with the third power, the results, of course, are greatly dependent upon the value chosen. The radius of the mercury atom was calculated from the density of the crystal, assuming spherical close packing. Consequently the radii of the noble gas atoms were determined on the same basis, according to the work of Simon (16) and Ruhemann (R_a). To obtain an idea of the possible limits of variation, the amounts derived from the critical volume (R_b) and from the liquid densities (R_c) are also given in table 3, as well as the "spectroscopic" heats of adsorption (A_d), the heats of evaporation (L) (15), and the ionization potentials (I).

The heats of adsorption found experimentally had to be extrapolated to the absolute zero point. This was done upon the supposition that the specific heat of the adatoms equals that of the adsorbent (A_0).

While the agreement between theory and experiment was satisfactory for charcoal only as regards the order of magnitude, the observed values for mercury tend to coincide with the lower theoretical limit, which might have been expected since, as a first approximation, the forces of repulsion were disregarded.

SUMMARY

The surface tension of mercury in contact with krypton and xenon was measured at several temperatures and pressures. With the accuracy available (± 0.05 dyne per centimeter) the influence of argon could not be ascertained. The adsorbed quantities were calculated by means of the Gibbs equation, and the heats of adsorption derived from these isotherms were compared with the theoretical values according to the dispersion theory of the van der Waals forces.

We wish to express our thanks to Dr. Pollitzer, chief chemist of Linde's Eismaschinen, München, Germany, through whose kindness we obtained samples of the noble gases, and to Professor J. W. McBain of Stanford University for his kind interest.

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TIN VANADATE AS A CATALYST IN THE OXIDATION OF TOLUENE TO BENZOIC ACID[1]

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INTRODUCTION

It has been known for centuries that certain gums are capable of preventing decay. Some of these gums were used by the Egyptians in the preservation of their dead. It was found that the preserving action of these gums was due to benzoic acid, one of their constituents. The insects caught by some insectiverous plants are preserved for long periods of time by the benzoic acid excreted from the leaves of these plants. At the present time use is made of the preserving action of this acid and its salts in the treatment of certain foods to prevent spoilage. The acid and its salts also find some use in medicine as well as in the manufacture of certain dyes.

When the acid or its salt is to be used in medicine or for the preservation of foods, the presence of certain impurities is considered to be particularly harmful. Much of the acid produced from chlorinated toluene contains combined chlorine as an impurity. Since the removal of this material presents a difficult problem, some other method for preparing benzoic acid from toluene is being sought.

In 1875 Coquillion (2) found that toluene vapor could be oxidized to benzoic acid by air in the presence of certain catalysts. Weiss and Downs (7) have given a review of the literature on the subject of catalytic oxidations, along with a report concerning their own work in this field. One of the most outstanding researches on the catalytic oxidation of toluene is that of Maxted (6) in which he used a catalyst of tin vanadate.

Advantages of a vapor phase catalytic process for the preparation of benzoic acid from toluene are obvious. The product may be made to sublime from the reaction chamber in a comparatively pure state with no inorganic contamination. Air has a sufficiently high concentration of oxygen to bring about the desired reaction, providing other conditions are properly chosen. Since the reaction is exothermic, external heating of the

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[1] This paper is based upon a thesis submitted to the Graduate School of Indiana University by Roy Huitema in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1934.

apparatus should be unnecessary. Any by-products of the catalytic process for the oxidation of toluene should be of such a nature as to present no difficulty in their disposal.

Numerous patents have been granted covering the use of certain materials as the contact mass in the vapor phase catalytic oxidation of toluene and related compounds. The catalysts which find the greatest favor with the investigators are the compounds of vanadium. In fact many oxidations, both organic and inorganic, are catalyzed by compounds of this element. Although vanadium pentoxide was one of the compounds first used in this type of work, it has been supplanted to some degree by the vanadates. Since tin vanadate has been reported to be especially active in the oxidation of toluene to benzoic acid, it was thought advisable to investigate the behavior of this catalyst a little more closely.

THEORETICAL CONSIDERATIONS

Several possible reactions may take place in the oxidation of such a compound as toluene. The nature of the reactions and the extent to which they occur are determined largely by the following conditions: temperature of the reaction chamber, pressure, nature of the catalyst, nature and proportion of diluent gases, and the proportion of oxygen to toluene vapor.

From a technical point of view the question of greatest importance is that concerning the ratio of the quantity of toluene converted to the desired product to the total amount of toluene consumed in the process. The reaction, too, must be of such a nature as to proceed with a sufficiently high velocity to be profitable.

A number of non-reactive vapors or gases have been suggested for use as diluents for the air used in vapor phase oxidation. It may be that in some cases a diluent tends to blanket side reactions which take place. Other diluents merely decrease the concentration of one or more of the reactants and thereby lessen the speed of the reaction.

Water vapor added to the reacting gases may serve as a means of carrying some of the less volatile products from the reaction chamber. However, if water is a product of the desired reaction, its addition may have a detrimental effect. The addition of any vapor or gas to the reactants increases the velocity with which they pass over the catalyst surface and therefore decreases the time of contact.

Perhaps the greatest benefit of the addition of inert materials to the reaction mixture is the tendency of these materials to maintain a more uniform temperature of the catalyst by absorbing some of the heat liberated in the reaction. If the reaction takes place at points on the surface of the catalyst, the heat liberated at these points may raise their temperature to such an extent that the products of the reaction will be different from those which would have been obtained had the temperature been held constant. Investigators (8) using glass apparatus report that when air and toluene vapor are mixed and passed over a catalyst heated to a temperature of from 200 to 300°C., points on the surface of the catalyst are heated to redness by the heat liberated in the reaction.

The following thermal equations show that a large quantity of heat will be liberated when the desired reaction takes place.

$$C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O + 935.6 \text{ kg-cal.}^{2} \qquad (1)$$
$$C_6H_5COOH + 7.5O_2 \rightarrow 7CO_2 + 3H_2O + 771.2 \text{ kg-cal. (3)} \qquad (2)$$

By subtracting equation 2 from equation 1 we get the following equation:

$$C_6H_5CH_3 + \tfrac{3}{2}O_2 \rightarrow C_6H_5COOH + H_2O + 164.8 \text{ kg-cal.} \qquad (3)$$

If one molecular weight of toluene is completely oxidized, there are 935.6 kg-cal. of heat liberated. Nine molecular weights of oxygen will be consumed in the process. However, if nine molecular weights of oxygen are utilized to oxidize toluene to benzoic acid, there will be 6 × 164.4 kg-cal. of heat liberated. This amounts to 50.8 kg-cal. more than the amount liberated when this same weight of oxygen is consumed in the complete oxidation of toluene.

The temperature at which a particular reaction may be catalyzed is dependent upon the catalyst used. For example, if a mixture of air and toluene vapor is passed over a vanadium pentoxide catalyst, the temperature must be nearly 400°C. before an appreciable amount of benzoic acid is formed. If some other catalyst is used, this same mixture will react at a different temperature.

EXPERIMENTAL PROCEDURE

The work herein reported was done in an attempt to determine the applicability of a tin vanadate catalyst to the vapor phase oxidation of toluene to benzoic acid. The effect of preliminary heating upon the activity of tin vanadate and the effects of such variables as reaction temperature, concentration of oxygen, and the addition of diluent gases were studied. Not only was the percentage of toluene converted to benzoic acid determined, but also a measure was taken of the extent to which the toluene was completely oxidized.

The apparatus consisted of a reaction chamber of black iron 3 in. long and $1\frac{1}{2}$ in. in diameter fitted at the bottom end with a cap and at the top with a reducer, T. The lower cap was drilled and threaded to take a $\frac{1}{8}$-in. pipe through which the gases might enter the reaction chamber. The gases passed up through the catalyst and out of the chamber through the

[2] This is the average of the values given by Kharasch (5).

side arm of the T. The upper opening of the T was bushed down to take a ¼-in. pipe which extended down to the top of the catalyst. This last named pipe was capped at the lower end and carried a copper-advance thermocouple for measuring the temperature of the gases as they came from the catalyst. Since the position of maximum temperature in the

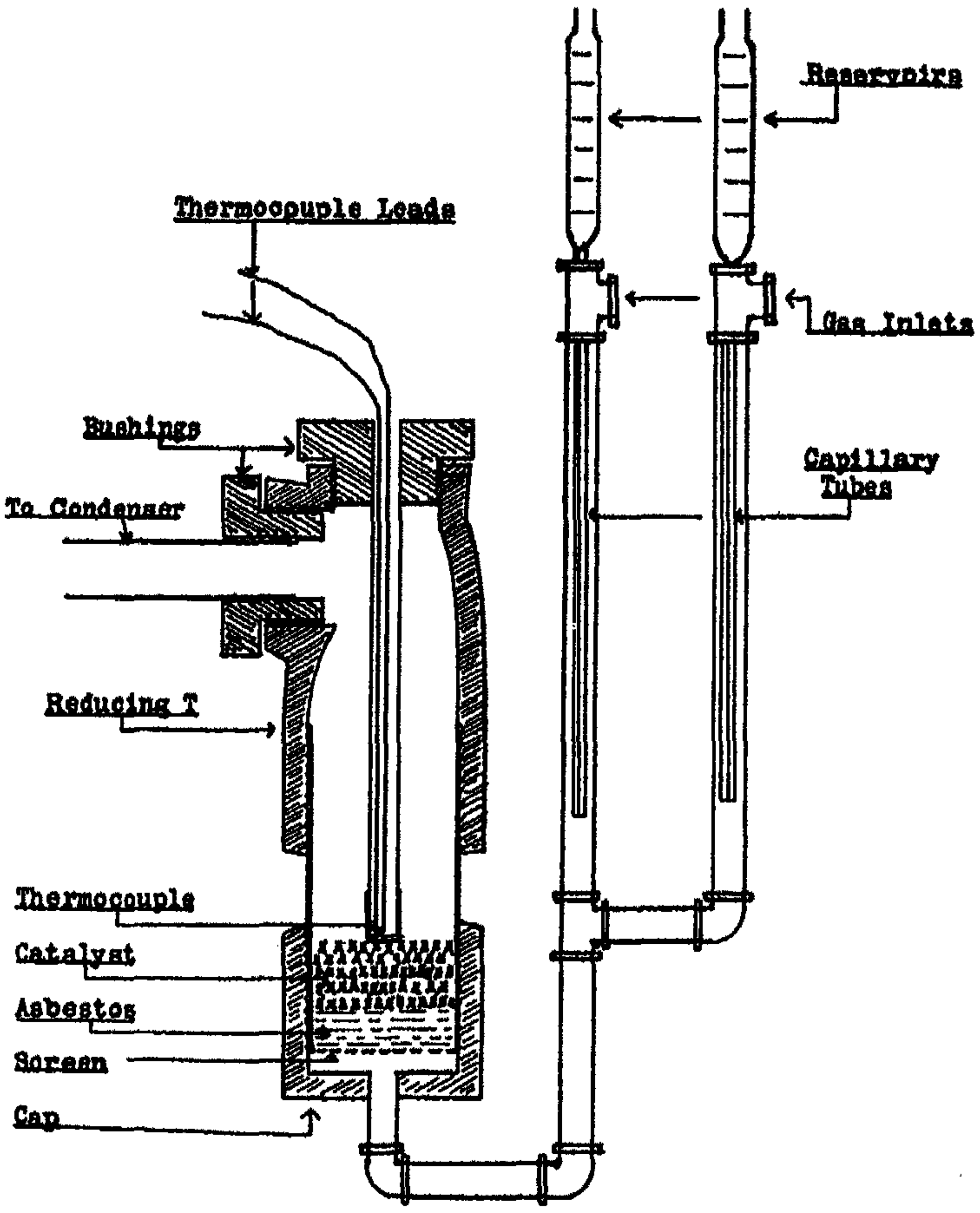

FIG. 1. Diagram of the apparatus (approximately two-thirds actual size)

body of a catalyst varies from time to time and is dependent upon the age of the catalyst, rate of gas flow, and other conditions, the temperature of the gas coming from the catalyst was taken as the working temperature of the catalyst. A diagram of the apparatus used is shown in figure 1.

The entire apparatus with the exception of the reservoirs and the condenser was placed in a tin can 8¼ in. tall and 6⅛ in. in diameter on the inside of which 30 ft. of No. 16 B. and S. gauge chromel wire was imbedded in alundum cement. The chromel wire acted as the heating unit and was placed in series with an outside resistance. After the apparatus was placed in the can in the desired position the remainder of the can was filled with sand. This was done so that all parts of the apparatus would be held at a uniform temperature. The variation in temperature of the gases coming from the catalyst never amounted to more than 2°C. for a given run.

Toluene was placed in the reservoir by means of a calibrated pipet and forced into the furnace at the desired rate through the connecting capillary. Since the capillary tube was heated to a temperature well above the boiling point of toluene, this material was vaporized before it reached the bottom end of this tube. At this point the vapor came in contact with the incoming air. Ample mixing of the vapor with the air took place as the two materials passed through the iron tube leading to the catalyst chamber and in their passage through the asbestos catalyst support. The desired rate of toluene flow was obtained by means of mercury leveling bulbs which regulated the pressure on the surface of the toluene in the reservoirs.

The gas flow into the furnace was kept constant throughout the run and for 90 minutes after the last of the toluene had entered the furnace. This was done in order that the greater portion of the benzoic acid which had been formed would be carried from the furnace.

In all of the work to be reported here 2 cc. of toluene (1.707 g.) was fed into the furnace in thirty minutes. After the washing period was finished the benzoic acid which had been formed was washed from the condenser with alcohol and water.

Any carbon dioxide which remained in the solution washed from the condenser was removed before the benzoic acid was titrated. This was done by bubbling carbon dioxide-free air through the solution for forty minutes. The acid was then titrated with $N/10$ sodium hydroxide solution which had been standardized against C.P. benzoic acid. Phenolphthalein was used as indicator.

The first run made under a given set of conditions was discarded; data were collected from subsequent runs. The 90-min. wash period was not sufficient to remove all of the benzoic acid from the furnace, but it was considered reasonable to assume that the amount of acid which was carried over from one run to the next would be constant. Any inaccuracy due to this carry-over from one run to the next was less than the inaccuracies due to errors which might develop from other sources.

The escaping gas from the condenser was passed through concentrated sulfuric acid to remove the vapors of water and toluene. Next, it passed through two weighed tubes of potassium hydroxide solution (sp. gr. 1.27), and finally through a weighed tube of concentrated sulfuric acid with a glass wool filter on the end. The difference in the sum of the weights of the potassium hydroxide tubes and the weighed sulfuric acid tube before and after the run was taken as the weight of the carbon dioxide produced. The removal train was connected to the condenser during the time toluene was being fed into the furnace and for five minutes after the last of the toluene had entered the furnace. The weight of carbon dioxide found in this manner was not entirely accurate, but the method served as a means of determining the relative losses of starting material.

The back pressure created by the carbon dioxide removal train was relieved by means of an aspirator. In this way it was possible to keep the pressure within the reaction chamber equal to that of the atmosphere.

The tin vanadate used as catalyst in this work was prepared by precipitation. A hot solution of carefully purified ammonium metavanadate was added to a dilute solution of stannic chloride (sp. gr. 1.075) to precipitate the tin vanadate. The product was washed several times by decantation. It was then filtered on a Büchner funnel and washed until the filtrate was practically free of chlorides.

When the washing was completed, the material was transferred to a large evaporating dish and dried for thirty-six hours at 110°C. The drying process was hastened by breaking up the lumps and by stirring the material occasionally. The dried tin vanadate was a rather hard, brittle material and was chocolate colored. It was broken up by means of a mortar and pestle until it would pass through a 20-mesh sieve.

The tin vanadate prepared as described above was divided into three parts, one of which was used directly as the contact mass in the oxidation of toluene to benzoic acid. This unheated material will be spoken of as catalyst A. Another portion of the material was placed in a cold muffle furnace and slowly heated to 400°C., maintained at that temperature for thirty minutes, and then allowed to cool. Tin vanadate treated in this manner will be spoken of as catalyst B. The third portion of the untreated material was heated in a furnace at 700°C. for thirty minutes. This material will be called catalyst C. When the temperature of the furnace in which catalyst C was being heated reached 450°C., some ammonium chloride was expelled from the material. The heated catalysts took on a yellowish color.

The apparent volume of catalyst used in each case was 30 cc. The material was spread evenly over the asbestos base, so that the reacting gases would pass through equal thicknesses of the contact mass.

Before any data were taken the catalysts were used for several days in the oxidation of toluene so that they would reach a constant degree of activity. This precaution was apparently unnecessary, as there was little or no change in the activity noticed after a few runs had been made.

RESULTS

The data in table 1 are made up of the results of a series of runs carried out in an attempt to determine the temperature at which the conversion of toluene to benzoic acid would be most practical. These data are represented graphically in figures 2 and 3. It is apparent that the temperature at which the highest percentage of toluene is converted to benzoic acid is 243°C., and that the percentage of toluene completely oxidized increases rapidly with increasing temperature.

On comparing the different catalysts, it is seen that the heating of tin vanadate changes its nature to a considerable extent. The exact nature of this change has not been determined, but it may be due to the driving off of occluded ammonium chloride. It is possible, too, that a change in crystalline structure took place during the heating period. Appreciable sintering of tin vanadate takes place at a little higher temperature than that to which catalyst C was heated.

TABLE 1

Determination of most practical temperature for the conversion of toluene to benzoic acid

Air flow: 7 liters per hour, which represents 100 per cent of the amount of oxygen required to oxidize the toluene to benzoic acid. Toluene flow: 3.414 gm. per hour (2 cc. in 30 minutes)

TEMPERATURE IN °C.	PER CENT TOLUENE CONVERTED TO BENZOIC ACID USING CATALYSTS			PER CENT TOLUENE CONVERTED TO CARBON DIOXIDE USING CATALYSTS		
	A	B	C	A	B	C
210	8.50	6.45	3.83	5.51	5.95	2.64
221	9.72	8.59	5.25	11.02	11.42	3.73
228	10.55	9.55	7.90	14.10	13.79	8.45
243	11.00	9.75	11.90	19.80	17.93	20.62
246	9.80	9.29	9.80	22.82		
261	7.17	7.85	7.17	25.42	19.48	21.60
270	6.45	7.61	6.45	27.43	22.70	21.70

In order to ascertain the effect of oxygen concentration upon the amount of toluene converted to benzoic acid and upon the amount of toluene completely oxidized, a series of runs were made using different rates of air flow. The temperature chosen for these runs was 236°C. At this temperature the conversion of toluene to benzoic acid was of the same order for all three catalysts, and there was no danger of exceeding the optimum operating temperature of any of them. The results of this series of runs are shown in table 2.

The data in table 2 indicate the effect of variation of oxygen concentration upon the percentage of toluene changed to benzoic acid and upon the percentage of toluene completely oxidized. The data show clearly that even though the percentage of toluene converted into benzoic acid is somewhat higher at the higher oxygen concentrations, the loss of toluene as carbon dioxide and water is very much greater at these concentrations. In the production of benzaldehyde from toluene by the use of air as the oxidizing agent in the presence of a vanadium pentoxide catalyst, Green (4) states that equimolecular quantities of oxygen and toluene vapor give good results and that Gibbs has indicated that two and one-half times that concentration is desirable. The data in table 2 show plainly that even lower oxygen concentrations are desirable in the production of benzoic acid from toluene by the use of a tin vanadate catalyst. The great change in the amount of carbon dioxide produced with changing oxygen concentrations makes it apparent that a delicate means of control for the air flow is essential in this type of work. A graphical representation of the effect of oxygen concentration upon the percentage of toluene converted to benzoic acid is given in figure 4.

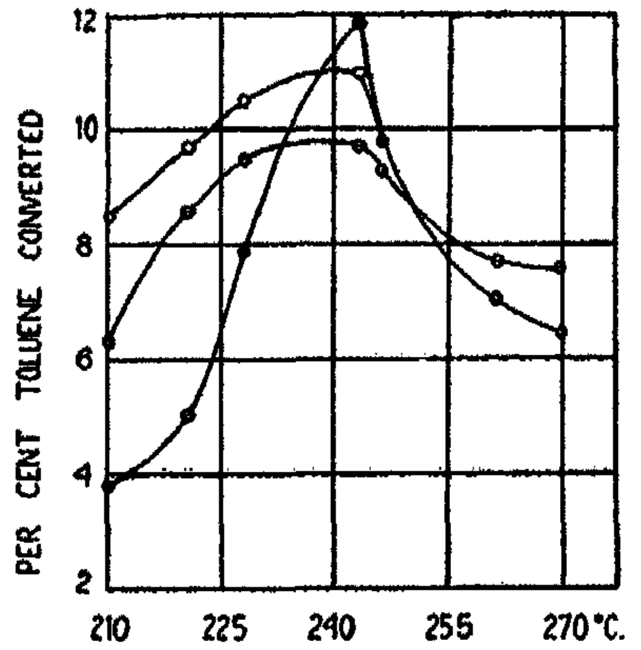

FIG. 2. The effect of temperature upon the per cent of toluene converted to benzoic acid. ○, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

TABLE 2

The effect of oxygen concentration

Temperature: 236°C. Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

AIR USED IN PER CENT OF THEORY	PER CENT OF TOLUENE CONVERTED TO BENZOIC ACID USING CATALYSTS			PER CENT OF TOLUENE CONVERTED TO CARBON DIOXIDE USING CATALYSTS		
	A	B	C	A	B	C
50	8.57	8.04	6.05	11.05	9.95	4.18
71.5	8.66	8.43	6.13	11.31	11.32	4.54
100	9.29	9.47	9.47	19.37	16.05	11.91
143	9.15	10.12	11.10	20.95	20.59	18.92

A relative measure of the amount of toluene consumed per pass which was converted to benzoic acid is given in the data in tables 3 and 4. The data in these tables were compiled by adding the per cent of toluene converted to benzoic acid to the per cent lost by complete oxidation. The per cent converted to benzoic acid was divided by this sum; the quotient obtained in this manner was then multiplied by 100. This final value shall be called the conversion ratio.

The data in table 3 show the effect of temperature upon the conversion ratio. Since there may have been some error in the carbon dioxide determination the values given are only relative. These data show that the conversion ratios for all three catalysts decrease with increasing temperature. Although the ratio for catalyst B is lower than the ratios of the other two catalysts at the lower temperatures, it is higher than the other ratios at the higher temperatures. The values of the different ratios were almost the same at the temperature at which the greatest percentage of toluene was converted to benzoic acid per pass (243°C.).

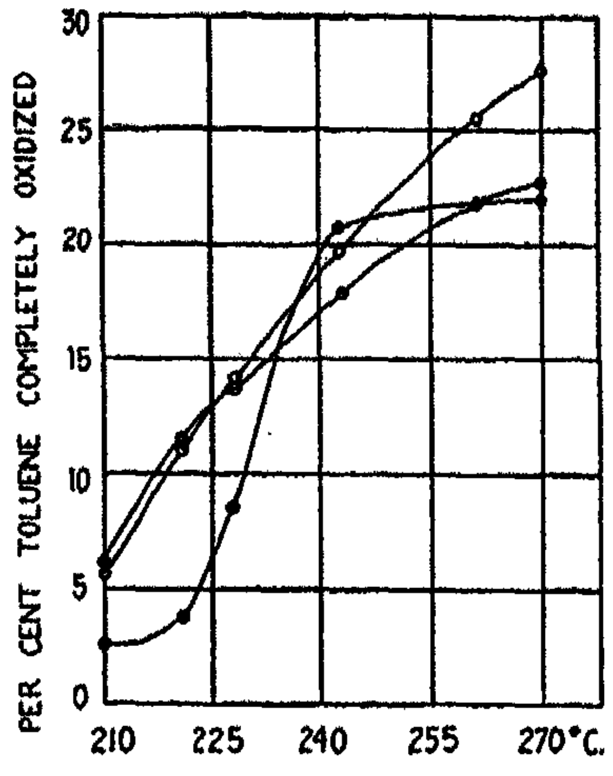

Fig. 3

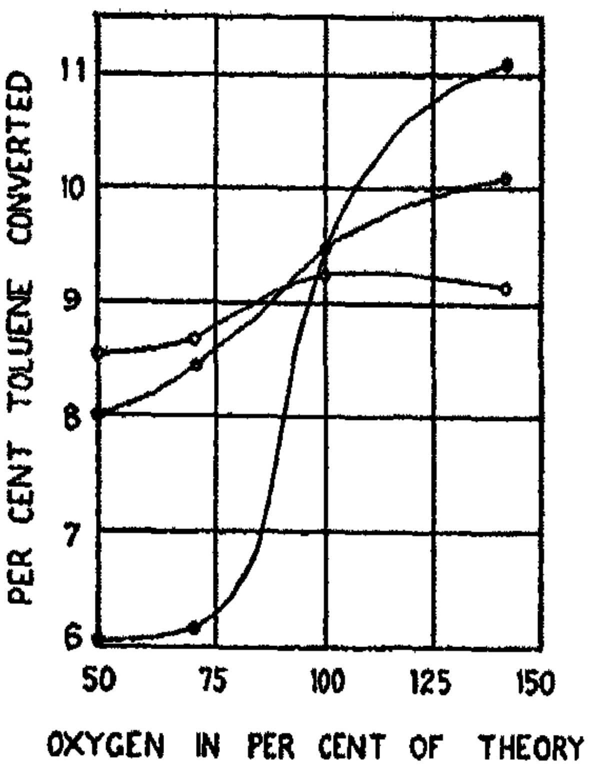

Fig. 4

Fig. 3. The effect of temperature upon the per cent of toluene completely oxidized. O, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

Fig. 4. The effect of oxygen concentration upon the per cent of toluene converted to benzoic acid. O, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

The data in table 4 show the effect of oxygen concentration upon the conversion ratios of the different catalysts studied. It is shown by these data that the higher the oxygen concentration the higher the losses of toluene by complete oxidation. At the temperature chosen the conversion ratio for catalyst C is consistently higher than the ratios of the other two catalysts.

The variations of conversion ratios from one catalyst to another indicate that there is an essential change brought about in the catalytic activity of tin vanadate by preliminary heating. These differences suggest the possibility of finding a catalyst which under the proper conditions would convert a greater portion of the toluene consumed to benzoic acid. Had this ratio been the same for all of the catalysts under the same set of conditions, the prospects for finding a better catalyst would have been small. It may be possible to find some foreign substance which when added to tin vanadate will blanket the reaction in which carbon dioxide is formed and thus produce a higher conversion ratio. This assumption is substantiated by the work of Charlot (1) in which he used various catalysts in the oxidation of toluene and its derivatives and found that there was a close relation between the extent of complete oxidation and the catalyst used. This relation was different for different catalysts, but it was essentially the same for a given catalyst irrespective of the compound oxidized.

TABLE 3

The effect of temperature upon the conversion ratio

Air flow: 7 liters per hour (100 per cent of the amount necessary to oxidize all of the toluene to benzoic acid). Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

TEMPERATURE IN °C.	PER CENT OF TOLUENE CONSUMED WHICH WAS CONVERTED TO BENZOIC ACID USING CATALYSTS		
	A	B	C
210	60.7	52.1	59.1
221	46.9	42.9	58.4
228	42.8	40.8	48.2
243	35.7	35.2	36.6
261	22.4	28.7	25.0
270	18.7	25.2	23.8

TABLE 4

The effect of oxygen concentration upon the conversion ratios of the catalysts

Temperature: 236°C. Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

AIR USED IN PER CENT OF THEORY	PER CENT OF TOLUENE CONSUMED WHICH WAS CONVERTED INTO BENZOIC ACID USING CATALYSTS		
	A	B	C
50.0	44.5	44.7	59.0
71.5	43.5	42.6	57.5
100.0	32.4	37.1	44.3
143	30.4	33.1	37.0

In order to determine whether or not the addition of carbon dioxide to the reacting gases would produce a higher percentage of benzoic acid from toluene, a series of runs was made in which carbon dioxide was added to the mixture of air and toluene vapor. The results of this series of runs are shown in table 5.

The data in table 5 indicate that the addition of carbon dioxide to the reacting gases has no beneficial effect,—at least there is no increase in the amount of benzoic acid produced per pass. Since no measure was taken of the extent of complete oxidation, we are not in a position to say definitely how the presence of carbon dioxide affected the conversion ratio, but in view of the other work which has been done on this subject, it is likely that the conversion ratio was not affected to any great extent. The decrease in the benzoic acid yield was probably due to the increased velocity of gas over the catalyst. A run was made with an air velocity of 3.5 l. per hour and with the same velocity of carbon dioxide. The oxygen concentration in this case was 50 per cent of the theoretical amount required to oxidize the toluene to benzoic acid, while the total gas velocity was essentially the same as when the oxygen concentration was 100 per cent and no carbon dioxide was added. The benzoic acid produced under these conditions was the same as when none of the diluent was added.

TABLE 5

Runs made in which carbon dioxide was added to the mixture of air and toluene vapor

Catalyst: tin vanadate heated to 400°C. Temperature, 286°C. Air flow: 7 l. per hour (100 per cent theoretical oxygen)

CARBON DIOXIDE ADDED IN LITERS PER HOUR	PER CENT TOLUENE CONVERTED TO BENZOIC ACID
None	10.67
5	8.91
10	7.26

When water vapor was added to the reacting gases, the extent of complete oxidation was the same as when no water vapor was added, and the benzoic acid yield was appreciably decreased.

In all of the work herein reported small quantities of anthraquinone and benzaldehyde were formed. Although no measure was taken of these quantities, the anthraquinone production appeared to increase with increasing temperature and also with the addition of carbon dioxide to the reaction mixture.

CONCLUSIONS

1. Tin vanadate is an excellent catalyst for the oxidation of toluene to benzoic acid.
2. Heating previous to use has a marked effect upon the behavior of tin vanadate as a catalyst in the reaction studied.

3. The temperature at which the reaction takes place and the concentration of oxygen affect the ratio of carbon dioxide to benzoic acid produced in the reaction.

4. The addition of diluents to the reacting gases gave no beneficial results in any of the experiments carried out.

5. Delicate control of air flow and temperature are essential in the type of work herein reported.

6. Anthraquinone and benzaldehyde are by-products of the reaction.

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AN EXPERIMENTAL TEST OF THE IDENTITY OF ELECTROKINETIC POTENTIALS

Electrosmosis and Streaming Potential Measurements with a Glass Slit

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Because of the extensive use and the great importance of electrokinetic methods in the study of adsorption from solution, the stability of colloidal systems, the electrical charges on colloids, living cells, etc., and a variety of other properties dependent on the existence of an electrical double layer at an interface, it is of importance to know whether the results of different electrokinetic experiments can be compared with each other, or, more specifically, whether the electrokinetic, or zeta, potentials obtained by one type of electrokinetic measurement are identical with those obtained by another method.

It has generally been assumed that cataphoresis, electrosmosis, or streaming potential experiments would yield identical values of the ζ-potential provided the system being studied were in exactly the same condition in each case. This assumption is partly due to a rather prevalent notion that the classical mathematical formulations of electrokinetics require such an identity and partly to Saxén's (23) experimental demonstration of the so-called reciprocal relation between electrosmosis and streaming potential

$$\left(\frac{V}{I} = \frac{E}{P}\right)$$

which he showed must obtain if the identity assumption is made with regard to the ζ-potentials.

Since the Saxén experiments of 1892 very little has been done to supply additional evidence on this important point. Thon (24) called attention to the fact that electrokinetic potentials calculated from cataphoresis measurements passed through maxima or minima at electrolyte concentrations considerably different from those at which maxima or minima occurred in streaming potential or electrosmosis experiments. Kanamaru

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(12) has made extensive electrosmosis and streaming potential measurements on cellulose and cellulose derivatives in contact with water and numerous electrolyte solutions, and reports that the streaming ζ-potentials were 2.6 times as large as the electrosmosis values. Since our own experiments were completed Bull (5) has reported a careful investigation of the same question. Electrosmosis, streaming potential, and electrophoretic measurements were made with Pyrex glass coated with protein. The ζ-potentials were found to be identical in the three cases.

Briggs (4) measured streaming potentials produced by streaming buffer solutions through diaphragms made of quartz particles covered with egg albumin. The ζ-potentials calculated from his data are in remarkably close agreement with those reported by Abramson (1, 10) on the basis of measurements of cataphoresis of quartz particles coated with egg albumin. However, the buffer solutions used in the two sets of experiments differed in electrolyte content, and Abramson (2) repeated the cataphoresis measurements with protein-covered quartz particles and buffers identical in composition with those used by Briggs. The ζ-potentials were now found to be about 50 per cent higher than Briggs' values, and Abramson concluded that the proteins used must have differed in some way.

In addition to these direct comparisons of electrokinetic potentials, it may be mentioned that deviations from the Helmholtz equations have been reported and discussed by various workers, including Gösta Köhler (13), Manegold and Solf (16), H. Reichardt (20, 21, 22), and Ettisch and Zwanzig (7). H. B. Bull has recently repeated the measurements of Ettisch and Zwanzig (6) and finds the deviations not to exist.

In order to provide a further, independent test of the identity of electrokinetic potentials we undertook to make combined measurements of electrosmosis and of streaming potential on a single system. We chose for the experiments a glass slit made of optically polished glass and of known dimensions. This was generously put at our disposal by Professor J. W. McBain and was the largest (slit No. 10) of the glass slits used in his careful measurements of surface conductivity (15). A detailed description of the preparation of these slits is given in the paper referred to. The dimensions of the slit were checked by us and found to agree with those published; namely, thickness (*t*), 0.00125 cm.; width (*w*), 1.001 cm.; length (*l*), that is, the thickness of the supporting block containing the slit, 0.5014 cm.; cross section of slit (*wt*), 0.00125 cm.^{2}

APPARATUS

The Pyrex glass apparatus in which the slit was mounted is shown in figure 1, the letters of which refer to the following parts: S, glass block containing the slit; BB, glass end blocks about 2.5 cm. square, with an opening through them about 1.3 cm. square; F, ebonite clamps holding together slit block, end blocks, and main cell; CC, capillary tubes about 30 cm. long, graduated in millimeter scale divisions and calibrated at 1-cm. intervals along their length by a weighed mercury thread,—used for observing displacement of liquid through slit; E, saturated calomel electrodes, separated from the rest of the apparatus by porous plugs, PP, of sintered glass; E_p, probing electrodes of bright platinum; R, connections of rubber tubing; D, screw clamps.

This apparatus (denoted cell IV) was designed to replace an earlier form equipped with platinized platinum probing electrodes and glass stopcocks throughout. The difficulties experienced with the earlier apparatus (denoted cell III) were (a) contamination of the very dilute solutions by foreign electrolyte previously adsorbed on the porous platinum surfaces of the probing electrodes, (b) persistent leakage through the glass stopcocks, and (c) contamination by stopcock grease. The new apparatus was entirely free from these sources of error. To test the rate of contamination from the rubber tubing and other sources in cell IV the solution used in experiments 21 and 22 was allowed to remain in the cell ninety-one hours and experiment 23 was conducted. The results showed that the rate of contamination was no greater than would be expected for conductivity water in any type of container. The rate of increase of the specific conductance of the conductivity water in the special Jena glass storage flasks was about 1 per cent per day.

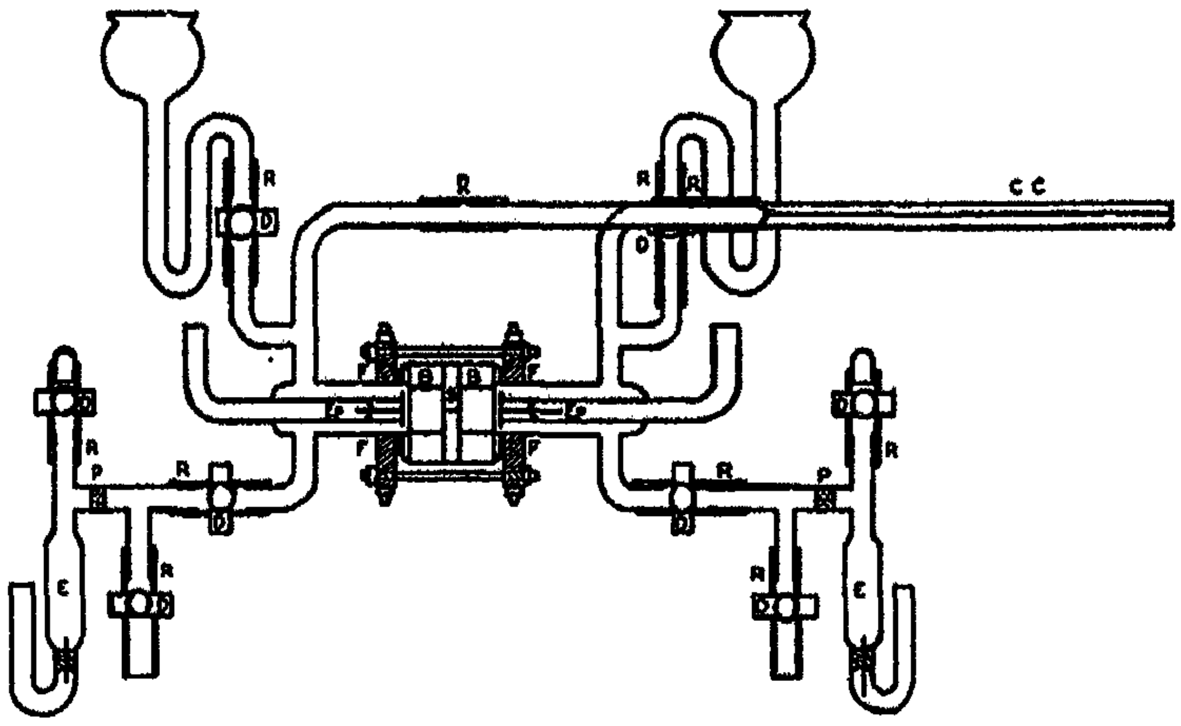

FIG. 1. Apparatus for electromosis and streaming potential measurements with glass slit. S, block containing slit; C,C, capillary tubes; E,E, calomel electrodes; E_p and E_p, platinum probing electrodes; F,F, ebonite clamps; B,B, glass end block; R, rubber tubing; D, screw clamp; P, P, porous plug of sintered glass.

At intervals the cell was cleaned with chromic acid without disassembling, and then rinsed with conductivity water for a period of about three days before resuming measurements, the water being forced through the slit by pressure. The cell was cleaned as described between the successive experiments 26–27, 43–54, and 61–87. Dilute nitric acid was used for cleaning between experiments 113 and 114. Mercury for the electrode arms was cleaned by distillation in the absence of air.

PREPARATION OF SOLUTIONS

The conductivity water used in these experiments was prepared in a special still (3) and was stored in Jena glass flasks properly protected against atmospheric contamination. The specific conductance was always determined immediately before use. The electrolyte solutions were made up to weight normality from samples of the salts, which were the purest obtainable on the market and were used without further purification. The glassware used was always steamed thoroughly and rinsed with conductivity water. The specific conductances of the more dilute electrolyte solutions were measured directly; the others were obtained from the International Critical Tables and the Landolt-Börnstein-Roth *Physikalisch-Chemische Tabellen*, were recalculated to 22°C., and were corrected for the conductivity of the solvent. The values are given in the later tables.

METHOD OF MEASUREMENT OF ELECTROSMOSIS

The quantities directly measured in the electrosmosis experiments and the methods of obtaining them are indicated in what follows.

V, the electrosmotic flow (cc. per second), was calculated from the average of the displacements of the liquid meniscuses in the two capillary tubes and the duration of the experiment.

E_T, the total E.M.F. applied at the calomel end electrodes, was obtained from 45 volt "B" batteries in series, which served excellently as sources of steady voltage because of the very slight current drain.

E_0, the potential drop across the probing electrodes. To measure this a compensating E.M.F. exactly equal and opposite to E_0 was applied to the probing electrodes by means of a potentiometer supplied by "B" batteries and shunted at the output terminals by a calibrated Weston voltmeter. Between one of the output terminals and its connection to the probing electrode was inserted a sensitive galvanometer. When the E.M.F.'s were balanced, as shown by the absence of any current through this galvanometer, the value of the compensating E.M.F. was read directly from the voltmeter. This method did not disturb the electrosmosis experiment in progress but, on the contrary, had a steadying effect on the working current, which had often varied considerably when a quadrant electrometer had been used to measure E_0. The values of E_0 appearing in the tables are the means of three such determinations made during each experiment.

I_0, the current passing through the slit during electrosmosis, was measured by means of a sensitive galvanometer connected in series with the slit and calibrated at frequent intervals. In experiments with highly conducting electrolyte solutions a 0 to 999.9 ohms four-dial resistance box was used as a shunt around the galvanometer to bypass part of the current.

E_{sl}, the effective E.M.F. across the ends of the slit, was obtained by multiplying the current I_0 by the resistance of the liquid in the slit, R_{sl} (see below). It is important to note that the magnitude of the electrosmotic effect depends on the value of the electrical field *within the slit*, that is, on E_{sl}/L, and the potential difference E_{sl} is somewhat less than E_0 because of the potential drops between the probing electrodes and the ends of the slit. In order to evaluate these IR drops an extended study was made of the series resistances in the circuit. As a result it was possible to evaluate separately the resistance R_{sl} and thus the potential difference E_{sl} ($= I_0 \times R_{sl}$).

ζ-potentials were calculated from the experimental data by use of equation 1, which was derived by Helmholtz for a capillary tube and can be shown to be applicable without change to a narrow slit:

$$\zeta = \frac{4\pi\eta}{D} \cdot \frac{L}{Q} \cdot \frac{V}{E} \qquad \text{(all quantities in absolute units)} \qquad (1)$$

where η is the viscosity of the liquid within which the double layer lies (taken equal to the viscosity of the bulk liquid), D is the dielectric constant of the liquid in the same region (taken equal to 80 here), L is the length of capillary or slit, Q its cross section, E the potential difference at its ends (equal to E_{sl} here), and V the electrosmotic flow (cc. per second).

With substitution of the numerical values and change to practical units,

$$\zeta \text{ (in millivolts)} = \frac{4 \times 3.1416 \times 0.01}{80} \times \frac{0.5014}{0.001251} \times (300)^2 \times \frac{V}{E_{sl}}$$

METHOD OF MEASUREMENT OF STREAMING POTENTIAL

The data obtained from the streaming potential experiments and the methods used were the following:

V, the rate of flow of the liquid through the slit during the streaming, was obtained from the observed displacement of liquid in the capillary tube left open during the experiment.

P, the applied hydrostatic pressure, was obtained by the use of mercury in a reservoir whose height could be adjusted and which was separated from the reservoir containing the streaming solution by a glass tube to which was connected a mercury manometer. The readings of the manometer were corrected for the difference in water levels in the reservoir and the outlet of the cell.

E_s, the streaming potential. In the early experiments with cell III streaming potentials were measured directly by the deflections of a Compton electrometer connected to the calomel electrodes (one connection through ground). This was a sensitive quadrant electrometer (1000 mm. deflection per volt with scale at one meter), and although the instrument and all connections to it were carefully shielded, considerable difficulty was caused by the unsteadiness of the zero point arising from the large deflections obtained. In the later experiments with cell IV this difficulty was avoided by the use of an improved method of measurement. Figure 2 shows the circuit arrangement. The streaming potentials were measured with a Leeds and Northrup Type K potentiometer with the Compton electrometer as a null instrument. By this method the electrometer vane was subjected to only slight displacements while a setting was being obtained, so that the zero point was very stable. It was necessary to operate the potentiometer at the high range (0 to 16.1 volts) to accommodate the large streaming potentials often obtained. A group of 6-volt storage batteries supplied the working current for the potentiometer. These were always recharged slowly and gave a constant voltage over long periods of time.

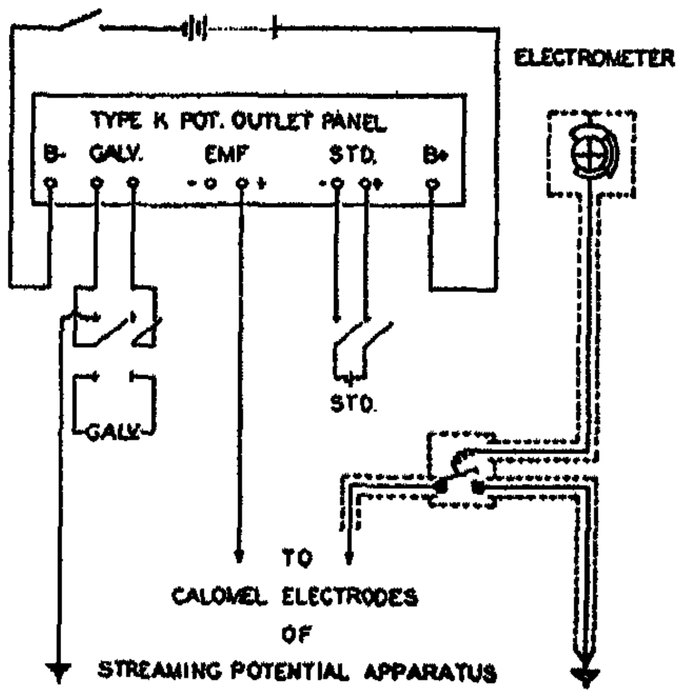

FIG. 2. Electrical circuit for measurement of streaming potential

Calomel electrodes saturated with potassium chloride were used for all streaming potential measurements. The maximum error in the measurements of E_s was not more than 0.1 per cent, except in the few experiments where E_s was only a few millivolts.

The potentiometer, cell, and reservoir were placed on plate glass resting on grounded sheet iron.

κ_s, the apparent specific conductance of the liquid in the slit, was calculated from the known dimensions of the slit and the observed conductance of the liquid in the slit. This slit conductance ($1/R_{sl}$) was determined before and after each set of streaming potential measurements. For this purpose the slit was flushed out with fresh solution, a known E.M.F. of, say, 90 volts, was applied to the calomel end electrodes (disconnected, of course, from the electrometer), and I_0, E_0, E_{sl}, and R_{sl} were determined as in the electrosmosis experiments.

TABLE 1

Electrosmosis experiments with conductivity water

NO.	TEMP. °C.	κ MHOS/CM. × 10^6	E_T VOLTS	E_0 VOLTS	E_{sl} VOLTS	V CC. PER SEC. × 10^5	I_0 AMPERES × 10^7	V/I_0, $\frac{\text{CC.}}{\text{AMP. SEC.}}$ ÷ 3 × 10^9 × 10^6	u_{EO} $\frac{\text{CM.}^2}{\text{VOLT-SEC.}}$ × 10^5	ζ MILLIVOLTS
19	23	0.53	135	105.0	104.2	−17.2	6.75	8.22	67.7	−95.8 ±2.5
20	24	0.53	22.5	16.7	16.1	−2.0	0.96	7.14	50.9	−72.0 ±4.7
21	23	0.53	45	30.4	29.4	−4.6	1.70	9.04	61.6	−84.7 ±5.5
22	23	0.53	90	56.7	54.6	−8.8	3.48	8.20	63.1	−89.3 ±7.5
24	22	0.73	135	106.8	104.2	−14.8	5.54	8.97	57.2	−81.0 ±4.8
25	22	0.73	135	104.2	101.7	−14.1	5.39	8.71	55.7	−78.8 ±5.0
26	22	0.73	90	71.6	69.9	−8.8	3.62	8.21	50.7	−71.7 ±4.7
27	22	0.56	225	122.3	116.0	−23.6	10.70	7.42	81.0	−114.6 ±7.3
28	22	0.56	180	115.5	87.8	−16.0	8.09	6.74	72.3	−102.2 ±7.7
29	24	0.56	135	72.0	68.3	−12.6	6.46	6.54	73.4	−103.9 ±11.9
30	24	0.56	90	49.1	46.6	−8.2	4.43	6.20	71.0	−100.4 ±11.4
31	25	0.56	45	25.4	24.1	−4.1	2.35	5.90	70.4	−99.5 ±19.0
Mean.								7.65	64.0	−91.6 ±7.2

The ratio V/I_0 is in absolute units—cc. per second per ampere/3 × 10^9—in order to facilitate comparison with the streaming potential ratio E/P, also in absolute units

ζ-potentials were calculated from the experimental data by the use of equation 2, valid for slit or capillary:

$$\zeta = \frac{4\pi\eta}{D} \cdot \kappa_s \cdot \frac{E_s}{P} \qquad \text{(all in absolute units)} \qquad (2)$$

or, in practical units,

$$\zeta = \frac{4 \times 3.1416 \times 0.01}{80} \times \kappa_s \times 9 \times 10^{11} \times \frac{E_s}{P} \times 10^3$$

(ζ in millivolts, E_s in volts, and P in dynes per square centimeter).

ELECTROSMOSIS EXPERIMENTS WITH CONDUCTIVITY WATER

Three series of electrosmosis experiments were carried out with three different lots of conductivity water of nearly the same conductivity

(0.5 to 0.7 × 10^{-6} mho per centimeter), fifty-seven separate determinations of ζ in all.[2] The results are given in table 1.

Before making a set of measurements the apparatus and the slit were rinsed thoroughly (while assembled) with conductivity water whose specific conductance had just previously been determined. The positions of the water meniscuses in the capillary tubes were then read after previous observations had shown them to be stationary without applied field. The desired voltage was then applied to the calomel end electrodes and the time noted to the nearest second. From two to four times during the ensuing electromosis the total current passing through the slit was read from the series galvanometer and the potential difference between the probing electrodes (E_0) was measured without interruption of the experiment. At the end of from three to ten minutes the current was interrupted; the water meniscuses in the capillaries instantly became stationary, and their positions were read.

Each set of data in the tables is the mean of the results of from four to six such experiments carried out in succession at the same applied voltage and without refilling the apparatus. The last column in table 1 gives the mean deviation of the individual ζ-potentials from the recorded mean.

The direction of electrosmosis was generally reversed in successive experiments by reversing the applied field. The mean of the ζ-potentials thus obtained was 11.7 per cent less for experiments in one direction (thirty experiments) than for those in the reverse direction (twenty-seven experiments), or 4.2 per cent less than the published mean for all experiments.

The work with conductivity water was entirely completed before that with electrolyte solutions was begun, in order to avoid as far as possible contamination of the slit by foreign electrolyte.

Relation of observed electrosmosis to strength of applied field

We were much interested in the possibility of finding a dependence of the ζ-potential on the applied field, which would show up in a variation of the quantity V/E. Toward this end the experiments were carried out over a tenfold range in the applied voltage. In figure 3 we have plotted the observed values of the ratio V/E_{sl} against the effective voltage E_{sl}, also the average values of the ratio V/E_T, for all experiments at the same total voltage, against E_T. The plot shows only a random variation in V/E_{sl} and only a very slight variation in V/E_T. It is evident that in the range of these experiments the charge distribution in the electrical double layer at the glass–water interface has been unaffected by the increase in the strength of the external electrical field applied parallel to the interface. It would perhaps be more accurate to say that the highest field strengths used

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[2] These do not include twenty earlier and much less reliable measurements made with the same slit mounted in a different apparatus (cell III, see p. 3).

were insufficient to effect a displacement of parts of the double layer which were sessile under the influence of the lowest fields. We are inclined to predict, however, that with sufficiently large applied electromotive force such a displacement, or slipping, might be brought about, with a consequent increase in the apparent value of the electrokinetic potential, ζ.

Absence of time effect in electrosmosis

In his early experiments on electrosmosis through a glass capillary tube Quincke (19) noticed that the electrosmotic flow was much more rapid just after the apparatus had been filled than after it had stood twenty-four hours. He attributed this fact to slow solution of the glass, which he actually demonstrated to have taken place. A parallel increase in the electrical conductivity of the water was found. In our own work each series of experiments with the same filling of conductivity water occupied an interval of several hours. In order to test for a similar source of error in our own work the following experiment was carried out. At the conclusion of experiment No. 22 the apparatus was allowed to stand without rinsing or refilling. At the end of ninety-one hours experiment No. 23 was performed, using water already in the apparatus and the same applied voltage. The results in table 2 show an almost negligible hourly change. The increase in the ratio E_0/E_T indicates the effect of passage of potassium chloride from the end electrodes into the tubes leading to the main cell; the constancy in the ratio E_{Sl}/E_0 shows that the electrolyte did not reach the slit.

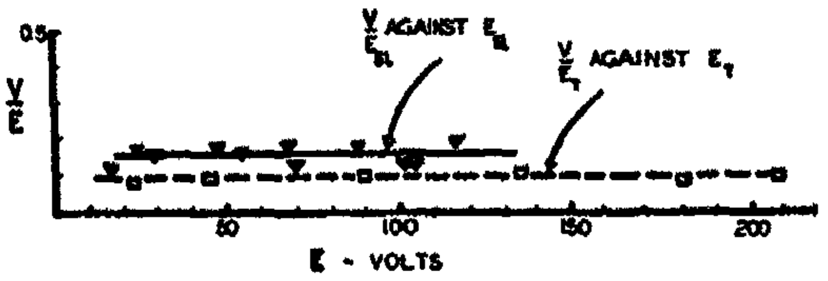

FIG. 3. Relation of electrosmotic flow, V, to applied field, E

TABLE 2

Absence of time effect in electrosmosis experiments

NO.	E_T VOLTS	E_0 VOLTS	E_{Sl} VOLTS	E_0/E_T	E_{Sl}/E_0	V cc./sec. $\times 10^5$	V/E_{Sl} cc./volt-sec. $\times 10^3$	ζ MILLIVOLTS
22	90	56.7	54.6	0.62	0.96	−8.8	0.16	−89.3
23	90	84.5	81.4	0.93	0.96	−9.6	0.12	−66.9
Hourly change							0.0004	0.25

Since examination of the results of the electrosmosis experiments fails to show any regular dependence on applied voltage or conductivity of the water used, we shall take as the most probable values of the ζ-potential and related quantities the mean values of all of the fifty-six experiments of the three series (exclusive of No. 23). These are given in table 1. The final value of the ζ-potential for the glass–water interface thus calculated is −92 millivolts.

STREAMING POTENTIAL EXPERIMENTS WITH CONDUCTIVITY WATER

At the close of the electrosmosis experiments just described the cell and slit were cleaned and rinsed thoroughly. An extended series of streaming potential measurements was then made at different pressures with various lots of conductivity water of about the same specific conductance (0.5 to 0.7 × 10^{-6} mho per centimeter); one hundred thirty-five separate measurements were made in all.

TABLE 3

Comparison of the results obtained with the early cell and the improved cell

CELL	ELECTROSMOSIS		STREAMING POTENTIAL		$\frac{\zeta_{SP}}{\zeta_{EO}}$
	Number of experiments	Mean ζ	Number of experiments	Mean ζ	
		mv.		*mv.*	
Cell IV	53	−92	135	−162	1.8
Cell III	20	−68	20	−134	2.0
Both cells	73	−85	155	−158	1.9

This number does not include two experiments which were evidently unreliable, and twenty earlier measurements with the slit mounted in cell III. Table 3 affords a comparison of the results obtained with the early cell (No. III) and the improved cell (No. IV).

At the beginning of each set of measurements at a given pressure a preliminary measurement was made of the rate of flow over a period of about two minutes. Before streaming was started again a reading was made of the zero point of the electrometer connected to one of the calomel end electrodes and to ground (the other calomel electrode being grounded). This reading was repeated at the close of the measurements in order to check the absence of any potential differences due to difference in the condition of the electrodes. The reading was always found to be within three millivolts of the initial value. Streaming was then started at the given pressure (always in the same direction in all experiments), and measurements of the streaming potential were made at intervals of a few minutes.

Time effect in streaming potential experiments

The streaming potentials were found to vary erratically during the first few minutes of streaming, but we found on continuing the measurements over an extended period of time that constancy was obtained after about ten minutes. In computing the published mean values of our results we have therefore excluded all observations made during the first ten minutes of streaming.[3] The collected results are given in table 4, each value given therein being the mean of from six to ten observations made during the next ten to twenty minutes.[4]

TABLE 4

Streaming potential experiments with conductivity water

NO.	TEMP. °C.	κ_v* MHOS/CM. $\times 10^6$	κ_s* MHOS/CM. $\times 10^6$	P DYNES/CM.^{2} $\times 10^{-4}$	V CC./SEC. $\times 10^3$	V/P CM.^{5}/DYNE-SEC. $\times 10^8$	E, VOLTS	E/P E.S.U./DYNES/CM.^{2} $\times 10^8$	ζ MILLIVOLTS
34	23	0.53	6.57	2.74	0.515	1.88	0.4688	5.70	−158
35	23	0.53	6.57	5.60	1.047	1.87	0.9026	5.37	−150
36	22	0.48	6.12	2.78	0.466	1.68	0.4449	5.34	−139
37	23	0.48	6.52	5.62	0.977	1.74	0.9702	5.82	−161
39	23	0.66	6.97	51.7	9.30	1.80	7.563	4.87	−145
40	22	0.60	6.35	2.73	0.474	1.74	0.4741	5.79	−156
41	24	0.60	6.17	5.66	1.210	2.14	1.1165	6.57	−172
42	22	0.54	6.87	5.81	1.15	1.98	1.1989	6.87	−200
43	22	0.54	6.03	2.78	0.556	1.99	0.5686	6.80	−174
54	23	0.56	5.48	48.8	12.56	2.57	12.4887	8.60	−204
55	23	0.56	5.48	23.4	5.32	2.27	4.5713	6.34	−151
56	23	0.56	5.48	7.90	1.92	2.43	1.480	6.25	−148
57	24	0.56	5.48	3.21	0.709	2.21	0.5771	5.99	−143
61.1	21	0.58	2.60	48.90	11.71	2.39	16.044	10.95	−120
61.2	21	0.58	2.60	22.10	5.32	2.41	6.805	10.60	−113
61.3	21	0.58	2.60	7.94	1.93	2.43	2.138	8.96	−99
61.4	21	0.58	2.60	3.26	0.711	2.18	0.8318	8.48	−94
Mean..						2.08		6.81	−162

*κ_v and κ_s are respectively the bulk conductivity of the water used, as measured outside of the slit, and the apparent conductivity of the same water in the slit, the increase being due to the surface conductivity.

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[3] Similar unexplained variations in the streaming potential have been observed by other experimenters. For example, Grumbach (11) was led to adopt a rule of selection similar to ours: "Je fus amené ainsi à m'imposer comme règle de n'admettre comme valable que les forces électromotrices qui demeurent fixes à pression constante pendant au moins 10 minutes."

[4] As a matter of fact the average value of ζ thus calculated from all measurements made after the first ten minutes of streaming (namely, −162.2 millivolts) is identical with the average obtained from *all* measurements both before and after this ten minute mark (−162.0 millivolts).

Careful plotting of the observed values of the E/P ratio against the applied pressure shows only random variation with this factor. We have therefore taken the mean of all determinations as representing the most probable value of the ζ-potential for the glass–water interface derived from streaming potential experiments. This value is −162 millivolts.

Streaming rate and applied pressure

The fundamental equations of electrosmosis and streaming potential are derived on the assumption that the flow of liquid through the slit, capillary, or porous diaphragm is non-turbulent. The usual experimental evidence of non-turbulence in streaming potential work is a constant proportionality between the rate of streaming (or the streaming potential) and the applied pressure. The data obtained from our own experiments (table 3, column 7) show that while the V/P ratio is satisfactorily constant in certain sets of measurements, it is not at all constant through the entire series of experiments. Now the rate of flow to be expected at any pressure can be calculated by use of the following equation derived for laminar flow through a slit in exactly the same way as is the Poisseuille equation for a circular tube:

$$V = \frac{wt^3P}{12\eta l}$$

where w, t, and l are respectively the width, thickness, and length of the slit, η is the viscosity of the liquid, P the difference in pressure at the ends of the slit, and V the flow rate in cc. per second. The value of the theoretical ratio V/P in the case of our slit is 3.28×10^{-8} cc. per second per dyne per cm.^{2} The observed ratio in most of our experiments is less than this; the average value is 2.46×10^{-8} in the experiments with electrolytes and 2.00×10^{-8} with water.

This discrepancy is in the direction to be expected if the flow was turbulent. Davies and White (6a) have established that the flow of liquid through a narrow slit becomes turbulent only after the mean velocity exceeds the limit $u = 890\ \eta/\rho t$, where η is the viscosity of the liquid, ρ is its density, and t is the thickness of the slit. The flow rates in all our streaming experiments were far below the critical value, and we are therefore of the opinion that turbulence did not occur in the flow of water through the slit.

The discrepancy noted forces us to suspect that the actual cross section of the slit, Q, was effectively smaller than that which we had calculated from the observed dimensions. Whether this was due to foreign intrusion in the slit, which resisted the repeated and thorough cleaning operations to which it had been subjected, or to an error in measuring the width of the slit (an error of about 0.0005 cm. would account for the discrepancy), we are unable to say. It is important, however, to point out (1) that all the ζ-potential values given here will be multiplied by a factor of 3.28/2.00 or

TABLE 5

Electrosmosis and streaming potential experiments with water and electrolyte solutions

LIQUID	ELECTROSMOSIS					STREAMING POTENTIAL				RATIOS		
	No. of expts.	κ_w mhos/cm. $\times 10^6$	κ_s mhos/cm. $\times 10^6$	$\frac{V}{I}$ cc./sec / E.S.U. $\times 10^{10}$	ζ mv.	No. of expts.	κ_s mhos/cm. $\times 10^6$	$\frac{E}{P}$ E.S.U. / dynes/cm.^{2} $\times 10^{10}$	ζ mv.	$\frac{\zeta_{SP}}{\zeta_{EO}}$	$\frac{E/P}{V/I}$	$\frac{\kappa_s - SP}{\kappa_s - EO}$
Water:												
Cell IV	53	0.6	3.0	765	−92	135	6.3	681	−162	1.76	0.89	2.12
Cell III	20	0.6	4.1	346	−68	20	4.1	769	−134	1.97	2.22	1.00
Cells III and IV	73	0.6	3.27	650	−85	155	6.0	693	−158	1.86	1.07	1.84
KCl												
10^{-4} *N*	10	14.89	14.1	132	−79	4	11.2	95.0	−45	0.57	0.72	0.79
5×10^{-4} *N*	6	70.68	108.9	11.2	−52	4	55.8	18.5	−44	0.85	1.65	0.51
10^{-3} *N*	8	139.99	116.7	9.9	−49	4	118.2	8.0	−40	0.82	0.81	1.01
$BaCl_2$												
10^{-4} *N*	8	13.47	11.6	77.9	−38	4	12.9	62.2	−34	0.89	0.80	1.11
5×10^{-4} *N*	8	64.87	51.4	12.4	−27	4	58.2	11.8	−29	1.08	0.95	1.13
10^{-3} *N*	2	127.59	112.3	4.8	−23	4	125.1	5.3	−28	1.22	1.11	1.11
$AlCl_3$												
10^{-5} *N*	7	1.98	1.51	722	−46	4	2.40	318	+32	−0.70	0.44	1.59
5×10^{-5} *N*	2	7.37	3.70			4	6.81	138	+40			1.84
10^{-4} *N*	3	14.16	13.8	70.9	+41	4	10.3	80	+34	0.83	1.13	0.75
5×10^{-4} *N*	4	68.06	61.0	15.7	+40	4	62.3	16.6	+42	1.05	1.06	1.02
10^{-3} *N*	2	135.56	118.4	7.0	+35	4	116.4	8.1	+40	1.14	1.15	0.98
Mean for electrolytes										0.94	1.04	0.93

3.28/2.46 (1.6 to 1.3) if an empirical value of the cross section is calculated from the observed V/P ratios, and (2) that both the electrosmosis and the streaming potential ζ-potentials will be multiplied by the *same* factor since both sets of values depend on the cross section, Q, in the same way. The V/P discrepancy does not therefore invalidate our general conclusions regarding the relative values of the ζ-potential obtained from electrosmosis and from streaming potential experiments.

COMPARISON OF ZETA POTENTIALS OBTAINED FROM ELECTROSMOSIS AND FROM STREAMING POTENTIAL MEASUREMENTS

The principal results of our experiments with water and with electrolyte solutions are summarized in table 5 for the purpose of comparison. The ζ-potentials calculated from these are plotted in figure 4.

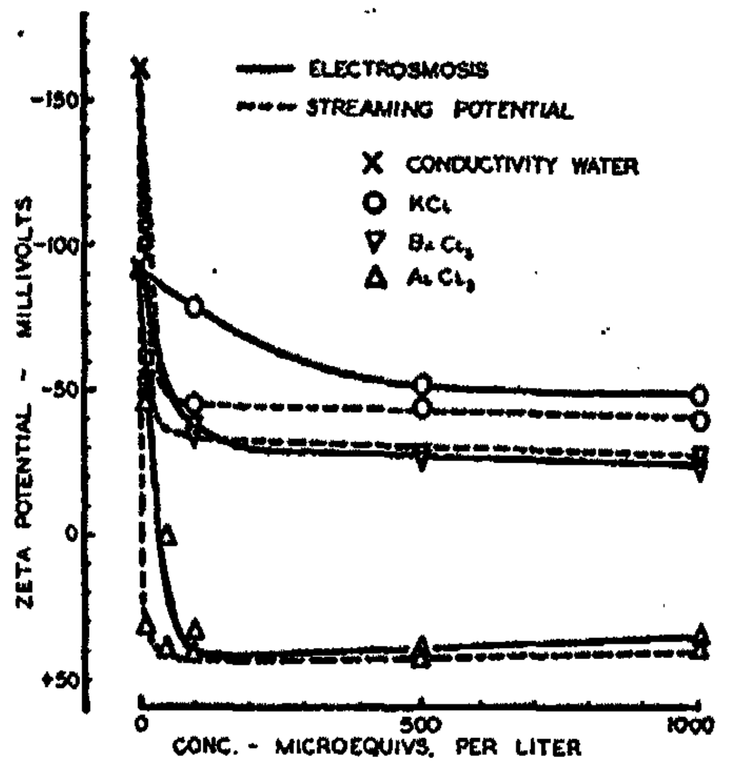

FIG. 4. Comparison of electrokinetic potentials obtained from electrosmosis and streaming potential measurements

The results of the experiments with conductivity water show a striking discrepancy in the ζ-potentials obtained from the two types of electrokinetic measurement, the electrosmosis values (−162 millivolts with cell IV and −134 millivolts with cell III) being almost twice as great as the streaming potential values (−92 millivolts and −68 millivolts with cells IV and III, respectively), the differences being well outside of the experimental error.

Such a difference in the ζ-potentials is not intrinsically a contradiction of the Helmholtz equations, for the following reason. These equations imply that—whatever the charge distribution in the electrical double layer—under the influence of an applied electrical field parallel to the wall (electrosmosis) or of a mechanical force (streaming potential), a lateral displacement of a mobile part of the double layer takes place relative to a sessile part fixed on the wall, and that somewhere very close to the wall there exists a limiting plane of shear where the lateral velocity of the liquid with respect to the wall is zero. The difference in the electrical potential at this distance from the wall and that in the interior of the solution is the zeta potential. The ζ-potentials calculated from the results of electrosmosis and streaming potential experiments will be identical only if the limiting planes of shear lie at the same distance from the wall in the two cases. There is no stipulation in the Helmholtz formulation that this condition shall be satisfied.

We had indeed looked for some difference in the two ζ-potentials as an indication that the condition may actually not be satisfied. The discrepancy actually observed does not, however, allow a definite conclusion of this sort to be drawn, because of a certain internal inconsistency in our own results. The large ratio of the ζ-potentials obtained from the forty experiments with cell III corresponds, as it should, to a similar ratio of the quantities E/P and V/I and an equality of the observed apparent conductivities of the liquid in the slit. In the one hundred eighty-eight experiments with cell IV, however, we find a similar high ratio of the ζ-potentials coupled with practical equality of the ratios E/P and V/I. This is an apparent contradiction of the usual assumption that equality of E/P and V/I indicates equality of the ζ-potentials.

The discrepancy is explained when we compare the measurements of the apparent slit conductivity made during the two sets of experiments and note that the value of κ_s observed in the streaming potential experiments was twice as great as that measured in the electrosmosis experiments, although the procedures were identical and the bulk conductivities of the water were practically the same in both cases.[5] Although the inconsistency noted robs our results of some of their theoretical import, it serves to point a warning that mere equality of the quantities E/P and V/I does not in itself demonstrate equality of the ζ-potentials without definite experimental proof that the specific conductances of the liquid in slit, capillary, or diaphragm are identical.

Identity of ζ-potentials obtained from experiments with electrolyte solutions

The results of the experiments with electrolytes show on the whole that ζ-potentials obtained from streaming potential measurements were identical with those obtained from electrosmosis measurements. They there-

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[5] This increase in ζ with increase in the specific conductance of the slit liquid is in the reverse direction from the effects noted by Lachs and Biczyk (14) with conductivity water, but is consistent with the initial rise in the ζ-concentration curve commonly observed in electrokinetic experiments.

fore point to the conclusion that the applied mechanical force acting on the liquid in the streaming potential experiment displaces the same fraction of the double layer as the applied electrical force in electrosmosis acting directly on the charged ions in the layer. The observed equality in the values of ζ *is not a fortuitous* result of a particular choice of applied field (electrosmosis) or of applied pressure (streaming potential), since the ζ-potentials were found to be independent of these factors.

Anomalous reversal of sign of the ζ-potential

The conclusion just stated rests on a comparison of the average values of all experiments with the three electrolytes. When we consider the individual experiments at different concentrations, we find random variations such as are generally observed in similar work. The usual valence effects are observable, including charge reversal in the case of solutions containing the trivalent Al^{+++} cation.

The most surprising result of all our work with electrolyte solutions was the observation that the electrosmosis and the streaming potential effects *were of opposite sign* in the measurements with 10^{-5} N aluminum chloride solution; that is, the direction of electrosmosis corresponded to a negative ζ-potential (-46 millivolts), while the streaming potential corresponded to a positive ζ-potential ($+ 32$ millivolts). This was so important a result that in order to establish the reality of the effect we disconnected the pressure apparatus just after completing the streaming potential measurement and immediately made another electrosmosis measurement. Electrosmosis again occurred as before in the direction corresponding to a negative ζ-potential. We are therefore forced to recognize that conditions may exist in an electrokinetic system where electrokinetic effects may differ not only in magnitude but even in sign. This suggests that in the neighborhood of the electrokinetic isoelectric point, where charge reversal takes place, the electrical double layer may have a complex structure involving several layers of charge of alternately positive and negative sign, as has been proposed by several writers (8, 9, 17). To complete the explanation of the effect we have observed it is necessary to suppose that when the tangential mechanical force was applied to such an interfacial layer in the streaming potential experiment, the limiting plane of shear (the "rigidity boundary" of Müller (18)) lay in a different part of this complex double layer than when the electrical force was acting in the electrosmosis experiment. That is, the rigidity boundaries in the two experiments lay in regions of the double layer where the electrical potential was of different sign.

SUMMARY

1. Electrosmosis and streaming potential measurements have been made with an optically polished glass slit in contact with conductivity water and

with solutions of electrolytes of different valence types. The measurements were made over the concentration range of 10^{-3} N down to about 10^{-6} N (conductivity water),—that is, the range in which electrokinetic effects change most rapidly with concentration.

2. The values of the ζ-potential for the glass-water interface were calculated from the results of these experiments. The electrokinetic potentials thus obtained from the electrosmosis experiments were nearly identical with those calculated from the results of the streaming potential measurements over most of the concentration range studied.

3. However, in the region of extremely low ionic concentrations large discrepancies were found. With water of specific conductance 0.6×10^{-6} mho per centimeter the streaming potential effects were relatively almost twice as great as the electrosmotic effects. The interpretation of the results, however, is complicated by the discrepancy in the observed values of the apparent specific conductance of the liquid in the slit.

4. With aluminum chloride solution of concentration 10^{-5} N a remarkable result was obtained when it was observed that the electrokinetic effects of electrosmosis and of streaming potential were of opposite sign, the values of the ζ-potential being respectively -46 millivolts and $+32$ millivolts. The two experiments were made in immediate succession without any reasonable chance for a change in the structure of the electrical double layer.

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39c-15b.

A STUDY OF SOME PHYSICAL PROPERTIES OF FLOUR DOUGHS IN RELATION TO THEIR BREAD-MAKING QUALITIES

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INTRODUCTION

Attempts to measure the physical properties of flour doughs were made by Kosutány (4) as early as 1907. This author pulled out a cylinder of flour dough at a constant rate, and measured the stress build-up.[2] Although not clearly distinguishing between viscous and elastic properties, the author's interpretation of his data points clearly to a number of the conclusions reached in the present work.

It is curious that this valuable work, in which Kosutány came so near to separating and measuring specific physical properties, should have lain fallow for so many years. From 1907 to 1932 work on the physical properties of flour doughs was confined almost entirely to the production of instruments measuring a complex mixture of properties, which, although in some cases of real value in the bread-making industry, threw little or no light on the physical nature of the problem. In 1932–33 three papers were published by Schofield and Scott Blair (8), in which certain of the physical properties of doughs were separated and independently measured. For the sake of convenience these papers will be referred to as I, II, and III.

In paper I it was emphasized that flour dough belongs to a group of materials in which a high degree of plasticity is combined with considerable elasticity. When under stress the relative amounts of plastic (non-

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

[2] Terzaghi (9) develops very similar ideas. The constant which he calls "degree of elasticity" (p. 79) is closely connected with relaxation time (vide infra). Terzaghi's work refers to soils and clays, but their behavior is in some ways strikingly similar to that of flour doughs. See also a recent paper by M. P. Wolarowitsch and K. I. Samarina (10) dealing with some physical properties of flour doughs.

recoverable) and elastic (recoverable) deformation depend on the time of duration of the stress. An extended significance was given to Maxwell's relaxation time, so that the equation

$$t_r = \eta/n$$

in which t_r = relaxation time, η = viscosity, and n = shear (rigidity) modulus,[3] could be applied to a material such as flour dough, in which neither η nor n is a constant.

It was found that η and t_r decrease with increasing stress and increase with increasing deformation. Fall in viscosity with increasing stress is a phenomenon well known in many colloidal systems, and has been called "structural viscosity" (6). Increase in viscosity with increasing strain is a common characteristic of metals, and is called "work-hardening."

In paper II, these two properties were more fully studied by observing the rate of shear of cylinders of dough hung vertically, and allowed to elongate under the action of gravity (the method of rheograms).

The Maxwell equation could only be tested satisfactorily after the most suitable value of modulus to use in calculating viscosities from relaxation times was known. Experiments to decide this point were described in paper III, and agreement was found to be as satisfactory as could be expected when the best value for the modulus was used. These experiments also made it clear that dough shows two other properties characteristic of metals, namely, elastic hysteresis and elastic after-effect.

The former causes the rigidity modulus to fall slowly as stress is raised, and also as stress is lowered, but at the point at which the sign of dS/dt changes,[4] the modulus increases abruptly. The latter means that elastic deformations are not recovered instantly, so that unless time is given for slow recovery to take place, certain deformations will be regarded as permanent which are in reality recoverable. This would lead to considerable errors in determining viscosity and modulus (see experimental section). In view of the partial understanding which this treatment had already given, it seemed advisable to investigate further the relationship between these fundamental physical properties, and those qualities of the dough which are of importance in the bread-making industry. For this purpose the Physics Department of the Rothamsted Experimental Station and the Research Association of British Flour Millers decided to coöperate in the further study of the problem.

[3] Note that for flour doughs, Poisson's ratio being 0.5, we can assume the rigidity modulus to be equal to one-third of Young's modulus. The shearing stress likewise is one-third of the loading stress. In the present paper, the term "rigidity modulus" is often abbreviated to "modulus," since no other modulus is discussed.

[4] Where S is shearing stress and t the time.

The general principles have now been elucidated, and although much detail requires yet to be filled in, the present paper gives a description of the conclusions to date.

EXPERIMENTAL

By far the most serious difficulties that have been encountered were those associated with the reproducibility of measurements on different test pieces from the same dough. In papers I, II, and III accurate replication on different test pieces was not attempted, and although the phenomena described could be repeatedly observed, it was realized that no fully satisfactory technique existed for such replication. In the course of the present investigation much time has been spent in developing such a technique, and the method finally adopted has proved on the whole to be satisfactory.

TABLE 1

The effect of mixing on the viscosity and modulus of the dough

TIME OF MIXING	TIME OF RESTING AFTER MIXING	VISCOSITY*	MODULUS*
minutes	*minutes*		
3	0	6.38×10^6	4.29×10^4
	30	4.92×10^6	3.94×10^4
	60	4.04×10^6	3.73×10^4
12	0	2.92×10^6	3.02×10^4
	30	3.55×10^6	3.41×10^4
	60	3.51×10^6	3.50×10^4

* All data for viscosities (η) and moduli (n) in this paper are given in C.G.S. units, but it must be borne in mind that they refer only to arbitrary fixed conditions of stress and strain.

It is necessary to make as homogeneous a dough as possible, and it has been found that machine mixing of the flour and water gives the most satisfactory results. The longer the time of mixing, the more homogeneous is the finished dough, but excessive mixing has a very marked effect on the dough's physical properties.

From the data in table 1 it can be seen that excessive mixing considerably lowers the viscosity and modulus of the dough, but that these increase again on resting. Such treatment, however, permanently lowers the tensile strength of the dough.

It will be shown later that the general tendency on aging a dough is for the viscosity and modulus both to fall. It is only after prolonged mixing that the opposite effect more than compensates for this fall, producing a net rise in both properties. Thus it appears in table 1 that after 3 minutes mixing, the effect of standing is the opposite of that produced by 12 minutes mixing.

The sample of dough is transferred from the mixer to a "gun," consisting of a hollow metal cylinder, 5 cm. long and 2.5 cm. in diameter, fitted with a plunger. To the bottom of the cylinder is fitted a solid piece of metal drilled with a hole 3.5 cm. long and 0.5 cm. in diameter. This first gun, into which the dough can be placed by means of a spatula, thus avoiding handling it, is too big to fit conveniently on to the apparatus, and therefore the extended dough cylinder is squeezed straight into a second smaller gun 15 cm. long and 1 cm. in diameter, which is fitted with an end piece similar to that of the first gun. The dough is forced from this second gun straight on to the surface of a bath of mercury.

Statistical analysis[6] showed that there was no greater error in comparing test pieces from different doughs than in comparing pieces from the same dough. It thus appeared that the chief source of error lay in the method of preparation of the test pieces. It was found that the force applied to the guns very largely affected the physical properties of the prepared dough cylinder. A system of pulleys and weights was therefore used for manipulation of the guns, and, provided that the weights were small, we found very little alteration of the properties of the doughs. The importance of a carefully standardized use of these guns cannot be too strongly emphasized.

During extrusion the dough cylinder swells, this swelling being in general greater for good than for poor quality flours. The exact connection, however, is not clearly understood.

The dough cylinders have been examined by the two general methods described in papers I, II, and III, namely (a) rheograms, and (b) the mercury trough extensimeter, but the technique of the latter method has been extended and developed.

(a) *The rheogram method.* This method has been further developed and has now reached a stage at which the results are excellently reproducible, and, although not free from errors, it provides the most satisfactory way at present available for separating the effects of work-hardening (rise in viscosity with rising strain) and structural viscosity (fall in viscosity with rising stress).

In most doughs these two properties appear, under the conditions of the rheogram experiments, approximately to cancel out. Without committing ourselves to any assessment of the degree of accuracy of individual samples, an examination of the data obtained from a study of some sixty doughs made from a series of twenty different flours, leads to the conclusion that certain flours tend to show higher or lower degrees of work-

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[6] Our best thanks are due to Mr. F. Yates of the Rothamsted Experimental Station Statistical Department for doing this analysis.

hardening than others, and that this property generally persists when different amounts of water and times of aging are used. Such differences do not, however, correlate directly with flour quality, and we conclude that weakness in a flour due to an unsuitable degree of work-hardening is the exception rather than the rule.

Certain practical difficulties are encountered in using the rheogram technique in the case of sticky doughs, and doughs of poor tensile strength. Moreover, both viscosity and rigidity modulus can be calculated from a single test on the extensimeter (*vide infra*); therefore the rheogram method was not employed further in this investigation.

(*b*) *The extensimeter.* This instrument, which is an improved model of the extensimeter described in papers I and III, is shown diagrammatically in figure 1.

A dough cylinder A, about 10 cm. long by 0.7 cm. in diameter, made as described above, is floated on a mercury bath. The ends of this cylinder are connected by means of cork "chairs" and cotton threads to two small scales B, which are observed through low-power microscopes, C. The smallest divisions on the scales are 0.013 cm. in length, and readings to one-tenth of this can be estimated with a fair degree of accuracy. To one scale is fastened a steel spring D, the other end of which is securely attached to the framework of the apparatus; the other scale is connected by cotton to a small winch (E), which can be wound either by hand or by a small motor.

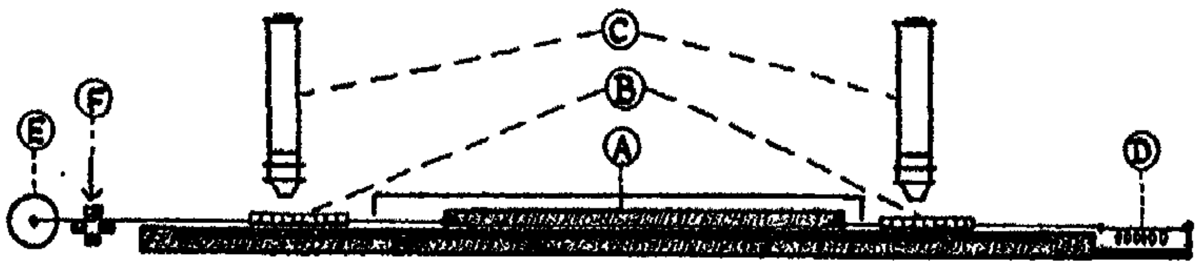

FIG. 1. The mercury bath extensimeter

During experiments the dough is protected by a cover, the felt lining of which is damped to provide a humid atmosphere to prevent drying out of the dough surface.

When the winch (E) is wound up, the dough and scales are moved to the left, and this extends the spring D. The dough is therefore subjected to a stress, the value of which is proportional to the extension of the spring, and inversely proportional to the cross section of the dough cylinder. The spring is calibrated by noting the extension caused by hanging weights of various sizes from it when placed in a vertical position. The diameter and initial length of the dough cylinder are measured with calipers.

In order to measure viscosity, which is defined (see paper I) as the ratio of shearing stress to velocity gradient (i.e., rate of change of non-recoverable strain), we can either fix the rate of change of strain and measure the stress, or fix the stress and measure the rate of change of strain. The latter has in practice been found to be by far the simpler method to use, and has been the basis for most of the experiments described in this paper.

Before doing an experiment, the necessary deflection of the spring to give the desired stress is first calculated from a knowledge of the constant for the spring and the cross section of the dough cylinder. The winch is then rapidly wound up until the shift in the scale attached to the spring corresponds to this required stress. For ordinary purposes we worked with an arbitrary tensile stress of 1500 dynes per square centimeter (shearing stress 500 dynes per square centimeter).

Under stress the dough cylinder extends, and for five minutes this extension is taken up by slowly winding the winch so that the deflection of the right-hand scale is kept constant. By this means the stress is kept almost constant, the rise in stress with slight thinning of the dough cylinder not being generally great enough to introduce any serious error, especially when relative, rather than absolute, viscosities of doughs are required.

By measuring the extension at minute intervals it would appear that the mean viscosity for each minute could be determined, and from this an indication of the amount of work-hardening (i.e., change in viscosity with strain) assessed. This is not, however, practicable, since elastic after-effect is taking place during the whole process (see introduction).

The stress is released at the end of the five minutes and the dough allowed to relax until no further change in length takes place (this takes about three to five minutes). The difference in the length of the dough cylinder before any stress is applied to it and at the end of relaxation gives a measure of the non-recoverable strain caused by the stress acting for five minutes.[6] From this a mean viscosity can be determined by dividing the non-recoverable strain per unit time into the stress. This is free from errors due to elastic after-effect.

The amount of recoverable or elastic deformation is obtained by noting the change in length of the dough cylinder between the time of releasing the stress and the end of relaxation. The value of the shear modulus which is given by the ratio

$$\frac{\text{change in shearing stress}}{\text{change in recoverable strain}}$$

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[6] Strictly speaking, the strains should be calculated from $\log_e l/l_0$, as in the rheogram calculation, but for the small strains used the method described here is adequate.

is a *mean* value for a change in stress from 500 to 0 dynes,[7] the modulus falling progressively during the lowering of the stress due to elastic hysteresis (see introduction).

Effect of temperature

Experiments have shown that the viscosity of a typical dough falls by about 10 per cent per degree Centigrade rise in temperature and the modulus by about 5 per cent. This makes it desirable to exercise careful control over the temperature. The extensimeter is not easily thermostated, and, moreover, the processes of dough preparation should also be carried out at a constant temperature. It would thus be best to carry out all measurements in a constant temperature room.[8]

Although a suitable constant temperature room has now been built, the fact that it was not available for the earlier work meant that we could only make direct comparison between results obtained over periods during which laboratory temperature did not fluctuate very widely, and in consequence we have had to forego making as full use of our data as we should otherwise have been able to do. Further, since the viscosity falls about twice as fast (with rise in temperature) as does the modulus, it is clear that the all-important[9] viscosity modulus ratio (relaxation time) is higher, the lower the temperature. This supports the view held by some bakers that dough should be fermented and put into the oven at as low a temperature as is consistent with the satisfactory working of the yeast.

The temperature coefficients also vary with the age of the dough, and it is thus clear that the temperature at which it is aged plays an important part in defining its physical properties at any given time, and hence in determining the quality of the resulting bread. Further experiments are needed to explore this field.

WATER ABSORPTION

When determining the value of a flour in the bakehouse the first step is to turn it into dough by mixing with water and other ingredients. The baker does not use a constant ratio of flour to water for all samples, otherwise some of his doughs would be too soft and sticky, while others would be too tough, extremes of condition which not only cause serious difficulties in the handling of the doughs, but which do not result in bread representative of the value of the flour. In view of this, the baker varies the

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[7] The stress is never allowed to fall quite to zero, owing to the necessity for keeping the cotton taut, but the final stress is very small, and is the same in all experiments.

[8] Care must be exercised to ensure proper ventilation and so prevent the danger of mercury poisoning (see Stock (9)).

[9] See later, under the section headed "general considerations."

amount of water he adds to each flour so that his doughs are easy to handle and in general bake into as good quality bread as his various flours are capable of making.

We are therefore faced with the problem of determining the significance of this optimum amount of water, or "water absorption" as it is called in the bakehouse, and also with the necessity of determining some method whereby it could be fixed. In assessing water absorption the baker relies on his sense of touch, and one of the impressions which helps in his judgment of correct absorption is the extent to which the dough sticks to his hands.[10]

It appeared to us that the baker made up his doughs so that the stickiness was just short of being a trouble, and on this assumption we based our first attempt to connect water absorption with a physical property, so that by the measurement of the latter we could fix the former.

TABLE 2

Effect of water content on viscosity and modulus of flour doughs

FLOUR	WATER CONTENT				
	− 1 gal.	− ½ gal.	Normal	+ ½ gal.	+ 1 gal.
No. 1 Manitoba:					
Viscosity ($\times 10^6$)	10.0	7.5	5.8	4.8	4.1
Modulus ($\times 10^4$)	4.1	3.6	3.1	2.6	2.1
Barusso Plate:					
Viscosity ($\times 10^6$)	15.0	8.3	5.7	4.4	3.5
Modulus ($\times 10^4$)	4.6	4.0	3.4	2.8	2.2
Australian:					
Viscosity ($\times 10^6$)	7.5	4.8	3.5	2.8	2.3
Modulus ($\times 10^4$)	5.5	4.6	3.6	2.6	1.6

Normal absorptions: No. 1 Manitoba, 15.6 gals. per sack; Barusso Plate, 15.3 gals. per sack; Australian, 14.0 gals. per sack.

Measurements of stickiness were made by measuring the force required to overcome the adhesion of a metal weight to the surface of a dough. The method used was a modification of those proposed by Kachinski (3) and others (1, 2, 5, 7) for measuring the stickiness of soils. It has, however, not been possible to make the measurements reproducible enough to use as a means of assessing water absorption.

The connection between water content and two other physical properties, namely, viscosity and rigidity modulus, was next investigated.

For this a series of flours was obtained, and from each flour several doughs were made containing different amounts of water. The data

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[10] For experiments on the psychological aspect of stickiness, see Zigler (12).

obtained by measuring the viscosities and moduli of the doughs made from three of these flours, a No. 1 Manitoba, a Barusso Plate, and an Australian are given in table 2.

Each flour was examined at the absorption chosen in the bakehouse which we have called "normal," and at four other water contents ±½ gallon and ±1 gallon per 280-lb. sack of flour.[11] Each dough was fermented for four hours, at the end of which time samples were taken for viscosity and modulus measurements. In figure 2 curves are drawn showing the relationship between these two properties at each of the five water contents for each of the three flours.

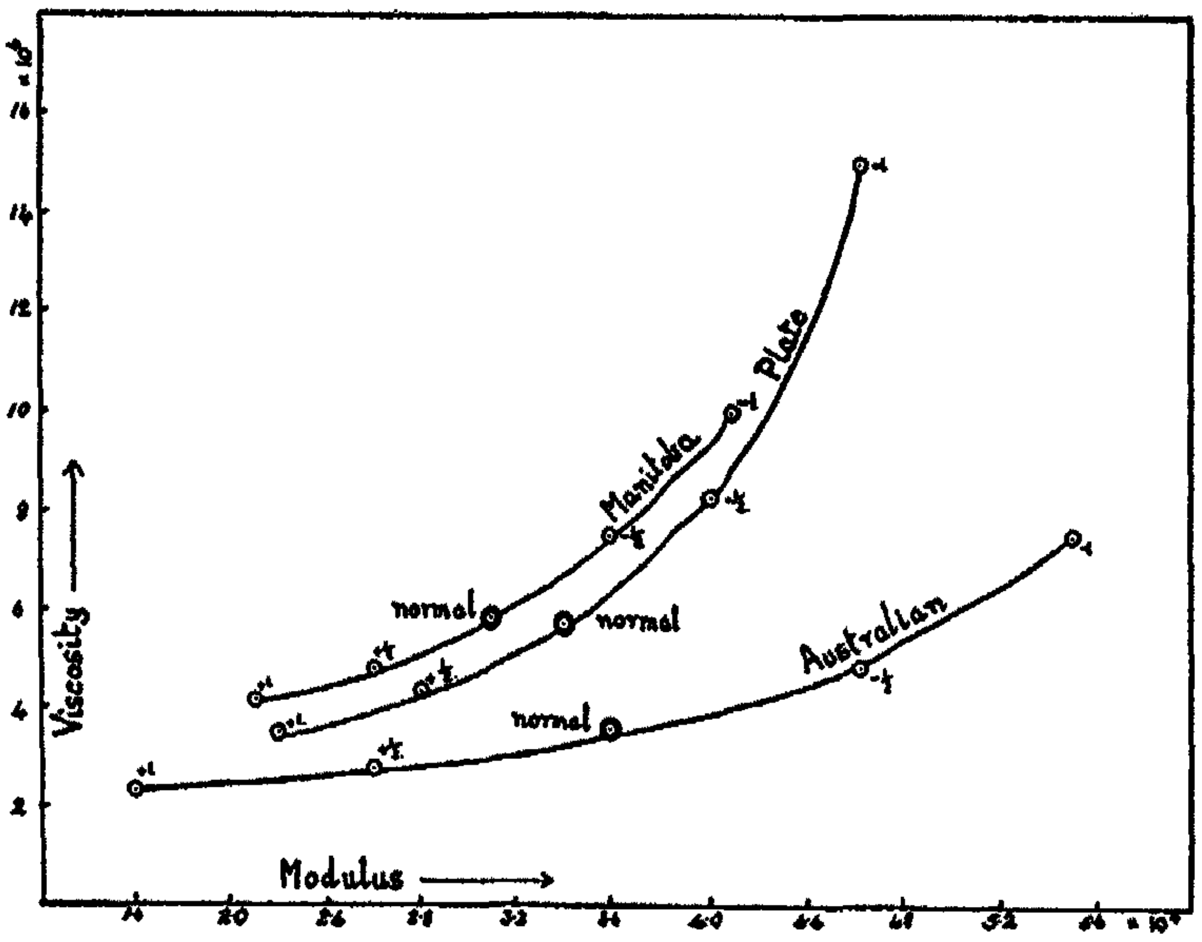

Fig. 2. The effect of water content of dough on the viscosity and modulus

An examination of these curves shows that with each flour both viscosity and modulus fell with increasing water content and vice versa. The relative effects on these two properties were not the same, and differed from flour to flour. The effects of a change of 2 gallons in water content on viscosity and modulus are given in table 3, the figures representing the difference in values for the driest and wettest doughs expressed as a percentage of the average.

These figures show that the effect both on viscosity and modulus was least in the case of the Manitoba, which is in keeping with the experience

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[11] One gallon per sack = 3.57 per cent on the flour.

of the baker that this type of flour has a much greater tolerance to changing water content than any other. The Plate flour differed from the Manitoba chiefly on account of the much greater effect of changing water content on viscosity, while in the case of the Australian both viscosity and modulus, and particularly the latter, were more markedly affected than in the case of the Manitoba. It is probable that a big upward change in viscosity with decreasing water content is of much less account in the bakehouse than a big increase in modulus, as the latter would make the doughs "dead" and lifeless (see later).

The three doughs of particular interest are the "normal" doughs, and it will be noticed that these doughs differed very considerably in viscosity, but only to a small extent in modulus. It is probable that the baker is unconsciously more influenced in choosing his water absorption by the moduli of his doughs than by their viscosities, and in consequence we may be able to use measurements of the former property as a means of determining correct water absorption. This point, however, needs much further investigation before it can be settled.

GENERAL CONSIDERATIONS

Although it is quite possible to make a dough from any flour whatsoever so that it shall have any desired viscosity or modulus (within wide limits), by using the appropriate amount of water, it is well known that a poor flour cannot by any such means be made to give a dough of satisfactory plastic and elastic properties. The reason for this is clearly seen from table 3. It is here apparent that if a "strong" flour dough (Manitoba) is compared with a "weak" (Australian) at the same viscosity, the modulus of the strong flour is much lower than that of the weak. If the comparison is made at the same modulus value, the strong flour has by far the greater viscosity. The intermediate Plate flour falls between the two extremes. This suggests that the relaxation time (η/n, see paper I) is of primary importance. This suggestion has been amply verified. It is, of course, clear that we cannot regard relaxation time as a constant of a dough, since it varies with both stress and deformation, but it has become increasingly evident during the course of this work that if doughs are compared under similar conditions of stress and strain, and if these conditions approximate as closely as possible to those obtained in the commercial dough, a comparison of relaxation times ("viscosity-modulus ratios") gives a primary measure of the differences in flour quality (although as is shown later, many other factors have to be taken into consideration as well). In paper I it is suggested that "the dough contains elastic elements which form a connected structure... (which elements) are not joined securely, but slide past one another whenever a sufficient stress is operative. The viscosity which has been determined is mainly governed by the behaviour of a plastic film by which the elastic elements are connected. It is quite possible that the elements are capable of complete elastic recovery, but there is at present no criterion for testing this. The time of relaxation is a characteristic of the connected structure as a whole and its value is as much determined by the elasticity of the elements as by the viscosity associated with their plastic junctions. . . . In relating these deductions to the known structure of the dough, one may safely identify the elastic elements with the protein part of the flour."

When a dough rises under the action of yeast, it is advantageous for as high a percentage as possible of the deformation to be elastic (recoverable). Non-recoverable deformations imply flow of the cell-walls, leading to their rupture, and collapse of the dough due to inability for it to hold its shape, resulting in a loaf having large and badly shaped holes, a poor volume, and bad over-all shape. Big elastic extension resulting from low modulus tends to produce a big rise when the dough is first placed in the oven, and hence big loaf volume.

TABLE 3

Effect of change in water content

	MANITOBA	PLATE	AUSTRALIAN
Viscosity	83	124	106
Modulus	64	70	105

The property by which an extended dough on release recovers a high percentage of its extension, is called by bakers "spring." It is clear that the extent to which the dough fails to return to its original length after such an extension will depend on how far the elastic elements have slipped past one another. This depends on the amount of friction between them, which, as we have seen, corresponds to the viscosity of the dough (as normally measured). The higher the viscosity, the less the slippage. But the amount of slippage depends not only on the viscosity, but also on the internal stress set up in the elastic elements. If we think of these as coiled springs, it is easy to see that the "lighter" the springs (i.e., the lower their moduli), the less stress will be built up for any given extension, and hence the less will be the slippage for a given viscosity. Thus a dough showing good "spring" will have a relatively high viscosity and low modulus, whereas a dough having bad spring will have a relatively low viscosity and high modulus.

It is now clear why the baker attaches so much importance to "spring" in his doughs. Good spring means a high viscosity modulus ratio (big relaxation time), and, as already stated, this is (other things being equal) the primary characteristic of a good flour.

It is pertinent to enquire as to the significance of the extent of the variation of viscosity and modulus with stress, strain, and stress history for different flours. Experiment has shown that even widely different flours show a very similar degree of elastic hysteresis, and no marked differences in their elastic after-effect behavior. As explained in paper III elastic after-effect is important in that unless attention is paid to eliminate its effect, it is liable to interfere seriously with the correct determination of viscosity.

TENSILE STRENGTH

In the bakehouse occasional doughs are encountered which "tear" badly during the baker's manipulation and during the rising of the doughs under the pressure of the gas generated inside them. Such doughs are said to be "short" and bake into unsatisfactory bread. Owing to the tearing, excessive gas leakage occurs which results in poor loaf volume, and the actual tearing gives the outside of the loaf a ragged appearance. In addition, the insides of such loaves easily crumble when pressed with the fingers. It thus appears that for such flours tensile strength is also a factor of major importance. This property is now being investigated.

AGING AND FERMENTATION OF DOUGHS

In the process of bread making the doughs are kept for some hours before baking into bread. Not only do their handling properties depend on the length of this period, but the type of bread also shows considerable variation.

In order to determine the changes with age in the physical properties of such doughs, and to find what connections exist between these changes and bakehouse behavior, a series of flours was obtained which had been previously examined by the baker. The doughs were made up with the same ingredients as had been used in the bakehouse and were kept at 27°C., samples being taken at hourly intervals for viscosity and modulus measurements, which were made at room temperature.

The data obtained on four of these flours, a No. 1 Manitoba, a No. 3 Manitoba, a Barusso Plate, and a South Australian, are given in table 4, and curves drawn from these data are given in figures 3, 4, and 5.

It will be noticed that no data are given for freshly made doughs. This is because of the difficulty of obtaining reproducible measurements on them. Rapid changes take place during this initial period and are probably connected with the rate of absorption of water by the flour. After one-half to one hour these effects disappear, and the physical properties then change in a normal and regular fashion.

In the case of the above four flours, the changes in physical properties were almost linear functions of time.

TABLE 4

Effect of fermentation on viscosity, modulus, and the η/n ratio

FLOUR	TIME IN HOURS	VISCOSITY × 10^4	MODULUS × 10^4	η/n RATIO
No. 1 Manitoba	1.23	3.97	3.16	126
	2.12	3.82	3.02	120
	3.05	3.79	3.21	118
	4.93	3.32	2.99	111
	6.00	3.27	3.21	102
	6.93	3.25	3.09	105
No. 3 Manitoba	1.10	3.25	2.61	124
	2.03	2.84	2.37	120
	3.08	2.68	2.53	105
	5.02	1.88	2.18	86
	6.07	2.04	2.18	93
	7.03	1.83	2.03	90
Barusso Plate	1.18	3.33	3.53	94
	2.03	3.46	3.47	100
	3.13	2.83	3.23	87
	5.02	2.56	3.08	83
	6.00	2.45	2.76	89
	7.07	2.07	2.39	89
Australian	1.07	2.52	3.21	78
	2.05	2.18	2.92	74
	3.00	1.97	2.82	70
	5.00	1.39	2.32	60
	6.13	1.00	2.06	48
	7.00	0.76	1.58	48

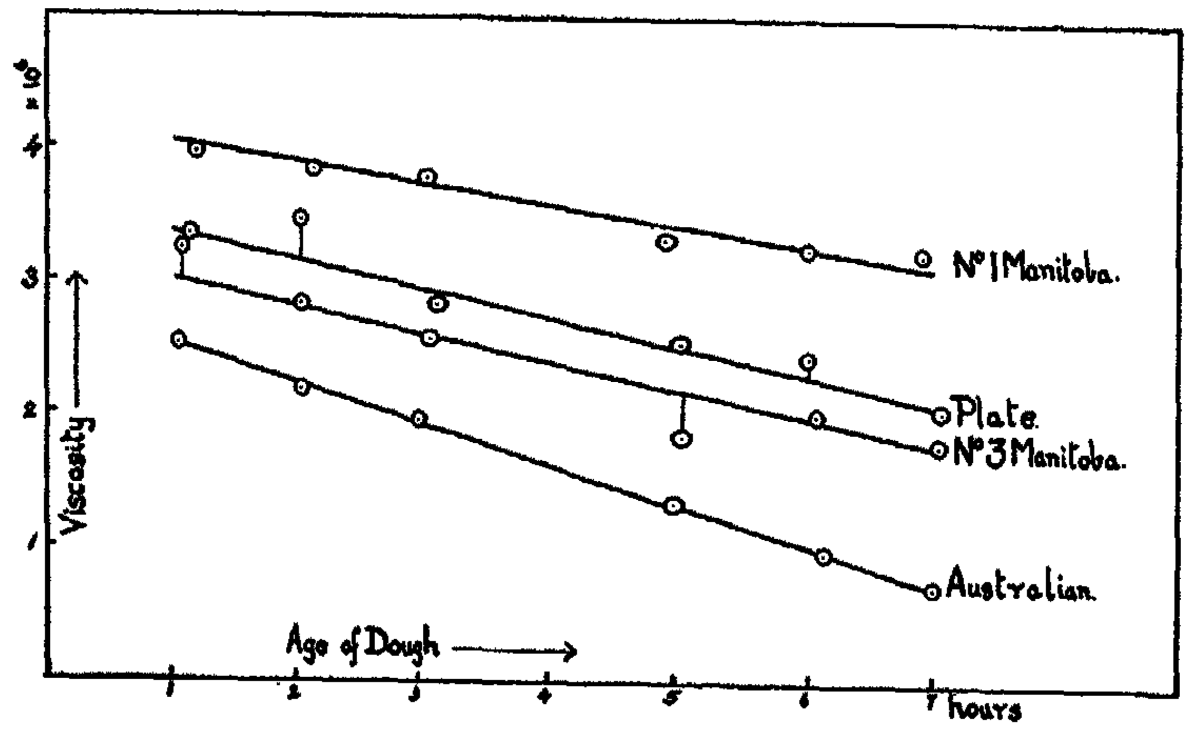

FIG. 3. The effect of age of the dough on the viscosity

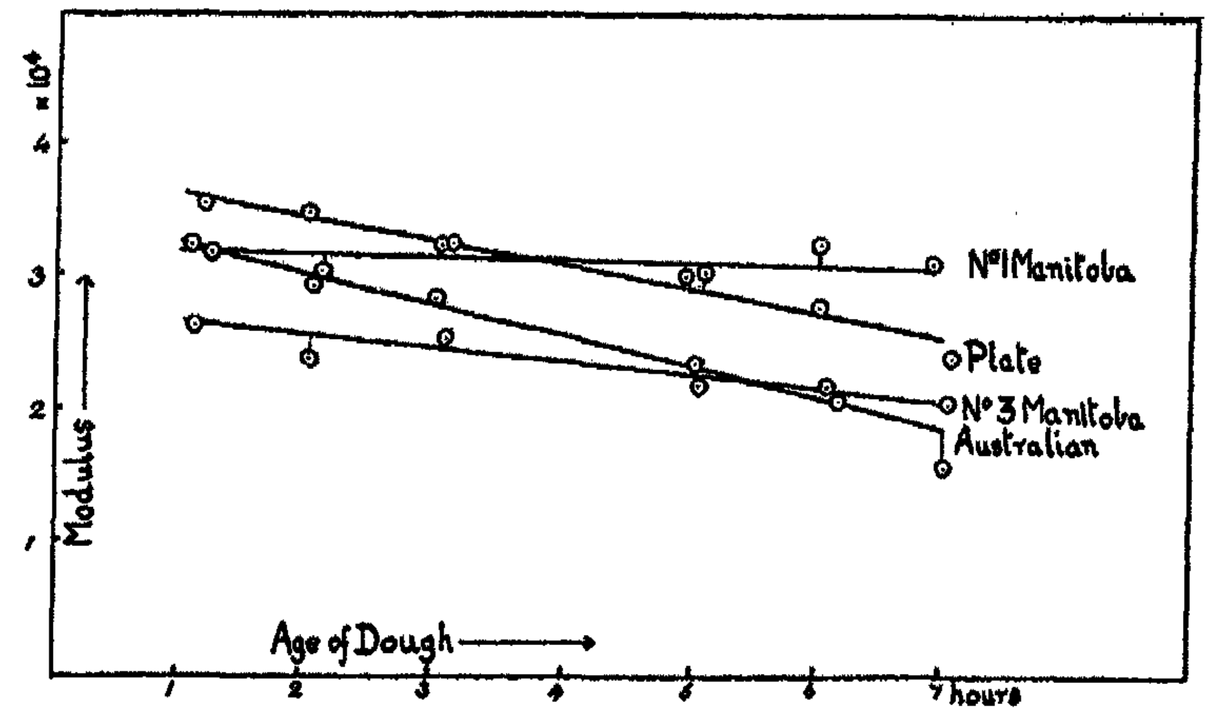

FIG. 4. The effect of age of the dough on the modulus

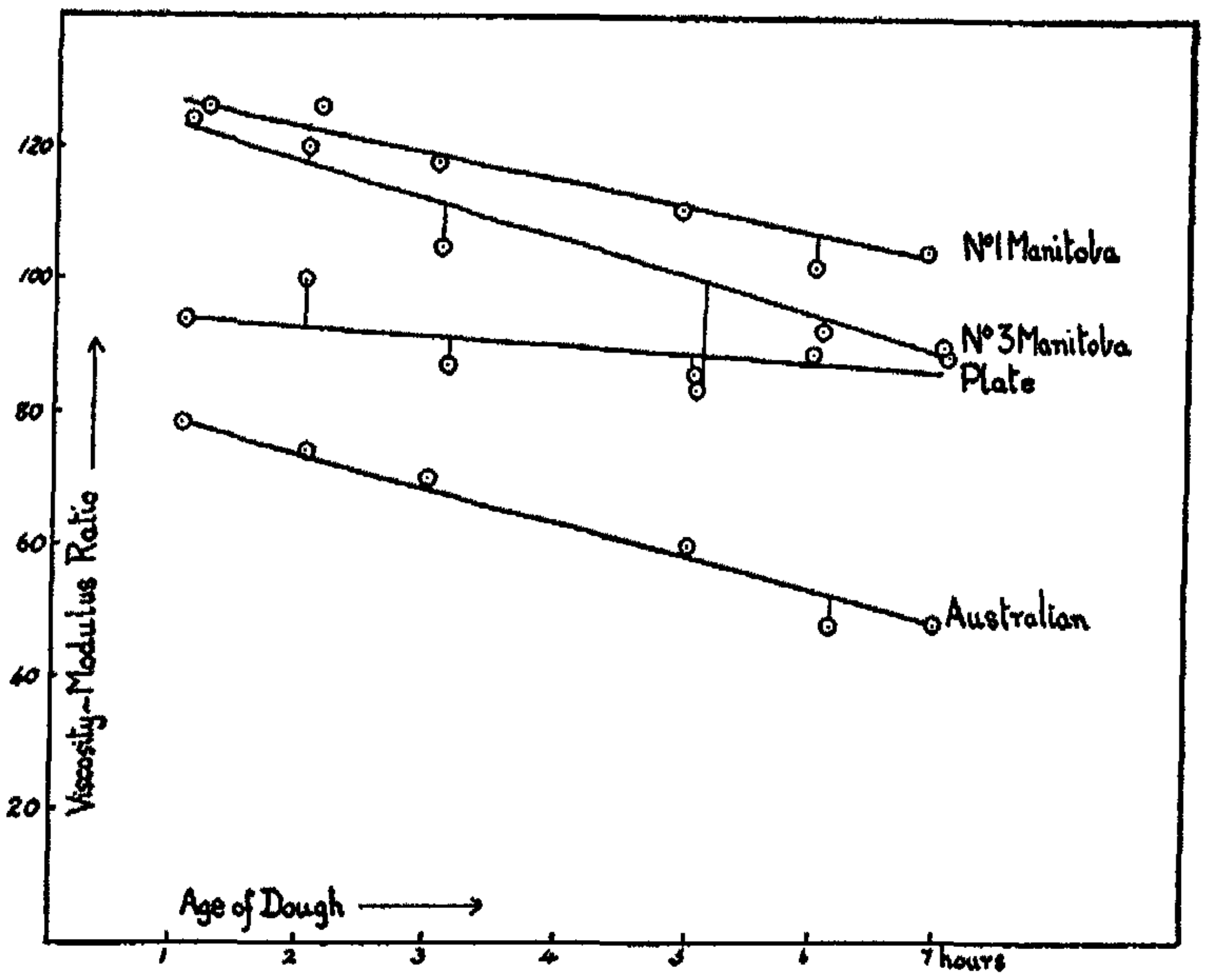

FIG. 5. The effect of age of the dough on the viscosity-modulus ratio

The data given in table 5 have been obtained from the curves (see figures 3, 4, and 5). An examination of the data shows that both viscosity and modulus fell with time of fermentation, and that in the case of each flour the viscosity fell more rapidly than the modulus, resulting in the ratio of these two properties also falling with increasing time.

In attempting to correlate these changes with the changes which took place in the handling properties of the doughs in the bakehouse, we were at once confronted with the fact that the baker reported that the No. 1 Manitoba dough improved in body and spring as fermentation progressed, that the Plate remained unchanged, and that the No. 3 Manitoba and Australian doughs became softer with increasing time.

TABLE 5

Change in physical properties with time

FLOUR	VISCOSITY AT		ACTUAL DECREASE	PERCENTAGE DECREASE
	1st hr.	7th hr.		
No. 1 Manitoba	4.05×10^6	3.17×10^6	0.88×10^6	22
No. 3 Manitoba	3.01×10^6	1.83×10^6	1.18×10^6	39
Plate	3.37×10^6	2.12×10^6	1.25×10^6	37
Australian	2.84×10^6	0.77×10^6	2.07×10^6	70

FLOUR	MODULUS AT		ACTUAL DECREASE	PERCENTAGE DECREASE
	1st hr.	7th hr.		
No. 1 Manitoba	3.19×10^4	3.05×10^4	0.14×10^4	4
No. 3 Manitoba	2.66×10^4	2.04×10^4	0.62×10^4	23
Plate	3.62×10^4	2.55×10^4	1.07×10^4	30
Australian	3.23×10^4	1.87×10^4	1.36×10^4	42

FLOUR	VISCOSITY-MODULUS RATIO AT		ACTUAL DECREASE	PERCENTAGE DECREASE
	1st hr.	7th hr.		
No. 1 Manitoba	127	104	23	18
No. 3 Manitoba	123	89	31	28
Plate	94	87	7	7
Australian	79	48	31	39

This improvement or toughening is associated by bakers with good quality. Several flours which have shown this response to fermentation in the bakehouse have been examined in the laboratory, and in every case both viscosity and modulus have been found to decrease with aging; in fact, no flour has yet been examined which showed a rise in either property during fermentation. It has been noticed, however, that those flours which have been reported as toughening in the bakehouse, were those which showed the smallest fall-off in physical properties when examined in the laboratory.

In the actual stretching of the dough during hand manipulation by the baker, dough does toughen,[12] but this happens with all flours, and in addition the effect disappears on resting. The toughening the baker speaks of in connection with good quality flours only, is considered by him to be due to the action of fermentation.

Careful tests have now been carried out in the bakehouse in which freshly made doughs were compared with fermented doughs made from the same Manitoba flour, which the baker considered had toughened. When the doughs were moulded side by side, one in each hand, and then allowed a few minutes to rest, it was reported by the baker that when tested by "feel" the older dough was very slightly the softer. It thus appears that bakers have been mistaken in their impressions that certain doughs toughen during fermentation.

When a series of replicate doughs is made from the same flour and allowed to ferment for varying times, it is found that with increasing time the volume and crumb quality of the bread at first improves, and then falls off. This improvement is considered by the baker to be due to what is called the "ripening" of the dough, the actual time to obtain maximum improvement varying with the amount of yeast, and with the type of flour used. "Strong" flours like Manitoba require much longer fermentation for optimum results than "weak" flours like English or Australian. Increasing the amount of yeast in the dough decreases the time of ripening.

Since viscosity, modulus, and relaxation time all fall consistently as the dough ages, it is difficult to explain the initial improvement in bread quality with time of fermentation in terms of the changes taking place in these physical properties.

The decrease in rigidity modulus with time is in itself desirable, but since it is the ratio of viscosity to modulus which is of primary importance in determining flour quality, the general result would be expected to be a fall-off, and not an improvement in bread quality. Also, if a fall in both of these physical properties were desirable, then a similar improvement in bread quality to that which takes place with fermentation could be brought about by using more water in the dough. This is not so, and even when the baker adds too much water to the flour, he still gets an improvement in bread quality with increasing fermentation time.

Although this improvement or "dough ripening" may be partly due to changes taking place in some physical property other than viscosity or modulus, it is possible to account for it on purely mechanical lines. Before a good loaf can be made, the necessary cell structure has to be built up in the dough, and this cell structure must be determined by the number and distribution of the yeast cells. Now normal bakehouse mixing is comparatively crude, and in consequence this distribution is probably anything

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[12] See paper II, figure 6.

but uniform. Owing to the activity of the yeast, however, the dough swells, and this probably helps to spread the yeast cells. In addition, at various stages of fermentation, the baker knocks the gas out of the dough and moulds it up, thus again helping towards more uniform distribution. During fermentation the yeast cells multiply, and thus as time goes on the gas-producing centers increase in number.

If the above picture is correct, and it is the building up of the necessary cell structure which determines how much fermentation is required for any flour to give its best bread, then it should be possible to cut down this time by the use of more yeast and/or thorough mixing. That this is so is well known, and it has moreover been verified experimentally by us.

During fermentation we therefore have two processes going on side by side, an improvement due to the multiplication and better distribution of the yeast, and a falling-off in bread-making quality due to the decrease in value of viscosity and relaxation time. The improvement due to the yeast appears to be comparatively independent of the physical properties of the dough. With a good quality flour such as Manitoba, the fall-off in physical properties is so slight that good bread is produced over a large range of time, while on the other hand the fall-off in physical properties is so great with a poor quality flour like English, that the best bread is produced early, and is followed by a rapid fall-off in quality.

Returning to the data in table 5, the No. 1 Manitoba had the highest initial viscosity and showed the smallest decrease in this property with time. This flour also had the highest viscosity–modulus ratio either after one or after seven hours. This is all in keeping with the general quality of the flour as shown in the bakehouse, where it behaved as by far the best of the four.

The No. 3 Manitoba, however, had a much lower initial viscosity and a much greater fall in this property with time. This low viscosity was accompanied by a low modulus, so that the initial value of the ratio of these two was high, although it fell considerably with time. This flour was not up to standard for its grade, and although it produced bread of excellent volume (low modulus) the best loaf was "thrown" relatively early, and the later loaves had much poorer "crumbs," owing to the fall in viscosity.

The Plate flour had a much higher viscosity than the No. 3 Manitoba throughout the seven hours, but this was accompanied by a rather high modulus. The ratio was lower than that for the No. 3 Manitoba at the beginning of fermentation, but decreased very little, so that at the later times the two flours approached one another in this respect. The Plate was a very good sample for its grade and gave its best bread late. The bread was of good volume, and would probably have been better if the flour had been given more water at dough making. By increasing the water content, however, the viscosity would have been lowered, so that although the best bread would probably have had greater volume, it would have been made earlier, and might have had a poorer crumb structure.

The Australian flour with its low initial viscosity, low viscosity-modulus ratio, and considerable fall in both with time, would be expected to be much the poorest flour of the four, and this was found to be so in the bakehouse.

So far we have only dealt with doughs containing yeast. This ingredient is necessary to produce the gas which builds up dough structure, but has it any other function in bread-making?

Tests have been carried out in which the physical properties of doughs with and without yeast have been compared. The general results of these tests show that in small amounts such as are used in commercial bread-making, the effect of the yeast on the viscosity and modulus of the dough is probably not great enough to be of importance in the bakehouse. Very large amounts of yeast do affect viscosity, for example, in one case 8 per cent yeast lowered the viscosity from 3.6×10^6 to 2.9×10^6. The effect on the modulus and on the rate of change of either property with age of the dough was, however, insignificant.

CONCLUSIONS

1. Viscosity and rigidity modulus appear to be of major importance. The viscosity must be high enough to prevent undesirable flowing-out of the dough, but on the other hand the modulus must be low, to allow big elastic expansion under the relatively low pressure of gas inside a fermenting dough. The relaxation time (which is the ratio of these two properties) is perhaps the most important single criterion of quality.

2. The water content of a dough determines the magnitude of its viscosity and modulus, and it is desirable that variations in water content should have as small an effect on these properties as possible, thus helping towards making the flour more fool-proof in the bakehouse. Whether water absorption is important in other ways, apart from financial considerations to the baker, is not known.

3. The degree to which viscosity and modulus change during the aging of the dough is of the utmost importance. The fall in viscosity with time is probably a major factor in determining the fermentation tolerance of a flour, and not only is the absolute rate of fall of this property important, but equally so is its relative rate compared with the rate of fall of modulus, since this determines the fall in relaxation time.

4. Tensile strength is a major factor in determining the extensibility and gas-holding properties of a dough, and this is of the utmost importance, since a deficiency in these properties ruins the quality of a flour even when other factors are up to standard.

5. Stickiness is important in affecting the dough's handling properties; the dough must not be too sticky to work over that range of moisture best suited to its other properties, nor should excessive stickiness develop during fermentation.

6. It is realized that such properties as work-hardening, structural viscosity, elastic hysteresis, and elastic after-effect must play their parts in determining the behavior of dough in the bakehouse, but although their significance is not yet fully understood, it is certain that they are only of secondary importance in determining the relative values of different flour samples except perhaps in certain abnormal cases.

7. It is considered that measurements of the physical properties of doughs, as far as possible in absolute units and under standard reproducible conditions, should lead to a far better appreciation of flour quality than any number of empirical tests, and should afford a sound basis for the control of quality in flour.

SUMMARY

Methods described in earlier papers for measuring the viscosity and rigidity modulus of flour doughs have been extended and developed.

The physical properties of dough are markedly affected by excessive handling, either during the preparation of the dough itself or during the preparation of the test piece. The methods used have therefore to be carefully controlled.

Viscosity and modulus measured under standard conditions of stress and strain both decrease with increasing water content or with increasing age of the dough.

Good bread-making quality is associated with a relatively high viscosity and low modulus; the relaxation time, i.e., viscosity-modulus ratio, therefore appears to be the chief single criterion of quality.

Yeast in small amounts has little effect on viscosity or modulus, and its importance in bread-making appears to be entirely due to its gas-producing activities.

Tensile strength is a major factor in determining the extensibility and gas-holding properties of a dough, but work on this property is still at too early a stage to be discussed.

Stickiness is an independent property which can be roughly measured. Its principal importance lies in its effect on the handling properties of the dough.

The investigations have proceeded far enough to show definite relations between the physical properties of flour doughs and their bread-making qualities. It is suggested that it is along these lines that further insight into the nature of flour quality will be obtained.

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LIQUID AMMONIA AS A SOLVENT. V

METALLIC SOLUTIONS

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This field has been ably reviewed by Johnson and Meyer (7), Johnson and Fernelius (6), Kraus (8), and Franklin (4), so that references to the literature need not be cited here. The experimental data of liquid ammonia solutions of metals is explained by a theory—namely, the dissociated metal theory—which we consider open to question. In liquid ammonia some metals, lithium, sodium, and potassium in particular, are claimed to dissociate to give a metallic cation and an electron which is solvated in dilute solutions. In more concentrated solutions even the existence of free electrons is claimed to account for the enormously low resistance of the solutions. The theory may be summarized into two equations:

$$M = M^+ + e^-$$

where M represents Na, K, etc., and

$$e^- (NH_3)_n = e^- + nNH_3$$

The "solvated electron" is used to explain the anomalous conductance data, vapor pressure data, photoelectric properties, transference values, the blue color of the metallic solutions, electrolysis, and absorption spectra.

In this paper we shall report a number of experiments which directly conflict with the "dissociated metal" theory, and also give our interpretation of the data in the literature.

EXPERIMENTAL

Electrolysis

A dilute solution of ammonium chloride was electrolyzed at −60° to −80°C., using small platinum electrodes. A blue color was detectable on the cathode surface. This blue color does not exist at the boiling point of liquid ammonia. Furthermore the evolution of hydrogen at the cathode shows that very little metallic ammonium is being formed. The small amount of blue color, however, must be due to the presence of metallic ammonium. Other data lead us to believe that the ammonium metal exists in the solution as $NH_4(NH_2^-)_x$. When a pure mercury cathode was used, with only a trace of ammonium chloride present as an electrolyte, no gas was liberated at the cathode, but there was a large amount of gas evolved at the anode. This we interpret to mean that ammonium metal is plated out and forms ammonium amalgam. A part of the cathode surface was a deep blue color during the plating process. When the amalgam was removed, it decomposed and hydrogen was liberated. NH_4 was first prepared in (l)NH_3 solutions by Moissan (9) and Rich and Travers (11). The ammonium amalgam resembles the ammonium amalgam prepared in aqueous solutions.

We then used sodium amalgam (unsaturated amalgam) as a cathode, and the only electrolyte present in the liquid ammonia was the small amount of sodium amide formed by reaction of the sodium in the amalgam with the ammonia. This solution was a very poor conductor, and it was necessary to use 220 volts across the system with the electrodes only a few centimeters apart. As soon as the current was applied blue streamers shot out from the cathode toward the anode. The speed of these particles is so high, a centimeter per second, that most of their energy must be supplied mechanically by surface tension effects and gas formation. Polarization causes the sodium and ammonium to plate out locally. The metal forms a colloidal particle and then moves away. Before reaching the anode the blue became fainter, and bubbles of hydrogen appeared which rose to the top of the liquid. There is no gas evolution at the cathode surface. In our discussion we will explain how the blue color is due to a colloid, that is, free metal with adsorbed amide ions. This negative particle is pulled away from the cathode by the applied potential. Out in the solution it becomes electrically an unstable sol. The hydrogen is produced by the decomposition of the ammonium metal, two molecules of ammonium metal giving two molecules of ammonia and one of hydrogen. According to the dissociated metal theory the blue color would be due to a solvated electron, but the decomposition of this ion could not give gaseous hydrogen. The liquid ammonia solution containing the sodium amalgam was perfectly colorless before the current was applied.

Reactions

Sodium reacted very rapidly with ammonium chloride at room temperature. At low temperature, about −70°C., there is practically no reaction. The rate of the reaction was determined by the volume of hydrogen given off per unit of time. At room temperature, roughly 5 cc. of hydrogen was produced per minute. At the low temperature ten hours was required to produce 1 cc. The reaction rate is easy to follow qualitatively by the disappearance of the blue color. Ionic reactions should reach equilibrium very rapidly, but a reaction with a metal with adsorption interfering would be relatively slow. The reaction

$$NH_4^+ + e^-(NH_3)_n = (n + 1)NH_3 + H$$

would certainly proceed very rapidly and

$$2H \rightarrow H_2$$

is known to go very rapidly with the production of much heat.

Schlubach and Ballauf explain the deficit in the hydrogen evolution by the formation of ammonium metal. They observed that only 35 per cent of the theoretical hydrogen was given off when ammonium chloride acted upon potassium solutions in liquid ammonia at −70°C. (12).

Pure mercury was added to blue, unsaturated solutions of sodium in liquid ammonia. The mercury was shaken with these solutions for several hours. The solutions were in sealed glass tubes; some of them were kept cold and some were allowed to react at room temperature. As soon as the formation of amalgam stopped, as judged by hardness and swelling, the amalgam was removed to dry tubes and the solvent ammonia allowed to evaporate. From these solid amalgams ammonia and hydrogen were liberated. When this latter decomposition took place the amalgams softened and decreased in volume.

Tyndall cone

A blue solution of sodium in liquid ammonia in a closed tube was allowed to settle carefully so that the undissolved metal and the sodium amide precipitated fell to the bottom. Dilute solutions prepared in this manner always showed a Tyndall cone.

Dialysis

Several membranes were found which were not attacked rapidly by liquid ammonia. Sodium and amide ions would diffuse through these membranes. A commercial viscose product was very satisfactory. Metallic sodium was placed in such a bag and suspended in a glass cell between platinum electrodes. Ammonia was condensed in the cell and bag. The sodium dissolved, forming a deep blue solution in the bag and some sodium amide. The amide diffused throughout the cell, but there was no blue color outside the bag. Electrodialysis was then carried out, using 220 volts. With this large potential no blue color could be pulled outside the bag. Sufficient sodium and amide ions were dialyzed to make the solution a poor conductor. This we consider as good evidence that the metal exists as a colloid.

Photoelectric properties

Kraus' experiment on the photoelectric properties of a lithium solution is confusing, since he reports a positive as well as a negative charge of the electrometer. We tested the photoelectric properties of sodium solutions in a closed cell at a low temperature, so that the ammonia vapor pressure was only 1 to 5 mm. The electrodes were of platinum and the anode was about 6 mm. above the solution. No current was detectable in a sensitive galvanometer, even when a 220-volt driving force was applied. The experiment was performed under different light intensities with the same negative result. Under the same experimental conditions pure metallic sodium showed photoelectric properties. We found that unless extreme care is used to prevent it, the ammonia will condense on the wall of the cell and thereby produce an electrical leak between the solution and the anode. Such a leak may explain the data of Kraus.

Densities of solutions

We hoped to determine the densities of solutions of alkali metals and of salts as well as of their mixtures at 25°C. However, we found that the dilute blue solutions of sodium became colorless with gas evolution when sodium bromide was added. This cannot be interpreted as common-ion effect. Surely it is due to a breaking down of the colloidal system.

If concentrated solutions of sodium were used we obtained two layers, a dense blue solution which settled to the bottom like an oil and a less dense bronze-blue layer. These latter solutions are both stable for days.

The so-called solutions of alkali metals when saturated, as at the break in the vapor pressure curve, are not homogeneous in appearance, but are sludge-like.

These data we cannot explain by the theory of Franklin and Kraus, and therefore we are offering a colloidal metal theory. The colloidal theory was first suggested by Ostwald (10). He did not propose the existence of ammonium metal in the alkali solution and therefore he tried to explain only the blue color of the solutions.

THEORETICAL INTERPRETATION OF THE DATA IN THE LITERATURE

The authors think that the alkali metals are dispersed into colloidal particles when they come in contact with liquid ammonia. They are not dispersed to atomic or ionic dimensions. At the time of peptization the metal displaces ammonium metal from the liquid ammonia according to the reaction

$$M + NH_4^+ \rightleftarrows M^+ + NH_4 \qquad (1)$$

This makes the colloidal particle a colloid of an alkali metal and ammonium metal. The blue solutions can be obtained only in alkaline solution. It is impossible to prepare ammonia so pure that it will not destroy a part of the blue color when a dilute blue solution is added to it. We do not think that the disappearance of the blue color is due to reaction with water adsorbed on the glass container. The extent to which reaction 1 takes place depends upon the activity of the two metals, the temperature, and the presence of impurities. The ion which is adsorbed in the peptizing process is the amide ion. Consequently the colloidal micelle is negatively charged. The ammonium and amide ions come from the reaction

$$2NH_3 \rightleftarrows NH_4^+ + NH_2^- \qquad (2)$$

K, the dissociation constant, of which is reported to be 10^{-33} in pure NH_3, but the reaction rate can be increased by removing the products as they are formed. The value of K increases very little with increase in temperature, but may increase markedly in the presence of alkali metals. The alkali ions from equation 1 are removed by the amide ions that are left from reaction 2 to the extent of the solubility of sodium amide. The reaction

$$M + n(NH_4^+, NH_2^-) \rightleftarrows nNH_4^+ + C(NH_2^-)_n$$

(where C represents colloidal metal) leaves NH_4^+ ions in the solution, that is, this reaction produces ammonium ions in solution equivalent to the colloid in solution until the electrical characteristics of the sol are such that the system is stable. The theories of metals have not been developed to the point where they would predict the appearance of a completely dispersed metal. Therefore we cannot judge the color of the solutions. On the other hand almost all colloidal solutions are colored, the color being dependent upon the particle size.

There is a point of apparent saturation of the metal in liquid ammonia. This fact can be explained using the colloidal metal theory if it is assumed that a certain definite concentration of amide ions is necessary to peptize the metal. This type of fact is known in the case of the peptization of iron in aqueous solutions of sodium hydroxide (2). The process of sol formation uses up amide ions, and when they are exhausted to a critical concentration then another type of colloid, such as the copper-colored colloid, is formed. The less active the metal the fewer amide ions required, and consequently the higher its solubility.

There is a very small change in the solubility of the metal with the change in temperature. There is obviously, therefore, very little heat of solution. This fact is very hard to explain using the metal dissociation theory. If this theory should be completely vindicated, the solution of a largely ionized substance with an infinitesimal heat of solution such as lithium in liquid ammonia would remain a remarkable phenomenon, since the solvation of the electron would give off a large amount of heat energy. The small change in the solubility with change in temperature is much more plausible in the light of the colloidal metal theory; however, little is known about the energy of peptization of metals. The heat of reaction 1 is also an unknown quantity.

There is a decrease in the vapor pressures of the solutions with increased concentration of the metal, that is fairly reproducible. Very little is known experimentally about the effect of colloids upon the vapor pressure of solvents, but theoretically the particles should serve as ions in the solution. Effectively we should have ammonium colloid in solution. If this is the case, then the vapor pressure data at least do not disprove our theory. Concentrated lithium solutions have very low vapor pressures,—much lower than Raoult's law could possibly explain. If the limiting factor is not the concentration of the lithium ion, but the adsorption of NH_3 on the metal atom as NH_4 and NH_2^-, then one does not have to postulate a large ratio of adsorbed particles per lithium atom to have a large percentage of the solvent molecules tied up. The enormous increase in activity with a slight dilution cannot possibly be due to metallic dissociation; it must be due to a decrease in the per cent of solvent adsorbed.

The molecular weight and activity of sodium have been calculated from the change in the vapor pressure with concentration of the metal. The molecular weight approaches less than 20 in dilute solutions. All of the calculations in the past have been carried out either to find out what value of molecular weight is approached at dilute solutions or to determine what the activity of the metal is, assuming Kraus' theory. The facts might be considered as some substantiation of the "dissolved and dissociated metal" theory if more were known about the extent to which salts dissolved in liquid ammonia obey Raoult's law. One of the authors (5) has carried out the determination of the activity coefficient of salts in liquid ammonia at room temperatures and has discovered marked deviations from Raoult's law. The facts about the change in the vapor pressure of the solution with change in metal concentration can be accounted for qualitatively on the basis of the formation of ammonium colloid electrolyte in solution and the marked departure from Raoult's law which would be expected in solutions of such electrolytes. The charge on the colloid particle per atom of sodium determines whether or not Raoult's law could be considered as being obeyed by these solutions. By postulating the necessary charge on the colloid (not unreasonable charges) the data could be accounted for assuming Raoult's law.

The disappearance of the blue color around the anode when a dilute metallic solution is electrolyzed we explained by the oxidation of NH_4 to NH_4^+, which immediately reverses equilibrium 2 with an increase of NH_3 or solvent in the anode compartment. Amide ions are plentiful, since they were adsorbed on the colloidal metal. This, of course, removes the source of the blue color, and since the ions are removed the solution immediately around the anode will become a very poor conductor. Furthermore, at the same time NH_4^+ is removed from the anode by attraction to the cathode. This explains the absence of visible products of electrolysis at the anode. The NH_4^+ will be an excellent carrier of electricity in its parent solvent (1). The cathode compartment will become richer in the blue color because

$$NH_4^+ + e \text{ (furnished by cathode) } \rightleftarrows NH_4$$

and secondly because of transference of the existing blue particle. The ionic atmosphere of the fast moving ammonium ion will contain the colloidal negative particle $C(NH_2^-)_x$. If the sodium or potassium ion is present it will also act as a positive carrier. These ions are not liberated, however, since this would require a greater potential. By our theory or the accepted theory, the free metal simply would ionize again. Reaction 1 will go to completion only at the anode. If the concentration of the solution is increased the conduction should become more and more metallic, owing to the increase in concentration of the colloidal particles. This will also shift the fraction of the current carried by the positive and negative carriers. The NH_4^+ will carry most of the current in the dilute solutions, since the larger colloid particle is less mobile, but when the concentration reaches a certain limit, the mobility of the negative carrier will no longer be an important factor, as the conduction is by electronic transfer (3). As a higher metal concentration is reached one would expect the ionic concentration to decrease and consequently the apparent molecular conductance. The two will not necessarily counterbalance, and we should expect a minimum conductance. This minimum has been reported by all investigators in the neighborhood of 0.05 normal. Our theory would predict a higher conductance than for a similar concentration of a salt because of the nature of the conductors.

The specific conductance of mercury is approximately two and six times, respectively, the specific conductance of a saturated and a 2 N solution of sodium. Preliminary experiments in this laboratory showed that the resistance offered a D.C. current by a sodium solution is decreased roughly 50 per cent by the addition of sodium chloride. This must be explained by an orientation of the conductors into a complicated "bridge-work" which favors electronic conduction. The addition of a common ion should decrease the concentration of the free electron, and therefore greatly increase the resistance of the solution.

There is a large positive temperature coefficient of the electrical conductivity that does not decrease in value with increasing temperature. This fact cannot be explained using the dissociated metal theory. Ordinary electrolytes have their conductivities pass through a maximum. Metals have negative coefficients. The increasingly large positive temperature coefficient is just what the colloidal metal theory would predict. There would be an increasing number of collisions between metal particles, and consequently an increasing percentage of metallic conductivity with the increase in temperature.

The absorption spectra of the alkali metal solutions are the same. This interesting fact can be interpreted as indicating that the colored component of all these dilute solutions is the solvated electron. The colloidal metal theory postulates that the metal colloid, especially in the dilute sol, is largely ammonium metal with a core of alkali metal. In the formation of a dilute colloidal solution the procedure is quite uniform. Since the composition of the outer part of the colloidal particles (no matter what alkali metal is dispersed) is the same, since the methods of formation of the various colloids are the same, and since all of the colloids are quite stable, it follows from the principle of Hevesy that the rotational-vibrational-electron-transition spectra should be quite similar for the sols of the various alkali metals.

The densities of the solutions of the alkali metals in liquid ammonia pass through a maximum density with increasing concentration of the metal. The change in density of these solutions is credited to the existence of electrons associated with ammonia molecules. It seems to the authors that this explanation is especially weak, since metals are in general very dense and the more dense the metal, the greater the possibility of having more free electrons per atom. It is well known that colloids greatly change the internal energy of liquids under most circumstances. Colloids lower the surface tension of a liquid; thereby they decrease the force compressing a liquid, and the density would be decreased. The charged forces in the colloidal solution will increase the free space between particles, so that the density will be decreased. The density of the free ammonium metal is an unknown factor, but we predict that it is less than 0.5 g. per cubic centimeter and that it will therefore decrease the density of the solution. The relative amount of free ammonium metal will change with the concentration of the dissolved metal as well as the closeness of packing of the adsorbed particles, so that the magnitude of the final density cannot be estimated. The closeness of packing should be greater for potassium than for sodium; therefore, one would predict a smaller increase in volume for potassium than for sodium solutions. This prediction agrees with the experimental data. The metallic ionic radii of sodium and potassium are of the wrong relative order to explain it, and the "solvated electron" should have the same density in both solutions.

Metals such as platinum will catalyze the decomposition of NH_4 through the removal of H_2.

$$2NH_4 = 2NH_3 + H_2$$

Therefore the rate of formation of sodium amide from liquid ammonia and metallic sodium will be increased. If the metal furnishes a colloidal metal surface under the experimental conditions, it will be a better catalyst for the reaction.

SUMMARY

1. Methods for producing ammonium metal in liquid ammonia have been described. Its presence in alkali metal solutions has been proven.
2. The "dissociated metal" theory of metallic ammonia solutions is critically discussed, and a colloidal metal theory is outlined to explain the properties of these solutions.
3. The alkali solutions are evidently mixtures, and therefore the physical data are not capable of interpretation on the basis of the well-known laws of physical chemistry.

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THE FLOCCULATION OF THE STANNIC OXIDE SOLS

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INTRODUCTION

The character of the stannic oxide sols was first studied methodically in the laboratory of Zsigmondy, where Franz (1) compared the peptizing ability of potassium and sodium hydroxides for the so-called alpha and beta stannic oxides. Varying amounts of alkali were used to give sols with stannic oxide: alkali ratios of 2, 10, 25, 50, and 100. It was found that potassium hydroxide was definitely better than sodium hydroxide, and that the β-oxide gels were more difficult to peptize than the α-oxide gels.

Heinz (2) investigated the flocculation of the sols from freshly precipitated or α-stannic oxide by certain salts whose action was found to be divided into two groups. Salts such as sodium chloride, sodium nitrate, sodium sulfate, and sodium acid sulfate produced flocculation at greater concentrations than those of the type of calcium chloride, barium chloride, aluminum chloride, and silver nitrate, the concentrations of the latter group in each case being the same as that of the peptizing alkali for the standard 10-cc. samples. Also, upon the addition of water the first group was reversible while the second was not. These values are summarized by Kruyt (van Klooster) (3).

From these experiments, Zsigmondy (8) assumed that peptization of stannic oxide by alkali formed particles of hydrous stannic oxide with stannate ions adsorbed to give the double layer. Discharge of the double layer was accomplished by the first group of electrolytes, whereas the second group produced insoluble stannates and destroyed the double layer to produce precipitation.

Varga (5) and Wintgen and coworkers (7) investigated the conductivity and transport of the sols to obtain an idea of the structure of the micelle expressed as the number of SnO_2 atoms associated with K_2O. It was shown that for sols with a SnO_2:KOH ratio of 50, about 15 per cent of the potassium stannate molecules occurred in the mobile part of the double layer, while 85 per cent were outside.

This work was undertaken to prepare similar sols, using ammonium hydroxide and lithium hydroxide as peptizing agents for the α-stannic oxide gel in addition to potassium hydroxide and sodium hydroxide, and to determine flocculation values for salts of potassium, ammonium, lithium, and sodium. It has been shown that the α- and β-forms of the stannic oxide are not allotropic forms but have the same crystal structure; the terms so used mean freshly formed and aged products, respectively (6).

EXPERIMENTAL

In the preparation of potassium hydroxide, Küster's (4) method was used. Water vapor acted slowly upon metallic potassium to give a 40 per cent alkali solution, which was diluted to about 1 normal and standardized.

The sodium hydroxide solution was made up to about 17 normal, when the carbonate was precipitated, and after decantation and filtration was diluted to 1 normal. Lithium hydroxide was prepared in like fashion.

The electrolytes used for flocculation were of analytical purity and were made up to exactly 1 normal.

The stannic acid gel was prepared after Zsigmondy and Heinz (2). 7.300 g. of $SnCl_4 \cdot 5H_2O$ (Eimer and Amend) was dissolved in about 1 l. of doubly distilled water and allowed to remain in a dark place at room temperature for a period of three days, until the white gelatinous precipitate had settled. The supernatant liquid was siphoned off and more water was poured in its place. The oxide was washed repeatedly until the off-coming liquid gave no test for chloride and the conductivity reached 4×10^{-6} mhos. The last washings were made with distilled water having a conductivity of 1.0×10^{-6}. In all, fifteen to twenty washings were required.

The gel was transferred gradually to a 250-cc. volumetric flask, allowing the water to separate until the volume of gelatinous oxide was approximately 235 cc. It was found that if the total volume of gel was below 220 cc., difficulty in peptization was experienced, particularly in sols with SnO_2:KOH ratios of 25, 50, and 100.

The calculated amount of alkali necessary for peptization was pipetted into the flask, the volume made up to exactly 250 cc., and the flask shaken vigorously until the peptization was complete. Finally, the solutions were transferred to Pyrex flasks and tightly closed with stoppers coated with tin foil.

In the sols of ratio 50 and 100, heat had to be applied. Sols of ratio 50 required heating for at least an hour, while those of ratio 100 required heating for five hours on a water bath. The sols of ratio 100 for lithium hydroxide could not be prepared, and for sodium hydroxide the stability was less than twenty-four hours. Likewise the ammonium hydroxide sol of the same ratio was not any more stable than that of sodium hydroxide.

The sols of ratio 2 were clear and without color, except in the case of lithium hydroxide where a decided blue was evident, reminiscent of the appearance of dilute mastic sols. The colloids with stannic oxide: alkali ratio of 10 were transparent but possessed a slight tinge of blue, noticeably more intense in the ammonium hydroxide sol. The Tyndall effect was more evident in the sols of ratio 25, while the sols in which the ratio of stannic oxide to alkali was 50 and 100 were opalescent and opaque, respectively. The sols of ratio 2 and 10 were basic in reaction, showing the presence of free alkali; in the ammonium hydroxide sol of ratio 2, an odor of ammonia was present.

Sols of ratios 2, 10, and 25 were stable after remaining in a cupboard for more than a year without any outward change, except that the SnO_2–NH_4OH sol of ratio 2 became opalescent. Sols of ratio 50 for ammonium hydroxide and lithium hydroxide and all of ratio 100 were found, after four months, to have settled into an opaque layer, below a transparent layer. On shaking, these sols became apparently homogeneous, but after some time again separated into layers.

In performing the flocculation experiments, a certain technique was always employed. The sols were chosen so that two weeks had elapsed since the beginning of hydrolysis to the gel form, with the exception of the sols of ratio 100, which were used as soon as peptized.

The peptized sols were pipetted into Pyrex test tubes of dimensions 16 x 150 mm. The initial concentrations of stannic oxide in the sols were adjusted so that 8 cc. of sol contained 0.666 milliequivalent of stannic oxide, while the alkali used for peptization was such as to give the proper ratios.

Eight cubic centimeters of the sol was pipetted into a Pyrex test tube previously steamed. The precipitating electrolyte in varying amounts was added to the test tubes and the total volume made up to 10 cc. in each case. The tubes were closed with tin foil-covered stoppers, inverted ten times, and set in a rack. After exactly 1 hour the tubes were inspected for flocculation. The procedure was carried out at approximately 25°C., and the colloids were shielded from sunlight throughout. A sol was considered as flocculated when a clear ring was seen below the whole of the meniscus, separating the opaque gel.

Usually series of experiments were run with the interval between quantities of added electrolyte made less until the accuracy was in the vicinity of 5 per cent. In sols of higher ratios, the accuracy was somewhat below 10 per cent.

Alcohol numbers were determined with 5 cc. of sol as standard. A quantity of alcohol (purified with silver oxide) that would cause precipitation in 1 hour was the alcohol number. This precipitation was reversible, as were those with the electrolytes.

Experiments were carried out on the flocculation by electrolytes of alcohol-containing sols. A total volume of 15 cc. was used, excepting in sols of ratio 2. Five cubic centimeters of alcohol were added to 8 cc. of sol in the test tube, and the remainder made up with electrolyte and water. The procedure was otherwise identical with the flocculations with electrolytes.

RESULTS

The results are shown in tables 1 to 4.

TABLE 1

Flocculation value of stannic oxide-potassium hydroxide sols

Milliequivalents per 10 cc. (total volume)

SALT	SnO_2 : KOH RATIO				
	2	10	25	50	100
$NaCl$	1.8	0.85	0.145	0.070	0.085
$NaNO_3$	1.9	0.80	0.140	0.070	0.085
Na_2SO_4	2.2	0.75	0.155	0.075	0.085
KCl	>10	0.85	0.155	0.080	0.090
KNO_3	>10	0.90	0.160	0.075	0.090
$LiCl$	0.48	0.30	0.105	0.075	0.080
Li_2SO_4	0.50	0.32	0.105	0.070	0.085
NH_4Cl	1.5	0.44	0.155	0.065	0.080
Alkali per 10 cc.	0.333	0.066	0.0266	0.0133	0.0065
C_2H_5OH (in cc.) to 5 cc. of sol	3.08	>500	>500	>500	

TABLE 2

Flocculation values of stannic oxide sols

Milliequivalents per 10 cc. (total volume)

SALT	SnO_2 : ALKALI RATIO					
	SnO_2-NaOH sols		SnO_2-LiOH sols		SnO_2-NH_4OH sols	
	2	10	2	10	2	10
$NaCl$	1.7	0.75	0.85	0.60	1.7	0.65
$NaNO_3$	1.8	0.70	0.85	0.45	1.15	0.60
Na_2SO_4	2.0	0.65	1.20	0.85	>10	0.65
KCl	>10	0.70	>10	0.80	>10	0.80
KNO_3	>10	0.80	>10	0.80	>10	0.75
$LiCl$	0.43	0.30	0.30	0.28	0.52	0.31
Li_2SO_4	0.42	0.30	0.35	0.30	0.56	0.31
NH_4Cl	1.40	0.40	0.80	0.88	1.5	0.40
Alkali per 10 cc	0.333	0.066	0.333	0.066	0.333	0.066
Alcohol number	1.36	>500	1.70	>500	>250	>500

TABLE 3

Flocculation values of stannic oxide–potassium hydroxide–alcohol sols

Milliequivalents per 15 cc.

SALT	SnO_2 : KOH RATIO			
	2	10	25	50
	4 cc. C_2H_5OH added	5 cc. C_2H_5OH added	5 cc. C_2H_5OH added	5 cc. C_2H_5OH added
NaCl	0.13	0.135	0.055	0.009
KCl	0.10	0.160	0.065	0.009
LiCl	0.12	0.110	0.060	0.008
NH_4Cl	0.52	0.125	0.070	0.009
$NaNO_3$	0.090	0.105	0.070	0.007

TABLE 4

Flocculation values of stannic oxide–alkali–alcohol sols

Milliequivalents per 15 cc.

SALT	SnO_2 : ALKALI RATIO					
	SnO_2-NaOH sols		SnO_2-LiOH sols		SnO_2-NH_4OH sols	
	2	10	2	10	2	10
NaCl	Flocculated by C_2H_5OH	0.12	Flocculated by C_2H_5OH	0.100	0.140	0.125
KCl		0.14		0.125	0.190	0.135
LiCl		0.10		0.100	0.140	0.125
NH_4Cl		0.12		0.110	0.155	0.160
$NaNO_3$		0.15		0.110	0.140	0.120
C_2H_5OH	2	5	2	5	5	5

DISCUSSION

From the results of peptization, it is seen that potassium hydroxide produces the sols most easily, whereas lithium hydroxide gives the greatest difficulty. Sodium hydroxide and ammonium hydroxide rank in between, in the order named. The order is evident if the time for conversion of the opaque gel of the hydrous oxide to the sol is compared qualitatively, and then it is seen that potassium hydroxide produces a clear sol by mixing thoroughly for a few seconds, sodium hydroxide taking a longer time, while ammonium hydroxide requires several minutes. The stannic oxide–lithium hydroxide sol of ratio 2 has not been obtained without the bluish appearance that is characteristic of the usual sols of ratio 50. Likewise it is seen in the sols of stannic oxide : alkali ratio equal to 100, that the potassium hydroxide sol is relatively stable, while the lithium hydroxide sol could not be prepared at all.

From the flocculation experiments, it is seen that the cations may be arranged in the order of decreasing flocculation values: K > Na > NH_4 > Li. The order is most evident in sols with a stannic oxide:alkali ratio of 2 and 10, less so for 25, and not at all for 50 and 100, where flocculation values are approximately the same for a single sol and for different sols of like ratio. This order however, is the reverse of the lyotropic series for hydrophobic sols such as Oden's sulfur and arsenic trisulfide sols and for the molybdenum pentoxide and vanadium pentoxide sols (3), but agrees with the usual series for emulsoids and is thus interpreted as a salting-out effect, so that hydration is a factor for consideration.

It is known that lithium has the greatest amount of water attached to the ion, while potassium has the least. Also it is indicated that the stannic oxide colloid is composed of particles of hydrous SnO_2 and has hydrophilic properties.

In considering the mechanism of peptization, the alkali has the effect of breaking up the gel into small particles of SnO_2, with the adsorbed stannate formed by chemical reaction giving rise to the double layer. As more alkali is introduced, the particles are expected to be smaller and the opacity of the gel to decrease with the greater dispersion. It is seen, however, that the ion with the greatest amount of water associated with it peptizes the stannic oxide gel with the greatest difficulty and conversely, so that the water of the ion may be viewed as a hindrance. From the experiments of Zsigmondy and Glixelli (9), it is found that compressing the micelles as in ultrafiltration or even ordinary filtration increases the amount of alkali needed for peptization, probably owing to the removal of some water from the gel, and this process may be responsible for the aging of the α-oxide into the β-form.

In the flocculation experiments, it is noted that the ion with the greatest amount of water coagulates the sol with the greatest ease. Possibly an equilibrium of the water carried with the ion has to be considered. By lowering the hydration, the stability factor induced in hydrophilic colloids is reduced so that smaller amounts of cation will be needed to discharge the double layer to cause coagulation. If an ion that tends to dehydrate a particle be used for peptization, smaller flocculation values for these sols are expected as compared with sols of an alkali ion with a smaller water mantle. This seems to be borne out by the sols prepared from lithium hydroxide.

The flocculation values for the sols from potassium hydroxide are not in numerical agreement with the values of Heinz (2) because of a difference in technique.

The alcohol numbers show that sols of ratio 2 are coagulated while the others are not. Since the stannates are only slightly soluble in ethyl alcohol, it may be that the alkali stannate has its solubility reduced so as to cause flocculation, which is reversed with the addition of more water.

It is seen that the addition of alcohol lowers the amount of electrolyte needed to bring about coagulation. The lyotropic series is evident in the presence of alcohol, but the flocculation values are smaller. The values of table 3 express this clearly. Table 4 shows a decrease for the sols prepared with sodium hydroxide and lithium hydroxide, except that for these two sols no values were obtained for the ratio 2 because of coagulation by the alcohol alone. Stannic oxide–ammonium hydroxide sols are less sensitive to alcohol. Alcohol may be said to possess two actions,—one of reducing the solubility of the adsorbed stannate, the other a dehydrating action.

SUMMARY

Stannic oxide sols were made with lithium hydroxide and ammonium hydroxide so that the ratios of stannic oxide to base varied from 2 to 50, together with those peptized by potassium hydroxide and sodium hydroxide, previously studied by Heinz (2).

Flocculation values were determined with salts of potassium, sodium, lithium, and ammonium, and also for the same sols containing alcohol.

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LIESEGANG RINGS OF MANGANESE SULFIDE. II

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Some years ago Chatterji and Dhar (1) published an account of a number of experiments on the formation of Liesegang rings in many gelatinous media, among them silica gel. They reported that they obtained rings of cadmium and antimony sulfides in this gel. However, they gave no detailed directions as to concentrations and other conditions under which the rings formed.

For some years we have been interested in the formation of bands of metallic sulfides in gels, and have recently tried to form bands of such sulfides in silica gel. The experiments were not altogether successful, as only faint rings were obtained, and these under varying conditions which could not always be reproduced. The rings so formed were those of zinc, cadmium, and antimony sulfides. As we had obtained excellent bands of manganese sulfide in gelatin (4), we tried to form rings of this substance in silica gel. We found the best procedure to be the following: Commercial water glass was diluted to a density of 1.07 and was mixed with an equal volume of 0.5 *N* acetic acid. This mixture, which reacted acid toward litmus, was poured into test tubes 1 in. in diameter until they were three-fourths full, and then the whole was saturated with hydrogen sulfide gas. The tubes were then allowed to stand until the contents set to a gel, after which the upper portion of the tube was filled with a solution of manganese chloride. The concentrations of manganese chloride giving the best bands were from 0.5 to 1 molar. The bands obtained are shown in figure 1. The rings usually obtained were like figure 1 a and b, but occasionally rings of the type shown in figure 1 c were produced. As far as the concentration of the manganese chloride is concerned, there seemed to be no difference whether the fine banded or coarsely banded ones were obtained, so the cause of this difference must have lain in the nature of the silica gel or in the concentration of the sulfide ion in it, as it is obvious from the method of preparation that the latter could not be accurately controlled. Attempts to control the concentration of the sulfide ion by using definite concentrations of sodium sulfide were unavailing, as this rendered the medium alkaline and the mixture failed to gel.

APPLICATION OF HUGHES' DIFFUSION THEORY

E. B. Hughes (3) has recently developed a theory of the formation of Liesegang rings, based on diffusion. The theory is essentially in accord with that originally advanced by Wo. Ostwald, but Hughes has worked out mathematically the conditions for the formation of a new band on the basis of the upper electrolyte diffusing in and building up a sufficient concentration to attain the solubility product of the insoluble substance anew. In order to apply the equations it is necessary to determine the distance between bands and the time of the formation of each band.

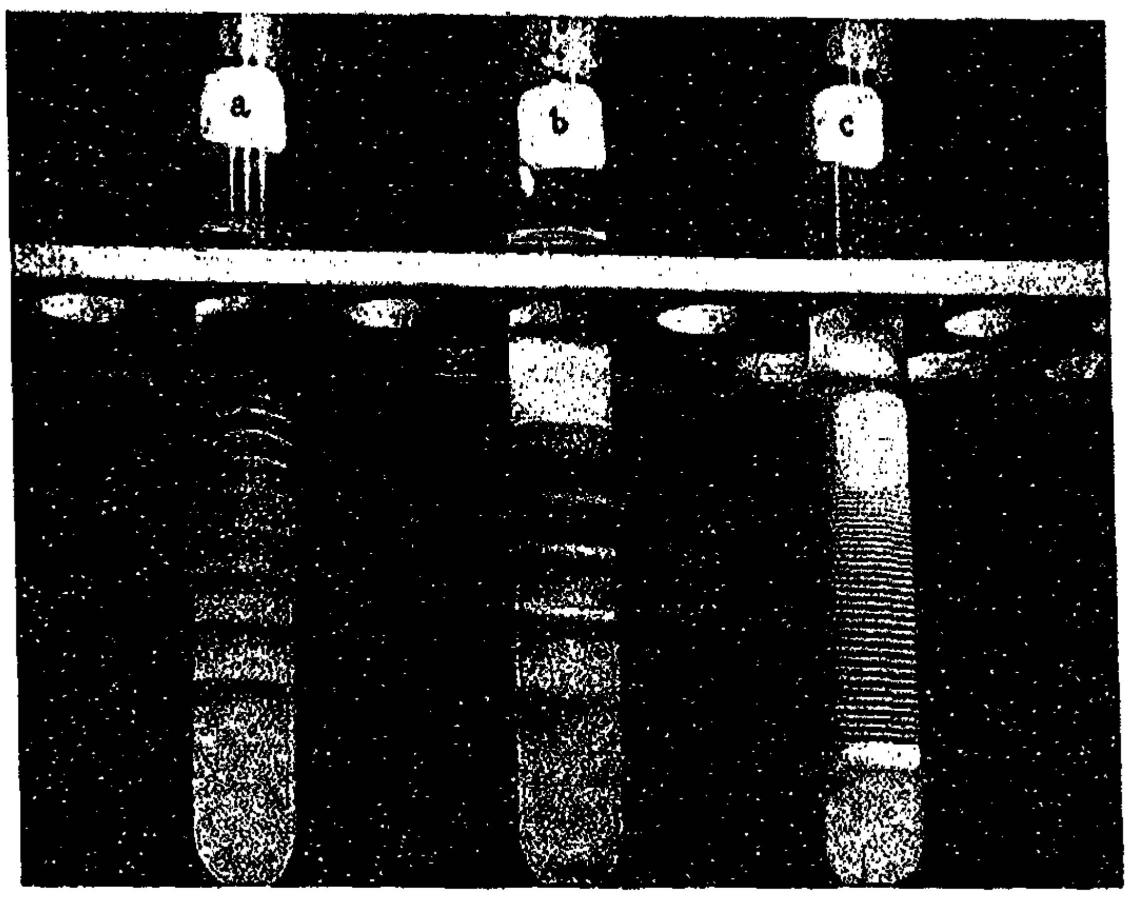

FIG. 1. Liesegang rings of manganese sulfide in silica gel

As bands of manganese sulfide could be reproduced very readily in gelatin, bands of this material and in this gel were used to test the theory. As seen in figure 1 a and b, a heavy precipitate of manganese sulfide was always produced at the junction of the two electrolytes. The thickness of this precipitated area varied greatly in different cases, and in general was greater the greater the difference in concentration of the Mn^{++} ion above from that of the S^{--} ion in the gel. The thicker this precipitated band, the more slowly the Mn^{++} ion diffused through it and the longer was the initial period before the first Liesegang ring formed. Another difficulty in measuring the time of formation of the bands was the long time consumed in completing the formation of the rings, viz., ten to twenty days. Naturally, therefore, some of the rings would form in the middle of the night, and the time of their formation would not be exactly fixed. However, since the time between the formation of successive rings was long, this error was small. On account of the varying thickness of the initial banded precipitate, the time was measured from the end of the formation of this band. The appearance of the rings in gelatin can be observed in figure 1 of the former article (5). The results obtained from two such experiments are given in table 1. In the first column are the distances of each ring from the point of beginning, and in the second column the time of the beginning of the formation of each band. h_n/h_{n-1} represents the distance of each band divided by the distance of the preceding band. $h/\sqrt{t}$ represents the distance of each ring divided by the square root of the time of its formation.

TABLE 1

Measurements made on rings of manganese sulfide

1 M $MnCl_2$; 0.15 M $(NH_4)_2S$				0.35 M $MnCl_2$; 0.15 M $(NH_4)_2S$			
h in cm.	Time in hours	$\frac{h_n}{h_{n-1}}$	$\frac{h}{\sqrt{t}}$	h in cm.	Time in hours	$\frac{h_n}{h_{n-1}}$	$\frac{h}{\sqrt{t}}$
1.45	14		0.3875	1.06	11		0.3915
1.85	24	1.276	0.3776	1.35	18	1.276	0.3182
2.35	38	1.270	0.3812	1.72	27.5	1.274	0.3280
2.95	54	1.255	0.4014	2.20	39	1.279	0.3523
3.70	82	1.254	0.4084	2.75	62	1.250	0.3492
4.45	116	1.203	0.4132	3.40	90	1.236	0.3584
5.25	162	1.180	0.4125	4.15	128	1.220	0.3668
6.20	217	1.181	0.4209	5.00	193	1.205	0.3599
7.35	280	1.184	0.4393	6.00	269	1.200	0.3659
8.80	400	1.197	0.4400	7.25	391	1.208	0.3667
Thickness of initial precipitate, 3 cm.				Thickness of initial precipitate, 1.9 cm.			

According to Hughes' theory the numbers in the last two columns should be constant. This is seen to be the case approximately. The numbers in the third column being approximately constant show that the rings are in geometrical progression, which has been found to be the case in most experiments of this kind. Many determinations of these values were made in other experiments, and the average found for rings of manganese sulfide of varying distances apart was 1.21.

Hughes has derived an equation[1] giving the value of this constant in

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[1] Equation (ii), Kolloid-Z. **72**, 213 (1935). To illustrate his theory he uses the results obtained by Morse and Pierce (Z. physik. Chem. **45**, 589 (1903)) with bands of silver chromate in gelatin. These bands were all complete in from one to one and three-quarters hours after the beginning of the experiment, and consequently results are to be expected differing considerably from those described here, where the time taken for the formation of a series was from ten to twenty days.

an independent manner, which requires for its solution the value of the solubility product of the substance forming the bands. The solubility product of manganese sulfide in water is 1.4×10^{-15}. Its solubility product in gelatin would have to be about 3.6×10^{-3} in order that Hughes' equation ii should have a value for K equal to 1.21. This of course is highly improbable. However, from the appearance of the bands when they begin to form, it is evident that the solution is highly supersaturated, for a band appears rapidly in voluminous quantity and then gradually increases in density and thickness. This seems to show that the sulfide ions build up a concentration considerably in excess of that required for the solubility product of manganese sulfide before a band begins to form. Furthermore, the strong adsorption of manganese[2] ions by the bands previously formed (2) delays the formation of a new band. For these reasons it is somewhat remarkable that the numbers in the fourth column in the table are as constant as they are.

SUMMARY

1. A method for obtaining Liesegang rings in silica gel is described.
2. Manganese sulfide bands in sillica and other gels are spaced approximately in geometrical progression, the multiplier having the average value of 1.21.
3. Although in general the bands of manganese sulfide are formed by a process of diffusion essentially in accord with Hughes' theory, the time of formation of the bands is considerably influenced by supersaturation and adsorption.

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[2] Analysis of the manganese sulfide precipitate, which composes the rings, shows an excess of manganese over sulfur of 25 per cent above that required for the formula MnS.

ACTIVATION OF REDWOOD AND ASH-FREE SUGAR CHARCOAL IN A CURRENT OF AIR

92-81

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It is difficult to ascertain from the literature[1] exactly what are the optimum conditions for the air activation of charcoal, or exactly what happens during the processes of activation. Attempts at activation in a current of air are easily frustrated by a lack of attention to detail or to conditions in different parts of the mass of the charcoal. Similarly, so numerous are the factors involved that occasionally an exceptional success is achieved which it may prove impossible to duplicate.

The present studies have been carried out over a series of many years, first with charcoal derived from redwood (*Sequoia Sempervirens*), as studied by Dr. F. Carlyle Harmon, and then by one of us (R.F.S.) with sugar charcoal, which is practically the only source of highly active, ash-free charcoal.

It early appeared that these results differed from the finding of Lamb, Wilson, and Chaney and their associates (6) that the optimum temperature for air activation lies between 350° and 450°C. We find indeed that there is a peak of activation at this temperature, but also find that an even more pronounced peak with still better activation occurs between 920° and 960°C. Above this, usually the activity of charcoal falls off very rapidly. However, the very best sugar charcoal ever obtained was that made by H. Greville Smith (8) in the chemistry department at Bristol University. He prepared a large sample by heating Kahlbaum sugar charcoal in a slow current of air at 1130°C., with an intermission required for repairing the horizontal Hereaus tube platinum resistance furnace. Its activity (81 per cent) equalled that of good activated wood or commercial charcoal. We find that the activity of charcoal activated at a particular temperature may be improved or impaired by subsequently submitting it to another temperature. Generally it is much improved by reactivating with air at the same temperature after an intermediate cooling to room temperature with exposure to air.

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[1] For a recent résumé of the patent literature see reference 5. For modern conceptions of the nature of activated charcoal, see references 5 and 1.

EXPERIMENTAL

Preparation of redwood charcoal

The redwood charcoal used for these determinations was made by carbonizing redwood strips 4 cm. wide and 0.7 cm. thick in an atmosphere of nitrogen at very low pressure at 450°C. The carbonized strips were crushed and only the pieces passing a 6-mesh but retained by a 10-mesh screen were used for activation. The original activity of this charcoal was 15.1 per cent, as determined by the percentage of iodine removed from 50 cc. of 0.2 *N* solution by 1 g. of 200-mesh carbon in 3 minutes.[3] The slow distillation of dry redwood yields a harder charcoal than the rapid distillation of wet material. Sapwood produced the hardest and light wood the softest charcoal. Carbon tetrachloride tests of activated redwood charcoal, whether from heartwood or bark, indicated that although highly satisfactory for sorption from solution, it has but little retentive value for gases, being only somewhat better than bone char.

Preparation of sugar charcoal

Five different grades of sugar charcoal were used in these experiments. These will be referred to henceforth as Nos. 1, 2, 3, 4, and 5.

Charcoals No. 1 and 2 were prepared from Baker's sucrose ("C.P. analyzed crystals"). Five pounds of sucrose were carbonized in an 18-quart aluminum kettle, the highest temperature attained being about 200°C. The charred mass was then removed to an aluminum pan, placed in an electric furnace, and the temperature raised to 400°C., being at 360° to 400°C. for 30 minutes. At the end of this period, the charcoal was cooled in air, ground to 20-mesh, washed three times in warm distilled water, drained, and dried for 15 hours at 105°C.

The first portion of this charcoal (No. 1) was not covered immediately upon removal from the furnace, and as a result there occurred a glowing of the charcoal that probably caused the temperature to go much above 400°C. The activity of this charcoal was 27.02 per cent before washing and 21.57 per cent after washing. The second portion (No. 2) was covered immediately upon removal from the furnace and then allowed to cool. Its activity was 3.53 per cent before washing and 8.84 per cent after, both activities being determined by the iodine method.[3]

Sugar charcoal No. 3 was also Baker's sucrose ("C.P. crystals"). It was caramelized or possibly carbonized in an aluminum kettle at 200°C., and

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[3] Standard method of determining "activity" (Chaney, N. K., Ray, A. B., and St. John, A.: Ind. Eng. Chem. **15**, 1248 (1923)). However, we have found that the results have a high temperature coefficient; thus, an "activity" determined as 7 per cent at 4°C. becomes 15.5 per cent at 25°C. and 27 per cent at 65°C. We have therefore measured at 20°C.

removed to porcelain crucibles; the latter were covered to keep out as much air as possible, and then placed in a muffle furnace and heated to 900°C. for 15 minutes. Upon removal from the furnace, sample No. 3 was chilled rapidly and stored in glass bottles. Its activity before being heated to 900°C. was 14.5 per cent, and after heating was 20.25 per cent. The ash content of these three sugar charcoals was less than 0.00 per cent.

Sample No. 4 was Kahlbaum's "charcoal from sugar" with an original activity of 14.5 per cent. Its temperature of formation is unknown. Its ash content was 0.12 per cent.

Sample No. 5 was prepared by C. I. Glassbrook by dropping pure sugar through crossed electric arcs operating at 400 volts and 6 amperes and at 100 volts and 26 amperes, respectively. After washing, it was a spongy, wet, black mass, with an activity of 14.7 per cent. After drying at 105°C., this fell to 5.8 and 6.4 per cent. Upon air activation at 920°C., two different specimens showed activities of 30 per cent and 20 per cent, respectively.

ACTIVATION OF REDWOOD CHARCOAL

The activities of the redwood charcoal after heating in an iron retort for 6 hours at a fixed temperature in a current of air at low pressure are shown in table 1 and figure 1. The results in this table indicate two maxima, one at about 368°C. and the other at 800°C. with a marked minimum between. Dr. Harmon suggested that the lower maximum might be due to combustion to carbon dioxide and the second to carbon monoxide. It appears more likely that these two peaks are connected with the fact that at these two temperatures different types (3, 12) of active charcoal are formed, both as regards sorption of alkali and as regards the order of the Traube series.

These results were repeated by H. W. Hobbie and then again by one of us (R.F.S.) to a substantially similar effect, with the additional information that very little difference was observed when the air was at 14 mm. or at atmospheric pressure. Furthermore, when redwood charcoal which had already been activated at temperatures between 370° and 770°C. and cooled in air, was heated in an atmosphere of nitrogen or helium, the activity was still further increased. A sample air-activated at 770°C. with a value of 33 per cent, upon heating to 920°C. in nitrogen showed a final activity of 64 per cent. Even charcoal which has not been activated but merely exposed to air at room temperature becomes moderately activated upon heating to 800° or 900°C. *in vacuo.*

As seen from table 1, the activated charcoal loses an appreciable fraction of its activity merely upon standing.

Three samples of Dr. Harmon's redwood charcoal were sealed in glass tubes with air at atmospheric pressure immediately after activation. At this time, their activities were 31.7, 34.5, and 56.6 per cent, respectively. The first had been activated at 722°C. at 14 mm., the second at 860°C. at atmospheric pressure, and the third at 685°C. in air and then again at 1000°C. in nitrogen. Twenty-eight months later these tubes were opened and the charcoals again tested. All three samples showed a distinct loss in activities, which were 18.06, 19.2, and 45.8 per cent, or a decrease of 43, 44, and 19 per cent, respectively.

TABLE 1

The activity of redwood charcoal heated for six hours at a fixed temperature in a current of air at low pressure

TEMPERATURE	PER CENT BURNED	"ACTIVITY"		PER CENT DECREASE
		Harmon	Sessions*	
340	16.5	30.7	24.3	21
368	22.5	37.9	28.8	24
400	32.8	32.8	27.1	17
514	30.0	24.9	15.7	37
590	27.5	23.7	10.5	56
720	35.0	20.6	7.6	63
730	26.5	19.6	16.0	18
800	36.5	37.6	29.8	23
865	36.0	36.1	37.6	
960	37.5	32.4		

* Original activity was determined by Harmon at the time of activation. Sessions' determinations were made after keeping four months in glass-stoppered bottles. One sample of Harmon's redwood charcoal with an original activity of 17.1 per cent was tested by one of us (R. F. S.) after standing for over two years in a corked tube and found to have an activity of 13.64 per cent, or a decrease of 21 per cent.

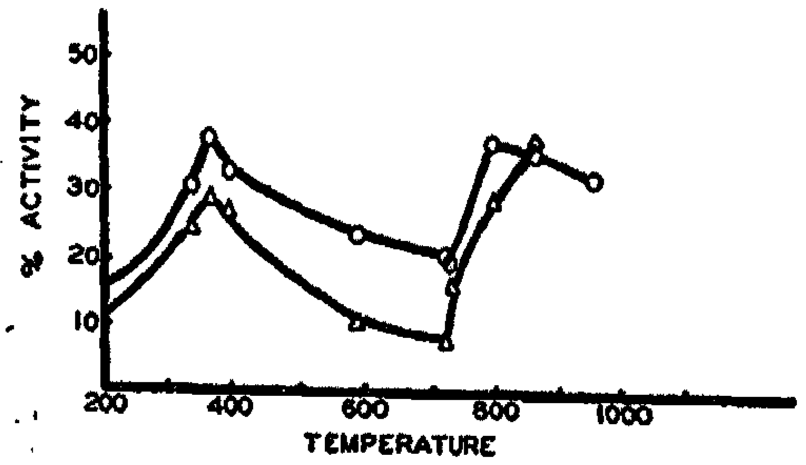

FIG. 1. Redwood charcoal. O, original activity; △, activity after four months

ACTIVATION OF SUGAR CHARCOAL

For temperatures below 1000°C., platinum- or nichrome-wound resistance furnaces were used. For those above 1000°C. a small inclined hydrogen arc induction furnace, and for the highest temperatures a large induction furnace with vertical graphite vessel were employed. Temperatures below 1100°C. were measured with calibrated thermocouples, those above with the standardized optical pyrometer.

Sugar charcoal may be made as highly activated as any wood charcoal. It also exhibits its optimum activation at just over 900°C.

The results of the air activation of sugar charcoals (Nos. 1, 2, and 4) are shown in figure 2. All except four of these results were obtained in a stationary furnace inclined at an angle of 30° at atmospheric pressure.

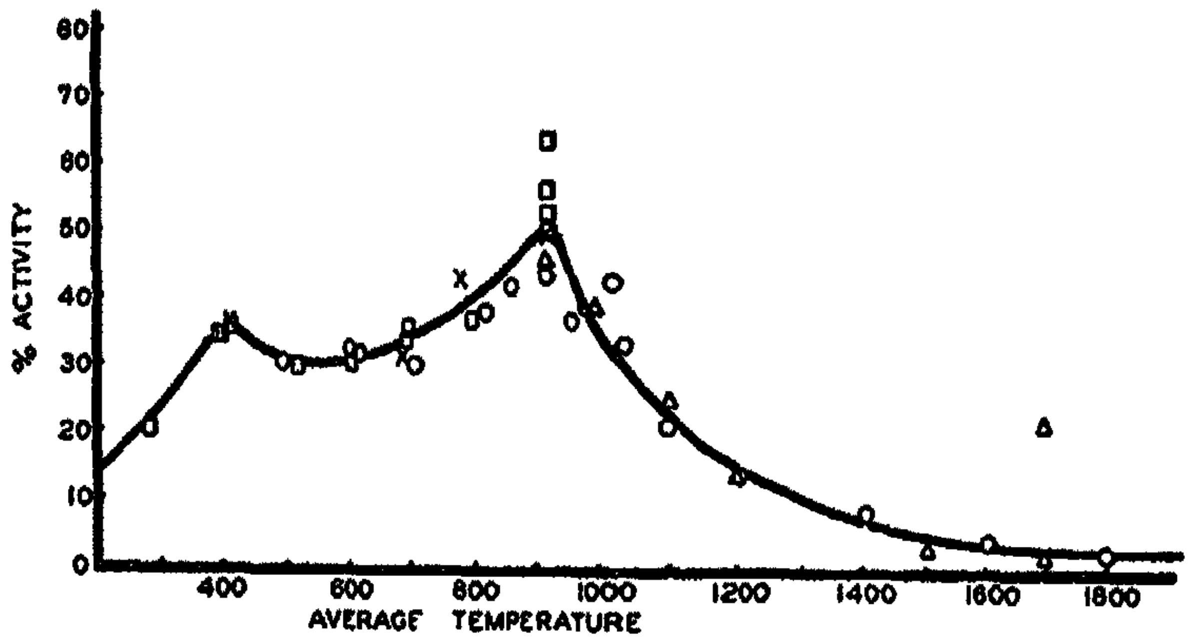

FIG. 2. Sugar charcoal. ○, charcoal No. 1 in inclined furnace; △, charcoal No. 2 in inclined furnace; □, charcoal No. 4 in inclined furnace; ×, charcoal No. 4 in horizontal rotary furnace.

Usually the heating lasted one hour, but in a few cases this was extended to from two to five hours. Usually the charcoal lost from 13 to 30 per cent of its weight. Four samples of charcoal No. 4 were activated in a horizontal rotary furnace (2), with results which fully confirm the existence of the two peaks. Two other experiments, not shown on the graph for lack of space, yielded 3.0 per cent at 2014°C. and 0.5 per cent activity at 2530°C., 14 per cent being burned in each case as in the experiment at 1804°C.

It is of great interest and some significance that a specimen of charcoal No. 1 that had been air "activated" by heating for 15 minutes at 2187°C., which reduced its activity from 21.6 per cent to only 3.0 per cent, upon being air-activated again for 80 minutes at 920°C. was restored to 6.1 per cent, with a loss of one-quarter of its weight.

A series of specimens of charcoal No. 2 were also activated in a stationary horizontal furnace, with results somewhat less satisfactory than in the inclined and rotary types, yet still showing a definite peak at about 920°C. These results are plotted in figure 3, which also shows two attempts to activate charcoal No. 2 in a stationary vertical furnace, with very mediocre success. All of the results shown in this figure were obtained after runs of approximately one hour at atmospheric pressure.

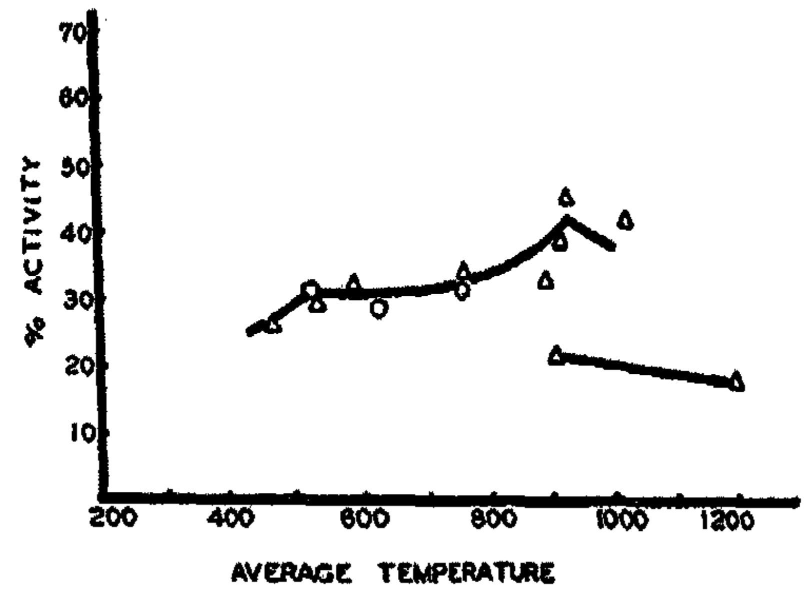

FIG. 3. Sugar charcoal in horizontal furnace. ○, charcoal No. 1; △, charcoal No. 2. Short lower curve shows results in vertical furnace.

TABLE 2

Nitrogen activation of sugar charcoal

TEMPERATURE	FURNACE	LOSS OF WEIGHT	ACTIVITY
°C.		*per cent*	*per cent*
500	Horizontal	14.0	14.6
600	Horizontal	22.0	28.2
697	Horizontal	27.0	24.2
793	Horizontal	30.0	22.5
894	Horizontal	29.0	22.2
949	Horizontal	29.0	12.3
1000	Horizontal	28.0	11.5
1190	Vertical	29.6	5.4
1600	Vertical	28.0	1.6

Similar heating in a current of nitrogen instead of air also activated charcoal No. 2 at temperatures up to 1000°C., but the activities shown in table 2 lie well below those given for air in figure 3. The activities fall from a peak value of 28.2 per cent at 600°C. to 1.6 per cent at 1600°C.

Charcoal No. 3, originally carbonized at 900°C., which has heretofore been thought to destroy the ability to be activated, showed a surprising degree of activation at 920°C. when one sample reached a peak of 58.5

per cent after being heated for three hours in an inclined furnace at atmospheric pressure. Other activities are mentioned in the discussion.

In a few tests of the activity of the charcoals in figure 3, using phenol instead of iodine, it was found that the values were parallel with those shown for iodine. Krczil (4) states that sorption of phenol likewise runs parallel with sorption of mercuric chloride and of benzoic acid.

DISCUSSION

The experiments indicate that charcoal is better activated in air at atmospheric pressure than in nitrogen. A good flow of air rids the charcoal of volatile matter and usually shortens the time of activation. In some experiments active charcoal, activated at over 900°C., on subsequent heating at 365°C. lost from one-third to one-half of its activity, whereas charcoal graphitized at 2187°C. was partially restored at 920°C. Again, a mixture of samples of charcoal No. 3, activated at 600° and 920°C., which then had an activity of 43.5 per cent, upon heating at 210°C. with 10 liters of air with 3.0 per cent loss of weight, lost activity, being reduced to only 30.5 per cent. Presumably the loss of activity which occurs on standing at room temperature is greatly accelerated at 210°C.

Temperature is apparently the most important determining factor in the degree of activation. It is also important that the charcoal lose at least 10 or 12 per cent of its weight. Further loss of weight is distinctly advantageous, but does not have so great an effect. Presumably, the shorter the time of heating, all other factors such as per cent loss in weight being kept constant, the better the activation, or, rather, the less the concurrent inactivation. At low temperatures loss of weight is slow or opposed by another concurrent process, so that, for example, in a series of 10-g. samples of charcoal No. 3, one at 255°C., over which was passed 3000 cc. of air in the course of one hour, neither gained nor lost weight, but yielded an activity of 22.4 per cent; at 450°C. 2 per cent was burned and the activity was 26.2 per cent. When 3 per cent loss of weight was brought about by using 10,000 cc. of air in 80 minutes at 210°C., the activity became 30.5 per cent. Five per cent loss at 695°C. gave 26.3 per cent activity and at 980°C. gave 35.0 per cent, while the use of 30,000 cc. of air at 600°C. gave a loss of weight of 23 per cent and an activity of 41.0 per cent. Here, clearly, the factor of initial loss of weight outweighs all effect of temperature. Then at 920°C. losses of 4, 10, 12, and 28 per cent in weight brought about with steadily increasing supplies of air (3000 to 28,000 cc.) gave activities of 29, 45, 46, and 58.5 per cent, although the respective times were 17, 120, 70 and 190 minutes. A temperature of approximately 920°C. for a period of one hour gave consistently good results in an inclined or rotary furnace. The most promising method is to heat the charcoal at 920°C. for two or even three periods of one hour each, with a period of about twelve hours at room temperature and exposure to air between each heating.[3]

Olin, Lykins, and Muro (10) have very recently described a series of peat charcoals activated "in different gaseous media" at temperatures between 450° and 925°C. There is a peak at 850°C. for adsorption of air or carbon dioxide or for velocity of cataphoretic migration. This activity peak at 850°C. is several times greater than at 450°C.

Roychoudhury (11) found that sugar charcoal was more active when activated in small quantities at 900°C. for four hours, instead of at 600°C. Longer heating greatly diminished the activity. Shorter periods were not studied.

Referring to figure 1, activated charcoal shows a large loss in activity merely on being kept in a stoppered bottle[4] or in a sealed tube. Such unused samples may lose from 30 to 60 per cent of their activity. This is in striking contrast to the constant activity preserved by activated sugar charcoal when it is sealed up with saturated organic vapors, showing no change even over periods of many years (9). The large adsorbed organic molecules serve as wedges to hold open the structure, whereas in the charcoal, merely exposed to enclosed air, the residual valencies of the carbon atoms, which must remain partially unsatisfied on account of steric hindrance (7), cause a shrinking or compacting of the porous structure.

CONCLUSIONS

1. There are two optimum temperatures at which sugar or redwood charcoal may be activated in a current of air, one at 350° to 450°C., and a still better one at 920° to 960°C.

2. Contrary to usual opinion or description, it has been found that sugar charcoal originally "carbonized" at 900°C. may still be activated. Activities as high as 58.5 per cent were obtained with sugar charcoal prepared ostensibly at this temperature. Sugar passed through the electric arc may then be air-activated.

3. When kept over a long period of time, even in sealed tubes, our charcoals show a decrease in activity of from 17 to 63 per cent. This is in great contrast to similar charcoal which has sorbed organic vapors and is kept in contact with the vapor. Then the charcoal loses none of its activity over a period of many years.

4. Although a stationary horizontal furnace may be used to activate charcoal with a fair degree of success, a stationary furnace inclined at an angle of 60° was found to give consistently better results, while a horizontal rotating furnace as used by Dubinin was the most promising of all.

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[3] For a more detailed examination of the effect of degree of burning see B. Bruns and O. Zarubina (Kolloid-Z. 64, 279 (1933)).

[4] See the similar observations of J. B. Firth (J. Chem. Soc. 119, 929 (1921)).

5. Charcoal attains a much higher degree of activity when activated in air than when merely heated in nitrogen or helium.

6. Temperature, loss of weight (especially the first fraction), and duration of heating are the most important considerations in activating charcoal in a current of air.

Our sincere thanks are due to the California and Hawaiian Sugar Refining Corporation Ltd., to the Air Reduction Corporation of Los Angeles, to the Western Precipitation Company of Los Angeles, and to Mr. J. C. Bauer for courtesies and facilities extended.

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THE MECHANISM OF THE PHOTOCHEMICAL REACTION BETWEEN BROMINE AND WATER

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The mechanism of the photochemical reaction between bromine and water, which yields hydrobromic acid and oxygen, apparently has never been studied. Several qualitative experiments, however, are given in the literature. Balard (1) states that bromine water exposed to sunlight slowly decolorizes with the formation of hydrobromic and bromic acids. Löwig (4), however, found that the reaction products are hydrobromic acid and oxygen. Pebal (5) found that saturated bromine water in a sealed container does not appreciably decolorize after three months exposure to sunlight. He was unable to detect any increase of gaseous pressure upon opening the container; however the solution was found to be slightly acid and gave a positive test for bromide. Joseph (2) showed that only 2 per cent of the theoretical amount of hydrobromic acid is formed if bromine water is exposed to sunlight for over one month in colorless glass bottles. The results of the quantitative investigation carried out in this laboratory are described below.

MATERIALS AND APPARATUS

Water was prepared by distilling tap water from alkaline permanganate, followed by redistillation. To oxidize possible volatile organic matter, the water was further treated with a small portion of pure bromine and allowed to stand in sunlight for several hours. The bromine was then completely boiled out and the residue distilled, and the distillate finally redistilled. A 12-liter, all Pyrex glass still was used. Grasselli's C.P. hydrochloric acid was likewise treated with bromine, followed by gentle boiling and aeration to remove the bromine. Mallinckrodt's C.P. bromine was purified by agitating with potassium bromide solution for several hours, followed by five washings with conductivity water in a separatory funnel. To remove small amounts of insoluble impurity the bromine was then dissolved in a large volume of conductivity water and reclaimed by distillation, using the still previously mentioned. The purification was completed by distilling once from concentrated sulfuric acid and finally redistilling. Upon evaporation, the bromine left no residue and gave negative tests for sulfuric acid. Sodium thiosulfate solutions, 0.05 N and 0.12 N, were prepared from Baker's C.P. analyzed chemical. Mallinckrodt's "Reagent quality" potassium iodide was used. This showed no trace of iodate. In order to duplicate titration conditions, the temperature of the iodine solutions to be titrated was controlled to 20 ± 2°C., and a mechanical stirrer operating at constant speed was used.

The photochemical reactions were carried out in Pyrex reaction chambers resembling a volumetric pipet. These had a capacity of about 55 cc., and were 15 cm. in length by 25 mm. in diameter. A 4 cm. x 5 mm. tube was sealed on one end, and a 6 cm. x 11 mm. tube was sealed on the other end. The reaction chambers were cleaned with sulfuric acid-dichromate cleaning solution, thoroughly washed, and finally steamed. Accurately weighed amounts of bromine were dispensed in small sealed glass bulbs. A 200-watt, frosted, Mazda electric light bulb was used as the light source. This was mounted vertically and rotated mechanically at about 20 R.P.M. to provide average uniform illumination in a horizontal plane. The photochemical reactions were carried out in a photographic dark room, with temperatures thermostatically controlled to 25.0 ±0.5°C.

PROCEDURE

The smaller tube on the reaction chamber was first sealed. The bromine bulb was then introduced into the chamber through the larger tube, followed by a solid glass plunger 8 cm. long by 6 mm. in diameter. A measured amount of water (45 cc.) was then added. The larger tube was then heated well away from the open end and drawn to a slender curved constriction. This was then connected to an aspirator pump for several minutes and sealed, while evacuated, at the constricted point. By quickly inverting the reaction chamber the glass plunger was allowed to strike and break the bulb, thus liberating the bromine into the water. The reaction tubes were then mounted vertically, equidistant from the light source. The amount of reaction which had taken place during the various time intervals was then found by iodometrically determining the amount of bromine remaining. The following technique was used to avoid loss of bromine vapor: A file mark was cut about 1 cm. from the sealed end of the smaller tube on the reaction chamber, and a calcium chloride tube was connected by means of a rubber coupling. One gram of potassium iodide in 10 cc. of 0.5 N hydrochloric acid was then added into the calcium chloride tube. By applying transverse pressure the tube was broken at the file mark, thereby forming a valve within the rubber coupling. After the iodide solution had been introduced into the reaction chamber, the latter was vigorously shaken to extract all of the bromine vapor in the free space. The reaction chamber was then lowered into a 500-cc. Erlenmeyer flask containing 200 cc. of 0.1 *N* hydrochloric acid and 1 g. of potassium iodide. By applying firm downward pressure the curved constricted end of the larger tube was then broken open against the bottom of the flask. This now permitted free drainage and thorough rinsing of the reaction chamber. The liberated iodine was then immediately titrated with thiosulfate. The latter was always standardized immediately after completing the analyses as follows: Weighed amounts of bromine in the sealed glass bulbs were introduced into a 500-cc. glass-stoppered Erlenmeyer flask containing the same volume of acid solution and potassium iodide as used in the analysis. The tightly stoppered flask was then vigorously shaken to break the bromine bulb and also insure complete reaction of the bromine vapor before titration.

TABLE 1

Reaction between bromine and water

SERIES A			SERIES B			SERIES C		
Time in hours	Bromine reacted*	$K \times 10^{-4}$	Time in hours	Bromine reacted*	$K \times 10^{-6}$	Time in hours	Bromine reacted*	$K \times 10^{-6}$
12	1.51	0.89	12	1.26	1.42	12	1.75	1.30
24	2.28	0.91	24	1.85	1.34	24	2.97	1.48
60	3.49	0.91	48	2.72	1.36	48	4.05	1.48
108	4.58	0.96	96	3.72	1.38	96	5.05	1.41
180	4.82	0.87	180	4.51	1.34	144	5.79	1.44

* Calculated to moles per liter $\times 10^{-4}$.

EXPERIMENTAL

Three series of experiments were carried out: series A, using 0.0221 *M* bromine at 50 cm. from the light source; series B, using 0.0221 *M* bromine at 71 cm.; and series C, using 0.0469 *M* bromine at 50 cm. The data and reaction velocity constants found are tabulated in table 1.

DISCUSSION

The reaction appears to take place as follows:

$$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HBrO$$
$$HBrO + h\nu \rightarrow H^+ + Br^- + \tfrac{1}{2}O_2$$

The reaction velocity constants given above were determined as follows: The initial concentrations of hypobromous and hydrobromic acids were calculated from the hydrolysis equilibrium equation (3)

$$\frac{[H^+][Br^-][HBrO]}{[Br_2]} = K_{eq.} = 5.8 \times 10^{-9}$$

The number of moles of hydrobromic acid formed at any stage of the reaction always equals twice the moles of bromine reacted, as determined iodometrically. Since the hydrolysis reaction rapidly attains equilibrium (3), the concentrations of both hypobromous and hydrobromic acids can be calculated by inserting $\{[\mathrm{HBr}]_{\mathrm{initial}} + [\mathrm{HBr}]_{\mathrm{formed}}\}$ into the hydrolysis equilibrium equation. By integrating the curves $[\mathrm{HBrO}]/[\mathrm{H}^+][\mathrm{Br}^-]$, it was found that the reaction velocities can be expressed:

$$-\mathrm{d}[\mathrm{Br}_2]/\mathrm{d}t = IK[\mathrm{HBrO}]/[\mathrm{H}^+][\mathrm{Br}^-]$$

The following mechanism appears logical:

$$\mathrm{HBrO} + h\nu \rightarrow \mathrm{Br}^{+\prime} + \mathrm{OH}^-$$

therefore,

$$-\mathrm{d}[\mathrm{Br}^{+\prime}]/\mathrm{d}t = Ik[\mathrm{HBrO}]$$

The $\mathrm{Br}^{+\prime}$ reacts simultaneously,

$$\mathrm{Br}^{+\prime} + \mathrm{OH}^- \rightarrow \mathrm{H}^+ + \mathrm{Br}^- + \tfrac{1}{2}\mathrm{O}_2 \qquad \text{(a)}$$

and

$$\mathrm{Br}^{+\prime} + \mathrm{Br}^- \rightarrow \mathrm{Br}_2 + \mathrm{E} \qquad \text{(b)}$$

From reaction a,

$$-\mathrm{d}[\mathrm{Br}^{+\prime}]/\mathrm{d}t = k'[\mathrm{Br}^{+\prime}][\mathrm{OH}^-]$$

Within the range studied, the bromine concentrations remain practically constant, owing to the reversal of the hydrolysis reaction with increasing hydrobromic acid concentrations, therefore we may assume

$$-\mathrm{d}[\mathrm{Br}^{+\prime}]/\mathrm{d}t = k''[\mathrm{Br}^{+\prime}][\mathrm{Br}^-]$$

for reaction b. The mole fractions of $\mathrm{Br}^{+\prime}$ taking part in the competing reactions a and b are thus directly proportional to $k'[\mathrm{OH}^-]$ and $k''[\mathrm{Br}^-]$, respectively. The rate equation may then be written

$$-\mathrm{d}[\mathrm{Br}_2]/\mathrm{d}t = IK[\mathrm{HBrO}][\mathrm{OH}^-]/[\mathrm{Br}^-]$$

to explain the observed decrease in reaction rate with respect to the increasing concentrations of hydrobromic acid.

SUMMARY

1. The photochemical reaction between bromine and water has been studied.

2. The reaction velocity equation was found, and a reaction mechanism shown to be in logical agreement with it has been discussed.

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THE DIELECTRIC CONSTANTS OF SOLUTIONS OF SOME ORGANIC ACIDS IN ETHYL ALCOHOL AND BENZENE[1]

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There are factors influencing the production of mobile ions other than the partial dissipation of the forces of interionic attraction in the solute through the orientation of the polar molecules of the solvent. The dielectric constant, however, measured at the proper frequency, is a measure of this factor of the ionizing power of a solvent that is due to the dissipation of interionic forces by the molecules of the solvent, through their orientation. In any theory proposing to establish a relationship that quantitatively describes the behavior of ionic solutes, the dielectric constant cannot be neglected. In modern theories it is assumed that the dielectric constant of the solvent remains unchanged in the presence of the intense electrical field surrounding each ion of the solute. It is doubtful that this assumption is justified. It might be well to consider briefly the effect of strong electric fields on the dielectric constant of a polar solvent.

Debye has derived an expression that indicates that the mean moment of a polar molecule tends to reach a saturation value as the field intensity is increased (5). If the dielectric constant of a liquid is to be considered, it will make a difference whether we have present a small electrical field or a more intense one. If we measure the dielectric constant of a liquid in the presence of a strong, constant, superimposed field, we should expect a decrease in the dielectric constant, inasmuch as the strong, superimposed field, in itself, will have brought the mean electric moment of the liquid molecules nearer the electrical saturation value.

Usually we are not concerned with electrical saturation effects because of the small field intensities. In the presence of ions, however, the electrical saturation effects are of importance. In the case of water as the solvent containing a number of ions we have the equation

$$E = e/r^2\epsilon$$

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[1] This article is part of a thesis submitted to the Graduate School of Indiana University by Robert C. Gore in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1933.

where E is the field intensity, e is the ionic charge, r is the ionic radius, and ϵ is the dielectric constant. If we take $r = 10^{-7}$ cm., $\epsilon = 80$, and $e = 4.77 \times 10^{-10}$ we get

$$E = \frac{4.77 \times 10^{-10}}{80 \times 10^{-14}} = 590 \text{ E.S.U.}$$

or 177,000 volts per centimeter, which is a great enough field intensity to cause appreciable saturation effect.

If the solution contains a number of ions, there will be a region around each ion containing electrically saturated water. If now a small field is superimposed in order to measure the dielectric constant of the solution, there will be, around the ions, regions of water molecules which cannot be oriented because of electrical saturation. Consequently, we may think of the solution as containing cavities of dielectrically inactive material. The radii of these cavities will depend upon the extent of the electrical saturation.

If ethyl alcohol is used as the solvent, owing to its less ability to absorb or dissipate energy as evidenced by its lower dielectric constant, the saturation effect caused by a single ion is greater. In this case

$$E = \frac{4.77 \times 10^{-10}}{24 \times 10^{-14}} = 2070 \text{ E.S.U.} = 594{,}000 \text{ volts per cm.}$$

Provided that there are the same number of ions in the alcoholic solution as in the water solution, the effect of electrical saturation would be approximately four times as great in alcohol as in water.

An approximate picture of what takes place around each ion and throughout the solution has been drawn by Debye. For small concentrations of ions in aqueous solutions, experiments seem to indicate that the apparent dielectric constants of solutions containing ions diminish with the increasing concentration and e^*, the apparent dielectric constant, may be expressed by an equation such as:

$$e^* = e\,(1 - \gamma C)$$

where e is the dielectric constant of the pure solvent, C is the concentration in moles per liter, and γ is a constant dependent upon the ionogen and the solvent.

The decrease of the apparent dielectric constant of the solution from that of the pure solvent can be accounted for by the introduction of highly charged ions, which electrically saturate the solvent and produce cavities of dielectrically inactive solvent throughout the main body of the solution. As the number of ions increases, however, a minimum in the apparent, or macroscopic, dielectric constant is reached, and then an increase is obtained. This increase can be thought of as due to the formation of electrical doublets or ionic dipoles between the ions as they increase in concentration and thus are forced into closer proximity. Several investigators have measured the dielectric constants of solutions of electrolytes by several methods and have obtained results which, in general, follow the theory only qualitatively. There are some exceptions to the theory even in qualitative agreement of the experimental results. The theory calls for a minimum in the apparent dielectric constant. Carman (4), however, in checking the results of Blüh (2) finds that urea continuously increases the apparent dielectric constant of an aqueous solution as the concentration is increased. Carman has also studied the effect of binary salts such as barium chloride and has found that their behavior is much more complex than the theory of Debye and Walden would lead one to believe. Other investigators have found points of inflection in the curves of other electrolytes dissolved in water.

It has been our purpose to determine the effect of the concentration of various ionogens on the apparent dielectric constant of alcoholic and, in some cases, benzene solutions. The relatively low conductivity, as compared with water solutions, of alcoholic solutions was expected to decrease the difficulties of measurement to such an extent that common methods of measuring the dielectric constants of solutions, with proper precautions, could be employed.

EXPERIMENTAL METHOD

At present impedance bridge networks and resonance or heterodyne circuits are used to measure the dielectric constants of liquids. We used both systems to obtain some of our measurements, but we made most of them with an impedance bridge. This bridge was an equal-arm, 1000-cycle, Vreeland oscillator-actuated network constructed from Leeds and Northrup's parts according to the principles laid down by Jones and Josephs (7). The precautions mentioned by Ball (1) were observed also.

Three cells were used for the measurements. The cell used in most of the measurements was made of two concentric platinum cylinders 70 x 12 mm. and 70 x 16 mm. enclosed in a Pyrex bulb fitted with side arms for filling and suitable mercury cups for electrical contact. The capacitance of this cell was determined by calibration with benzene, having a dielectric constant of 2.2725, and was found to be 24.3887 mmf. The second cell was a silver-plated, radio, variable condenser mounted so that no solid dielectric came into contact with the solutions. The third cell was a slightly modified copy of Ball's (1) best cell. During all measurements, the cells were immersed in a constant-temperature bath filled with water or transformer oil at 25°C.

All readings of refractive index were made with a Pulfrich refractometer and are for the D line of sodium.

PURIFICATION OF MATERIALS

The absolute alcohol was made from commercial 95 per cent alcohol by three treatments with lime, which was activated by heating the hydrated lime in an electric furnace to just below the sintering temperature. The aldehydes were removed by lead acetate or by sodium hydroxide and lead dioxide. When the alcohol was ready to be used, it was first distilled through a four-bulb fractionating column in order to remove the major portion of lime. It was then fractionated twice through a sixteen-bulb Young fractionating column, the first and last fractions being discarded. The purity of the alcohol was determined through the use of Schiff's reagent, aluminum ethylate, and transformer oil and by the measurement of its dielectric constant and refractive index. Various other methods of purification were tried, but none yielded as pure a product as the one used.

The anhydrous benzene was prepared from Mallinckrodt's crystallizable thiophene-free benzene by adding 20 g. of phosphorus pentoxide per liter and allowing the mixture to stand for several months. The anhydrous benzene was distilled from the phosphorus pentoxide and twice fractionated through a sixteen-bulb Young column, only the middle fraction being saved. The boiling points were determined and checked against the variations of the vapor pressure with temperature as given by Smith and Menzies (8).

The various solutes were either from the Eastman Kodak Company or from Dr. Theodor Schuchardt and were the purest obtainable. Their purity was checked by determinations of their melting points. Each solute was dried over phosphorus pentoxide, over calcium chloride, or in a vacuum. Solids having a sufficiently high melting point were dried in an electric oven at 110°C. for several hours.

PREPARATION OF SOLUTIONS

A 0.1 molar solution of each solute was prepared by weight. Other concentrations were prepared from these solutions by careful dilution. All solutions were kept in desiccators until they were measured, which was as soon as possible after preparation.

RESULTS

The results of the measurement of the dielectric constants of alcohol and benzene solutions of various organic acids are given in tables 1 and 2. The dielectric constants are referred to air as unity and are probably correct to the first decimal place, and in some instances are correct to the second decimal. The dielectric constants of solutions exhibiting values above 30 are not as accurate as the lower values, owing to errors introduced in assuming that the equivalent shunt capacitance of the cell is its true capacitance when the parallel resistance becomes relatively small, which is the

TABLE 1

Dielectric constants of solutions of organic acids in ethyl alcohol

ACID	CONCENTRATION OF ACID IN MILLIGRAM-MOLES PER LITER							
	0	1	5	10	15	20	50	100
Benzoic	24.47	25.34		25.57				26.73
m-Chlorobenzoic	24.31	27.12		50.77	78.70	111.5		>110
o-Chlorobenzoic	24.18	24.35	25.29	24.74	25.21	25.97		34.70
p-Chlorobenzoic	24.43	24.33	24.72	24.36	24.51		26.97	28.02
p-Nitrobenzoic	24.34	24.81	25.36	25.70	26.72	28.78	39.04	56.87
o-Nitrobenzoic	24.27	24.85	25.26	26.37	27.88	29.14	42.16	69.23
m-Nitrobenzoic	24.21	24.77	26.34	29.10	32.72	37.37	74.22	>115
p-Aminobenzoic (impure alcohol)	26.39	26.43	26.54	26.51	26.59	26.72	26.94	28.72
m-Aminobenzoic	24.81	25.37	26.32	29.18	30.58	33.71	61.75	>115
o-Aminobenzoic	26.21	27.43	29.04	31.90	34.72	38.94		>115
p-Hydroxybenzoic	24.79	24.99	27.84	33.12	38.47	44.48	96.00	>115
m-Hydroxybenzoic	23.91	25.41	25.54	25.90	26.05	26.63	28.31	32.98
o-Hydroxybenzoic	24.24	25.78	24.46	24.56	24.76	25.09	26.70	30.85
o-Toluic	24.36	24.22	24.50	24.83	24.83	26.06	27.21	30.83
m-Toluic	24.43	24.68	31.32	45.82	64.25	81.44		>156
p-Toluic	24.09	24.37	24.6	24.79	25.05	24.81	26.54	29.38
Propionic	24.30	24.21	24.40	24.36	24.66	24.65	25.28	25.28
n-Butyric	24.20	24.39	24.28	24.08	24.46	24.36	24.57	25.12
Isobutyric	24.30	24.34	24.40	24.58	24.74	24.56	24.71	25.53
n-Valeric	24.42	24.43	24.32	24.18	24.46	24.36	24.79	25.61
Isovaleric	24.38	24.34	24.26	24.35	24.34	24.54	24.73	25.37
n-Caproic	24.27	24.48	24.34	24.44	24.44	24.44	25.61	27.43
Isocaproic	24.29	24.37	24.08	24.65	24.83	25.08	26.85	32.86
Acetic	24.37	24.86	24.57	24.81	25.10	24.99	25.37	26.24

TABLE 2

Dielectric constants of solutions of acids in benzene

CONCENTRATION OF ACIDS IN MILLIGRAM-MOLES PER LITER	*m*-NITROBENZOIC ACID	*m*-TOLUIC ACID	ISOCAPROIC ACID
0	2.273	2.273	2.273
5			2.274
10	2.288	2.281	2.274
15			2.273
20	2.305	2.282	2.273
50		2.283	2.279
68.07	2.377		
100		2.289	

case with the more highly conducting solutions. Even in the extreme cases, with very high dielectric constants, the error should not be greater than 2 or 3 per cent.

CONCLUSIONS

We find that ten of the solutes show, with increasing concentrations of their solutions, minima in the values of the dielectric constants. These ten solutes also show minima in the values of the refractive index and maxima in the values for the balancing resistances at the concentrations exhibiting the minima in the dielectric constants. Tables of these values have not been included for lack of space. Four other solutions show minima in the dielectric constants and refractive indices or resistances, but not in all three of these variables.

TABLE 3

Dielectric constants of solutions of organic acids

ACIDS SHOWING MINIMA IN THE CONCENTRATION, DIELECTRIC CONSTANT, REFRACTIVE INDEX, AND RESISTANCE FUNCTIONS	ACIDS SHOWING NO MINIMA IN THESE FUNCTIONS
o-Chlorobenzoic, D.E.K., R.I., R.	Benzoic
p-Chlorobenzoic, D.E.K., R.I., R.	*m*-Chlorobenzoic
p-Aminobenzoic, D.E.K., R.I.	*p*-Nitrobenzoic
o-Hydroxybenzoic, D.E.K., R.I., R.	*o*-Nitrobenzoic
o-Toluic (?), D.E.K., R.I.	*m*-Nitrobenzoic
p-Toluic, D.E.K., R.I., R.	*m*-Aminobenzoic
Propionic, D.E.K., R.I., R.	*o*-Aminobenzoic
n-Butyric, D.E.K., R.I., R.	*p*-Hydroxybenzoic
Isobutyric, D.E.K., R.I., R.	*m*-Hydroxybenzoic
n-Valeric, D.E.K., R.I., R.	*m*-Toluic
Isovaleric, D.E.K., R.I., R.	
n-Caproic, D.E.K. (?)	
Isocaproic, D.E.K., R.I.	
Acetic, D.E.K., R.I., R.	
Benzene solutions	Benzene solutions
Isocaproic, D.E.K., R.I., R.	*m*-Nitrobenzoic
	m-Toluic
	Benzoic

Ten acids show no minima in the dielectric constants of their solutions with increasing concentration. One solution of one acid in benzene shows minima in the dielectric constant, the refractive index, and the resistance. Three acid solutions in benzene show no minima with increasing concentration. These results are shown in table 3.

From these results our only conclusion concerning the validity of the electrical saturation theory for acids in ethyl alcohol and benzene solutions is that, although the theory may hold qualitatively in some instances, it does not hold quantitatively.

It is interesting to note that the meta-substituted benzoic acid solutions do not show minima in any case. The values for the dielectric constants of solutions of meta-substituted acids are greater than the corresponding values for the ortho- and para-isomers.

All of the solutions of the aliphatic acids showed minima, even isocaproic acid dissolved in benzene. The stronger acids, as determined by Bright and Briscoe (3), did not show minima to any greater extent than did the weaker acids.

The *o*- and *m*-aminobenzoic acids showed no minima, while the para-isomer showed a slight minimum. In this case, however, the solutions of the para acid were measured by the heterodyne method and, in view of their conductances, their dielectric constants were subject to error. The change in the dielectric constant of the alcohol, due to the addition of equivalent quantities of the *o*- and *m*-aminobenzoic acids, was not the same for both isomers, as was found to be the case in water solutions by Hedestrand (6), who failed to obtain an increase in the dielectric constant of water by the addition of these three aminobenzoic acids.

It must be remembered that the electrical saturation theory is based upon the existence in solution of free ions carrying electrical charges. The theory has been developed from a physical viewpoint and is admittedly highly hypothetical. From our data it is obvious that the physical viewpoint is entirely inadequate in the case of acids dissolved in alcohol and even in benzene.

Other factors which would tend to change the picture as presented by the physical viewpoint would be: the possibility of the production of dipoles made up of the hydrogen ions from the acids and the hydroxyl part of the alcohol; the formation of water and ester molecules, although all determinations were made immediately after the preparation of the solutions (this is not a factor in the case of benzene solutions of the acids); the production of dipoles between the $C_2H_5OH_2^+$ ion and the negative acid radical; and the possibility that ionization is very slight and is offset by the preponderance of the undissociated molecules having large electric moments.

Inasmuch as it is difficult to find in the literature accurate values for the dielectric constant and refractive index of ethyl alcohol, it is of interest to report the following figures obtained from twenty-four samples of alcohol: dielectric constant = 24.331 at 25°C., and $n_D^{25°} = 1.35921$.

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THE PHYSICAL PROPERTIES OF THE TERNARY SYSTEM ETHYL ALCOHOL–GLYCERIN–WATER[1]

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INTRODUCTION

This and a previous investigation (10) were undertaken to obtain data to be used in the study of distillation of ternary mixtures. The densities, surface tensions, viscosities, refractive indices, and specific heats for the ternary system ethyl alcohol–glycerin–water are reported in this paper. A later paper will contain latent heats, boiling points, vapor pressures, and liquid–vapor composition data for the two ternary systems.

Densities (4), specific heats (13), refractive indices (11), and viscosities (19) of the binary system glycerin–water have been determined previously by various experimenters. The binary system ethyl alcohol–water has been investigated by Bose (6), who determined specific heats, and by Winkler (22) for density. This investigation includes the determination of densities, surface tensions, viscosities, refractive indices, and specific heats of the ternary system ethyl alcohol–glycerin–water.

EXPERIMENTAL

Materials. Glycerin of the C.P. grade was purified by repeated distillation under reduced pressure. C.P. ethyl alcohol was treated successively with metallic calcium, sodium hydroxide, and finally with metallic sodium, and distilled after each addition. The water was treated with potassium permanganate and distilled; then treated with barium hydroxide and distilled repeatedly. The physical constants of the purified materials are given in table 1.

Preparation of samples. The samples were prepared on a weight per cent basis in increments of 10 per cent. The composition of these samples is shown in table 2.

Apparatus. Densities were determined by using a Geissler pycnometer. An Ostwald-Poiseuille viscosimeter (23) was employed for the determination of viscosities. The surface tension was measured by means of the

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rise in a capillary tube (21). An Abbé refractometer (1) was used in obtaining refractive indices. Specific heats (17) were determined by introducing a measured quantity of electricity into the liquid and recording the temperature rise. A portable watt-second meter (Sangamo Electric Co.) and a thermometer with 0.1° graduations were used to determine these values. A carbon resistor was used as a heating element. This apparatus was inclosed in a silver-plated glass tube surrounded by an evacuated jacket.

TABLE 1

Physical constants of purified materials

MATERIAL	DENSITY	VISCOSITY	SURFACE TENSION	REFRACTIVE INDEX	SPECIFIC HEAT
Ethyl alcohol	0.7851* 0.78506 (14)† 0.78510 (22)	1.10* 1.101 (9)	22.0* 22.03 (3)	1.3596* 1.35941 (2)	0.536* 0.54 (16)
Glycerin	1.2580* 1.2580 (4) 1.25802 (5)	934* 945 (19)	62.5* 63.0 (8)	1.4729* 1.4730 (11)	0.555* 0.541 (13) 0.589 (13)
Water	0.99707 0.99707 (20) 0.99707 (7)	0.893 0.894 (12) 0.893 (18)	72.0 72.0 (16)	1.3332* 1.3325 (15) 1.3333 (10)	1.00

* Author's experimental values.

† The numbers in parentheses refer to the bibliography.

DISCUSSION

The results of the experimental work are shown in table 3. From the data obtained, both binoidal and triangular diagrams have been drawn for each physical property. The binoidal curves are plotted with the composition of the sample on the abscissa versus the particular property under consideration as the ordinate. The constant property lines on the triangular diagrams were prepared from the binoidal curves.

Relative density. Figure 1 is a binoidal graph of the relative densities against composition. The line representing the densities of the ethyl alcohol–water system curves upward, indicating a decrease in volume upon mixing. These values agree with those of Winkler (22). The densities of the ethyl alcohol–glycerin system lie between the values for alcohol and glycerin, but likewise show a decrease in volume upon mixing. The water–glycerin curve slopes downward, denoting a slight increase in volume when mixed, agreeing with Bosart and Snoddy (4).

The constant per cent glycerin curves and the constant per cent ethyl alcohol curves show a curvature similar to the ethyl alcohol–water and the glycerin–water curves, respectively. The characteristic curvature of the lines on the triangular diagram (figure 2) is to be expected because of the change in volume when the different components are mixed.

TABLE 2

Composition of the samples

SAMPLE NUMBER	WEIGHT PER CENT GLYCERIN	WEIGHT PER CENT ETHYL ALCOHOL	WEIGHT PER CENT WATER	SAMPLE NUMBER	WEIGHT PER CENT GLYCERIN	WEIGHT PER CENT ETHYL ALCOHOL	WEIGHT PER CENT WATER
1		100		34	50	10	40
2	100			35	40	10	50
3			100	36	30	10	60
4		10	90	37	20	10	70
5		20	80	38	10	10	80
6		30	70	39	70	20	10
7		40	60	40	60	20	20
8		50	50	41	50	20	30
9		60	40	42	40	20	40
10		70	30	43	30	20	50
11		80	20	44	20	20	60
12		90	10	45	10	20	70
13	90		10	46	60	30	10
14	80		20	47	50	30	20
15	70		30	48	40	30	30
16	60		40	49	30	30	40
17	50		50	50	20	30	50
18	40		60	51	10	30	60
19	30		70	52	50	40	10
20	20		80	53	40	40	20
21	10		90	54	30	40	30
22	10	90		55	20	40	40
23	20	80		56	10	40	50
24	30	70		57	40	50	10
25	40	60		58	30	50	20
26	50	50		59	20	50	30
27	60	40		60	10	50	40
28	70	30		61	30	60	10
29	80	20		62	20	60	20
30	90	10		63	10	60	30
31	80	10	10	64	20	70	10
32	70	10	20	65	10	70	20
33	60	10	30	66	10	80	10

Surface tension. The curve (figure 3) representing the binary system ethyl alcohol–glycerin is smooth but rises abruptly from the 80 per cent glycerin composition. The constant per cent water lines have the same characteristic curvature.

The surface tensions of the water–glycerin mixtures are between the

TABLE 3

Physical properties

SAMPLE NUMBER	DENSITY	VISCOSITY	SURFACE TENSION	REFRACTIVE INDEX	SPECIFIC HEAT
1	0.7851	1.10	22.0	1.3596	0.537
2	1.2627	934.0	62.5	1.4729	0.555
3	1.0000	0.893	72.0	1.3332	1.000
4	0.9833	1.33	46.6	1.3399	1.036
5	0.9692	1.76	37.7	1.3453	1.040
6	0.9535	2.13	32.3	1.3510	0.995
7	0.9342	2.34	29.6	1.3552	0.964
8	0.9125	2.33	28.3	1.3587	0.915
9	0.8895	2.24	26.9	1.3610	0.859
10	0.8659	2.04	26.1	1.3628	0.784
11	0.8415	1.72	25.2	1.3630	0.700
12	0.8160	1.41	24.4	1.3624	0.618
13	1.2356	155.6	64.5	1.3472	0.579
14	1.2089	55.8	65.7	1.4435	0.610
15	1.1819	18.5	66.5	1.4281	0.665
16	1.1545	9.38	66.9	1.4145	0.715
17	1.1272	5.34	67.4	1.3992	0.770
18	1.1003	3.18	67.9	1.3858	0.810
19	1.0738	2.14	68.5	1.3708	0.870
20	1.0484	1.54	69.5	1.3582	0.930
21	1.0237	1.09	70.5	1.3451	0.967
22	0.8199	1.52	22.9	1.3701	0.550
23	0.8566	2.23	23.9	1.3799	0.550
24	0.8947	3.49	24.2	1.3898	0.549
25	0.9368	5.83	25.4	1.4005	0.548
26	0.9806	10.4	26.1	1.4109	0.550
27	1.0288	20.6	27.7	1.4226	0.549
28	1.0797	45.3	29.6	1.4344	0.549
29	1.1366	103.3	32.7	1.4470	0.551
30	1.1932	254.0	38.9	1.4597	0.552
31	1.1724	74.6	40.4	1.4462	0.581
32	1.1484	26.2	39.9	1.4321	0.622
33	1.1212	14.1	40.4	1.4193	0.675
34	1.1004	7.42	41.3	1.4063	0.741
35	1.0776	4.75	42.7	1.3917	0.790
36	1.0514	3.13	44.0	1.3769	0.856
37	1.0270	2.22	45.4	1.3639	0.921
38	1.0025	1.69	46.4	1.3511	0.966
39	1.1165	41.1	32.7	1.4343	0.588
40	1.0988	16.9	33.5	1.4220	0.635
41	1.0753	9.29	34.6	1.4096	0.681
42	1.0525	5.91	34.9	1.3961	0.735
43	1.0318	4.04	35.1	1.3827	0.810
44	1.0101	2.92	35.9	1.3705	0.885
45	0.9882	2.20	37.0	1.3573	0.953
46	1.0618	19.50	30.4	1.4235	0.591

TABLE 3—*Concluded*

SAMPLE NUMBER	DENSITY	VISCOSITY	SURFACE TENSION	REFRACTIVE INDEX	SPECIFIC HEAT
47	1.0460	10.80	30.1	1.4112	0.644
48	1.0273	6.63	31.3	1.3990	0.690
49	1.0090	4.60	31.6	1.3871	0.754
50	0.9888	3.47	32.0	1.3749	0.831
51	0.9690	2.69	32.8	1.3631	0.910
52	1.0149	12.3	28.8	1.4120	0.592
53	0.9984	7.04	28.9	1.4006	0.642
54	0.9821	4.73	28.9	1.3900	0.702
55	0.9655	3.57	29.6	1.3787	0.775
56	0.9486	2.84	29.9	1.3672	0.860
57	0.9670	6.63	27.2	1.4011	0.591
58	0.9553	4.59	28.0	1.3907	0.648
59	0.9430	3.52	27.5	1.3810	0.720
60	0.9272	2.78	28.3	1.3700	0.809
61	0.9282	4.26	26.3	1.3911	0.582
62	0.9143	3.26	26.3	1.3817	0.660
63	0.9016	2.59	27.0	1.3717	0.741
64	0.8889	2.88	24.5	1.3812	0.610
65	0.8796	2.36	25.6	1.3721	0.677
66	0.8505	2.00	24.6	1.3720	0.616

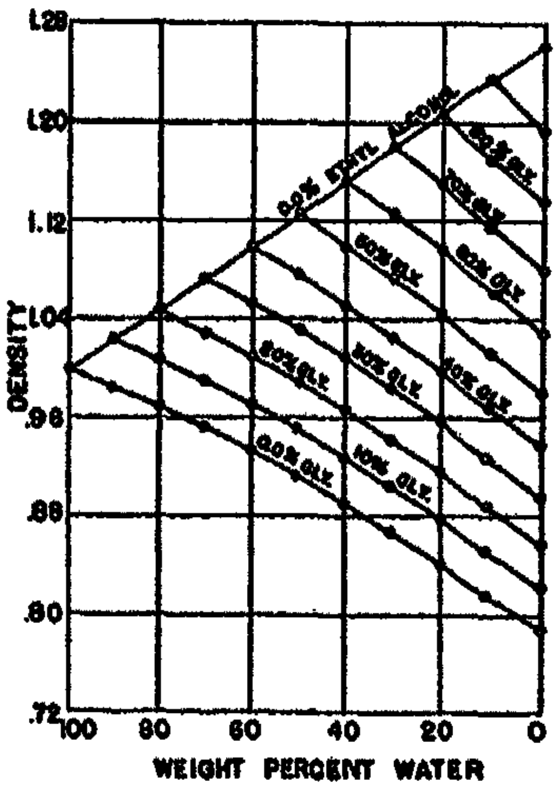


Fig. 1

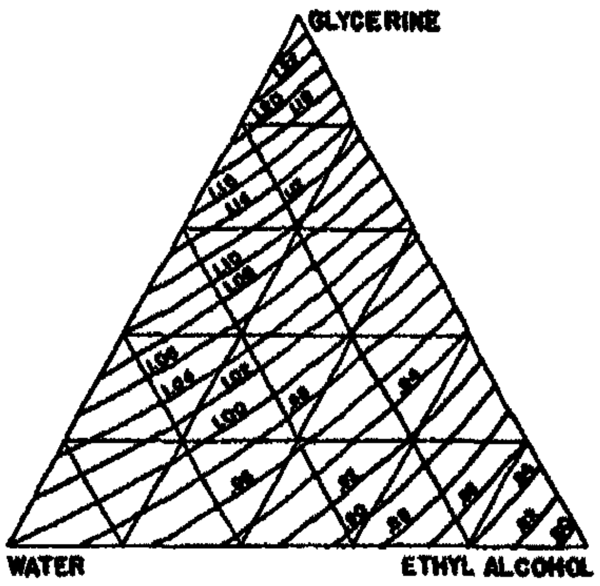
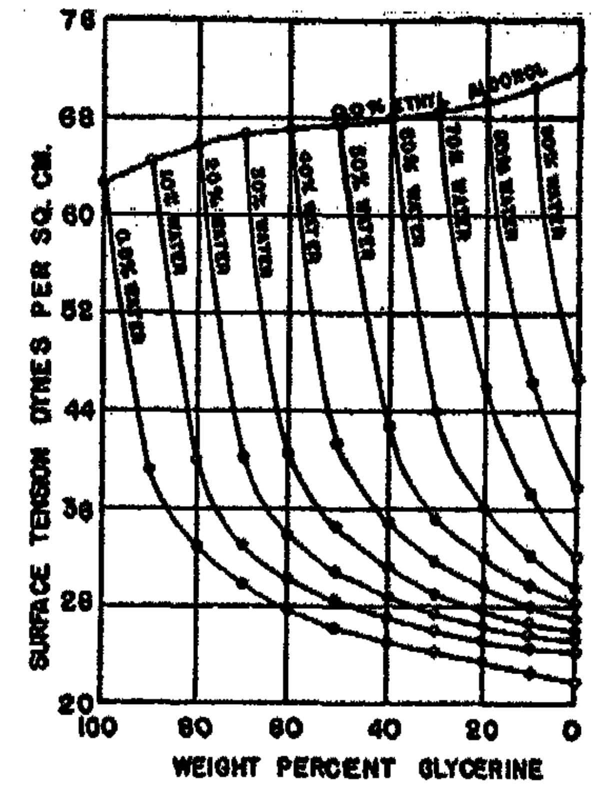


Fig. 2

Fig. 1. Relative density glycerin–ethyl alcohol–water at 25°C.
Fig. 2. Relative density glycerin–ethyl alcohol–water at 25°C



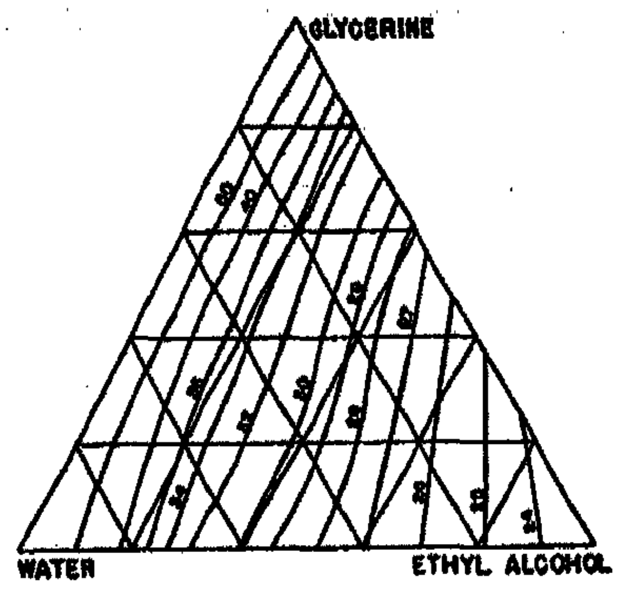
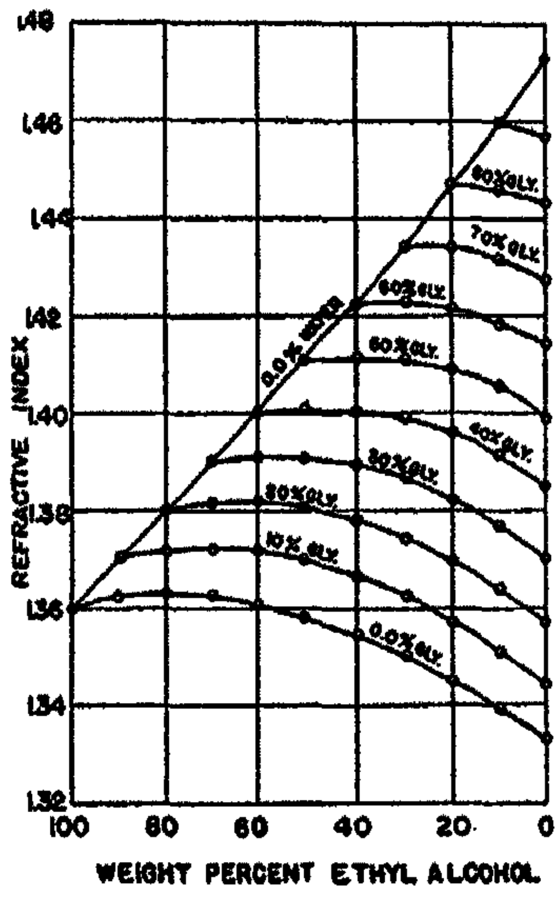


Fig. 3 Fig. 4

Fig. 3. Surface tension glycerin-ethyl alcohol-water at 25°C.
Fig. 4. Surface tension glycerin-ethyl alcohol-water at 25°C.



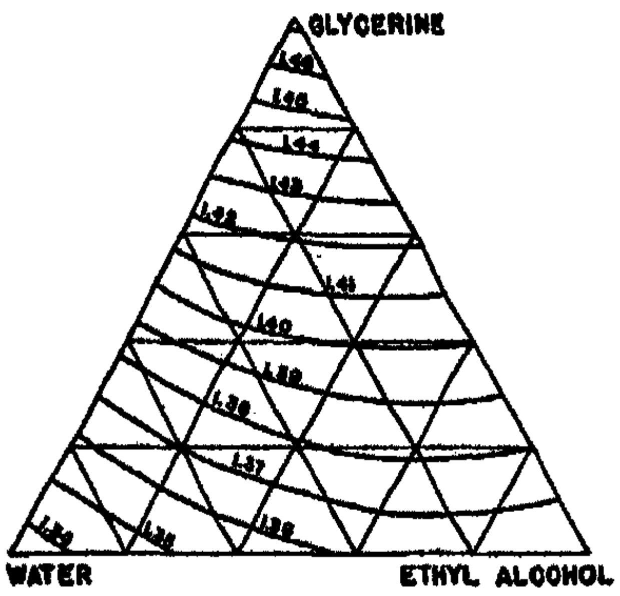


Fig. 5 Fig. 6

Fig. 5. Refractive index glycerin-ethyl alcohol-water at 25°C.
Fig. 6. Refractive index glycerin-ethyl alcohol-water at 25°C.

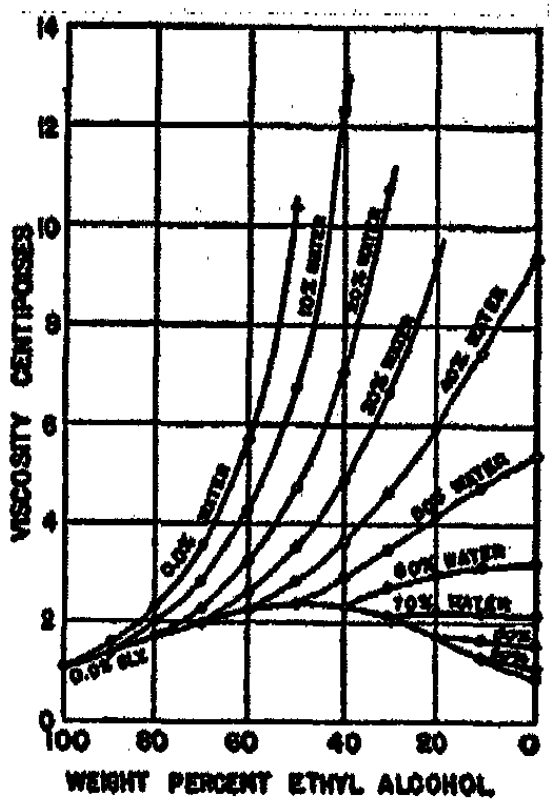


FIG. 7

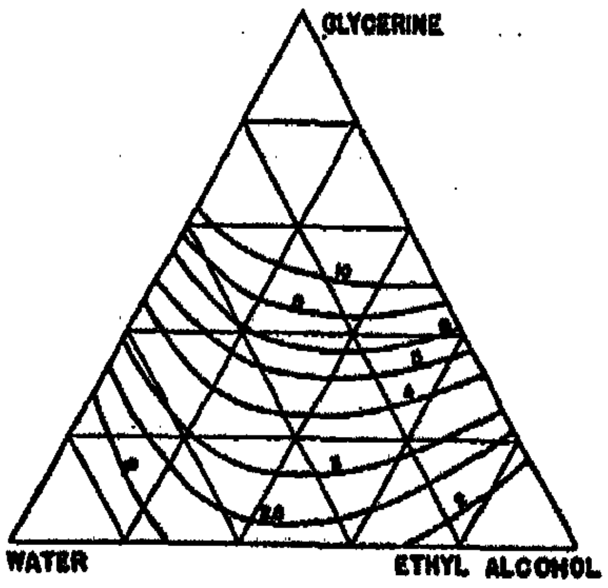


FIG. 8

FIG. 7. Viscosity glycerin-ethyl alcohol-water at 25°C.
FIG. 8. Viscosity glycerin-ethyl alcohol-water at 25°C.

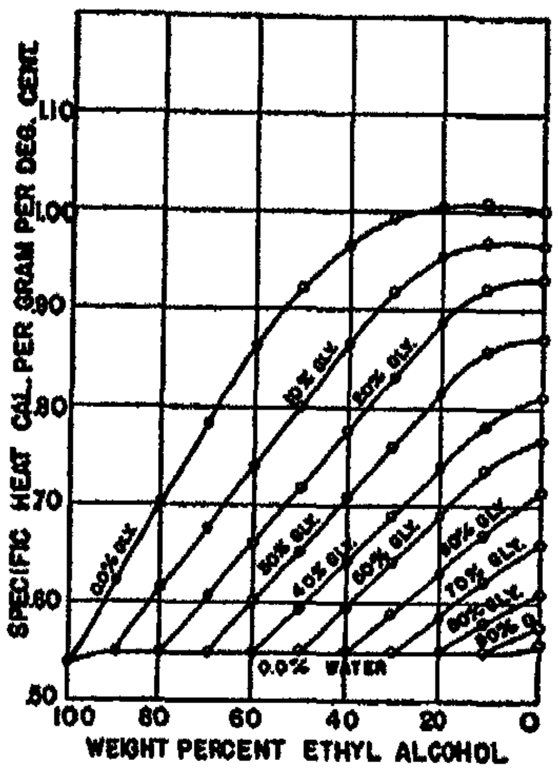


FIG. 9

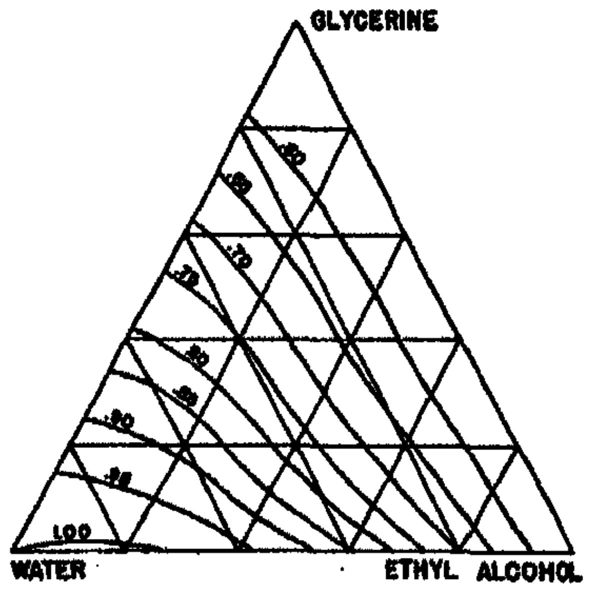


FIG. 10

FIG. 9. Specific heat glycerin-ethyl alcohol-water at 25°C.
FIG. 10. Specific heat glycerin-ethyl alcohol-water at 25°C.

values for the pure components; they lie on a smooth curve but not in a straight line.

In figure 4 the line representing compositions having a surface tension of 34.0 is a straight line. The lines on either side are convex with respect to this constant property line.

Refractive index. The refractive indices are shown graphically in figure 5 and figure 6. The values of the alcohol–water mixtures lie on a smooth curve reaching a maximum at 80 per cent alcohol. The constant per cent glycerin lines show similar maximum points.

The glycerin–water values curve slightly but are intermediate between the refractive indices of the pure components. The constant per cent water lines have the same curvature as the glycerin–alcohol curve. The constant property lines in figure 6 show a similar curvature throughout.

Viscosity. Because of the high viscosity of glycerin, namely 945 centipoises (19), when compared to that of alcohol and water, the curves showing viscosities include only those samples whose glycerin percentages are below 40 per cent. In figure 7 the alcohol–water mixtures have maximum viscosity at 50 per cent alcohol. The constant per cent glycerin curves show similar maximum points. These maxima explain the shape of the lines in figure 8.

Specific heat. Figure 9 shows the specific heat of the system plotted against composition. The specific heat of the water–alcohol system reaches a maximum at 80 per cent water and drops on a smooth curve to pure alcohol. The glycerin–alcohol line is almost straight. The constant per cent glycerin lines show similar curvature, but approach straight lines at 60 per cent glycerin.

The slopes of the lines on the ternary diagram (figure 10) are explained by the constant per cent glycerin lines reaching a maximum.

CONCLUSION

Densities, surface tensions, viscosities, refractive indices, and specific heats for the ternary system glycerin–ethyl alcohol–water have been determined. Both binoidal curves and ternary diagrams have been prepared for each property and are included in this paper.

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MIXED CRYSTAL FORMATION OF ZINC SULFIDE POSTPRECIPITATED WITH MERCURIC SULFIDE. THE AGING OF MERCURIC SULFIDE AND OF ZINC SULFIDE

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In an extensive study regarding the postprecipitation of zinc sulfide with mercuric sulfide to be reported in this journal, it was found that the zinc sulfide could not be completely removed from the mixed precipitate by extraction with 3 *N* hydrochloric acid at room temperature. This suggested a possible mixed crystal formation of zinc sulfide with mercuric sulfide. Such a view was supported by an x-ray investigation described in this paper.

X-ray diagrams were made by the powder method, using a Siegbahn (15) metal x-ray tube with a copper target as the source of the x-rays. The finely divided materials investigated were coated on a copper wire 0.5 mm. in diameter by means of collodion. The pattern thus obtained from the copper wire provided a means of calibrating the photographic film. The lattice constant (*a*) of copper was taken to be 3.61 A.U. (6), and upon this value are based the corrections applied to observed values of the angles of reflection. In calculating lattice constants, only lines due to the K_α radiations of copper were considered.

MERCURIC SULFIDE

Mellor (13) lists four different forms in which mercuric sulfide may exist. Three of these are crystalline, while black amorphous mercuric sulfide is given as the fourth. Of the three crystalline forms reported, the existence of two, namely α-HgS or ordinary red cinnabar and α'-HgS or black metacinnabar, is unquestioned; these two forms have been known for a long time to exist in nature. The third crystalline form listed by Mellor is the supposed new form reported by Allen and Crenshaw (1), which is not found in nature and which is a red hexagonal form differing from cinnabar. Allen and Crenshaw based their report of the existence of this new modification on evidence gained by microscopic examination. Kolk-

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[1] This article is based upon a thesis submitted by R. 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.

meijer, Bijvoet, and Karssen (9), employing the powder method of x-ray investigation, found none of the modifications described by Allen and Crenshaw to contain crystals different from the ordinary black and red forms.

Cinnabar is the most commonly occurring natural form, and was considered by Allen and Crenshaw (1) to be the most stable modification at all temperatures up to the sublimation temperature (580°C.). Rinse (14), however, found that vapor pressure data indicated the existence of a transition point at about 386°C., above which the black form was the stable modification. The change in color from red to black, which takes place when cinnabar is heated under certain conditions, has been observed and reported by other investigators (1, 16).

The structure of red trigonal cinnabar has been determined by Mauguin (12) using the Bragg method of x-ray analysis, by which the dimensions of the unit cell were found to be: $a = b = 4.15$ A.U., $c = 9.51$ A.U. It was found that with a slight deviation, the particles were arranged on a rhombohedral lattice. The work was later confirmed by Kolkmeijer and coworkers (9), using the Debye-Scherrer method of x-ray analysis.

The structure and properties of natural and artificial black metacinnabarite have been investigated by various workers (7, 9, 10). There is entire agreement that the black form usually precipitated from acid solution is identical in structure with that of naturally occurring metacinnabarite, the atoms of mercury and sulfur being arranged on a face-centered cubic lattice of the zinc blende type. The edge of the unit cell is listed by Wyckoff (18) as 5.84 A.U. In agreement with this value the authors likewise determined the lattice constant to be 5.84 A.U.

Mercuric sulfide freshly precipitated from acid medium exists as very imperfect submicroscopic crystals. While Böhm and Niclassen (3) report that mercuric sulfide precipitated at 0°C. gave at once a sharp interference pattern, it was found in this work that under the conditions of radiography employed only a few diffuse interference maxima were obtained. The period of aging necessary before the precipitate achieves a condition making possible a clear pattern was, however, found to be rather short. Mercuric sulfide precipitated from a medium which was quite strongly acid (2 N sulfuric acid) and aged in the supernatant liquid for three days at room temperature yielded a well-defined diffraction pattern characteristic of the cubic metacinnabar form.

In general, black cubic mercuric sulfide undergoes upon aging a transformation to the red cinnabar form. The observation has previously been made that the red modification is readily formed by digestion of the black gel with soluble alkali sulfides. According to Weiser (17) this process consists in the solution of the black form, with subsequent precipitation of the less soluble red form, although no experimental proof has been given that such a mechanism is the actual case. It was found in this work that alkalinity is not a necessary condition for the formation of the red form, but that transformation occurs upon aging in the supernatant liquid at room temperatures even in quite strongly acid medium. However, the speed of transformation decreases with increasing acidity. If the mercuric sulfide is precipitated from a neutral solution of the perchlorate and allowed to age in the resulting supernatant liquid saturated with hydrogen sulfide, transformation to the trigonal form as indicated by the color change of the precipitate is apparent within a few hours and is apparently complete within a day or two, whereas in more strongly acid solution (2 to 3 *N* sulfuric acid) a week or so will elapse before the change becomes convincingly apparent. Proof of the transformation and of the identity of the crystal forms involved was obtained by x-ray methods, as well as by visual observation of the color changes taking place. Transformation in case the precipitate is suspended in pure water or in dilute ammonium hydroxide was not detected. From the observations made, it is apparent that conversion from the cubic to the hexagonal form is hastened by low hydrogen-ion concentration, high concentration of hydrogen sulfide (or sulfide ion), and by higher temperatures of the supernatant liquid in which aging takes place. The presence of certain substances, such as potassium iodide and sodium acetate, was found to retard the transformation, as did likewise the presence of postprecipitated zinc sulfide. In the light of the proven occurrence of mixed crystal formation exhibited by mercuric sulfide and postprecipitated zinc sulfide, the fact that the latter inhibits the transformation of the former is construed as indicative of a stabilization of the metacinnabar form by virtue of the presence of zinc sulfide in the lattice.

ZINC SULFIDE

Two different crystal modifications of zinc sulfide are known to exist in nature. The regular form, or zinc blende, is by far the more abundant and is the stable form at ordinary temperatures, passing to the hexagonal or wurtzite form at or above the conversion point of 1020°C. (1). Wyckoff gives the lattice constant of the zinc blende form as 5.43 A.U. Values reported in the literature show a considerable deviation from this figure, ranging from 5.395 (4, 5) to 5.437 (10). In our work an aged precipitate of zinc sulfide yielded a value of 5.40 A.U.

Böhm and Niclassen (3) report that zinc sulfide precipitated at 0°C. from solutions of zinc sulfate was amorphous, but that after being digested on a water bath for several days, an x-radiogram of the product showed sharp interference maxima, indicating that crystallization had taken place. Likewise, in the work reported here, the diffraction pattern obtained from a product freshly precipitated at room temperature from a 0.1 *M* solution of zinc sulfate at an initial acidity of 0.1 *N* sulfuric acid was barely visible, while that obtained employing a product precipitated under like conditions, but aged at room temperature for one month in the supernatant liquid saturated with hydrogen sulfide, was sharply defined. A marked change in solubility accompanying aging was also observed. In 2 *N* sulfuric acid saturated with hydrogen sulfide, the solubility of the fresh product was in the neighborhood of 0.035 *M*, in contrast to 0.005 *M* for the aged product. Aging in the dry condition apparently does not affect the crystalline nature of precipitates of either zinc sulfide or mercuric sulfide. After existing in a dry condition at room temperature for one year, precipitates which had been separated from the mother liquor shortly after precipitation did not yield any definite diffraction pattern.

It is generally accepted that only the more stable blende form is precipitated from alkaline solution (1, 17). However, some question arises as to the identity of the crystal form assumed by zinc sulfide precipitated from acid solution by the action of hydrogen sulfide. Levi and Fontana (11) found only the blende form to have been precipitated from solutions of the sulfate and acetate. Allen, Crenshaw, and Merwin (1) found by microscopic examination of crystals formed in sealed tubes in the presence of the supernatant liquid at temperatures between 200° and 400°C. that, while only crystals of the blende structure were formed from alkaline solution, from acid solution both the wurtzite and zinc blende forms were produced. From their investigations concerning the crystalline forms and genetic conditions of the sulfides of zinc, iron, cadmium, and mercury, they drew the general conclusion that the higher the temperature, the greater the quantity of stable form, while the higher the acidity of the solution from which precipitation takes place, the greater the quantity of the unstable form. From this generalization they were led to predict that the acid concentration required to give pure wurtzite was probably close to neutrality at ordinary temperatures. In our work an x-radiogram of the aged product previously described yielded no indication of the presence of any but the zinc blende form. The possibility of a minor percentage of the wurtzite form being present is not, however, excluded on the basis of this evidence.

Employing the values 5.84 A.U. and 5.40 A.U. as the respective lattice constants of metacinnabar and zinc blende, the difference is found to be 7.8 per cent of the average value. On the basis of the work of Havighurst, Mack, and Blake (8) and of Barth and Lunde (2) regarding the limitations of miscibility in systems of the alkali halides and the halides of monovalent copper, silver, and thallium, respectively, we should expect that at least a limited mixed crystal formation of the sulfides of mercury and zinc is possible. The possibility is further strengthened by the fact that there is a mineral, bearing the name of guadalcazarite (Hg, Zn) (S, Se) and containing about 10 mole per cent zinc sulfide, which according to Hartwig (7) has a lattice constant of 5.781 ± 0.006 A.U.

TABLE 1

Study of a precipitate of mercuric sulfide containing postprecipitated zinc sulfide (Hg-Zn)S mounted on a copper wire for exposure. Copper radiation; 30 kv.; 10 ma.; 4 hours exposure. Diameter of specimen (S) = 0.7 mm. Diameter of camera = 57.3 mm.

LINE NO.	ESTIMATED RELATIVE LINE INTENSITY	$(2d - S)$ MM. 2θ (DEGREES)	2θ CALCULATED FOR Cu LINES	2θ CORRECTED	$\sin^2\theta$	RADIATION	hkl
1	vw[a]	24.4		23.9	0.04287	K_β	111
2	s	27.0		26.5	0.05253	K_α	111
3	vw	28.8		28.3	0.05976	?	?
4	m	31.3		30.9	0.07097	K_α	200
5	m	43.7	43.3			K_α	111 (Cu)
6	s	44.7		44.3	0.14215	K_α	220
7	vw	47.7		47.3	0.16092	K_β	311
8	m	50.9	50.5			K_α	200 (Cu)
9	ms	52.7		52.3	0.19424	K_α	311
10	vw	55.3		54.9	0.21250	K_α	222
11	vw	56.8		56.3	0.22258	?	?
12	vw	65.1		64.6	0.28317	K_α	400
13	vw	66.4	65.9			K_β	220 (Cu)
14	mw	71.2		70.8	0.33557	K_α	331
15	vw[a]	73.2		72.8	0.35215	K_α	420
16	s	74.6	74.2			K_α	220 (Cu)
17	vw[a]	79.9	79.2			K_β	311 (Cu)
18	w	81.7		81.3	0.42437	K_α	422
19	w	87.7		87.3	0.47645	K_α	333 511
20	ms	90.4	90.0			K_α	311 (Cu)
21	m	95.4	95.2			K_α	222 (Cu)
22	vw	97.3		97.2	0.56267	K_β	620
23	mw	103.7		103.7	0.61842	K_α	531
24	mw	114.1		114.1	0.70417	K_α	620
25	mw	117.0	117.0			K_α	400 (Cu)
26	vw	119.1	119.2			K_β	420 (Cu)
27	s (broad)	137.0	136.6			K_α	331 (Cu)
28	s (broad)	145.2	144.8			K_α	420 (Cu)

$\sin^2\theta = 0.017656(h^2 + k^2 + l^2)$. $a = 5.79$ A.U.

[a] Reflection appeared only on one side of the film.

A precipitate of mercuric sulfide containing postprecipitated zinc sulfide was prepared by saturating a solution which was 0.021 *M* with respect to zinc sulfate and mercuric chloride, respectively, at an acidity of 2 *N* sulfuric acid with hydrogen sulfide and allowing the mixture to stand for one month. It has been shown[1] that in this precipitation the mercuric sulfide is first precipitated in a pure form, zinc sulfide entering the precipitate upon further standing. At the end of one month, the precipitate was filtered off, washed with water and alcohol in the order named, and dried over concentrated sulfuric acid at reduced pressure. The composition of the precipitate was determined to be 39 mole per cent zinc sulfide and 61 mole per cent mercuric sulfide. The specimen had the usual black color of metacinnabar. The diffraction pattern obtained employing this product is represented by the data in table 1. A precipitate consisting of 48 and 52 mole per cent respectively of postprecipitated zinc sulfide and mercuric sulfide precipitated from an equimolar solution of zinc sulfate and mercuric chloride at an acidity of 0.5 N sulfuric acid and aged for three days in the supernatant liquid, yielded a value for the lattice constant identical within experimental error with that determined employing the first described precipitate. The diffraction pattern, however, was not as sharply defined in the case of the second precipitate as in the case of the former.

Referring to the table, reflections No. 3 and No. 11 present difficulties in their interpretation. Line No. 3 assumes a value of 2θ, which is too large to allow its identification as the K_β reflection from (200) planes. Moreover with K_α as weak as 4 and 12, one would not expect the corresponding K_β reflections to be detectable. Reflections from pure zinc sulfide possessing approximately these values (No. 3 and No. 11) for 2θ are strong. Consideration of the total amount of zinc sulfide present, the fact that aging in the sense of increasing crystalline perfection may have been greatly retarded by the presence of mercuric sulfide, and finally the fact that many of the stronger reflections from zinc sulfide fall in positions very close to those occupied by lines due to the bulk of the precipitate, suggests an explanation as to why no definite evidence of a second phase consisting either of pure zinc sulfide or possibly of a very dilute solid solution of mercuric sulfide in zinc sulfide is to be found in the diffraction pattern.

The decrease in lattice constant from 5.84 A.U. to 5.79 A.U. is a strong indication that mixed crystal formation occurs. By application of the formulation by Havighurst, Mack, and Blake (8) for the general rule of additivity regarding the relation between composition and change in lattice constant as applicable to mixed crystals of cubic habit, it is indicated that mixed crystal formation takes place to the extent of about 12 mole per cent zinc sulfide.

No indication was found in this work that mixed crystals of hexagonal habit exist.

SUMMARY

1. Aging of the sulfides of zinc and mercury in the supernatant liquid at room temperature after precipitation from acid solution by hydrogen sul-

fide results in a perfection of the crystalline state, as evidenced by increased clarity and sharpness of the diffraction patterns obtained.

2. Some of the variables affecting the transformation of mercuric sulfide from the black cubic form of metacinnabar to the red trigonal form of cinnabar upon aging in the supernatant liquid have been noted.

3. Evidence has been obtained by x-ray methods that a limited mixed crystal formation to the extent of about 12 mole per cent of zinc sulfide takes place between freshly precipitated black mercuric sulfide and post-precipitated zinc sulfide.

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QUANTITATIVE ANALYSES OF LIESEGANG RINGS

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As part of a program of careful quantitative study of the Liesegang phenomenon, we have performed analyses for the ions present in both bands and clear spaces in a copper chromate structure in silicic acid gel. By removing the banded structure from the test tube and subjecting the sections to analyses, we have shown both copper and chromate ions to be present together in the lower sections of this gel without the formation of a precipitate.

Very few studies of this type have been made. Earlier work by Hedges and Henley (1) on magnesium hydroxide made no attempt to distinguish between the soluble portion and the widely dispersed precipitate. Hughes (2) has recently made a very careful and complete survey of the distribution of ions in a large number of different systems. Our present work extends and corroborates his recent findings.

Banded structures of copper chromate were prepared by a technique previously described (3). After formation, these were removed from the tubes, cut into sections, the soluble salts extracted, and the copper, sulfate, and chromate ions determined. In all cases the copper and sulfate ions were distributed throughout the whole tube in a manner compatible with diffusion from the top, while the chromate ion was exhausted in all the upper sections. However, in most tubes both copper and chromate ions were found together in the lowest clear space, below which a band was just forming. The concentrations were such as to cause a precipitate in the absence of the gel.

Since no definite information could be found on the solubility product of this salt, tests were made to determine whether the actual concentrations found did cause a precipitate in the absence of a gel. Solutions were made which upon mixing yielded exactly the same concentrations as found. Heavy precipitates formed in all cases. Additional solutions were made containing the exact amount of free acetic acid present in the gels, and also, both the acid and the large amount of sodium acetate formed in precipitating the silicic acid. In these cases also a precipitate formed, although somewhat slowly.

For the preparation and analysis of the gels we are indebted to Mr. John Main.

EXPERIMENTAL

The gels were formed from equal volumes of 1.06 sp. gr. sodium silicate solution and 0.65 *N* acetic acid solution by a technique previously described (3). The gels were made 0.1 *M* and 0.2 *M* with respect to potassium chromate. Concentrations of 0.3 *M* and 0.4 *M* copper sulfate were used on top.

After the completion of the reaction the bottoms of the tubes were filed and cracked off. The gels were then pushed out with a rod, loosening first by momentary immersion in hot water if necessary. The gel was then cut into sections by means of a razor blade. Usually two clear spaces and one ring were analyzed.

TABLE 1

Results of typical analyses

REACTION	SPACE		DISTANCE FROM TOP	WEIGHT OF SAMPLE	PER CENT OF SO_4^{--}	PER CENT OF Cu^{++}	PER CENT OF CrO_4^{--}
			inches	*grams*	*per cent*	*per cent*	*per cent*
I. K_2CrO_4, 0.08 *M*; $CuSO_4$, 0.3 *M*	1st clear space	A	½	1.3169	0.86	0.43	None
		B	½	1.4948	0.87	0.46	None
	1st band	A	1	1.2948	0.78	0.39	None
		B	1	1.4598	0.79	0.40	None
	2nd clear space	A	1½	4.7322	0.68	0.19	0.10
		B	1¾	3.1824	0.68	0.19	0.12
II. K_2CrO_4, 0.2 *M*; $CuSO_4$, 0.3 *M*	1st clear space	A	½	1.0689	0.69	0.28	None
		B	½	1.2486	0.69	0.27	None
	1st band	A	1	1.3846	0.58	0.25	None
		B	1¼	1.3519	0.57	0.24	None
	2nd clear space	A	1½	3.8695	0.28	0.09	0.19
		B	1¾	3.4502	0.29	0.09	0.18
III. K_2CrO_4, 0.1 *M*; $CuSO_4$, 0.4 *M*	1st clear space	A	½	1.7517	0.83	0.39	None
		B	½	1.6385	0.83	0.39	None
	1st band	A	1	1.3690	0.71	0.35	None
		B	1¼	1.4006	0.73	0.35	None
	2nd clear space	A	1½	4.7593	0.58	0.18	0.10
		B	1¾	3.8891	0.58	0.20	0.08

Analytical procedure

The portions selected for analysis were placed in weighing bottles and carefully weighed. The soluble salts were extracted with boiling water and filtered. The extraction was repeated five or six times.

Chromate ions were first reduced by boiling with dilute hydrochloric acid and ethyl alcohol (4). After expelling the excess alcohol, the sulfate was precipitated as barium sulfate and weighed as such, according to the standard procedure. The filtrate from this precipitation was then treated with hydrogen sulfide to precipitate the copper, which was redissolved, and determined iodometrically. Finally, chromium was precipitated as the hydroxide, taking the usual precautions to eliminate excess ammonia, ignited to the oxide, and weighed.

The results of typical analyses are shown in table 1.

Precipitation in the absence of gel

Two solutions were made containing respectively 1.416 g. and 0.756 g. of $CuSO_4 \cdot 5H_2O$ in 100 ml., and two solutions containing respectively 0.402 g. and 0.666 g. of K_2CrO_4. These were twice the amounts found in the corresponding sections of the same gels. When equal volumes of the corresponding solutions were mixed, the final solutions should contain exactly the same concentrations as found in the gel. Heavy precipitates formed in both cases.

The copper sulfate solutions of the same concentration were prepared containing (1) 3.0 ml. of acetic acid per 100 ml. and (2) 7.7558 g. of $NaC_2H_3O_2 \cdot 3H_2O$ and the acid as in (1). Adding these to the corresponding chromate solutions produced a heavy precipitate of copper chromate.

SUMMARY

By quantitative analyses of rhythmically banded copper chromate structures in silicic acid gel it has been shown that, while the copper and the sulfate ions are distributed throughout the tube in a manner to be expected from simple diffusion, there are present in the lower clear space both copper and chromate ions in moderate concentration.

Copper chromate has been found to precipitate when the ions are present in the concentrations found in these spaces, even in the presence of the same amount of free acetic acid and of sodium acetate present in these gels. It appears that the presence of silicic acid inhibits the precipitation of this compound until higher concentrations are reached, and so aids in the formation of banded structures.

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THE SOLUBILITY AND ACTIVITY COEFFICIENT OF SILVER ACETATE IN MIXED SOLVENTS[1]

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INTRODUCTION

The experimental work described in this paper was undertaken in order to furnish an additional test of the applicability of the theory of Debye and Hückel (2) to strong electrolytes dissolved in mixed solvents. With this purpose in mind, we measured the solubility of silver acetate in various mixtures of water and ethyl alcohol in the presence of various amounts of a soluble nitrate. The nitrates used were those of lithium, sodium, potassium, calcium, strontium, and barium.

The solubility of silver acetate in water at 25°C. has been determined by a number of investigators. We give herewith the results obtained in moles per liter: Raupenstrauch (10), 0.0671; Goldschmidt (3), 0.0669; Jaques (5), 0.0663; Hill and Simmons (4), 0.0667; Knox and Will (6), 0.0667; MacDougall (7), 0.0664; MacDougall and Rehner (8), 0.0663. The value obtained in the present research was 0.06634.

MATERIALS USED

The silver acetate, obtained from Mallinckrodt, was 64.62 per cent silver (theoretical, 64.64 per cent) and was used without further purification. It was kept in black lacquered bottles and stored in the dark. The nitrate salts were recrystallized from "conductivity" water and dried at 150°C. The water was "conductivity" water, prepared by distillation of distilled water in a tin-lined vessel in the presence of sodium hydroxide and potassium permanganate. The ethyl alcohol used was approximately 95 per cent by volume and was tested according to Murray (9). It was found to be free from acetone, aldehyde, other organic impurities, and heavy metals. It was used without further purification.

EXPERIMENTAL PROCEDURE

The mixed solvent was prepared by mixing weighed amounts of 95 per cent alcohol and conductivity water, but the exact alcoholic content of

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[1] This paper gives the essential portions of the dissertation presented by Charles E. Bartsch to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

the mixture was calculated from its density. Mixtures containing approximately 10, 20, and 30 per cent by weight of alcohol were used as solvents.

Weighed amounts of the solvent and of the nitrate salt were brought together in a glass-stoppered flask. When the nitrate had dissolved, equal portions of the solution were transferred to two amber-colored glass-stoppered bottles containing an excess of silver acetate. The bottles were sealed immediately with a heavy layer of paraffin. They were then rotated end over end in a water bath at 25.00 ± 0.05°C. for at least forty-eight hours. For the purpose of sampling, the bottles were removed from the rotator and clamped upright and almost completely immersed in the bath. After half an hour, the paraffin was removed from the stopper, a siphon (containing a small cotton wad in the "bottle" end) was inserted in the liquid, and about 125 cc. of the liquid was blown by compressed air into a 250-cc. Erlenmeyer flask, immersed as completely as was permissible in the water bath. The Erlenmeyer flask was fitted with a rubber stopper to minimize evaporation. From this flask two samples of 50 cc. each were withdrawn by means of an accurately calibrated pipet and weighed in glass-stoppered weighing bottles. Results for density and for analysis were accordingly obtained in quadruplicate for each concentration of added nitrate.

The solutions containing 10 or 20 per cent alcohol were analyzed gravimetrically for silver; all other solutions were analyzed volumetrically. The volumetric analysis was carried out by the Volhard method for silver as suggested by Professor I. M. Kolthoff. The samples were transferred to 250-cc. Erlenmeyer flasks, acidified with 5 cc. of concentrated nitric acid, and diluted to 100 cc. Then 5 cc. of ferric nitrate indicator solution was added. The solutions were titrated immediately with 0.04 N potassium thiocyanate to a reddish-brown coloration. The solutions were then shaken until the color disappeared. The titration with potassium thiocyanate was continued until a faint rose coloration remained after vigorous shaking. The thiocyanate solution was standardized with a solution containing a known amount of silver acetate. The standardization was checked with a solution containing a known weight of silver nitrate.

METHODS OF EXPRESSING COMPOSITION OF THE SOLUTIONS

If p is the fraction of alcohol in the mixed solvent, the number of moles of water, N_{0_1}, and of ethyl alcohol, N_{0_2}, in 1000 g. of solvent can be found from the equations

$$\begin{aligned} N_{0_1} &= \frac{1000\,(1-p)}{18.016} \\ N_{0_2} &= \frac{1000p}{46.045} \end{aligned} \qquad (1)$$

The molar concentration, *c*, of a solute salt is the number of moles of the salt in a liter of the solution. The molal concentration, *m*, is the number of moles in 1000 g. of mixed solvent. In calculating the mole fraction of a component of the solution we have assumed that the dissolved silver acetate and added nitrate salt are completely ionized. If x is the mole fraction of Ag^+ or of $C_2H_3O_2^-$ in a solution in which the molalities of silver acetate and added nitrate are m and m_s respectively, then

$$x = \frac{m}{N_{0_1} + N_{0_2} + 2m + \nu m_s} \qquad (2)$$

where ν is the number of ions obtainable on complete ionization of one molecule of added nitrate salt.

The density of the solvent (alcohol–water mixture) is represented by d_0, that of the solution saturated with silver acetate and containing various amounts of nitrate salt by d.

ACTIVITY COEFFICIENTS

If f, γ, and γ_c are the mole-fraction, molality, and molarity activity coefficients respectively of any solute then

$$\gamma = \frac{f}{1 + \dfrac{2m + \nu m_s}{N_{0_1} + N_{0_2}}} \qquad (3)$$

$$\gamma_c = \frac{d_0}{d}\left(1 + \frac{mM + m_sM_s}{1000}\right)\gamma \qquad (4)$$

M and M_s are the molecular weights of silver acetate and added nitrate salt, respectively.

According to Debye and Hückel (2), the activity coefficient of a univalent ion (or of a uni-univalent salt) at 25°C. is given by the equations

$$\log_{10} f = \log_{10} x_0 - \log_{10} x = -\frac{BS^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} \qquad (5)$$

$$B = \frac{352.61}{D^{\frac{3}{2}}} \qquad (6)$$

$$A = \frac{2.914 \times 10^8}{D^{\frac{1}{2}}}\, a \qquad (7)$$

where D is the dielectric constant of the solvent and a is a suitable mean ionic diameter. In equation 5, x is the mole fraction of silver ion in a given saturated solution and x_0 is the extrapolated value of x for an ionic strength equal to zero; in other words, x_0 is the activity of silver ion in any solution saturated with silver acetate.

The dielectric constant of an alcohol-water mixture was calculated by linear interpolation from the values given by Åkerlöf (1).

EXPERIMENTAL DATA

In table 1 we give the solubility at 25°C. of silver acetate in alcohol-water mixtures containing from 0 to 50 per cent ethyl alcohol. In tables 2 to 7 we give the solubility in the presence of added nitrates in solvents containing approximately 10, 20, and 30 per cent ethyl alcohol. The data are also represented graphically in figures 1, 2, and 3. An examination of the tables and of the figures will show that the solubility of silver acetate increases with the concentration of added nitrate, and that for a solution

TABLE 1

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water

PER CENT ALCOHOL	DENSITY OF SATURATED SOLUTION	MOLAR CONCENTRATION OF SILVER ACETATE	PER CENT ALCOHOL	DENSITY OF SATURATED SOLUTION	MOLAR CONCENTRATION OF SILVER ACETATE
0.00	1.0048	0.0663	25.06	0.9616	0.0294
5.00	0.9955	0.0577	29.82	0.9530	0.0251
7.62	0.9898	0.0523	30.05	0.9526	0.0249
9.00	0.9882	0.0506	40.27	0.9323	0.0180
15.03	0.9784	0.0413	50.14	0.9102	0.0124
19.96	0.9696	0.03			

TABLE 2

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing potassium nitrate

9.41 PER CENT ALCOHOL $D = 73.14$			20.37 PER CENT ALCOHOL $D = 66.78$			30.02 PER CENT ALCOHOL $D = 61.09$		
m KNO_3	d Satd. soln.	$10^3 \times Ag^+$	m KNO_3	d Satd. soln.	$10^3 \times Ag^+$	m KNO_3	d Satd. soln.	$10^3 \times Ag^+$
0.0	0.9875	0.9649	0.0	0.9709	0.7449	0.0	0.9520	0.5811
0.05131	0.9909	1.0311	0.05006	0.9742	0.8196	0.04949	0.9581	0.6488
0.09865	0.9939	1.0710	0.09945	0.9776	0.8612	0.09996	0.9615	0.6910
0.2004	1.0010	1.1333	0.1998	0.9838	0.9191	0.2004	0.9669	0.7506
0.3006	1.0075	1.1751	0.2982	0.9897	0.9623	0.3007	0.9728	0.7974
0.4057	1.0153	1.2190	0.3958	0.9952	0.9892	0.3990	0.9774	0.8298
0.5012	1.0174	1.2462	0.4959	1.0009	1.0271	0.4984	0.9838	0.8591
0.6013	1.0271	1.2662	0.5994	1.0070	1.0507	0.6265	0.9906	0.8931
0.8046	1.0381	1.3114	0.7923	1.0180	1.0925	0.8813	1.0028	0.9452
1.0049	1.0495	1.3517	0.9898	1.0281	1.1285	1.0365	1.0103	0.9705
1.2957	1.0655	1.3868	1.2539	1.0422	1.1686			
1.6227	1.0828	1.4313	1.4916	1.0540	1.1964			

of a given ionic strength the effect of a given nitrate is given in general by the order $KNO_3 < NaNO_3 < Ba(NO_3)_2 < Sr(NO_3)_2 < LiNO_3 < Ca(NO_3)_2$.

TABLE 3

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing sodium nitrate

9.17 PER CENT ALCOHOL $D = 73.27$			20.37 PER CENT ALCOHOL $D = 66.75$			30.02 PER CENT ALCOHOL $D = 61.09$		
m $NaNO_3$	d Satd. soln.	$10^3 \times Ag^+$	m $NaNO_3$	d Satd. soln.	$10^3 \times Ag^+$	m $NaNO_3$	d Satd. soln.	$10^3 \times Ag^+$
0.0	0.9879	0.9815	0.0	0.9709	0.7449	0.0	0.9520	0.5811
0.04711	0.9910	1.0485	0.04819	0.9735	0.8141	0.05054	0.9558	0.6452
0.09579	0.9948	1.0892	0.09547	0.9762	0.8591	0.1002	0.9590	0.6931
0.1911	1.0001	1.1548	0.1937	0.9823	0.9251	0.2011	0.9652	0.7565
0.2864	1.0047	1.2009	0.2880	0.9859	0.9652	0.3012	0.9704	0.8066
0.3859	1.0102	1.2395	0.3821	0.9921	1.0023	0.3996	0.9745	0.8375
0.4702	1.0147	1.2660	0.4776	0.9971	1.0355	0.5001	0.9800	0.8757
0.5822	1.0206	1.3042	0.5738	1.0022	1.0637	0.6014	0.9856	0.9060
0.7735	1.0309	1.3464	0.7626	1.0116	1.1103	0.8003	0.9948	0.9573
0.9579	1.0405	1.3826	0.9571	1.0214	1.1557	0.9983	1.0048	0.9990
1.1903	1.0522	1.4123	1.1894	1.0336	1.1923	1.3026	1.0192	1.0594
1.4411	1.0644	1.4466	1.4258	1.0437	1.2327	1.6015	1.0343	1.1034
1.9095	1.0861	1.4934	1.8935	1.0646	1.2920	2.0047	1.0509	1.1583
2.3876	1.1077	1.5292	2.3764	1.0861	1.3353			
2.8732	1.1284	1.5555	2.8061	1.1047	1.3659			

TABLE 4

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing barium nitrate

9.17 PER CENT ALCOHOL $D = 73.27$			19.39 PER CENT ALCOHOL $D = 67.35$			30.02 PER CENT ALCOHOL $D = 61.09$		
m $Ba(NO_3)_2$	d Satd. soln.	$10^3 \times Ag^+$	m $Ba(NO_3)_2$	d Satd. soln.	$10^3 \times Ag^+$	m $Ba(NO_3)_2$	d Satd. soln	$10^3 \times Ag^+$
0.0	0.9879	0.9815	0.0	0.9722	0.7456	0.0	0.9520	0.5811
0.02541	0.9941	1.0877	0.01036	0.9749	0.8013	0.01028	0.9568	0.6328
0.05050	0.9994	1.1412	0.02463	0.9780	0.8506	0.01978	0.9589	0.6684
0.1012	1.0107	1.2326	0.05384	0.9842	0.9226	0.04002	0.9628	0.7229
0.1454	1.0198	1.2824	0.1241	0.9986	1.0235	0.06038	0.9669	0.7643
0.2021	1.0314	1.3462				0.08023	0.9711	0.7979
0.2343	1.0381	1.3798				0.09930	0.9748	0.8274
0.2978	1.0456	1.4187						

APPLICATION OF THE DEBYE-HÜCKEL THEORY

Values of A and x_0 of equation 5 were obtained for each series of solutions by substituting in the equation the observed values of x and $S^{\frac{1}{2}}$ for two

TABLE 5

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing strontium nitrate

9.90 PER CENT ALCOHOL $D = 72.86$			19.95 PER CENT ALCOHOL $D = 67.03$			30.45 PER CENT ALCOHOL $D = 60.83$		
m $Sr(NO_3)_2$	d Satd. soln.	$10^3 \times Ag^+$	m $Sr(NO_3)_2$	d Satd. soln.	$10^3 \times Ag^+$	m $Sr(NO_3)_2$	d Satd. soln.	$10^3 \times Ag^+$
0.0	0.9866	0.9565	0.0	0.9712	0.0742	0.0	0.9534	0.5781
0.02672	0.9912	1.0664	0.02730	0.9768	0.8505	0.01236	0.9557	0.6425
0.05250	0.9964	1.1258	0.05039	0.9808	0.9202	0.02495	0.9581	0.6872
0.09925	1.0045	1.2116	0.09969	0.9893	1.0074	0.04085	0.9604	0.7305
0.1991	1.0206	1.3441	0.1988	1.0041	1.1348	0.07072	0.9858	0.7918
0.2986	1.0370	1.4381	0.2997	1.0210	1.2345	0.09976	0.9706	0.8403
0.4018	1.0530	1.5189	0.3973	1.0362	1.3162	0.2019	0.9865	0.9685
0.4995	1.0685	1.5898	0.4986	1.0514	1.3918	0.2998	1.0007	1.0711
0.5978	1.0832	1.6486	0.5965	1.0658	1.4620	0.4018	1.0163	1.1591
0.8013	1.1135	1.7717	0.7974	1.0950	1.5890	0.6033	1.0453	1.3073
1.0021	1.1425	1.8844	0.9896	1.1214	1.6968	0.7999	1.0722	1.4536
1.2463	1.1764	2.0015	1.2403	1.1561	1.8414	0.9954	1.0994	1.5780
1.4855	1.2088	2.0959	1.5377	1.1950	1.9961	1.4888	1.1651	1.8837
2.0065	1.2746	2.3012	1.9768	1.2497	2.1990			

TABLE 6

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing lithium nitrate

9.41 PER CENT ALCOHOL $D = 73.14$			19.39 PER CENT ALCOHOL $D = 67.35$			30.02 PER CENT ALCOHOL $D = 61.09$		
m $LiNO_3$	d Satd. soln.	$10^3 \times Ag^+$	m $LiNO_3$	d Satd. soln.	$10^3 \times Ag^+$	m $LiNO_3$	d Satd. soln.	$10^3 \times Ag^+$
0.0	0.9883	0.9647	0.0	0.9722	0.7456	0.0	0.9520	0.5811
0.05177	0.9909	1.0412	0.05225	0.9746	0.8232	0.04890	0.9550	0.6557
0.1018	0.9931	1.0877	0.09767	0.9767	0.8692	0.10622	0.9572	0.7097
0.2017	0.9977	1.1625	0.2030	0.9813	0.9479	0.19890	0.9606	0.7712
0.2991	1.0019	1.2192	0.2973	0.9855	0.9961	0.2979	0.9650	0.8217
0.4082	1.0062	1.2718	0.4053	0.9894	1.0433	0.3881	0.9685	0.8621
0.5092	1.0103	1.3103	0.5114	0.9936	1.0861	0.4969	0.9728	0.9047
0.6191	1.0145	1.3507	0.5981	0.9969	1.1191	0.5977	0.9764	0.9417
0.8042	1.0219	1.4178	0.7966	1.0042	1.1830	0.7969	0.9836	1.0085
1.0214	1.0303	1.4781	0.9913	1.0117	1.2422	0.9974	0.9912	1.0721
1.3229	1.0415	1.5552	1.2529	1.0213	1.3111	1.3072	1.0031	1.1552
1.6556	1.0536	1.6310	1.5749	1.0328	1.3915	1.5735	1.0119	1.2284
2.1024	1.0693	1.7288	1.9670	1.0462	1.4911	1.9970	1.0257	1.3294
2.5195	1.0836	1.8260	2.5001	1.0640	1.6226			
3.0930	1.1027	1.9543	3.0096	1.0809	1.7457			

TABLE 7

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing calcium nitrate

9.90 PER CENT ALCOHOL $D = 72.86$			19.95 PER CENT ALCOHOL $D = 67.03$			30.45 PER CENT ALCOHOL $D = 60.83$		
m $Ca(NO_3)_2$	d Satd. soln.	$10^2 \times Ag^+$	m $Ca(NO_3)_2$	d Satd. soln.	$10^2 \times Ag^+$	m $Ca(NO_3)_2$	d Satd. soln.	$10^2 \times Ag^+$
0.0	0.9857	0.9565	0.0	0.9712	0.7420	0.0	0.9534	0.5781
0.02581	0.9908	1.0758	0.02404	0.9754	0.8643	0.01338	0.9554	0.6548
0.04913	0.9935	1.1466	0.04886	0.9789	0.9394	0.02549	0.9575	0.7046
0.09891	1.00004	1.2510	0.09900	0.9848	1.0411	0.04072	0.9592	0.7524
0.1966	1.0118	1.4229	0.2022	0.9971	1.2199	0.07269	0.9626	0.8328
0.3028	1.0245	1.5420	0.3008	1.0085	1.3342	0.10118	0.9664	0.8929
0.3967	1.0354	1.6396	0.3938	1.0190	1.4418	0.1997	0.9775	1.0501
0.4956	1.0469	1.7366	0.4932	1.0313	1.5361	0.2974	0.9883	1.1749
0.6006	1.0586	1.8219	0.5919	1.0407	1.6241	0.4010	0.9997	1.2905
0.8013	1.0798	1.9879	0.7914	1.0615	1.8033	0.5994	1.0203	1.4818
0.9916	1.1002	2.1386	0.9958	1.0828	1.9712	0.7996	1.0409	1.6677
1.2375	1.1252	2.3090	1.2466	1.1074	2.1742	0.9991	1.0606	1.8486
1.5338	1.1544	2.5202	1.4687	1.1285	2.3428	1.4869	1.1056	2.2750
2.0224	1.1994	2.8394	1.9823	1.1759	2.7582			

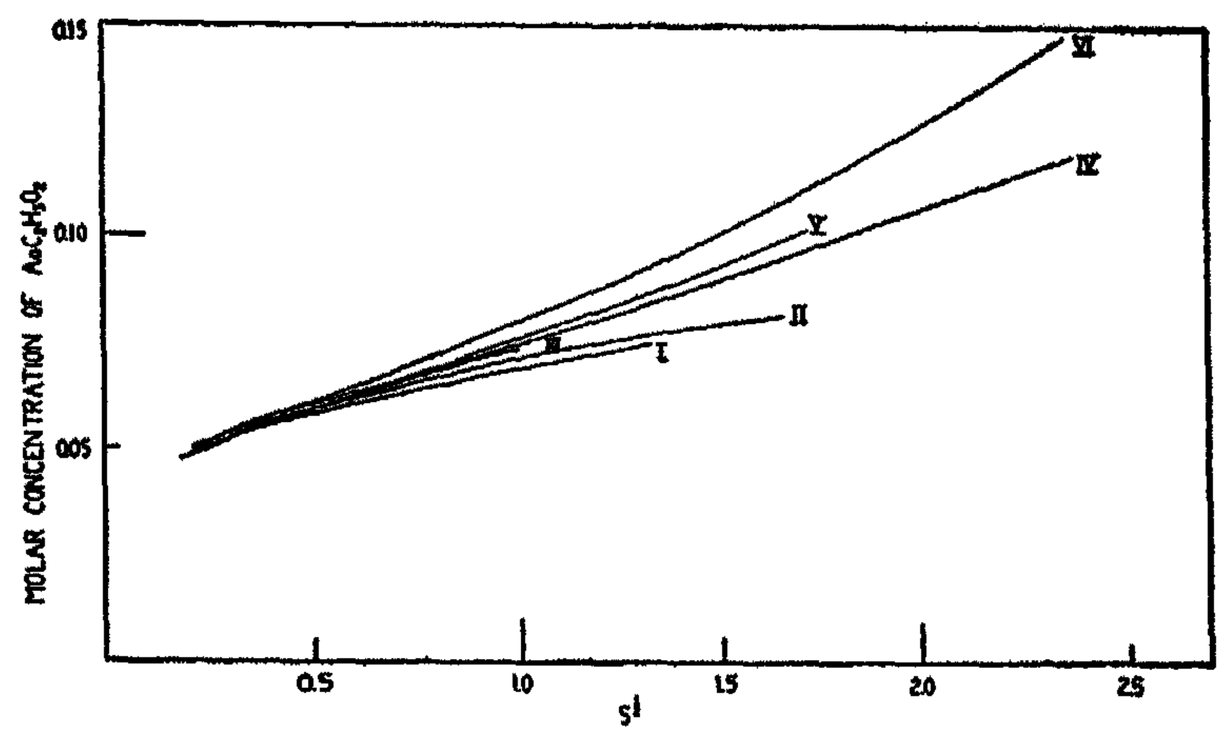

FIG. 1. Solubility of silver acetate in about 10 per cent alcohol in the presence of various nitrates. I. KNO_3; solvent, 9.41 per cent alcohol. II. $NaNO_3$; solvent, 9.17 per cent alcohol. III. $Ba(NO_3)_2$; solvent, 9.17 per cent alcohol. IV. $Sr(NO_3)_2$; solvent, 9.90 per cent alcohol. V. $LiNO_3$; solvent, 9.41 per cent alcohol. VI. $Ca(NO_3)_2$; solvent, 9.90 per cent alcohol.

solutions, one of which was always the solution that contained no added nitrate salt. From the two simultaneous equations so obtained, a value of A and a value of x_0 were calculated. We have summarized in table 8 the results of these calculations. One might infer from this table that the Debye-Hückel equation is in general valid up to approximately the same

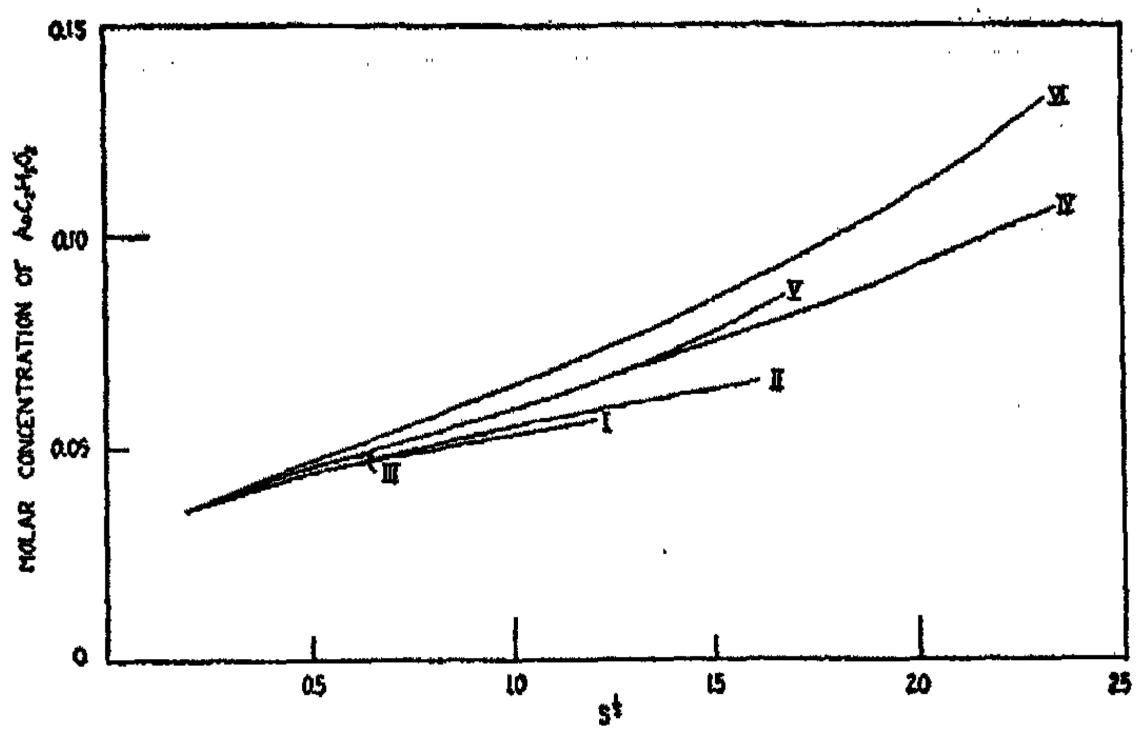

FIG. 2. Solubility of silver acetate in about 20 per cent alcohol in the presence of various nitrates. I. KNO_3; solvent, 20.37 per cent alcohol. II. $NaNO_3$; solvent, 20.37 per cent alcohol. III. $Ba(NO_3)_2$; solvent, 19.39 per cent alcohol. IV. $Sr(NO_3)_2$; solvent, 19.95 per cent alcohol. V. $LiNO_3$; solvent, 19.39 per cent alcohol. VI. $Ca(NO_3)_2$; solvent, 19.95 per cent alcohol.

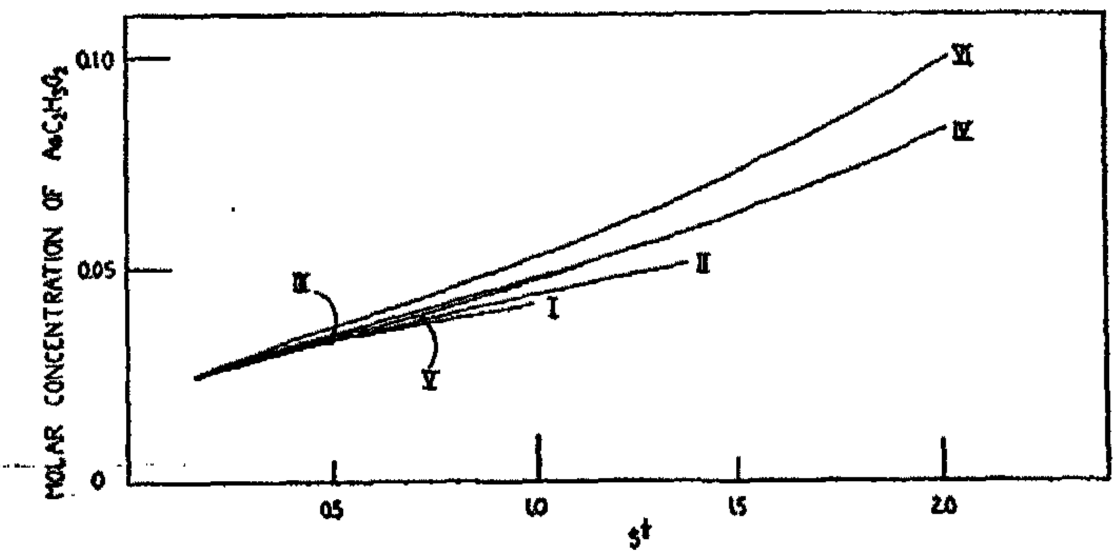

FIG. 3. Solubility of silver acetate in about 30 per cent alcohol in the presence of various nitrates. I. KNO_3; solvent, 30.02 per cent alcohol. II. $NaNO_3$; solvent, 30.02 per cent alcohol. III. $Ba(NO_3)_2$; solvent, 30.02 per cent alcohol. IV. $Sr(NO_3)_2$; solvent, 30.45 per cent alcohol. V. $LiNO_3$; solvent, 30.02 per cent alcohol. VI. $Ca(NO_3)_2$; solvent, 30.45 per cent alcohol.

ionic strength, irrespective of the nature of the added nitrate. For higher ionic strengths, there are marked differences in the effects of different nitrates. In the case of the less soluble barium nitrate, the validity of the Debye-Hückel equation extends up to solutions saturated with this salt. For all other nitrates investigated (except sodium nitrate in 9.17 per cent alcohol) there is a falling off in the calculated values of A when we go to solutions of higher ionic strengths than those given in table 8, but whereas this decrease in A is relatively slow when sodium nitrate and potassium nitrate are the added salts, it is more rapid in the case of strontium nitrate and lithium nitrate and still more so for calcium nitrate. It would therefore be more correct to say that the range of *approximate* validity of equation 5 is greatest for sodium nitrate and potassium nitrate, less for strontium nitrate and lithium nitrate, and least for calcium nitrate.

As will be pointed out in a later publication from this laboratory, the great increase in solubility of silver acetate in the presence of calcium nitrate is probably due to the formation of the intermediate ion $CaOAc^+$.

TABLE 8

Calculated values of A and x_0

ADDED NITRATE	ca. 10 PER CENT C_2H_5OH			ca. 20 PER CENT C_2H_5OH			ca. 30 PER CENT C_2H_5OH		
	A	10^3x_0	Valid to an ionic strength	A	10^3x_0	Valid to an ionic strength	A	10^3x_0	Valid to an ionic strength
KNO_3	1.43	0.775	0.5	1.37	0.597	1.0	1.39	0.466	0.6
$NaNO_3$	1.28	0.783	2.65	1.31	0.596	0.9	1.34	0.466	0.8
$Ba(NO_3)_2$	1.14	0.778	0.9	1.08	0.593	0.8	1.20	0.464	0.75
$Sr(NO_3)_2$	1.08	0.758	0.9	1.02	0.588	0.88	1.08	0.459	0.75
$Li(NO_3)_2$	1.14	0.766	0.8	1.10	0.593	0.85	1.23	0.464	0.75
$Ca(NO_3)_2$	0.86	0.750	0.9	0.75	0.582	0.98	0.80	0.455	0.75

Since the solvents referred to as approximately 10 per cent alcohol varied appreciably in composition (e.g., 9.17, 9.41, and 9.90 per cent alcohol) the calculated values of 10^3x_0 in table 8 for these solvents are not expected to be identical. Moreover the extrapolated value of x_0 depends somewhat on the value of A used in equation 5. If we assume that the value of x_0 and the value of the solubility, x, of silver acetate in a mixed solvent vary relatively in the same way with the per cent of alcohol, and if we take as most reliable the values of x_0 obtained in the presence of sodium nitrate, potassium nitrate, and barium nitrate, we readily find the following relation for the value of x_0 as a function of the per cent, p, of alcohol when p is in the neighborhood of 10 per cent; viz.,

$$10^3x_0 = 0.760 + 0.026\,(10 - p)$$

This relation gives

$$10^3x_0 = 0.783, \text{ for } p = 9.17 \ (NaNO_3, Ba(NO_3)_2)$$
$$10^3x_0 = 0.776, \text{ for } p = 9.41 \ (KNO_3, LiNO_3)$$
$$10_3x_0 = 0.767, \text{ for } p = 9.90 \ (Sr(NO_3)_2, Ca(NO_3)_2)$$

The solvents richer in alcohol differ relatively so little from exactly 20 per cent and 30 per cent, respectively, that we may infer from table 8 (giving greatest weight to the results with sodium nitrate and potassium nitrate) that

$$10^3x_0 = 0.596, \text{ for } p = 20 \text{ per cent alcohol}$$
$$10^3x_0 = 0.466, \text{ for } p = 30 \text{ per cent alcohol}$$

TABLE 9

Values of a in A.U.

PER CENT C_2H_5OH	VALUES OF a	
	KNO_3	$NaNO_3$
0.0	4.35	3.69
10.0	4.21	3.86
20.0	3.85	3.67
30.0	3.91	3.62

TABLE 10

Activity coefficient of silver acetate in saturated solutions at 25°C.

SOLVENT	10^3x_0	m_0	C_0	f
Water	0.960	0.0533	0.0531	0.800
10 per cent alcohol	0.760	0.0396	0.0388	0.797
20 per cent alcohol	0.596	0.0291	0.0281	0.803
30 per cent alcohol	0.466	0.0211	0.0201	0.802

IONIC DIAMETERS

The values of A obtained by application of equation 5 can be interpreted in terms of average ionic diameters, a, by means of equation 7. In table 9 we give the values of a so obtained for solutions containing potassium nitrate and sodium nitrate, respectively. The values of a for 0 per cent alcohol are taken from the papers by MacDougall (7) and MacDougall and Rehner (8).

ACTIVITY COEFFICIENTS

The mean activity coefficient, f, of silver acetate is given by the ratio $\frac{x_0}{x}$. The activity coefficients, γ and γ_c, may be calculated by means of equations 3 or 4 or from the equations

$$\gamma = \frac{m_0}{m} \qquad \gamma_o = \frac{c_0}{c} \tag{8}$$

where $m_0 = (N_{0_1} - N_{0_2})x_0$ (see equation 11) and $c_0 = d_0m_0$; d_0 is the density of the solvent. It will be observed that we have assigned a value of unity to the activity coefficient of an ion in any of our solvents (water, 10 per cent, 20 per cent, or 30 per cent alcohol) when the ionic strength approaches zero. We give in table 10 values of the mean activity coefficients of silver acetate in saturated solutions of that salt when the solvent is water, 10 per cent, 20 per cent, and 30 per cent alcohol, respectively. For the data in aqueous solutions containing no alcohol, see the papers by MacDougall (7) and MacDougall and Rehner (8). For the solutions listed in table 10 the values of γ and of γ_o do not differ appreciably from the corresponding values of f.

SUMMARY

This paper gives the solubility of silver acetate at 25°C. in 10, 20, and 30 per cent ethyl alcohol in the presence of the nitrates of potassium, sodium, lithium, calcium, strontium, and barium.

The Debye-Hückel equation seems to be valid for the solutions investigated up to values of the ionic strength listed in table 8.

Values of the mean ionic diameter are calculated for the solutions containing potassium nitrate or sodium nitrate.

Data are presented which will enable one to determine the activity coefficient of silver acetate in any of the solutions investigated.

The activity coefficient of silver acetate in solvents saturated with that salt but not containing any nitrate is given in table 10.

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THE PHYSICAL CHEMISTRY OF FLOTATION. VII

TRIMETHYLCETYLAMMONIUM BROMIDE AS A FLOTATION AGENT

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Solutions of trimethylcetylammonium bromide possess, to an unusual extent, certain surface properties that influence the flotation of minerals. Films thin enough to exhibit beautiful interference colors may persist for weeks, and solutions can be used for such experiments with bubbles as are described by Boys (1). The compound is one of the best frothing agents known, even a 10 mg. per liter solution giving a very stable froth. The stability of the bubbles is not due to the formation of a thick semirigid film of the type produced by saponin, for, in dilute solutions, the substance does not seem to be present in colloidal form. From aqueous solutions the salt is adsorbed by a wide variety of minerals, and since it possesses the polar–nonpolar structure characteristic of collectors, it is almost a universal flotation reagent of the collector class. The angle of contact, determined as described in previous contributions (11, 9), is 60° for chalcopyrite and antimonite. This maximum angle has not been obtained for galena and pyrite, however, nor for the oxidized and silicate minerals. For these minerals the angle is usually within a few degrees of 50°.

It is of interest that silver bromide is not precipitated from solutions of the compound immediately upon the addition of silver nitrate, but upon boiling a precipitate slowly forms. For the work to be described the compound was purified by recrystallizing twice from alcohol and washing with ether.

TRIMETHYLCETYLAMMONIUM BROMIDE AS A COLLECTOR

Dilute solutions of trimethylcetylammonium bromide induce flotation of chalcopyrite, pyrite, sphalerite, galena, and other sulfide minerals. Several silicate minerals also respond to it, quartz, for example, responding to acid, neutral, and alkaline solutions, and rhodonite to neutral solutions. Tinstone responds to alkaline solutions, but calcite does not float in acid, neutral, or alkaline solutions. Captive bubble tests with polished mineral specimens confirm these observations. The compound modifies the surface of glass in such a way that an angle of contact of about 40° is obtained;

it is therefore impossible to keep glassware "clean" when in contact with dilute solutions.

Solutions of the compound possess a property that is unusual among collectors, a property moreover that is general for all the minerals floated by it. As the concentration is increased from 0 to about 50 mg. per liter, the floatability increases steadily. Further increases in concentration decrease the floatability, until somewhere below 500 mg. per liter, not a single particle floats. Meanwhile the frothing power of the solutions has steadily increased. Parallel results are obtained when polished mineral specimens are tested by a captive bubble of air, contact ceasing to be possible at a concentration of about 100 mg. per liter. The mechanism of the process preventing contact was suggested by tests with galena in a 50 mg. per liter solution. A newly formed bubble effected contact with the center of the galena surface, but a bubble thirty seconds old did not. Whatever the age of the bubble, contact could be effected with the sharp edges of the specimen, and when once established, the contact could be retained as the bubble was moved across the plane surface,—even to the central area with which contact could not be established with an aged bubble. The galena specimen, when transferred to pure water exhibited, for a time, an air avidity; this indicates that a film of the collector had been adsorbed. It is presumed that the galena was in a suitable condition for contact with air, but the surface of the bubble, as it aged, passed into a condition that hindered contact; nevertheless, the sharp edges of the galena could still rupture the bubble surface. In slightly more concentrated solutions, contact with the center could be established only by starting at an edge, while in a 500 mg. per liter solution contact at the edges could not be established.

These results were not unexpected. It has already been suggested (11) that the difficulty of rupturing an orientated adsorbed film of frother at the surface of a bubble would hinder its contact with a collector-conditioned mineral surface. But it is only when the film is particularly stable, as here, that its presence can be demonstrated by the bubble test. Support for this interpretation is given by a test in which a chalcopyrite specimen, previously conditioned by amyl xanthate, was placed in a 500 mg. per liter solution of trimethylcetylammonium bromide. Contact with air could not be effected, though the specimen, when replaced in water, still carried an air-avid film with the characteristic amyl xanthate contact angle.

Reagents of the type of trimethylcetylammonium bromide—that is, substituted ammonium salts and amines containing a large nonpolar group—may be of value for the flotation of silicate and other oxygen-bearing minerals. They possess the advantage over soap solutions that they do not form insoluble salts with such cations as calcium, copper, and iron. Very low concentrations of the collector should suffice, since there would be no waste due to precipitation by cations derived from the ore or present in the water used.

DEPRESSANTS

Because a reagent is a depressant for a mineral when using a collector of the xanthate type, it does not follow that it will be a depressant also when using a nitrogenous collector. Thus 1 g. of $Na_2S \cdot 9H_2O$ per liter, which is much more than sufficient to prevent contact with the sulfide minerals in the presence of xanthates, does not prevent contact in the presence of 50 mg. per liter of trimethylcetylammonium bromide. Neither does it influence contact with or flotation of quartz. Similarly, a small concentration of sodium cyanide, though an excellent deactivator and depressant for sphalerite and pyrite respectively in xanthate flotation, is not a depressant with this reagent. The reagent causes flotation of so many minerals that its application in practice will depend upon the discovery of suitable depressants, which must be differential in their action. Depressants for some minerals have been found. Thus, galena is depressed by alkalis; in a solution containing 10 mg. per liter of the compound and 20 mg. per liter of lime, a partial separation of sphalerite from galena is possible. When the separation was attempted in a test tube, a little of the fine galena floated with the sphalerite. Copper sulfate and sodium cyanide when used together—but not singly—prevent the flotation of tinstone, sphalerite, and pyrite, but it has not been ascertained whether this action is differential between sphalerite and pyrite. Presumably the cupricyanide ion is the depressant. Acids and alkalis both prevent the flotation of rhodonite. In acid solutions quartz can be floated away from tinstone.

TABLE 1

Conditioned chalcopyrite in solutions of trimethylcetylammonium bromide

CONCENTRATION	CONTACT ANGLE	INDUCTION PERIOD ON PLANE SURFACE		DIRECT FLOTATION TESTS
		Extreme values	Mean value	
mg. per liter		*seconds*	*seconds*	
Nil	(54)	0.6 and 2.4	1.1	Slight film flotation
10	60	0.6 and 8.4	1.9	Excellent froth flotation
25	59	2.8 and 6.2	4.2	Excellent froth flotation
50	60	22 and 48	31	Good froth flotation
100	50*		>600	Fair froth flotation
500	Nil		>600	No flotation

* For this determination contact had first to be established with an edge.

INDUCTION PERIOD FOR CONTACT BETWEEN AIR AND MINERAL

Some tests now to be described have a bearing on the explanation of the "induction period" for the establishment of contact. Sven-Nilsson (8) has observed that *true* contact (spreading) does not usually take place until some time after a bubble has come into *apparent* contact with a suitably conditioned mineral surface. The time that elapses before spreading commences, he terms the induction period. It increases with the size of the bubble, but the manner of its dependence upon other variables has not yet been established. Using a stopwatch, the induction period has been determined for a chalcopyrite specimen in a series of solutions of trimethylcetylammonium bromide of different concentrations (see table 1). To ensure that the surface condition was as nearly as possible identical in all tests, the newly polished specimen was conditioned in a 500 mg. per liter solution and rinsed in water before it was placed in the test solution. Evidently the induction period is dependent upon the concentration of the compound. This is presumably because at high concentrations the adsorbed film is difficult to rupture.

TABLE 2

Dependence of angle of contact at a submerged paraffin surface on concentration of trimethylcetylammonium bromide

CONCENTRATION OF AMINE	ANGLE OF CONTACT	INDUCTION PERIOD
mg. per liter		
Nil	107, 106, 109°	Too small to be measured by a stopwatch
10	100	
25	94.5	
50	92	
100	80, 79	Up to 2 seconds
250	66	Very irregular
500	Nil	

CONTACT AT A PARAFFIN SURFACE

The condition of the surface of the bubble cannot account completely for the influence, recorded in table 2, of the concentration of trimethylcetylammonium bromide on the angle of contact at the surface of paraffin wax. The wax was purified first by heating with a strong sulfuric acid solution and then with a strong caustic soda solution. The test surface was formed on a glass base by allowing molten wax to solidify in contact with the air; the hysteresis effect was almost absent because of the smoothness of this surface. Since the angle of contact changed slowly with time even in distilled water, the recorded angles were measured immediately after immersion of the wax in the solution.

Variations in the surface tension of the solution, no matter how large, could not account for a reduction in the angle to below 90°, since in the Young equation for the cosine of the contact angle, the surface tension occurs only as the sole term of the denominator and therefore changes in it could not alter the sign of the cosine of the angle of contact, as happens when the angle passes through 90° (10). The results prove that the surface energy at the paraffin-water interface has changed in such a way as to render the paraffin more water-avid or less air-avid. Such a change may be a chemiadsorption of the amine, with the paraffin wax attracting the alkyl groups of the substituted ammonium salt and the polar group orientated outwards, or it may be a kind of Gibbs' adsorption at this interface. If a film is formed, it can have no very strong binding forces, for on placing the paraffin in pure water the usual contact angle (107.5°) was obtained.

SURFACE TENSION MEASUREMENTS

Perhaps the best method of studying adsorption is to attempt to apply the Gibbs' equation to measurements of the change in surface tension of a solution with concentration. Most of the methods of measurement of surface tension are inapplicable if, as here, the solution forms a finite contact angle with glass. The "maximum bubble pressure" method, which is stated to be applicable when the contact angle is finite, was therefore adopted (7). It was found, however, that the finite contact angles that *dilute* solutions of trimethylcetylammonium bromide form with glass, though they may not directly influence the maximum bubble pressure, do prevent the apparatus from functioning smoothly. Consequently results could not be obtained for solutions of concentration lower than 50 mg. per liter.

There is an unexplained lack of agreement between the results of those who have measured surface tensions of aqueous solutions of surface-active compounds. The work of Harkins and Brown (4) suggests that insufficient attention has been paid to the time necessary for the establishment of the equilibrium or static value of surface tension. Schmidt and Steyer (6) claim that equilibrium is not immediately established even in pure water.

The surface tensions of solutions of trimethylcetylammonium bromide, measured by the bubble pressure method, vary with the time interval between the formation of successive bubbles in the manner shown in figure 1. For each strength of solution the measured surface tension approaches a steady minimum value as the rate of bubble formation is decreased. This steady value is presumably the static value corresponding to the attainment of an adsorption equilibrium. The dynamic value, i.e., the value corresponding to a surface concentration equal to the bulk concentration, was not measured, but—whatever the concentration—it is evidently very much closer to, and may not differ greatly from, the value

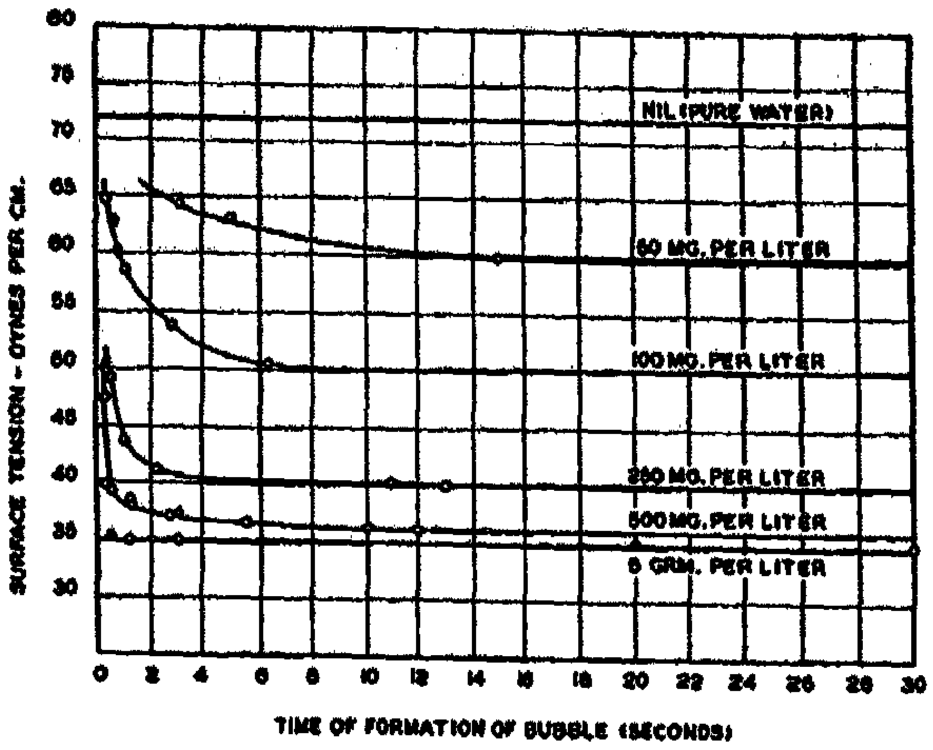

FIG. 1. Relationship between the value of the surface tension of solutions of trimethylcetylammonium bromide of various concentrations and the "age" of their surfaces. Temperature, 25 ± 1°C.

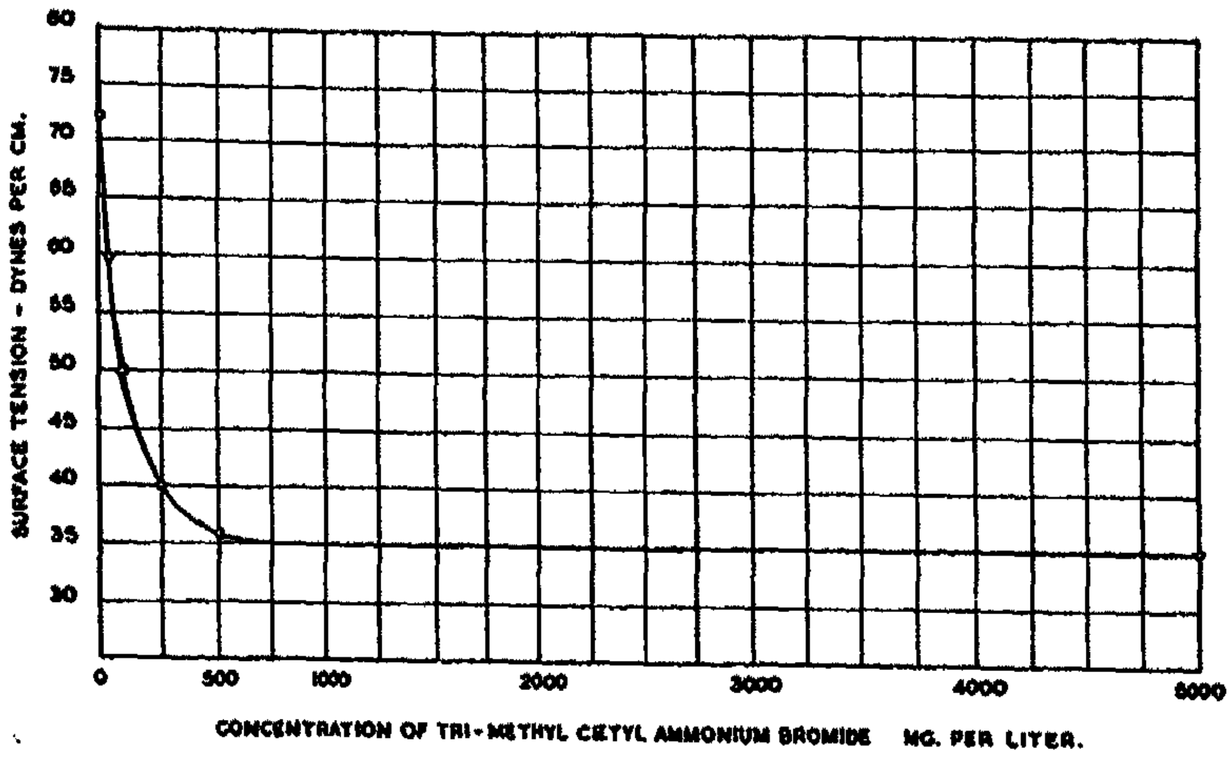

FIG. 2. Relationship between concentration of solutions of trimethylcetylammonium bromide and their static surface tensions. Temperature, 25 ± 1°C.

for pure water. The indicated slow attainment of equilibrium is due to the slow diffusion to the surface of such a large molecule as trimethylcetylammonium bromide. It is evident, moreover, that equilibrium is most rapidly established in the most concentrated solutions. This is because of the greater concentration of solute molecules that are available close to the surface for the formation of the adsorbed layer.

Figure 2, constructed from figure 1, shows the relationship between the concentration of trimethylcetylammonium bromide and the static surface tension. Up to a concentration of 1 g. per liter, the higher the concentration the lower is the static surface tension and, presumably, the more of the dissolved collector is adsorbed at the surface, but already in a 500 mg. per liter solution the surface must consist largely of orientated solute molecules. It is apparent that if the adsorbed layer around a bubble is a hindrance to contact with a suitably conditioned solid surface, contact will be most readily established in dilute solutions.

FROTHING

In figure 2 a condition has been reached at which an increase in concentration no longer lowers the surface tension. H. M. Cassel (2) in discussing a similar case, states that at a point of zero slope in the surface tension–concentration curve for sodium palmitate, the Gibbs' theorem indicates that no adsorption at all takes place. The application of the Gibbs' theorem is inadmissible, however, when complete, or almost complete orientated films of polar–nonpolar compounds are present. Langmuir (5) states that such films at the surface of aqueous solutions may possess the properties of liquids or solids.

Corresponding to the large difference between the static and dynamic values of the surface tension, even the stronger solutions froth strongly (compare Foulk (3)). This certainly indicates that there is an adsorption film at the interface, despite the horizontal nature of the concentration–surface tension curve beyond 1 g. per liter.

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THE REACTIVITY OF HALOGEN COMPOUNDS. II

The Rates of Reaction and the Energies of Activation of 2,4-Dinitrochlorobenzene with Aromatic Primary Amines

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In earlier papers (8, 9) it was pointed out that a relation existed between constitution and energy of activation for the reaction between benzyl chloride and *m*- and *p*-toluidine and the corresponding dimethyltoluidines. The relation observed was that which would be expected on the Lapworth-Robinson hypothesis, assuming that reactivity in this reaction is helped by electron accession to, or availability at, the nitrogen atom of the amino group; the *p*-methyl group lowered the energy of activation as compared with the *m*-methyl group. The correspondence between the behavior of the tertiary bases, where only the addition reaction took place, and that of the primary bases was taken as evidence that the step which governed the rate of reaction for primary amines was also the addition reaction and not the reactivity of the hydrogen atom of the primary amino group. These conclusions are supported by the behavior of *m*- and *p*-nitrobenzyl chlorides with aromatic primary and tertiary bases (7, 10).

Further confirmation of the connection between constitution and energy of activation has been obtained by a study of the reaction between 2,4-dinitrochlorobenzene and certain aromatic primary amines. This reaction has been studied by Rheinlander (11) for aniline at one temperature and different concentrations, and by Van Optall (13) for a series of aromatic amines. In addition to the results at two temperatures given in table 2 Van Optall also measured the rate of reaction at one temperature of 2,4-dinitrochlorobenzene with the following: *o*-toluidine, *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-nitroaniline, *o*-anisidine, *o*-phenetidine, *p*-aminoacetophenone, *o*- and *p*-aminodiphenyl, α- and β-naphthylamine, and the secondary bases methylaniline and piperidine. We have determined the velocity of reaction in ethyl alcohol solution at two temperatures; from these results the value of the energy of activation, E, and the quantity log A, in the equation $k = Ae^{-E/RT}$ have been determined. In table 1 are collected the results of our experiments.

The velocity constants given above represent in nearly every case the mean of at least two independent experiments, but the energies of activation calculated from them cannot be regarded as accurate to within less than about 300 cal. The extreme error for a difference in energy of activation is therefore about 600 cal. The error of 300 cal. in the energy of activation would cause an error of rather less than 0.3 unit in the value of log A and a maximum error of twice this amount in differences. This can be looked at in another way: if two reactions have the same value for A and if the ratio of the velocities is 2.7 or less, then the difference in E necessary to give this ratio is within the limits of experimental error. In such a case reliable evidence can only be obtained by a large number of determinations.

TABLE 1

Velocity constants, energies of activation, and action constants for the reaction between 2,4-dinitrochlorobenzene and some primary aromatic amines in ethyl alcohol solution

[Dinitrochlorobenzene] = 0.1 M. Unit of time, minutes

BASE	CONCENTRATION	$10^4k_{25°C.}$	$10^4k_{35°C.}$	E (IN CALORIES)	LOG A
	M				
Aniline	0.4	6.91	12.3	11180	5.8
Aniline	0.8	6.49	11.8	11520	5.9
o-Toluidine	0.4	0.384	0.785	13860	6.4
o-Toluidine	0.8	0.333	0.725	15080	7.2
m-Toluidine	0.4	9.75	17.7	11560	6.2
m-Toluidine	0.8	8.76	16.8	12620	6.9
p-Toluidine	0.4	21.3	35.7	10060	5.4
p-Toluidine	0.8	19.0	33.2	10810	5.9
o-Chloroaniline	0.8	0.01 (approx.)			
m-Chloroaniline	0.4	0.44	0.86	13010	5.9
m-Chloroaniline	0.8	0.395	0.770	12940	5.8
p-Chloroaniline	0.4	1.49	2.81	12300	5.9
p-Chloroaniline	0.8	1.34	2.57	12620	6.1
o-Bromoaniline	0.8	0.01 (approx.)			
m-Bromoaniline	0.4	0.419	0.912	15080	7.3
m-Bromoaniline	0.8	0.374	0.842	15730	7.7
p-Bromoaniline	0.4	1.08	2.29	14570	7.4
p-Bromoaniline	0.8	0.975	2.11	14960	7.6
o-Anisidine	0.4	2.63	4.72	11330	5.5
o-Anisidine	0.8	2.17	4.40	13700	7.1
m-Anisidine	0.4	5.00	8.31	9850	4.7
m-Anisidine	0.8	3.99	6.98	10840	5.3
p-Anisidine	0.4	67.4	111.0	9670	5.7
p-Anisidine	0.8	58.1	98.6	10250	6.0
α-Naphthylamine	0.4	0.222 (?)	0.363	9530	
α-Naphthylamine	0.8	0.149	0.279	12160	
β-Naphthylamine	0.4	2.73	5.03	11850	
β-Naphthylamine	0.8		3.92		

When meta-substituted derivatives are compared with para, it is seen that in every case the faster reaction has the lower energy of activation. For the reaction considered:

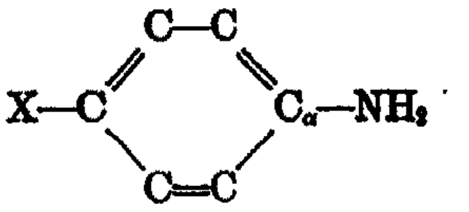
$$E_p - E_m = RT\,(\log_e A_p/A_m - \log_e k_p/k_m)$$

In tables 1 and 2 $E_p - E_m$ is always of the same sign as $\log_e k_m/k_p$. On the other hand the sign of $\log_e A_p/A_m$ varies, possibly through experimental error, and therefore the value of $\log_e k_m/k_p$ appears to be governed mainly by the changes in E. For these reactions, therefore, the change in energy of activation appears to be the chief factor in the alteration of the velocity constant. Secondly, the change in energy of activation is of the nature expected on the basis of the Lapworth-Robinson hypothesis. The argument for this need only be briefly reviewed, as it has already been dealt with elsewhere (1, 4, 5). The reactivity of these amines is determined by electron availability at the nitrogen atom of the amino group, and this in turn depends upon electron availability at, or accession to, the carbon atom to which it is attached; the greater the electron availability at this carbon atom, the greater the availability at the attached nitrogen atom. This can be looked at in another way. The dipole moment of aniline, its lower reactivity and basicity as compared with fatty amines, all suggest that the phenyl group is able to, and does, make a demand upon the two unshared electrons of the amino group, reducing their mobility. Increase of electron availability at the carbon atom to which the nitrogen atom is attached—i.e., reduction in the demand made by the phenyl group—increases the mobility of these unshared electrons of the nitrogen atom. This effect, relayed from the carbon atom to the nitrogen atom, would be expected to be less in the nitrogen atom than in the carbon atom from which it is relayed, as pointed out by Waters (14). Increased reactivity due to a sub-

TABLE 2

Energies of activation calculated from the results of Van Opstall (13)

BASE	$10^5k_{25°\text{C.}}$	k_{100}	E (IN CALORIES)
Aniline	8.5	0.286	10360
p-Toluidine	21.2	0.7057	10330
m-Toluidine	10.9	0.4248	10800
p-Anisidine	81.9	0.6718	6200
p-Phenetidine	85.7	2.026	9320



stituent X would therefore be expected to be greater at C_a than at the nitrogen atom. In other words, the reactivity of these amines would be expected to resemble that of the corresponding benzene derivatives towards electron-seeking reagents, but the differences would be less marked in the amines than in the originating benzene derivative.

It follows (1, 5) that a substituent which leads to increased electron availability at the para carbon atom, should lower the energy of activation of the amine in the para compound as compared with the meta, and raise the reaction velocity of the para compound as compared with the meta. Ortho-para directing substituents in the para-position in the amine should raise the reaction velocity and lower the energy of activation, as compared with the effect of the same substituent in the meta-position. Meta directing substituents should have the opposite effect. For reaction velocities these conclusions are supported by Van Optall's results and ours for the toluidines and chloroanilines, by Van Optall's for nitroanilines, and by our results for the bromoanilines and anisidine.

For the energies of activation the evidence is not so decisive. In every case, however, the difference between the energy of activation of the para compound and that of the meta compound is of the sign predicted by the Lapworth-Robinson hypothesis. In one case—the anisidines—the difference for both concentrations used is within the limits of experimental error. If the energies of activation for these meta and para compounds were really equal, then experimental error should give an equal number of values above and below equality. That all values for the meta compound are above those for the para—in many cases outside the range of experimental error—suggests that the meta compounds examined really have higher energies of activation than the para. The case of the anisidines is interesting. If the values of A were the same for the meta and the para compounds the difference in E required to produce the observed difference in velocity would be about 1400 cal., outside the range of experimental error. The observed differences are much smaller, and it may be that here the difference in reactivity is partially due to differences in A.

These results agree with those of Van Optall (13) in showing markedly the effect of para substituents. The order of reactivity is: $OCH_3 > CH_3 > H > Cl > Br$. The order is reversed for the energies of activation; the lower the energy of activation the greater the velocity of reaction. The effect on energy of activation is to a large extent that which would be expected from the Lapworth-Robinson hypothesis. The electron-repelling methyl group lowers the energy of activation. Chlorine and bromine have an inductive effect greater than their electromeric effect and both raise the energy of activation, bromine more than chlorine. Betti has also observed that bromine in some cases has a greater negative action than chlorine. The methoxyl group occupies a somewhat anomalous position which can possibly be ascribed to its large electromeric effect, and which agrees with its marked ortho–para directive effect. Baker (1) has also observed high velocities for substances containing the methoxyl group in the para-position to the reacting group.

Nathan and Watson (6) and Williams and Hinshelwood (4) have shown that for several reactions the differences in the energies of activation of substituted benzene derivatives are nearly proportioned to the dipole moments of C_6H_5X. For the reaction between benzoyl chloride and aromatic amines of the type $XC_6H_4NH_2$, Williams and Hinshelwood took the mean molecular diameter as constant and used the approximate equation:—

$$k = \text{const.} \times (1/M)^{\frac{1}{2}} \times e^{-E/RT}$$

Whence:

$$2.303 \log kM^{\frac{1}{2}} = \text{const.} - E/RT$$

TABLE 3

Values of E, log $kM^{\frac{1}{2}}$, μ C_6H_5X, and log A for para derivatives

BASE	E (IN CALORIES)	$10^3k_{25°\text{C.}}$	$\log_{10} 10^4kM^{\frac{1}{2}}$	$\mu \times 10^{18}$ (C_6H_5X)	LOG A
p-Anisidine	9670	67.4	1.7706	−1.2	5.7227
p-Toluidine	10060	21.3	1.2510	+0.4	5.4994
Aniline	11180	6.91	0.7418	0	5.8085
p-Chloroaniline	12300	1.49	0.1199	−1.5	5.9402
p-Bromoaniline	14570	1.08	0.0177	−1.5	7.4234

and the differences in E were found to run parallel with the differences in log $kM^{\frac{1}{2}}$. In table 3 are collected the values of E, calculated from the temperature coefficients, of log $kM^{\frac{1}{2}}$, of μ, and of log A.

From table 3 it is seen that, apart from p-anisidine, the results confirm the relationship established earlier (4, 6). p-Anisidine is anomalous in that it should have an energy of activation between that of aniline and chloroaniline to correspond with its dipole moment. The results of Van Optall (table 2) confirm this abnormality and show that it is true also of p-phenetidine.

For the meta compounds (see table 5) the order of velocity constants is $CH_3 > H > OCH_3 > Cl > Br$, and the order of energies of activation is $Br > Cl > CH_3 > H > OCH_3$. The electromeric effects are usually regarded as negligible in meta compounds, so that the effects here may be ascribed mainly to the inductive effect. Bromine and chlorine, electron-attracting groups, raise the energy of activation as would be expected. The methyl group should lower the value of E; the slight rise may be due to a steric effect exerted from the meta-position. The methoxyl group is again anomalous; it will be noticed that the group occupies its correct position in the order of velocity constants, and this case obviously needs further checking.

The effect of ortho substituents on the energy of activation has already been discussed (9) for the reaction between benzyl chloride and *o*-toluidine (cf. von Braun (2)). With dinitrochlorobenzene similar results were observed. The energy of activation for *o*-toluidine is markedly greater than that for the other toluidines and for aniline. The value of the action constant, although liable to experimental error, suggests that the probability of reaction is greater than for the para compound. The effect of the ortho substituent is thus not to hinder a reaction in a complex raised to the activated state but to increase the energy of activation. The methyl group as an electron-repelling group ought to exert in the ortho-position an effect similar to that which it exerts in the para-position, that is, it should make easier the displacement necessary for activation, and when the methyl group is directly attached to the nitrogen atom as in monomethylaniline, then the rate of reaction with benzyl halides is faster than with aniline, although one might expect steric hindrance to operate here. The *o*-methyl group therefore exerts some special influence on the amino group, which may be exerted in two ways. It has already been suggested (9) that this influence is of the nature of a coördination similar to that suggested by Sidgwick for *o*-nitrophenol and similar compounds. More recently Sidgwick (12) has pointed out that hydrogen shows little tendency to coördinate

TABLE 4

Energies of activation and dipole moments (Williams and Hinshelwood (4))

Reaction: benzoyl chloride and amine, $X \cdot C_6H_4NH_2$

X =	$100k_{25°C.}$	*E*	$\mu \times 10^{18}$ C_6H_5X
H	6.88	7350	0
p-CH_3	29.8	6800	+0.4
p-Cl	1.50	7600	−1.5
p-NO_2	0.0042	11800	−3.9

TABLE 5

Energies of activation and values of log $kM^{\frac{1}{2}}$ *for meta compounds*

BASE	$10^3k_{25°C.}$	*E*	$\log_{10}10^4kM^{\frac{1}{2}}$	LOG *A*
m-Anisidine	5.00	9850	1.6409	4.7200
Aniline	6.91	11180	1.7418	5.8085
m-Toluidine	9.75	11560	1.9116	6.2320
m-Chloroaniline	0.44	13010	0.5902	5.9195
m-Bromoaniline	0.419	15080	0.6065	7.3697

with nitrogen to form chelate rings, and the effect observed here may be, as he suggests for other cases, due to resonance. The effect of the methyl group is here exerted on the molecule containing it (cf. Von Braun(2)). There is another possibility, an intermolecular effect. The process of activation has been pictured by Eyring and Polanyi (3) as involving approach of two molecules, and consequent displacement of electrons and nuclei until the complex is brought to a state in which the reactive groups can be regarded as attached to either molecule indifferently and the complex may then rearrange itself to form the reaction products. The energy of activation is thus an energy barrier that has to be overcome. An ortho substituent group, irrespective of any dipole effect, will tend to hinder the close approach of another molecule, the two electron clouds will repel one another, and so tend to raise the energy of activation. *o*-Anisidine also has a high energy of activation.

Reference to table 1 shows that increase in concentration of the base lowers the velocity constant, raises the energy of activation, and increases the value of A. Rheinlander (11) found that increasing the concentration of aniline lowers the velocity constant of the reaction. The changes in E and A are for the most part within the limits of experimental error; but it is perhaps noteworthy that, with the exception of *m*-chloroaniline, they are in one sense.

The experiments were all carried out in absolute alcohol solution. The ethyl alcohol used was dried over quicklime for twenty-four hours, boiled under reflux with fresh quicklime for one hour, fractionally distilled, and the middle fraction used. The 2,4-dinitrochlorobenzene was crystallized from alcohol and melted at 51°C. The β-form, m.p. 43°C., was also obtained and gave the same values for the velocity constant. The bases, aniline, *o*-toluidine, *m*-toluidine, *m*-chloroaniline, *m*-bromoaniline, *o*-anisidine, and *m*-anisidine were purified by conversion to their acetyl compounds, whose melting points were as follows: after crystallization from water or aqueous alcohol acetanilide, 114°C.; acet-*o*-toluidide, 110°C.; acet-*m*-toluidide, 66°C.; acet-*o*-chloroanilide, 73°C.; acet-*m*-bromoanilide, 87°C.; acet-*o*-anisidide, 84°C.; acet-*m*-anisidide, 79°C. The acetyl derivatives were then hydrolyzed. The steam-distilled bases were dried and distilled under reduced pressure or at ordinary pressure for aniline and the toluidines. The solid bases were generally purified by crystallization from suitable solvents: *p*-toluidine, 44°C. (petroleum ether); *p*-chloroaniline, 70.5°C. (absolute alcohol); *p*-bromoaniline, 63°C. (absolute alcohol); *p*-anisidine, 57°C. (distilled under reduced pressure); β-naphthylamine, 111.5°C. (absolute alcohol).

Solutions of known strength of dinitrochlorobenzene and the base in absolute alcohol were prepared and brought to thermostat temperature. The calculated volumes of each solution were then mixed in a 50-cc. glass-stoppered flask and the volume made up to 50 cc. with absolute alcohol at the thermostat temperature; the time of mixing was taken as zero time. From time to time 10 cc. of the reaction mixture was withdrawn and run into a separating funnel containing 10 cc. of standard silver nitrate solution, dilute nitric acid, and 30 cc. of benzene. The excess silver nitrate was titrated with standard ammonium sulfocyanide, as described by Rheinlander (11). In some cases the crystalline product made difficult the withdrawal of samples, and in these cases the reaction was carried out in test tubes into which was put 10 cc. of a solution of each reactant of the proper strength and the tube then sealed up. In the case of the anisidines the color of the solution interfered with the endpoint in the volumetric estimation, and the chlorine was therefore estimated gravimetrically. The results of some typical experiments are given in table 6; in all cases the concentration of the 2,4-dinitrochlorobenzene was 0.1 M. The reaction is

TABLE 6

Results of some typical experiments at 45°C.

REACTANTS	TIME IN MINUTES	NH_4CNS IN CC.	AgCl IN GRAMS	x	$A/2 - x$	$B - x$	$k_{45°\mathrm{C}.}$
0.4 M aniline; 0.9950 $N/10$ $AgNO_3$; 1.0230 $N/20$ NH_4CNS	74	13.95		0.0282	0.1718	0.0718	0.0121
	108	12.1		0.0376	0.1624	0.0624	0.0122
	140	10.7		0.0448	0.1552	0.0552	0.0122
	156	9.8		0.0494	0.1506	0.0506	0.0127
0.8 M p-chloroaniline; 1.0105 $N/10$ $AgNO_3$; 1.0207 $N/10$ NH_4CNS	513	7.75		0.0615	0.3385	0.0385	0.00256
	699	5.60		0.0725	0.3275	0.0275	0.00260
	900	4.15		0.0799	0.3201	0.0201	0.00256
	1067	3.20		0.0847	0.3153	0.0153	0.00256
0.4 M p-anisidine	12.01*		0.0541	0.0378	0.1622	0.0622	0.111
	15.48		0.0652	0.0455	0.1545	0.0545	0.1095
	18.55		0.0725	0.0506	0.1494	0.0494	0.1095
	21.45		0.0797	0.0556	0.1444	0.0444	0.112

*12.01 means 12 minutes 1 second.

$$2XC_6H_4NH_2 + C_6H_3(NO_2)_2Cl = XC_6H_4NHC_6H_3(NO_2)_2 + XC_6H_4NH_3Cl$$

hence if [base] = A and [2, 4-dinitrochlorobenzene] = B

$$\frac{dx}{dt} = k(A - 2x)(B - x)$$

whence

$$k = \frac{1}{2t}\frac{1}{A/2 - B}\,2{\cdot}303\log_{10}\frac{A/2 - x}{B - x}\,\frac{B}{A/2}$$

The reaction was very sensitive to the purity of the bases used. The so-called pure, distilled aniline gave a distinctly higher velocity constant than that given by the base prepared from the pure acetyl compound. The best commercial *o*-toluidine gave interesting results; the velocity constant fell off during the progress of the reaction. When the base was purified through the acetyl compound, a much lower initial value of the velocity constant was obtained and no falling-off during the reaction was observed, indicating that the commercial product contained a small amount of a more rapidly reacting impurity. This reaction may, therefore, be used as a test of the purity of aromatic amines. β-Naphthylamine was too sparingly soluble in alcohol at 35°C. for results to be obtained at 0.8 *M* concentration. The figure for α-naphthylamine at 0.4 *M* and 35°C. is only approximate. Dinitrochlorobenzene had no action on ethyl alcohol under the conditions of these experiments.

SUMMARY

1. The velocity of reaction of 2,4-dinitrochlorobenzene at 35°C. and 45°C. with the following bases at 0.4 and 0.8 *M* concentration has been found: aniline, *o*-, *m*-, and *p*-toluidine, *m*- and *p*-chloroaniline, *m*- and *p*-bromoaniline, *o*-, *m*-, and *p*-anisidine, and α- and β-naphthylamine.

2. The energies of activation for these reactions have been calculated.

3. The effect on the energy of activation of transferring a substituent from the meta- to the para-position is that predicted by the Lapworth-Robinson hypothesis.

4. The changes in energy of activation for the meta and para compounds have been compared with the dipole moments; the position of *p*-anisidine is anomalous. In the meta series both *m*-toluidine and *m*-anisidine occupy anomalous positions.

5. The low rate of reaction of *o*-toluidine seems due to a high energy of activation. The steric effect is thus an energy barrier.

6. In general, energy of activation seems the chief factor in determining velocity of reaction, but the reaction probabilities are not constant and the results are not decisive.

We thank the University of Rangoon for a grant towards the cost of this investigation, which is being continued.

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STUDIES ON MOLECULAR WEIGHT CHANGES OF SULFUR MONOCHLORIDE[1]

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The following investigation was undertaken with a view to studying the anomalous behavior of sulfur monochloride in connection with its boiling-point elevation as contrasted with its depression of the freezing point.

Raoult (13), near the end of the last century, measured the freezing-point lowering of glacial acetic acid and of benzene due to the addition of sulfur monochloride. The molecular weight of the monochloride as calculated from these data was 135, which corresponds to the formula S_2Cl_2. This value agrees with those Dumas (9) and Marchand (9) found independently by vapor density measurements. Beckmann and Geib (3) and Beckmann and Junker (4) obtained similar results by the cryoscopic method, using a number of low-boiling solvents, e.g., ethyl chloride, sulfur dioxide, and phosgene.

The earliest mention of an investigation by a boiling-point method came in 1899. Oddo and Serra (12), using the Beckmann boiling-point apparatus, found the molecular weight of sulfur monochloride in benzene and carbon tetrachloride to be abnormal, i.e., 190 and 173, respectively. Two years later, however, Oddo (11) repeated the work more carefully and at the same time used a more rigorous method of calculation. This time he found the molecular weight in the same two solvents to be about 150, showing therefore no effect due to the solvent. However, he did find a slight increase in this value with increase in concentration.

From that time on the system sulfur–chlorine has been studied in more or less detail, but it was not until recently that more work was done on the molecular weight of sulfur monochloride in solution. Jones (6), by an ebullioscopic method, obtained a value in excess of 160 for the molecular weight of sulfur monochloride in carbon tetrachloride. His experiments also indicate that there is actually an effect due to the nature of the solvent. These results when taken in conjunction with those of Oddo indi-

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cate strongly that there is an inconstancy in the molecular composition of sulfur monochloride.

In view of the volatility of sulfur monochloride, with the resultant uncertainty in the composition of the solutions, it became necessary to limit the investigation to very dilute solutions. This limitation was advantageous from two standpoints. In the first place, change in the composition of the solution during ebullition was made negligible, and in the second place, no reasonable doubt could be entertained in regard to the application of Raoult's law.

Raoult's law may be applied in the following form if we take the vapor pressure of the solution at the boiling point to be equal to the sum of the partial pressures of the two components,

$$[760 + (\mathrm{d}P_A/\mathrm{d}T_A)\,\Delta T]x_A + [P_B^0 + (\mathrm{d}P_B/\mathrm{d}T_B)\,\Delta T]x_B = 760$$

The second term on the left is the correction due to the volatility of the solute, where P_B^0 is the vapor pressure of the solute at the boiling point of the solution and $\mathrm{d}P_B/\mathrm{d}T_B$ is the slope of the vapor pressure curve at that temperature. When the solute is non-volatile both of these terms equal zero and the familiar relationship $\Delta T = \mathrm{B}x_B$ remains.

EXPERIMENTAL

Materials

In order to get some information on the effect of temperature, solvents with boiling points as far apart as possible were used. Because of the reactivity of the sulfur monochloride, it was rather difficult to obtain a large number of inert solvents. The liquids finally used were benzene, carbon tetrachloride, chloroform, cyclohexane, and toluene.

Benzene that had been purified by the method described by Greer (5) was available. Since it was known to be free of thiophene and carbon disulfide it was used without further treatment. Baker's C.P. carbon tetrachloride was distilled on the 11-foot, modified Podbielniak still described by Zinc (14). The fraction which had the value for $n_D^{25°}$ of 1.4575 was used. The cyclohexane was of Kahlbaum's "reagent" grade, and it was deemed unnecessary to purify it further. Baker's C.P. chloroform, which contains 0.5 per cent of alcohol, was treated in the following manner. Several hundred cubic centimeters of the chloroform was refluxed with 1 to 2 per cent of sulfur monochloride for about thirty hours. The resulting solution was washed several times with a solution of pure sodium hydroxide and finally with distilled water. The chloroform was stored over calcium chloride for several days, and was then distilled in a closed system. Baker's C.P. toluene was treated in the same manner as that described for chloroform.

Merck's "technical grade" sulfur monochloride was distilled from 1 per cent of sulfur and 1 per cent of activated charcoal in the manner indicated by Mann, Vernon, and Pope (8). The final distillation was made in an all-glass still, using a 3-foot refluxing column filled with glass beads. In order to prevent contact with the air on transferring the sulfur monochloride from the receiver to the flask which was to hold it, the still was filled with dried nitrogen. The nitrogen was run through a three-way stopcock placed just in front of the pump. The sulfur monochloride was kept in a glass-stoppered Erlenmeyer flask from which the air had been displaced by dried nitrogen. The flask was then placed in a desiccator over calcium chloride.

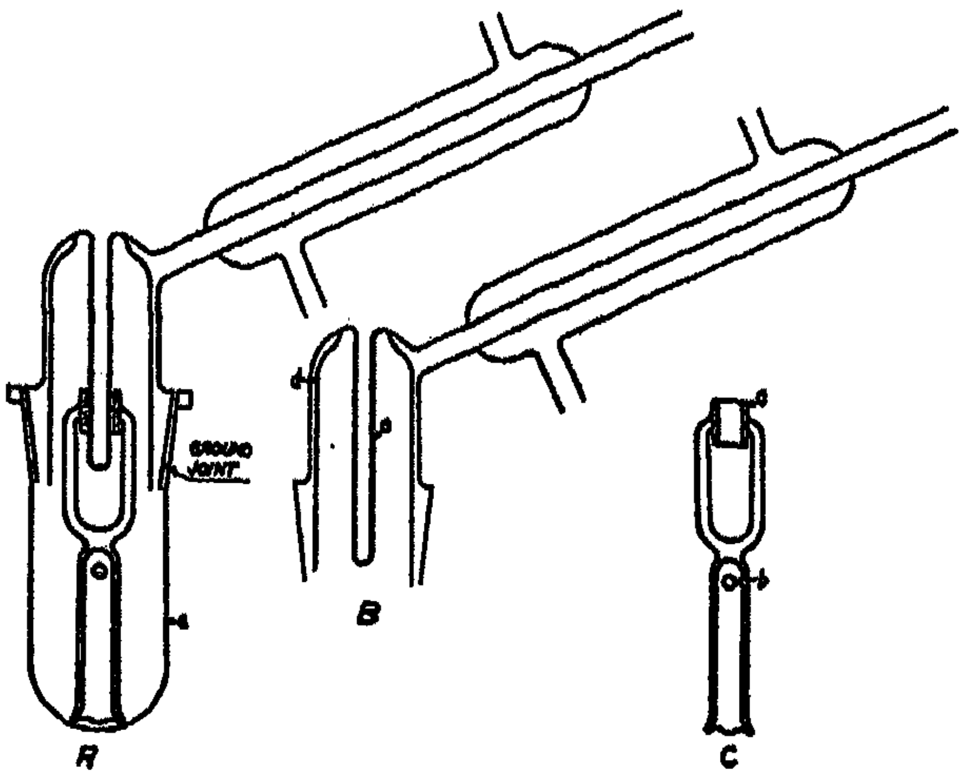


Fig. 1. The ebullioscope

Apparatus

Many types of ebullioscope are described in the literature, but it was thought best to design one modelled along the lines of the original Cottrell flask, which would be best adapted to the present purposes. The flask, consisting of three parts, is shown in figure 1. The lower body, a, is merely a piece of glass tubing 4.5 cm. in diameter, closed off at one end and ground at the other as the female of a ground-glass joint. The upper body, B, carries, besides the male of the ground joint, a shield and thermocouple well sealed into the top by a double ring seal. A condenser is sealed into the top on the outside at an angle of about 50°. The pump, C, is of a type used by Mair (7), the main difference being in the use of shorter arms and the absence of the heating element which he has sealed in the bottom.

The pump is flared at the bottom to cover a wider area which was a consequence of the use of external heating. Two identical flasks, one containing pure solvent and the other the solution, were used side by side in all the experiments in order to overcome the effects due to the fluctuation of the atmospheric pressure.

Because of the corrosive character of sulfur monochloride it was impossible to use the more efficient method of internal heating. The heat was supplied from the outside by two small, identical, electric heaters. The cores of the ovens were copper rods, shaped as tacks with concave heads. These were wound with 6 feet of No. 24 B & S nichrome wire, each oven having a resistance of 16.6 ohms. The ovens were connected in series with each other, so that voltage changes in the line would affect both similarly. A variable resistance was also placed in the heating circuit, in series, to control the current input.

A differential method of measuring the boiling-point rise, which is fully described by Jones (6) and Zinc (14), was used. It consisted merely of a galvanometer used as a deflection instrument and a simple two-junction thermocouple. The thermocouple consisted of No. 36 B & S double silk-covered copper wire and No. 30 B & S double silk-covered constantan, both of which were obtained from the Driver, Harris Co.

Procedure

The apparatus was calibrated by measuring the difference in temperature between boiling carbon tetrachloride and a solution of naphthalene in carbon tetrachloride of known composition. Baker's C.P. naphthalene, which contains only 0.002 per cent of non-volatile matter, was sublimed three times before being used in the calibration.

The actual measurements were made by first obtaining the galvanometer reading with no current flowing, merely as a reference point. Then with pure solvent boiling in each flask an initial reading was taken. After the flasks had cooled sufficiently the one which was to contain the solution was opened and a weighed amount of sulfur monochloride added. During the introduction of the solute a slow stream of dried nitrogen flowed through the flask continuously. The flask was then closed and both vessels were connected by pieces of rubber tubing, from the end of their condensers, to a large copper box containing calcium chloride. The box was open, at the far end, to the air. The heating current was started again, and after the liquid in both flasks was boiling evenly another reading was taken. The difference in the two positions on the scale gave the boiling-point rise directly. Several additions of solute were made in each experiment until the galvanometer mirror had swung over almost the whole scale.

TABLE 1

Sulfur monochloride and benzene (see figure 2)

x	W	x	W
0.02005	140.0	0.01240	136.6
0.03733	148.5	0.02470	143.6
0.04674	152.4	0.03704	148.4
0.05057	152.5	0.04653	153.7
0.06617	155.3	0.05945	153.9
		0.06645	154.4
+ (in figure 2) represents values of x and W obtained February 27, 1935		● (in figure 2) represents values of x and W obtained March 21, 1935	

TABLE 2

Sulfur monochloride and cyclohexane (see figure 3)

x	W	x	W	x	W
0.00491	149.5	0.01376	152.9	0.01694	155.2
0.02265	153.7	0.02640	158.2	0.03465	161.2
0.03697	160.2	0.04335	165.7	0.04715	167.6
0.04933	165.6	0.05078	167.8	0.05670	168.1
0.05946	168.7	0.06126	168.8	0.06840	172.2
0.06501	169.5				
○ (in figure 3) represents values of x and W obtained March 4, 1935		+ (in figure 3) represents values of x and W obtained March 6, 1935		● (in figure 3) represents values of x and W obtained March 15, 1935	

TABLE 3

Sulfur monochloride and chloroform (see figure 4)

x	W	x	W
0.00824	193.4	0.00943	187.9
0.02332	167.2	0.02156	169.0
0.03373	165.8	0.02992	166.2
0.04540	163.9	0.04050	164.7
0.05386	164.4	0.05685	165.4
○ (in figure 4) represents values of x and W obtained March 13, 1935		+ (in figure 4) represents values of x and W obtained March 14, 1935	

RESULTS

Calibrations were made at various intervals throughout the series of experiments and an average of all the values was obtained. Using 31.9

TABLE 4

Sulfur monochloride and toluene (see figure 5)

x	W	x	W
0.01542	89.4	0.01857	94.6
0.02902	102.5	0.04707	111.7
0.04851	107.1	0.06499	112.9
0.06338	112.6	0.08621	105.0
0.07840	113.5	0.11006	101.9
0.09235	109.6		
0.11277	99.8		
○ (in figure 5) represents values of x and W obtained March 27, 1935		+ (in figure 5) represents values of x and W obtained March 29, 1935	

TABLE 5

Sulfur monochloride and carbon tetrachloride (see figure 6)

x	W	x	W	x	W	x	W
0.01749	143.5	0.01519	146.8	0.01438	157.1	0.01618	183.6
0.02817	147.2	0.02345	151.4	0.02425	159.7	0.02599	182.1
0.04545	153.9	0.03649	157.4	0.03538	170.2	0.03551	180.9
0.05643	156.8	0.04730	162.6	0.04677	169.9	0.04350	180.8
0.06334	158.0	0.05715	166.2	0.05989	172.5	0.05013	182.0
						0.06099	183.0
Values obtained February 20, 1935		Values obtained March 1, 1935		Values obtained March 12, 1935		Values obtained April 8, 1935	

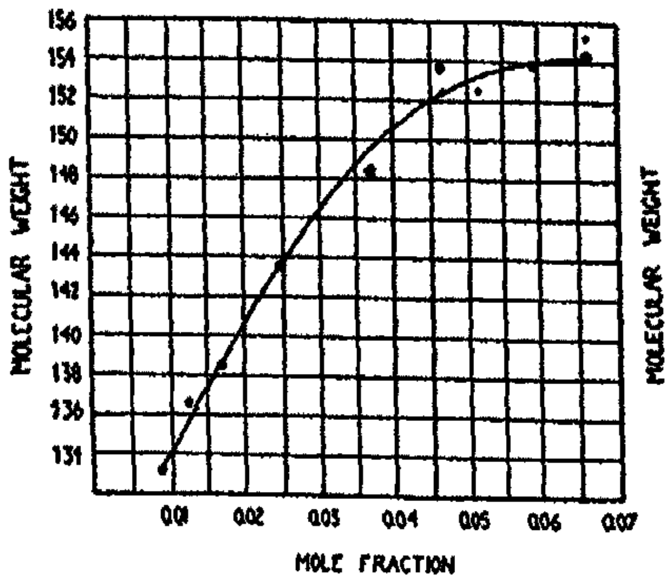


FIG. 2

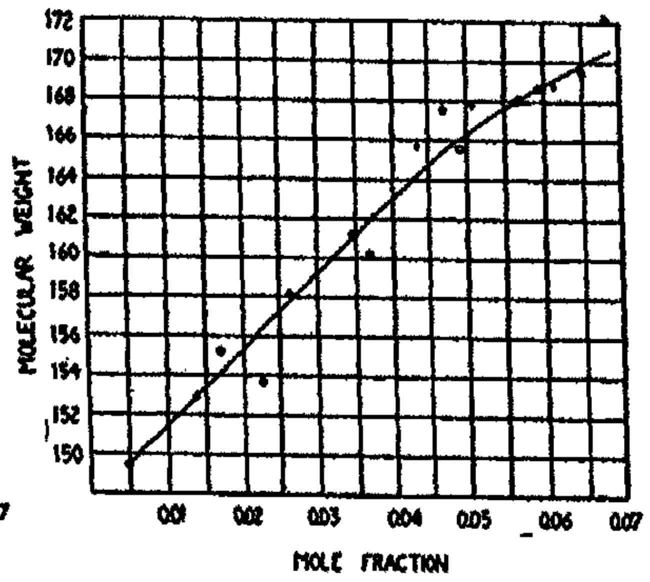


FIG. 3

FIG. 2. Sulfur monochloride and benzene. ○, February 22, 1935; +, February 27, 1935; ●, March 21, 1935

FIG. 3. Sulfur monochloride and cyclohexane. ○, March 4, 1935; +, March 6, 1935; ●, March 15, 1935

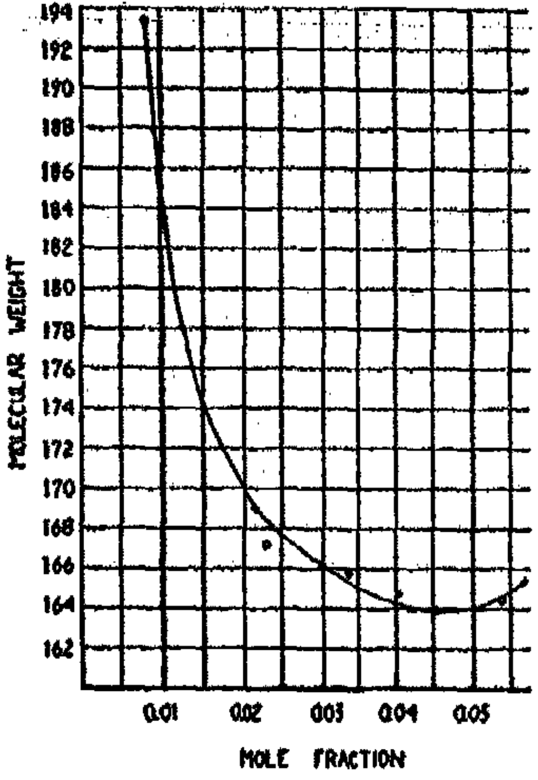


FIG. 4

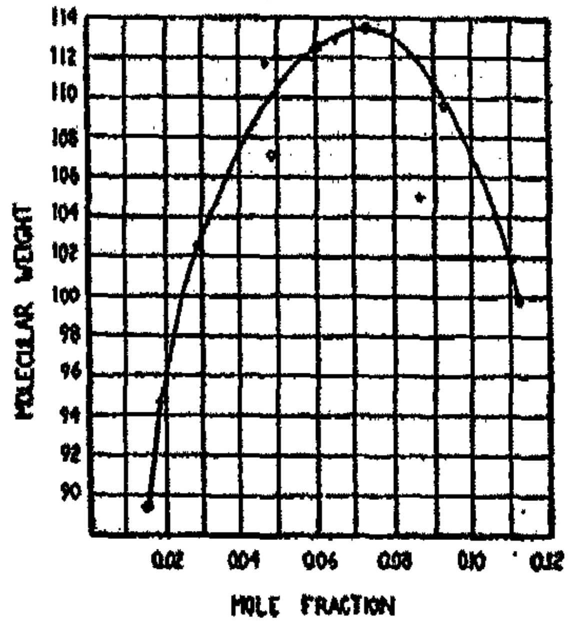


FIG. 5

FIG. 4. Sulfur monochloride and chloroform. ○, March 13, 1935; +, March 14, 1935

FIG. 5. Sulfur monochloride and toluene. ○, March 27, 1935; +, March 29, 1935

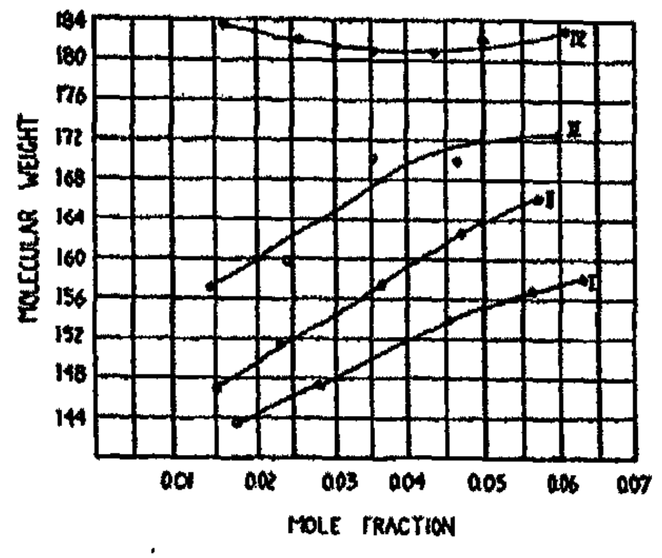


FIG. 6

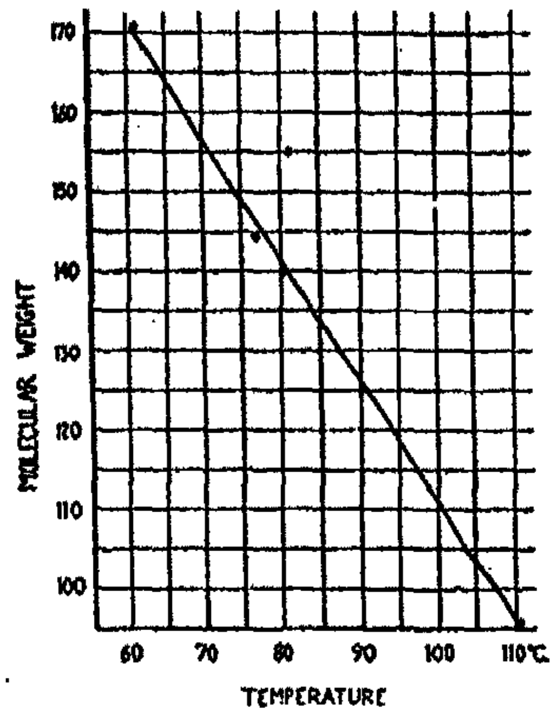


FIG. 7

FIG. 6. Sulfur monochloride and carbon tetrachloride. I, February 20, 1935, II, March 1, 1935; III, March 12, 1935; IV, April 8, 1935

FIG. 7. Effect of temperature on the molecular weight of sulfur monochloride

as the boiling-point constant, it was found that each division was equivalent to 0.0393°C.

In tables 1 to 5 x is the mole fraction of the solute and W is the molecular weight calculated from the boiling-point rise. Two or more series of measurements were made with each solvent in order to afford a check. The values of all the experiments in the same solvent are plotted on a single curve.

In the experiments listed the age of the sulfur monochloride was about the same with each measurement in any one solvent and at no time was it more than fifteen days old. In table 5 is listed an experiment in which sulfur monochloride which had been distilled on February 19, 1935 was used throughout.

One observation may be noted here in connection with the experiments in toluene. As the measurement progressed, the solution which had had the normal golden-yellow color of sulfur monochloride during the first hour of boiling, became gradually darker until at the conclusion of the experiment the liquid was a very definite pink. There was no indication of a color change in any of the other solutions.

DISCUSSION

We are forced to the conclusion that the molecular weight of sulfur monochloride exhibits a rather puzzling series of changes. It is obviously necessary to consider the method of preparation and the age of the compound, as well as the concentration and temperature of the solution in which the molecular weight is being determined. It might be well to mention here that the toluene experiments do not properly form a part of this study, since it is obvious that the high temperatures brought about the formation of sulfur dichloride, as evidenced by the pink color of the solutions. This causes complications of a nature which the data at hand are inadequate in solving. Moreover, the region past the maximum in figure 5 is somewhat outside the realm of dilute solutions and Raoult's law cannot be justly expected to apply.

Two simple conclusions may be drawn from the remaining experiments. First, we are dealing with a polymerized molecule which dissociates at higher temperatures. Figure 7 shows the molecular weight of sulfur monochloride, when x is approximately 0.02 in the various solvents, plotted as ordinate against the boiling point of the solvent as abscissa. Although the cyclohexane value is not in very good agreement, the effect of temperature is still unmistakable.

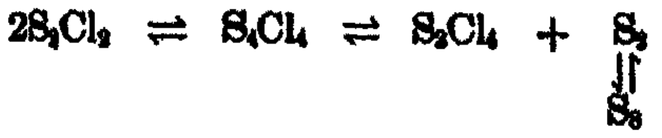
Second, the carbon tetrachloride experiments indicate that a progressive polymerization is taking place in the pure sulfur monochloride. From these results it would appear that the real equilibrium is not being measured in the boiling liquids, but that the true equilibrium rests on the side of the polymerized molecule (note the carbon tetrachloride experiment of April 8, 1935). It then becomes necessary to discover the cause of the sluggishness and the anomalous behavior of the reaction.

Furthermore the conditions of age and temperature are insufficient in explaining all of the facts. For example, when using chloroform as the solvent we find that the molecular weight increases with dilution. Such behavior is hardly consistent with the law of mass action. If

$$(AB)_2 \rightleftharpoons 2(AB)$$

dilution will certainly cause an increase in the right-hand member.

In the chloroform experiments one finds the molecular weight approaching 200 in the most dilute solutions and falling to 164 at a mole fraction of 0.044. A double molecule of sulfur monochloride should exhibit a molecular weight of 270, but such a condition should result in an increase in molecular weight with increasing concentration. The following assumption, however, offers some interesting possibilities:



$$\begin{tikzcd} 2S_2Cl_2 \arrow[r, leftrightharpoons] & S_4Cl_4 \arrow[r, leftrightharpoons] & S_2Cl_4 + S_2 \arrow[d, leftrightharpoons] \\ & & S_8 \end{tikzcd}$$

We have here a series of changes whereby sulfur monochloride breaks up to form S_2Cl_4 and S_8. From one mole of sulfur monochloride there would be formed $\alpha/8$ moles of S_8 and $\alpha/2$ moles of S_2Cl_4, where α is the fraction transformed. The total number of moles at equilibrium would be

$$1 - \alpha + \alpha/2 + \alpha/8 = 1 - 3\alpha/8$$

If $\alpha = 1$ the molecular weight is 216, and if $\alpha = 0$ it is 135. By such a mechanism it is possible to account for a variation in molecular weights from 135 to 216, which is approximately the range covered in the experiments.

The effect of concentration before the final stage of equilibrium is reached is probably best explained by the effect of the solvent and temperature on sulfur itself. If we assume a reaction such as that just above we are permitted to postulate a great many forms of sulfur. Mellor (10) cites examples of the many different forms of sulfur existing in various solvents and at different temperatures. Furthermore the presence of the sulfur monochloride may alter the form of the sulfur markedly. Aten (2), for example, reported that in a solution of sulfur in sulfur monochloride there existed a ternary mixture of S_2Cl_2, S_λ, and what he called S_π. In a previous paper (1) he showed that the molecule S_λ is S_8 and that of S_π is S_4. The latter form alone may be sufficient to explain the apparent change in molecular weight with concentration, but if it is not adequate, certainly with all the possible ramifications of sulfur there may well exist, to some extent at least, the molecule S_2. In this connection it is important to remember that the nature of the solvent may be profoundly altered by the presence of the sulfur monochloride.

SUMMARY

1. A modified Cottrell ebullioscope has been described.

2. The molecular weight of sulfur monochloride has been measured in various inert solvents at different concentrations.

3. It has been shown that the molecular weight of the sulfur monochloride seems to be affected by its age, the temperature, the nature of the solvent, and the concentration.

4. It has been postulated that the abnormal molecular weight is due to the presence of a polymer $(S_2Cl_2)_2$, which breaks up into S_2 and S_2Cl_4; also that the change in weight with concentration is due to an equilibrium between large and small molecules of sulfur.

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FERRIC SULFATE IN AQUEOUS SOLUTIONS OF OTHER SULFATES

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INTRODUCTION

Ferric sulfate, $Fe_2(SO_4)_3$, with aqueous hydrogen sulfate forms a three-component system, but it is only in high concentrations of the acid that ferric sulfate is truly a component. At lower concentrations it is hydrolyzed, and the stable solid in contact with the liquid is either a basic sulfate or a solid solution of basic character. Furthermore, at ordinary temperatures no ferric sulfate of definite composition can exist as stable solid in contact with an aqueous solution unless the ratio of SO_3 to Fe_2O_3 be greater in the liquid phase than in the solid (1). Consequently, it would be expected that the addition of ferric sulfate to the aqueous solution of another sulfate must necessarily produce a four-component system.

However, alums, pseudo alums, and other double salts have been reported as crystallizing from clear solutions. Similar observations have been made on analogous aluminum compounds. The crystallization of ordinary potassium or ammonium alum is commonplace. Dobbins and his coworkers have shown in this laboratory that sodium alum is stable over wide ranges of concentration and a fairly wide range of temperature (2). Occleshaw has reported the pseudo alum $FeSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ related to the mineral halotrichite (3); the manganese compound $MnSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and others are known. The possibility exists, therefore, under some conditions of temperature and concentration, of considering an aqueous solution of ferric sulfate and another sulfate as a three-component system.

From preliminary experiments it appeared difficult to obtain solutions from which *some* indefinite ferruginous material would not precipitate. It was attempted to add sufficient excess of sulfuric acid to prevent the indefinite solid from precipitating and to maintain a constant ratio between the excess acid and water. This latter condition was impracticable of complete realization. But the indefinite ferruginous material being apparently but slightly soluble, it was decided to ignore it with the slight

TABLE 1

Ferric sulfate in aqueous solutions of other sulfates at 25°C.

LIQUID PHASE			RESIDUE			SOLID PHASE
$(NH_4)_2SO_4$	$Fe_2(SO_4)_3$	Excess SO_3	$(NH_4)_2SO_4$	$Fe_2(SO_4)_3$	Excess SO_3	
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
1.4	44.5	+0.7				?
1.5	44.2	+1.1				?
1.7	44.4	+2.3				$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$ and indefinite mixture
1.9	43.1	0.98	0.7	41.9	0.7	$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$
2.2	39.2					$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$
3.3	32.8					$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$
4.8	28.7					$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$
11.7	20.6	0.9	14.0	40.9	0.9	$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$
14.8	18.0		14.2	41.1		$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$
17.3	16.3	2.5				$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$ and $(NH_4)_2SO_4$
26.6	9.0					$(NH_4)_2SO_4$
40.8	1.4					$(NH_4)_2SO_4$
44.2	0.5	0.8				$(NH_4)_2SO_4$
K_2SO_4	$Fe_2(SO_4)_3$	Excess SO_3	K_2SO_4	$Fe_2(SO_4)_3$	Excess SO_3	
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
2.83	27.8	0.4	28.8	37.3	4.4	$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
2.94	24.3	0.7	29.8	35.6	4.3	$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
3.34*	21.8	2.8	29.6	36.6	3.8	$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
3.38	20.8	0.9	29.8	36.0	4.2	$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
4.56	13.1	1.7				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
5.43	11.2	1.4				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
5.32	9.02	1.9	30.5	33.3	3.9	$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
6.21	6.04	2.1	29.4	32.3	3.6	$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
8.0	2.35	1.58				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$
11.7	0.85	0.59				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$ and K_2SO_4
11.9	0.69	0.68				K_2SO_4
11.8	0.31	0.55				K_2SO_4
11.5	0.10	0.26				K_2SO_4
11.3	0.02	0.11				K_2SO_4
12.2†	1.25	1.27				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$ and K_2SO_4
12.0†	1.28	1.41				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$ and K_2SO_4
12.5†	1.53	1.86				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$ and K_2SO_4
13.1†	1.68	2.24				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$ and K_2SO_4
13.7†	1.88	2.7				$2K_2SO_4\cdot Fe_2(SO_4)_3\cdot 14H_2O$ and K_2SO_4

TABLE 1—*Concluded*

LIQUID PHASE			RESIDUE			SOLID PHASE
$FeSO_4$	$Fe_2(SO_4)_3$	Excess SO_4	$FeSO_4$	$Fe_2(SO_4)_3$	Excess SO_4	
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
0.38	44.75	1.48	0.04	48.14	−4.43	Basic ferric sulfate
0.82	44.15	1.93	0.05	48.51	−4.09	Basic ferric sulfate
1.36	43.79	3.19	0.08	47.40	−4.08	Basic ferric sulfate
2.01	43.32	2.98				Basic ferric sulfate
2.53	42.25	2.47	1.63	44.74	−4.44	Basic ferric sulfate
2.61	43.25	1.12				Basic ferric sulfate
3.07‡	42.60	1.56	4.10	44.25	−4.05	$FeSO_4 \cdot 7H_2O$ and a basic ferric sulfate
3.26‡	41.71	1.99	7.90	40.10	−2.99	$FeSO_4 \cdot 7H_2O$ and a basic ferric sulfate
4.90‡	39.80	2.86	10.36	41.54	−3.95	$FeSO_4 \cdot 7H_2O$ and a basic ferric sulfate
5.30‡	38.42	3.61	6.91	43.41	−4.47	$FeSO_4 \cdot 7H_2O$ and a basic ferric sulfate
8.16	36.60	1.90				$FeSO_4 \cdot 7H_2O$ and ferric sulfate
10.47	28.36	0.25	49.89	6.26	−0.55	$FeSO_4 \cdot 7H_2O$
11.29	23.38	1.16				$FeSO_4 \cdot 7H_2O$
15.23	16.64	0.04	53.15	2.86	0.45	$FeSO_4 \cdot 7H_2O$
18.39	9.59	0.21				$FeSO_4 \cdot 7H_2O$
19.04	8.70	0.18				$FeSO_4 \cdot 7H_2O$
19.23	7.52	1.73				$FeSO_4 \cdot 7H_2O$
20.24	5.73	−0.21	22.96	1.07	0.20	$FeSO_4 \cdot 7H_2O$
21.30	3.02	−0.53				$FeSO_4 \cdot 7H_2O$
22.06	2.50	0.31				$FeSO_4 \cdot 7H_2O$
22.50	1.36	0.63	49.70	0.50	0.45	$FeSO_4 \cdot 7H_2O$

* Solution obtained by dissolving the alum $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ in water alone.

† Probably, points on a boundary curve of a four-component system.

‡ Probably, points on a boundary curve of a four-component system.

excess of acid and proceed as if dealing with a three-component system, meanwhile acquiring the data necessary to treat the several systems as of four components.

Series were made of aqueous solutions of ferric sulfate and either ammonium sulfate, potassium sulfate, or ferrous sulfate, and agitated continuously in thermostats for upwards of four months. From time to time the liquid phases were analyzed, until they had reached a steady state. The final results for 25°C. are given in table 1. Recalculated to the basis of moles per 100 grams of solution they are plotted on the right-angled isosceles triangle, in figure 1, as offering the best comparisons of them. The data are included for ferric sulfate in aqueous solutions of sulfuric acid, recalculated from analyses by Constable (3).

AMMONIUM SULFATE–FERRIC SULFATE–WATER

The system was studied at 25°C. by J. E. Hunter (5). Much difficulty was encountered in preparing solutions from which basic ferruginous solids would not precipitate on standing. In contact with solutions containing from 1.7 per cent ammonium sulfate and about 44.5 per cent ferric sulfate to 17.3 per cent ammonium sulfate and 16.3 per cent ferric sulfate, the stable solid is the alum $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$. At lower concentrations of ammonium sulfate the solid is a more basic precipitate of iron sulfates, while at higher concentrations the solid is ammonium sulfate. The tie lines for solutions and corresponding residues do not give a perfectly unique crossing for the alum, but ones reasonably close to one another. Analysis of a dry residue gave 41.5 per cent ferric sulfate and 13.6 per cent ammonium sulfate against 41.5 per cent ferric sulfate and 13.9 per cent ammonium sulfate as required by the alum formula.

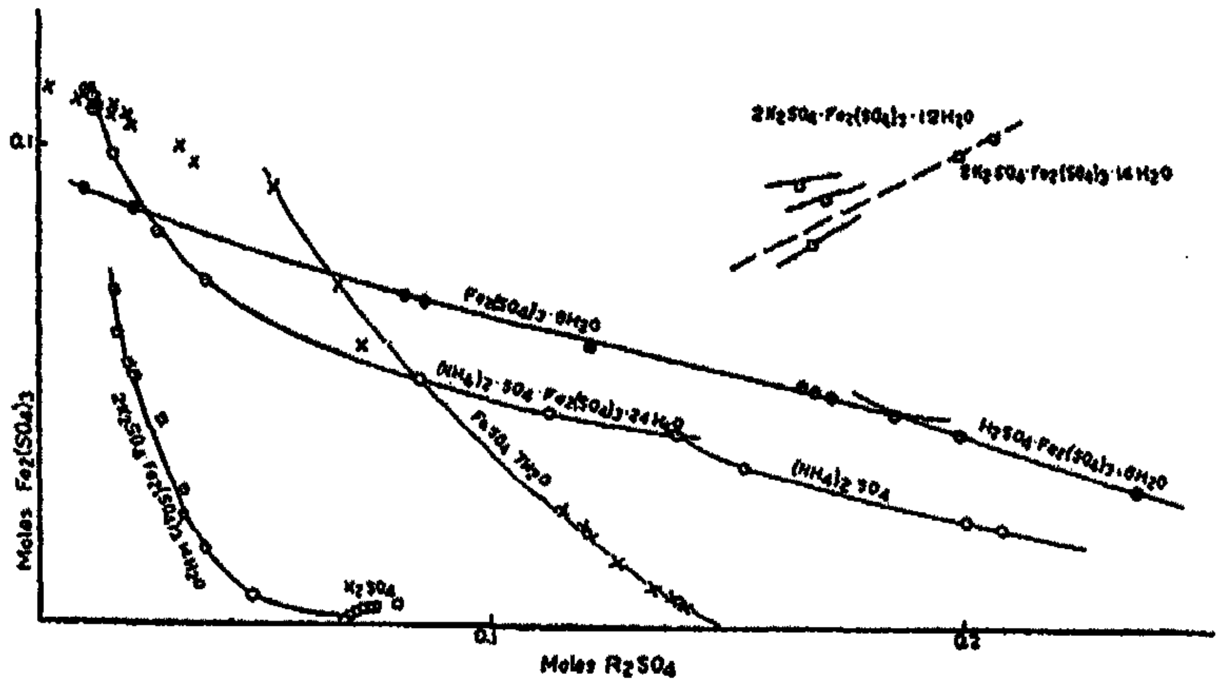

Fig. 1

The ammonium sulfate precipitates were all more or less contaminated by yellow ferruginous solids. A few only in which the contamination was slight are recorded here. To prevent this contamination would require the addition of much sulfuric acid and would markedly affect the solubility of the ammonium sulfate; the system would then become, inevitably, a four-component one. To prove the solid phase was ammonium sulfate, the carefully filtered, clear, mother liquors were placed in contact with solid ammonium sulfate for several days. Analysis of the liquid phase then showing no change in composition, it was concluded they were already saturated with respect to ammonium sulfate when filtered, and the residues were essentially that salt.

It was shown by dilatometer measurements that ammonium ferric alum is stable below 36°C., above which temperature it decomposes.

POTASSIUM SULFATE–FERRIC SULFATE–WATER

This system has been studied by D. A. Pickler (9). According to the International Critical Tables, potassium ferric alum, $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$, is stable to 33°C. (7). In contact with its aqueous solution, Pickler has found that it decomposes above 17°C. to form another double sulfate of potassium and iron with the simultaneous formation of a very basic iron complex of low solubility. Satisfactory crystals of the alum were obtained by crystallizing from solutions at 0°C. and removing adhering mother liquor and basic ferruginous material with filter paper. A series of solutions was prepared, from alum, ferric sulfate, potassium sulfate, and appropriate amounts of sulfuric acid and water, and agitated for four months at 25°C., when a steady state had been realized. The data in table 1 are results of the final analyses. In contact with solutions from 2.83 per cent potassium sulfate and 27.8 per cent ferric sulfate to 11.7 per cent potassium sulfate and 0.8 per cent ferric sulfate the solid phase is a double sulfate. At lower concentration of potassium sulfate the ferric sulfate hydrolyzes with precipitation of a more basic complex, and at higher concentrations the solid phase is potassium sulfate, K_2SO_4.

A plot of the tie lines between solution and corresponding residue data indicates with reasonable certainty that the double salt contains two reacting weights of potassium sulfate to one of ferric sulfate. On the line through the origin and corresponding to all mixtures in this proportion, points were selected corresponding to different proportions of water of crystallization. Tie lines from the point corresponding to 14 molecules of water of crystallization to the solution points passed more closely to the points for corresponding residues than tie lines from any other point. Consequently, and beyond reasonable doubt, the formula for the double salt is $2K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 14H_2O$. The solution and residue designated by an asterisk in table 1 were made from potassium ferric alum and water alone. The plotted tie line passes very close to the point representing the double salt.

The solutions designated by a dagger (†) in table 1 were obtained in an effort to realize a condition where pure potassium sulfate would alone exist in the solid phase. The solubility of this salt evidently increases much more rapidly with addition of sulfuric acid than do the ferric complexes present. A boundary curve, in part, was realized where the solid phases are potassium sulfate and the double salt just described. In the three-component system obtained by keeping excess sulfuric acid at a minimum, the range of concentrations is very short over which potassium sulfate alone is the solid.

FERROUS SULFATE–FERRIC SULFATE–WATER

The literature covering the effects of other sulfates on the solubility of ferrous sulfate has been summarized recently (8). In general, the solubility of ferrous sulfate is depressed in the presence of another sulfate. The formation of double salts is common. At high temperatures only is the hydrolysis of serious moment.

The effects produced by the addition of ferric sulfate to solutions of ferrous sulfate have been studied by C. C. Hudson (5). The data for solutions agitated at 25°C. for seven months are included in table 1. There is a transition point or "constant solution" containing 8.16 per cent ferrous sulfate and 36.6 per cent ferric sulfate. With higher concentrations of the ferrous salt, the stable solid phase in contact with the solutions is $FeSO_4 \cdot 7H_2O$. With concentrations less than 8.16 per cent ferrous sulfate, the nature of the solid phases is uncertain.

Examination of the data shows, at very low concentrations of ferrous sulfate and hydrogen sulfate in the liquid phase, the solid phase approximates in composition the basic sulfate $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$ recently described or a more basic ferric complex (solid solution) (1). As the concentration of ferrous iron increases in the liquid phase with more hydrogen sulfate the former increases in the solid phase, i.e., ferrous sulfate is a component of the solid phase. One is dealing with a four-component system and two phases are present in a mixture of solids. Calculated as oxides, for treatment as a four-component system, we find the solutions varying from one containing FeO, 0.18 per cent, Fe_2O_3, 17.9 per cent, SO_3, 28.26 per cent, and H_2O, 53.64 per cent, to one containing FeO, 2.51 per cent, Fe_2O_3, 15.37 per cent, SO_3, 28.94 per cent, and H_2O, 53.18 per cent. The range of concentrations covered is so narrow that graphical treatment is difficult, and the data are insufficient to justify definite statements regarding the composition of the solid ferric complex encountered. In table 2 are the results for a series kept at 50°C. for seven months. Again, at high concentrations of ferrous sulfate the heptahydrate, $FeSO_4 \cdot 7H_2O$, is the stable solid. The constant solution at the transition point contains 14.74 per cent ferrous sulfate and 32.94 per cent ferric sulfate. With very low concentration of ferrous sulfate in the liquid, the composition of the solid approaches the basic sulfate $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$, but as the concentration of ferrous iron increases in the liquid it becomes an essential constituent of the solid phase or phases in contact with the liquid. Ferric hydroxide is very slightly soluble in solutions of ferrous sulfate at ordinary temperatures. In table 3 are the results of agitating the hydroxide in contact with solutions of varying composition at 50°C. for seven months. Though small, the solubility is appreciable and increases relatively more as the concentraton of the ferrous sulfate increases. The analysis of the residues shows a relatively greater absorption of SO_4 than of ferrous iron in the solid. Consequently it would seem necessary to assume that basic ferrous sulfates are present in the solids as well as basic ferric compounds. The data for liquids appear to fall on a boundary curve for a four-component system, but the nature of the two coexisting solid phases is indefinite.

TABLE 2

Ferric sulfate in aqueous solutions of ferrous sulfate at 50°C.

LIQUID PHASE			RESIDUE			SOLID PHASE
$FeSO_4$	$Fe_2(SO_4)_3$	SO_4 excess	$FeSO_4$	$Fe_2(SO_4)_3$	SO_4 excess	
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
0.19	48.73	0.78				Basic ferric sulfate
0.67	46.54	2.59	0.49	58.06	−5.82	Basic ferric sulfate
3.67	44.50	1.33				Basic ferric sulfate
6.18	41.03	3.16	11.21	48.33	−6.21	Basic ferric sulfate and $FeSO_4 \cdot 7H_2O$
6.28	40.53	3.00	11.20	47.69	−6.17	Basic ferric sulfate and $FeSO_4 \cdot 7H_2O$
8.02	38.87	5.20				Basic ferric sulfate and $FeSO_4 \cdot 7H_2O$
10.55	36.61	2.50	22.17	46.43	−6.10	Basic ferric sulfate and $FeSO_4 \cdot 7H_2O$
14.74	32.94	1.09				$FeSO_4 \cdot 7H_2O$
19.40	25.35	0.95	54.95	10.74	0.30	$FeSO_4 \cdot 7H_2O$
21.76	19.85	1.01	66.20	4.61	0.20	$FeSO_4 \cdot 7H_2O$
27.88	9.67	0.22				$FeSO_4 \cdot 7H_2O$
30.35	5.40	0.30	53.97	2.80	0.51	$FeSO_4 \cdot 7H_2O$
31.99	2.79	0.67				$FeSO_4 \cdot 7H_2O$

TABLE 3

Composition of liquids and residues obtained by treating solutions of ferrous sulfate with ferric hydrate

LIQUID PHASE			RESIDUE		
Fe	Fe	SO_4	Fe	Fe	SO_4
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
3.50	0.15	6.34	0.96	40.03	5.95
4.27	0.19	7.61	0.14	38.18	6.80
5.15	0.22	9.55	0.14	38.18	6.80
6.72	0.25	12.00	2.10	45.00	8.43
8.38	0.36	15.47			

In dilute solutions of ferrous sulfate, the system is always a four-component one.

No double salt, nor pseudo alum analogous to that described by Occleshaw, exists between 25°C. and 50°C. at any concentration of ferrous sulfate.

SUMMARY

It is shown that, generally, the addition of ferric sulfate to an aqueous solution lowers the solubility of another sulfate. At extreme dilutions when hydrolysis is nearly complete, sulfates which form disulfates with sulfuric acid, such as ammonium sulfate and potassium sulfate, may become more soluble, but over a very small range of concentration.

With ferrous sulfate, no double salt is formed between 25°C. and 50°C. at any concentration of ferric sulfate.

With ammonium sulfate, an alum is formed below 36°C., and the range of concentrations over which it exists at 25°C. is shown, with approximate accuracy.

With potassium sulfate an alum exists below 16°C. over a wide range of concentration. It is not stable above 16°C., but a double salt, $2K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 14H_2O$ is stable over all but very high or very low concentrations of ferric sulfate. The concentration limits are shown with approximate accuracy.

At very low concentrations and at rather high concentrations of ferric sulfate in the presence of another sulfate, the system must be treated as composed of four components. But over wide ranges of concentration and temperature the system may be considered as composed of three components, and so treated, practically, with the addition of small excesses of sulfuric acid.

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NEW BOOKS

The Next Hundred Years: the Unfinished Business of Science. By C. C. Furnas. 434 pp. Baltimore: Williams & Wilkins Co., 1936. Price: $3.00.

Since the death of Slosson how often have we heard the lament that no one has risen to take his place in the popularizing of chemistry. In reading the present book the reviewer became convinced that this complaint need no longer be considered valid, although chemistry constitutes only a small part of the work. A freshness of viewpoint, an originality of treatment, a readiness of wit challenging our most cherished beliefs,—scientific and otherwise,—breadth of outlook and wide scope of subjects, all controlled by sound common sense, have been united with masterly genius.

Although the work makes no claim of especially drawing upon or contributing to the field of physical chemistry, yet frequent use is made of its methods in dealing with the subjects treated, and any physical chemist will profit from and be entertained by this keen analysis of the present status and future problems of science.

The topics are divided between the fields of biology, chemistry, physics, engineering, and sociology. One cannot fail to be impressed by the wide range of knowledge displayed and the variety of problems discussed. The specialist will probably be most interested by the subjects remote from his own field with which he does not so often have contact.

The usefulness and instructive features might have been enhanced by the introduction of some tables, for example, of the vitamins and hormones and their functions.

In spite of the caution and prevailing skepticism of the author, he occasionally displays a surprising degree of confidence in his predictions. Probably few, if any, biologists will show his optimism as to the possibility of unlimited extension of the span of human life, nor many engineers or scientists follow him in believing that the utilization of sunlight as a power source is imminent.

The book is not only thoughtfully written and instructive but is pervaded by an atmosphere of conviction and a sprightliness of presentation that make it a most readable work which can be recommended to any reader who looks to the future with an open mind.

S. C. Lind.

Electrolytic Oxidation and Reduction: Inorganic and Organic. By S. Glasstone and A. Hickling. Vol. IX of a Series of Monographs on Applied Chemistry edited by E. Howard Tripp. 22 x 14 cm.; x + 420 pp. New York: D. Van Nostrand Company, Inc., 1936. Price: $9.00. London: Chapman and Hall, Ltd., 1935. Price: 25s.

This is a well-balanced monograph on the preparation of inorganic and organic compounds by electrolytic oxidation and reduction, in which the basic theory is presented adequately and a wealth of practical information is to be found. Experimental methods are not discussed in detail, although the various factors affecting yields are treated systematically. Wherever possible the authors try to give an unbiased interpretation of the reaction mechanisms involved. They fully realize the limitations of our present knowledge of the subject. Although many problems are left unsolved, the discussions given should stimulate further research in this intriguing field.

The first three chapters (ninety-five pages) deal with "Reversible Electrode Potentials," "Polarization and Overvoltage," and "Diffusion Phenomena in Electrolysis." The theory underlying polarization is treated more extensively than in other texts, and is up-to-date. It is not quite clear why the saturated calomel electrode is less advantageous than the 0.1 *N* or 1 *N* calomel electrodes on account of a high temperature coefficient (p. 13). The oxidation potentials of *o*-phenanthroline ferrous iron, and diphenylamine are not known at pH = 7; the data tabulated on p. 31 should refer to acid medium. In the calculation of electrode potentials during electrolysis (p. 72) the migration of ions should have been considered. This is mentioned later, but it would have been more logical to mention this on p. 72.

The following chapters deal with reversible inorganic oxidation and reduction processes, irreversible organic and inorganic reduction processes, "polymerization of anions," oxidation of fatty acids and their salts, irreversible inorganic and organic oxidation processes, and "anodic substitution." An extensive list of literature references is given at the end of each chapter; the patent literature is considered throughout the text. It is regrettable that no attention is paid to the important investigations of Conant and coworkers on the "apparent oxidation potential" of various organic compounds.

The above remarks do not detract from the value of this timely monograph, which is recommended to all those who for theoretical or practical reasons are interested in electrolytic preparations, and in electrode reactions in general.

I. M. KOLTHOFF.

Inorganic Colloid Chemistry. II. The Hydrous Oxides and Hydroxides. By H. B. WEISER. 15.5 x 23.5 cm.; vii + 429 pp. New York: John Wiley and Sons, Inc., 1935. Price: $4.75.

The second volume in this series by Professor Weiser maintains the same high standard as Volume I. As the subtitle indicates, this work covers about the same field as was covered by the author in his book, *The Hydrous Oxides*, which he published about ten years ago. However the present work is in no sense a revision of the previous one. So much has been accomplished in this field in the ten year period that the work has been almost completely rewritten. X-ray analysis has proved that many of the substances considered to be hydrous oxides at that time are in reality hydrous hydroxides or hydrous oxide hydrates. These results have made extensive changes in the subject matter necessary.

After a general introductory chapter which considers the preparation, properties, and nature of hydrous oxide sols and gels, the author in the next three chapters deals with the hydrous oxides of iron, the aluminum family, and chromium. The hydrous oxides of the other elements are taken up, where practicable, in the order in which they come in the periodic table. The last four chapters deal with technical applications of these important types of substances and are titled "Mordants"; "Color Lakes of the Hydrous Oxides"; "Mineral Tanning"; and "Coagulants in Water Purification." These last chapters add considerably to the value of the book from the technical point of view. Like the first volume of the series, this one is well illustrated and a complete list of references to original work is given.

Those who have used Professor Weiser's previous work on this subject will welcome this new book. It is very complete and up-to-date. Colloid chemists will welcome this second member of the series on Inorganic Colloid Chemistry and will await the appearance of the third volume with interest.

L. H. REYERSON.

Colorimetric Methods of Analysis. Volume I, Inorganic. By Foster Dee Snell and Cornelia T. Snell. xxiii + 766 pp. New York: D. Van Nostrand Co., 1936. Price: $9.50.

Of the physicochemical methods in daily use in analytical laboratories, the colorimetric doubtless hold first place. The size of the present work, compared with that of F. D. Snell's *Colorimetric Analysis*, published in 1921, attests the rapid development of this branch of analysis. The first volume of the second edition embraces a brief account of the principles of colorimetry, a rather full description of colorimetric apparatus, and a comprehensive collection of methods for the colorimetric determination of both the common and the rarer elements; a few turbidimetric and nephelometric methods are included incidentally. A section of some fifty pages is devoted to the determination of hydrogen-ion concentration. Photoelectric colorimeters are described, and their application is discussed; the Pulfrich photometer receives mention.

The book gives evidence of careful preparation, and there are only a trifling number of typographical errors; on page 51, in a footnote, the names of Emich and Donau are incorrectly given. One might wish that the authors had given a fuller discussion of the principles of colorimetry. The volume should prove a useful one for those making use of colorimetric methods. Since the authors have intentionally confined themselves to the practical side of the subject, the book is of little value to those interested in the theoretical aspects of colorimetry.

E. B. Sandell.

Ueber katalytische Verursachung im biologischen Geschehen. (On Catalytic Causation in Biological Phenomena.) By Alwin Mittasch. 14.5 x 22 cm.; x + 126 pp. Berlin: Julius Springer, 1935. Price: 5.70 RM.

This is the publication in an extended form of an article which the author contributed to the periodical *Die Naturwissenschaften* with the subtitle "Auch ein Berzelius-Gedenken," as a tribute to the memory of Berzelius on the occasion of the centenary of the origination by Berzelius of the concept of catalysis in 1835. The present author is a chemist who urges many years experience in technical catalysis as an excuse for entering the field of biological catalysis, while admitting that the last word must rest with biologists. In the course of his review of the problem he deals with a large variety of subjects such as immunity, hormones, growth substances, vitamins, genes, and stimuli of various kinds. The treatment is largely philosophical and in the course of the argument such subjects as holism, causality, vital force, and metaphysics are introduced. A feature of the book is the liberal citation of literature references and of lists of books for further reading. The postscript ends with a quotation from Goethe: "Alles ist einfacher, als man denken kann; zugleich verschränkter, als man begreifen kann" (All things are simpler than one may think; at the same time more interlocked than one can conceive),—a statement which would seem quite appropriately to sum up the author's writing.

P. Haas.

Les Solutions Concentrées. Théorie et Applications aux Mélanges Binaires de Composés Organiques. By Jean Timmermans. 647 pp.; 540 figures. Paris: Masson & Cie, 1935.

It is difficult to give the reader an adequate idea of the wealth of material to be found in this book of Timmermans. Not only does he present the theory of various types of binary mixtures of organic substances but he also reproduces, in a very comprehensive manner, experimental data dealing with such properties of the mixtures as density, freezing point, boiling point, critical solution temperature, refractive index, viscosity, surface tension, etc. The data are sometimes given in tables, but usually by means of accurately drawn graphs.

The book includes a 26-page bibliography and a 49-page formula index of the binary systems discussed in the text.

The usefulness of the book is somewhat impaired by the very individualistic system of symbols used by the author and by the very small type employed for letters and numbers in the graphical figures.

F. H. MacDougall.

Solubility of Non-electrolytes. Second edition. By Joel H. Hildebrand. American Chemical Society Monograph Series. 203 pp. New York City: Reinhold Publishing Corporation, 1936. Price: $4.50.

The appearance of a second edition of Dr. Hildebrand's well-known book on solubility will be welcomed by those who are familiar with the first edition. They will be glad to have available a portrayal in moderate compass of the progress that has been made during the last dozen years in the study of solutions. Dr. Hildebrand's monograph can be heartily recommended to the attention of all students of the properties of solutions. It is to be noted that only non-electrolytes are treated by the author.

F. H. MacDougall.

Die Fermente und ihre Wirkungen. Supplement Bd I: Specieller Teil: Hauptteil VII–XV. By Carl Oppenheimer. The Hague, Holland: W. Junk Verlag, Scheveningsche Weg 74, 1935–36. Appearing in Lieferung of *ca.* 160 pp. each, 20.5 x 28 cm. Priced at $6.80 per Lieferung.

The chemist investigating enzyme reactions is dealing with organic catalysts elaborated by, and controlling the reactions in, living cells and tissues. Naturally the flood of papers appearing in this field is enormous. During 1924–1929 the massive four volumes of the fifth edition of Oppenheimer's *Die Fermente und ihre Wirkung* appeared and have been accepted as the standard reference work in the field of enzyme chemistry.

The present volume deals with the literature which has appeared since the main series of volumes was published. Lieferung 1 to 5 are already published. They maintain the high standards which characterized the parent volumes. No other work of equivalent grade is available in this field. It is encyclopedic in scope and is invaluable to students of enzyme phenomena.

Ross Aiken Gortner.

Fundamentals of Biochemistry in Relation to Human Physiology. Fifth edition. By T. R. Parsons. xii + 453 pp. Baltimore: William Wood and Company, 1935. Price: $3.00.

In 1923 the author, a member of the faculty of the University of Cambridge, published the first edition of this *Fundamentals of Biochemistry.* The book represented an "attempt to describe in a continuous story the more important generally-accepted principles which have been derived from the study of the changes occurring in the human body." The author's purpose that "any merit my book may possess may result from its containing *less* of information rather than more than other books contain" has been successfully achieved and has made this book a welcome novelty in these days when many elementary texts appear to be designed rather to impress fellow scientists with the erudition of the author than to present an "introduction suitable for readers new to the subject."

Despite the large number of important recent advances in biochemistry, the author has succeeded admirably in maintaining his original objective in this, the fifth, edition. The newer developments in the fields of pigments (flavins), hormones, sterols, and vitamins are presented in a satisfactory manner with excellent citations of the literature for those who would read further.

The reviewer knows of no elementary text in which the relations of physical chemistry to life are presented more simply and more effectively than in the two chapters under the headings of gas tensions, osmotic pressure, colloids, adsorption, the reaction of body fluids, and the functional importance of electrolytes.

While the material presented is neither designed nor adequate in amount for the courses in biochemistry of our professional schools in this country, it affords a worthy introduction to the more comprehensive texts and as such should be readily available for these students. It can also be recommended as an excellent general presentation for the layman who wishes to be informed in modern developments of chemistry as related to vital activity.

Howard B. Lewis.

Flame. By O. C. deC. Ellis and W. A. Kirkby. Methuen's Monographs on Chemical Subjects. 17 x 11 cm.; vi + 106 pp. London: Methuen and Co., Ltd., 1936. Price: 3/ net.

The study of the initiation and propagation of flame in gaseous mixtures has not only become increasingly important in recent years by reason of its relation to the internal combustion engine, but has also received much attention in the research laboratory. The authors deal not only with the physical aspects of combustion but also with such matters as the effect of temperature and pressure on flame equilibria, chain reactions, and free radicals. They give 160 references to literature, including very recent work, and in the space at their disposal they present a review of the subject which is both authoritative and interesting. The illustrations comprise a plate and fourteen diagrams.

J. R. Partington.

Aluminium-Legierungen. I Teil zugleich Anhang zu Aluminium Teil A in Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. By A. Grutzner and G. Apel. 26 x 18 cm.; 342 pp. Berlin: Verlag Chemie, 1936. Price: 26.25 marks (in Germany, 35 marks).

The book gives a list of aluminum alloys classified according to a system, with the compositions, properties, and applications, and references to literature and patents. To the metallurgist and technician it will be of great utility.

J. R. Partington.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 4: Stickstoff. Lieferung 3. 26 x 18 cm.; pp. 507–854. Berlin: Verlag Chemie, 1936. Price: 41.25 marks (in Germany, 55 marks).

The present section deals with the oxides of nitrogen. It includes a very detailed discussion of the technical formation of nitric oxide in the electric arc and by the oxidation of ammonia. The latter, as the most important modern process for the manufacture of nitric acid, receives special attention, and this section is perhaps the best and fullest account of the subject which has yet appeared. The rest of the volume is also of high standard and includes many discussions of physicochemical and technical interest. As an example, the account of the reaction $2NO + O_2 = 2NO_2$, with a wealth of numerical data, may be mentioned.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium. Teil A, Lieferung 3. 26 x 18 cm.; pp. 451–534. Berlin: Verlag Chemie, 1936. Price: 10.50 marks (in Germany, 14 marks).

This section deals solely with the surface treatment of aluminum and aluminum alloys, including oxide layers and metallic surfaces. It gives full references to literature and patents and contains material of physicochemical interest as well as much on the technical side.

J. R. PARTINGTON.

Reactions of Organic Compounds. By W. J. HICKINBOTTOM. 22.5 x 15 cm.; x and 449 pp. London: Longmans, Green and Co., 1936. Price: 16/—.

For its price and size this book is unique. The author has set out to describe the *facts* of organic chemistry by reference to laboratory practice rather than to classical theory, and in consequence the arrangement of the subject matter presents unusual features. The most obvious is simplicity of classification. Only eleven chapters are taken to describe the reactions of the commoner groupings and radicals in the various types of structural situation in which they occur. The consideration of benzene with methane, phenols and alcohols with enols, etc., in this way avoids repetition and enables the ground to be covered much more neatly than is done in many text-books where the conventional order is followed.

As a typical example the chapter headed "Aldehydes and Ketones" can be mentioned. Here are first detailed quite fully the various transformations of substances of these types without any references to the common subdivisions of organic chemistry, a very widely chosen selection of specific examples is then quoted, drawn from aliphatic, aromatic, and heterocyclic systems, the carbohydrates, and the quinones. Such a plan emphasizes the essential unity of the chemistry of the *carbonyl* compounds, and at the same time the wealth of experimental illustration given affords the very necessary indication of the limitations which "general" reactions are apt to display in practice.

As a complement to a standard text-book this work should prove valuable both to advanced students and to those who desire a book of reference which is convenient to read and up-to-date (the index is good and frequent citations are made to the original literature). From the point of view of the student the book is additionally attractive because it has a useful appendix dealing with the identification of organic substances, and throughout its contents are distributed some thirty five pages of tables of physical constants, derivatives etc., quite adequate for the general requirements of qualitative analysis. Full experimental details are included for several hundreds of preparations. It thus offers under one cover much of the material of three books.

R. J. W. LE FÈVRE.