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A STUDY OF THE SODA ALUM SYSTEM

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Soda alum was discovered by Gehlen in 1815 (6), and the existence of the double salt has been confirmed by the work of many other investigators. Astruc and Mousseron (1) investigated the 5°, 18°, and 42°C. isotherms and state that the salt does not exist below 11°C. or above 39°C. Dobbins and Addlestone (2) found that the alum does exist at 42°C., but that considerable hydrolysis occurs at that temperature. This study was undertaken with the purpose of investigating further the effect of increase of temperature on the system, and to find the full range of conditions under which the alum can exist and to determine if other compounds may exist in the system. The system was studied in a 10 per cent sulfuric acid solution at 50°, 42°, and 30°C.

EXPERIMENTAL PROCEDURE

Since the alum had been found to exist at 42°C., although hydrolysis had occurred to some extent, it was decided to cut down the hydrolysis by the addition of a small amount of sulfuric acid and to raise the temperature to 50°C. A 10 per cent solution of acid was found to be necessary to eliminate hydrolysis at this high temperature. Anhydrous sodium sulfate and aluminum sulfate with 18 moles of water were used in making the solutions. A series of solutions was prepared containing varying concentrations of aluminum sulfate in contact with solid sodium sulfate, and another series containing varying concentrations of sodium sulfate in contact with solid aluminum sulfate. One hundred cc. of solution in contact with the solid was prepared for each bottle. The bottles were placed in a constant temperature bath at 50°C. Equilibrium was reached only after nine months.

SAMPLING

After equilibrium was reached, the solutions were allowed to settle completely so that the supernatant liquid was perfectly clear. Samples of the liquid phase were withdrawn by means of pipets, transferred to weighing bottles, and weighed. These samples were then diluted to 250 cc.

The solid phase presented much difficulty in sampling, owing to the very finely divided condition of the solid. The very fluffy condition of the precipitate made it impossible to obtain a sample free of adhering liquid. Portions of the solid with adhering liquid were transferred to weighing bottles and the liquid drained off as much as possible. The residue was then weighed and made up to 250 cc.

METHODS OF ANALYSIS

The system was analyzed for aluminum, gravimetrically, by the method of Dobbins and Sanders (5), and for sodium, volumetrically, by the method of Dobbins and Byrd (4). Since additional sulfuric acid had been added and since the determination of sulfate in the presence of large amounts of aluminum is not very satisfactory, this determination was not made. The sodium and aluminum were calculated to sodium sulfate and aluminum sulfate, respectively. Since the small quantity of sulfuric acid was added in constant amount, it has been treated with the water as one component.

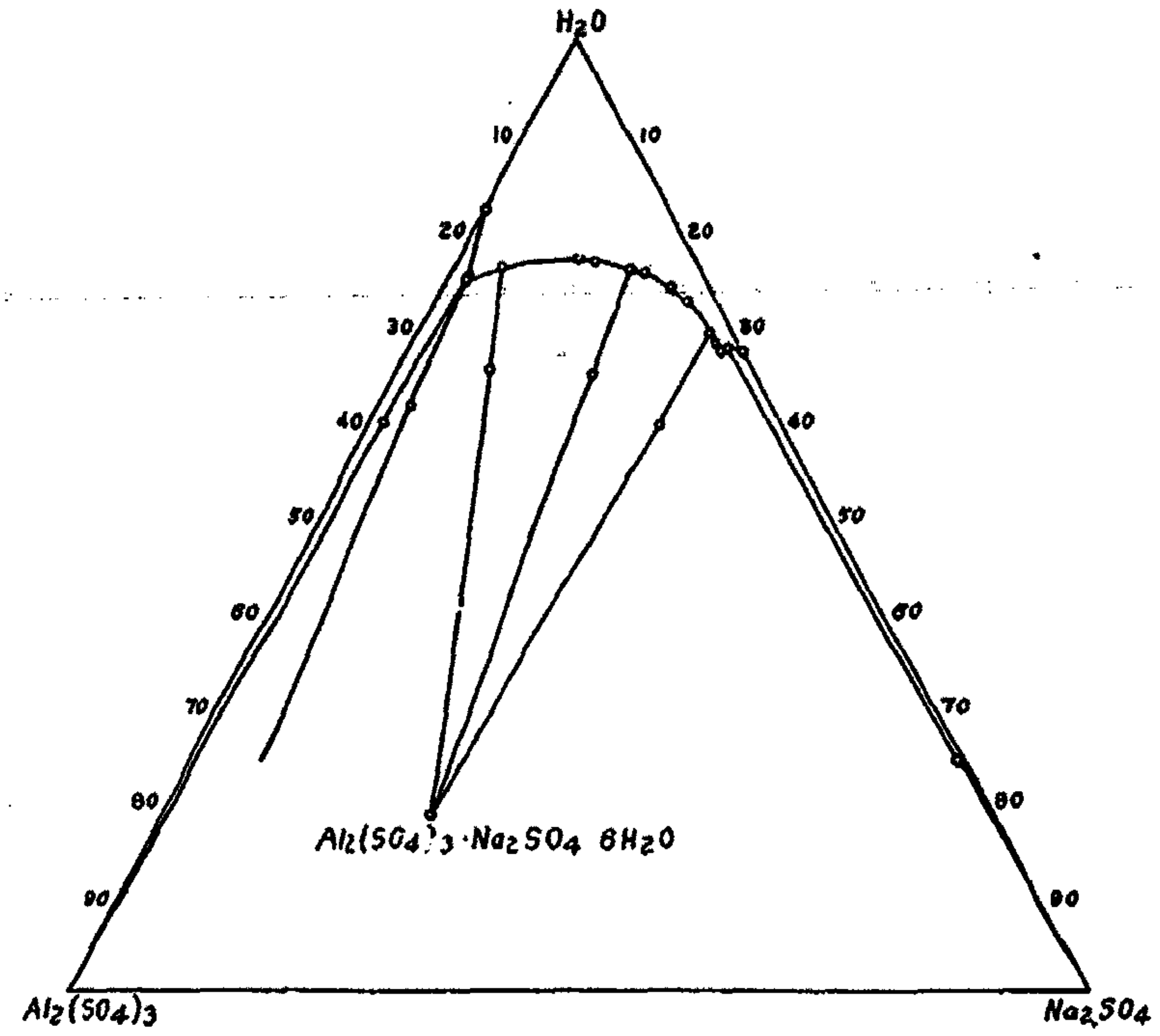

Fig. 1. The system Na_2SO_4–$Al_2(SO_4)_3$–H_2O at 50°C. in 10 per cent sulfuric acid

EXPERIMENTAL RESULTS

The data for the 50°C. isotherm are given in table 1 and the results are plotted in figure 1.

An examination of figure 1 shows that the 50°C. isotherm consists of three solubility curves, showing that compound formation had taken place. Tie lines connecting the wet residue to the liquid phase show that the solid phases are anhydrous sodium sulfate, anhydrous aluminum sulfate, and a double salt of the composition $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 6H_2O$.

TABLE 1

Data for the 50°C. isotherm

LIQUID PHASE			WET SOLIDS		
Na_2SO_4	$Al_2(SO_4)_3$	H_2O	Na_2SO_4	$Al_2(SO_4)_3$	H_2O
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
33.07	0	66.93			
30.93	1.64	67.43	75.44	0.49	24.07
30.66	2.23	67.11			
29.64	2.00	68.36	28.00	12.00	60.00
28.40	2.30	69.30			
27.13	3.05	69.82			
24.24	3.19	72.57			
23.29	4.17	72.54			
17.86	6.23	75.91			
16.46	7.00	76.54	18.40	16.22	65.38
13.35	9.40	77.25			
11.49	11.05	77.46			
5.04	18.40	76.56	9.03	25.34	65.63
1.97	23.43	74.60	3.50	34.43	62.07
1.81	23.10	75.09	1.73	36.58	62.69
	18.77	81.23			

TABLE 2

Data for the 42°C. isotherm

LIQUID PHASE			WET SOLIDS		
Na_2SO_4	$Al_2(SO_4)_3$	H_2O	Na_2SO_4	$Al_2(SO_4)_3$	H_2O
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
33.20	0	66.80			
32.00	1.52	66.48	66.47	0.81	32.72
31.79	1.87	66.34			
28.75	1.71	69.54	27.50	9.80	62.70
24.47	2.84	72.69			
17.42	6.51	76.07			
16.81	5.63	77.56			
10.93	10.49	78.58	13.54	18.85	67.61
4.72	17.11	78.17	9.81	26.00	64.19
1.75	18.59	79.66	1.14	38.00	60.86
0	16.45	83.55			

The double salt exists between the concentrations of 30.66 per cent to 1.97 per cent sodium sulfate and 2.23 per cent to 23.43 per cent aluminum sulfate. This is a much wider range than was found for the existence of the alum at 42°C. The hydrated double salt, $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 6H_2O$, found at 50°C. has not been reported previously in the literature. The corresponding double salt, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 6H_2O$, has been reported and is thought to be the most stable hydrate of this salt.

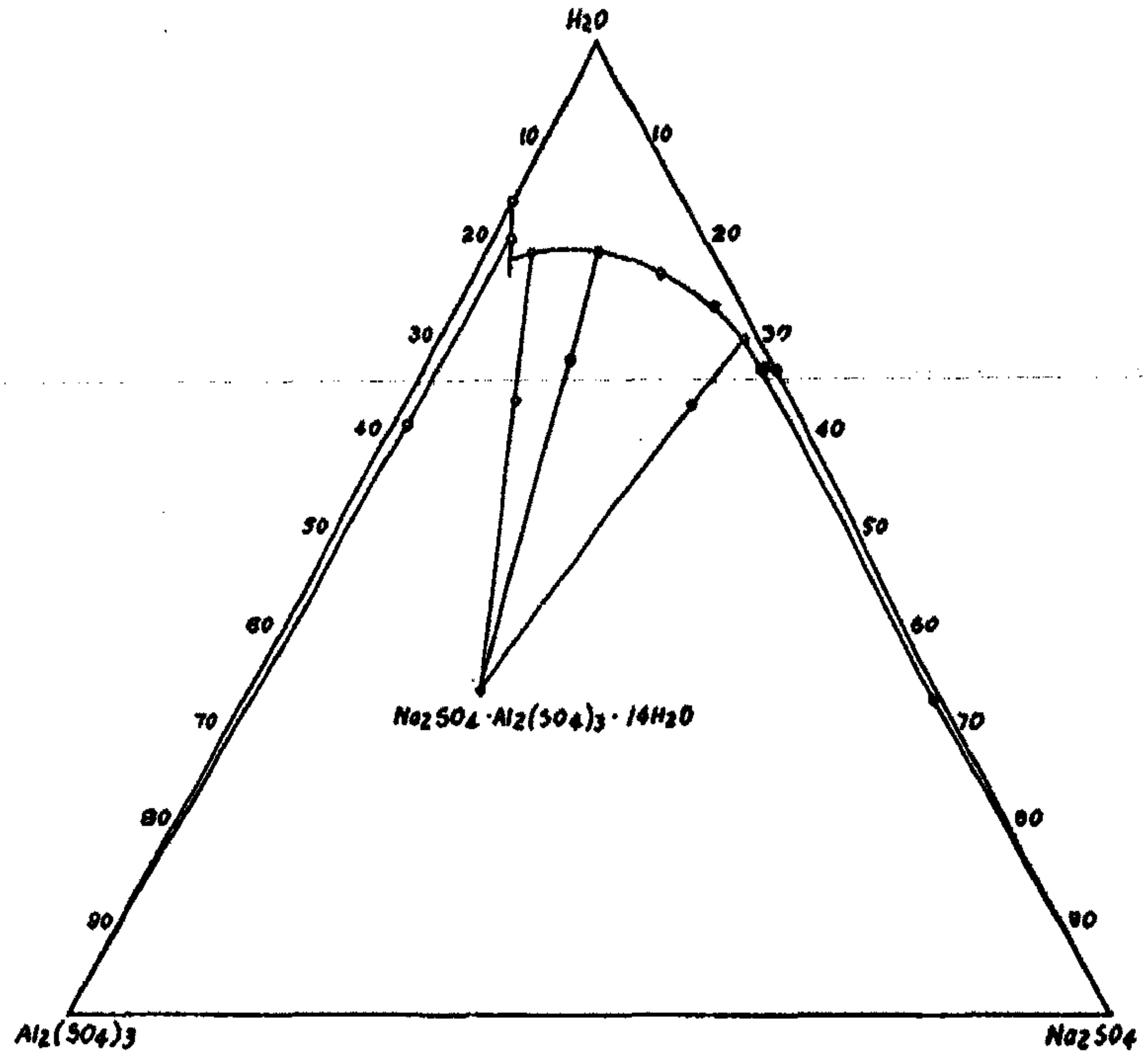

FIG. 2. The system Na_2SO_4–$Al_2(SO_4)_3$–H_2O at 42°C. in 10 per cent sulfuric acid

Since the alum was not found to exist under these conditions, the temperature was lowered to 42°C., where the alum had been found by Dobbins and Addlestone (2).

The data are given in table 2 and the results plotted in figure 2.

An examination of figure 2 shows that the 42°C. isotherm also consists of three solubility curves. Analysis of the wet residue shows that the solid phases are anhydrous sodium sulfate, anhydrous aluminum sulfate, and the double salt of the composition $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$, which exists between the concentrations 31.79 per cent to 2.70 per cent sodium sulfate and 1.87 per cent to 20.25 per cent aluminum sulfate. This double sulfate has been reported by Mousseron and Gravier (7) as existing at 37°C. The

TABLE 3

Data for the 30°C. isotherm

LIQUID PHASE			WET SOLIDS		
Na_2SO_4	$Al_2(SO_4)_3$	H_2O	Na_2SO_4	$Al_2(SO_4)_3$	H_2O
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
34.07	0	65.93			
32.09	1.38	66.53	80.08	0.55	19.36
31.80	1.72	66.48	30.00	8.62	61.38
30.03	2.19	67.78			
18.45	6.22	75.03			
11.69	10.55	77.78			
5.52	15.78	78.70	11.44	28.26	60.30
1.96	21.33	76.71	1.66	35.20	63.14
1.74	21.00	77.26	0.89	39.16	59.95
0	14.52	85.48			

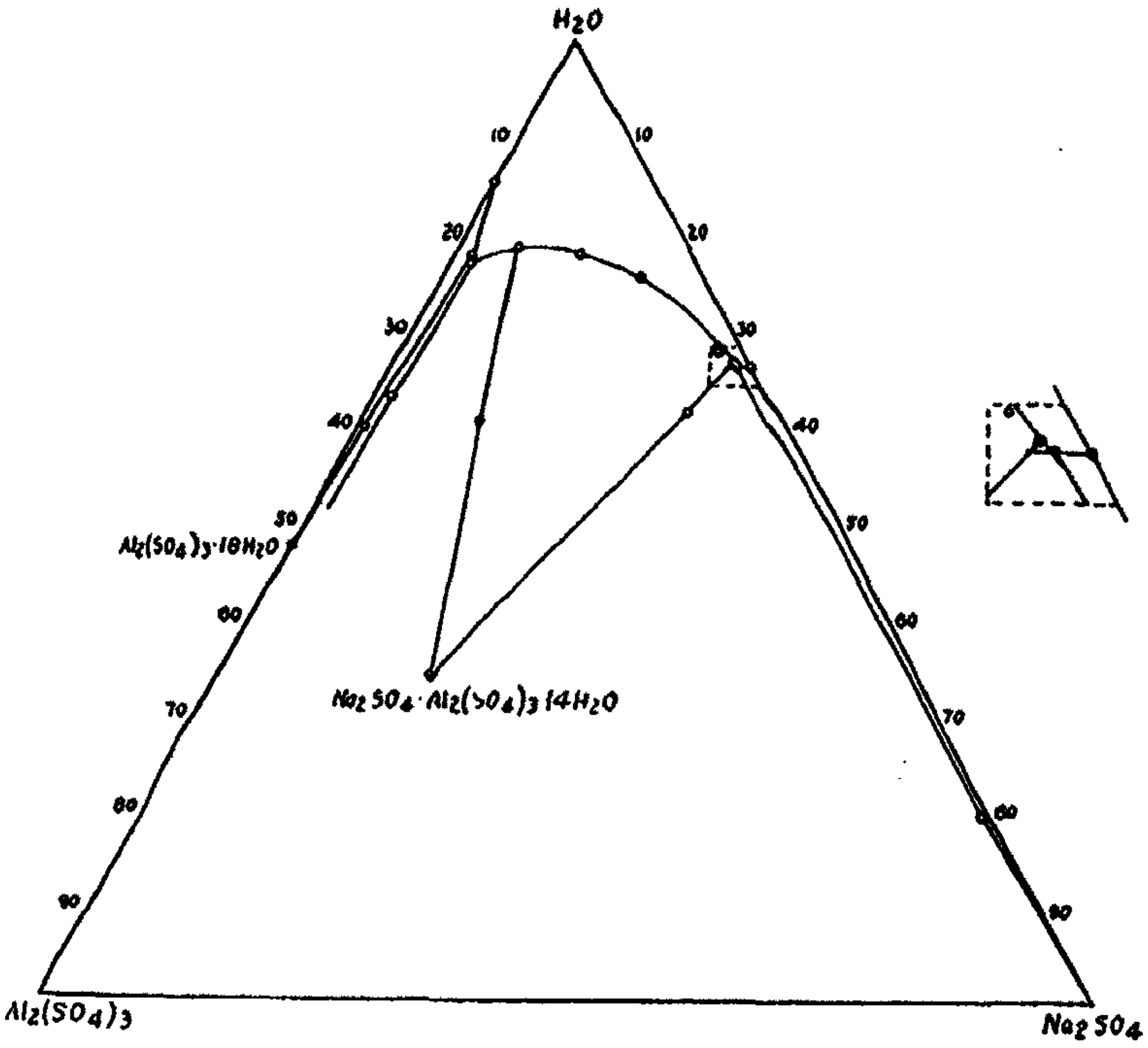

FIG. 3. The system Na_2SO_4–$Al_2(SO_4)_3$–H_2O at 30°C. in 10 per cent sulfuric acid

range of existence for the double salt with 14 moles of water is much wider than for the alum under the same conditions of temperature.

Since no alum was found at 42°C. and since the work of Dobbins and

Byrd (4) showed that at 30°C. the alum did form in aqueous solutions without hydrolysis, it was decided to study the system at that temperature to find out if any further hydration had taken place.

The data are given in table 3 and the results are plotted in figure 3.

An examination of figure 3 shows that at 30°C. there are three solubility curves, showing the formation of a compound. The solid phases existing are anhydrous sodium sulfate, aluminum sulfate with 18 moles of water, and the double salt of the composition $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$, existing between the concentrations 32.09 per cent to 1.96 per cent sodium sulfate and 21.33 per cent to 1.38 per cent aluminum sulfate. A microscopic examination of the solid phase showed octahedral crystals similar to the alum. A comparison of the 30°C. isotherm as studied by Dobbins and Addlestone (2) with figure 3 shows that the range of concentration for the alum is much less than for the hydrated salt with 14 moles of water at the same temperature.

TABLE 4

Dilatometer readings

TEMPERATURES	CAPILLARY READINGS	
°C.	*cm.*	
41.4	16.00	
42.4	17.10	
42.9	17.50	
43.4	18.00	1 hour
	19.50	12 hours
	20.01	24 hours
	20.00	36 hours
44.4	21.00	
45.4	22.00	
46.4	23.00	

DILATOMETER DETERMINATIONS

Since two hydrated salts had been found under the conditions studied, it was decided to determine the transition temperature at which the salt with 14 moles of water was dehydrated to the salt with only 6 moles. A dilatometer consisting of a bulb 2 in. in length and 0.5 in. in diameter and a very long capillary tube was used. The bulb was partially filled with partially dehydrated alum, and then thoroughly moistened with 10 per cent sulfuric acid; the bulb was then sealed. The remainder of the bulb was filled with Nujol by evacuating it and allowing the Nujol to flow in. The dilatometer, affixed to a meter stick, was then allowed to come to equilibrium at room temperature in a water bath. The temperature was slowly raised and the rise of oil in the capillary recorded. It was found that twelve hours were needed for the mixture to come to equilibrium after each increase in temperature. At the transition temperature it was necessary to keep the temperature constant for thirty-six hours before equilibrium was attained. The data are recorded in table 4.

An inspection of table 4 shows that the transition of the double salt with 14 moles of water to the salt with 6 moles occurs between 42.9° and 43.4°C. This slow transition is verified by the great length of time necessary for the system to come to equilibrium.

SUMMARY

The 50°, 42°, and 30°C. isotherms for the system sodium sulfate–aluminum sulfate–water in 10 per cent sulfuric acid have been studied. At 50°C. the double salt $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 6H_2O$ exists. At 42°C. and 30°C. the double salt $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$ is the stable salt.

The double salt $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 6H_2O$ has not previously been reported in the literature.

The transition temperature of the double salt with 14 moles of water to the double salt with 6 moles of water lies between 42.9° and 43.4°C.

A 10 per cent sulfuric acid solution prevents the formation of alum at 50°, 42°, and 30°C.

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A NEW SLIT PHOTOMETER FOR THE ANALYSIS OF THIN SECTIONS OF COLORED SOLUTIONS: EXPERIMENTAL CONFIRMATION OF THE DIFFUSION EQUATION

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In previous work (2) on this problem, a mathematical relation was derived which described the progress of a definite concentration of a diffusing substance as a function of the diffusion coefficient and the time. The relation gave rise to a simple and direct method for determining diffusion coefficients. In experimental work described previously (3), the usefulness of the method was demonstrated and data were obtained for the diffusion coefficient of the cupric ion in silica gels. However, the apparatus used in this work did not permit an actual measurement of the concentration gradient in the diffusion front.

The purpose of the present undertaking was to devise an apparatus for making this measurement, and to compare the experimental results with those predicted by the equation.

APPARATUS

The diffusion apparatus used in this work was essentially a refined model of that previously described (3). The apparatus (figure 1) consisted of a light source, a slit system, 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 32-c.p. bulb was operated from a 6-volt storage battery. Variable resistances in series with the lamp provided a means of adjusting the intensity of illumination. The lamp housing was surrounded by a water jacket to prevent excessive heating.

Immediately in front of the lamp was a gelatin light filter which passed nearly monochromatic red light to the glass water cell. The position of the lens was adjusted to illuminate the first slit with a slightly converging beam of light. After passing through the diffusion cell, the light beam was further confined by two parallel black plates which permitted the passage of a light beam about 3 cm. wide and 0.1 mm. thick to the photoelectric cell.

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The diffusion cell was formed by clamping rectangular pieces of plate glass (18 cm. × 10 cm.) on either side of a u-shaped, rubber-covered rod. The cell was always clamped to the same uniform thickness of about 1 cm. The cell fitted into an upright conveyer (figure 2) which was so arranged on a stand that it would be moved up or down at will by means of a screw adjustment. The screw adjustment extended through the bottom of the constant-temperature air bath which was maintained at a temperature of 25°C. Readings of the height of the cell were taken to 0.01 cm. by means of a cathetometer. A mark on the cell holder was illuminated by a miniature shaded bulb, and a cloth curtain over the glass window of the thermostat and the telescope of the cathetometer prevented external light from entering the bath.

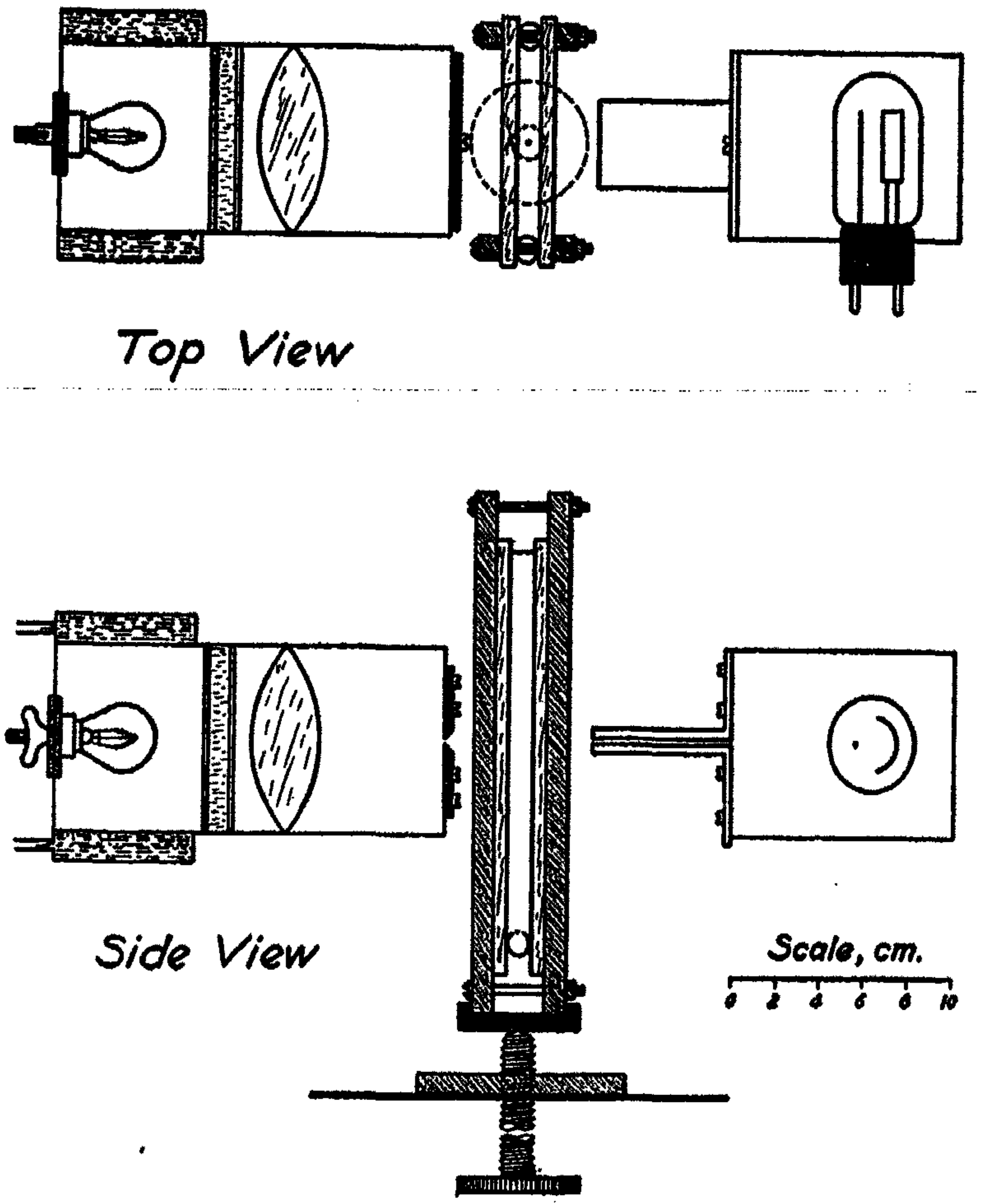

FIG. 1. Diagram of diffusion apparatus

The photoelectric cell was connected to a vacuum tube amplifier (figure 3). The tube was a General Electric F. P. 54, and the circuit was practically that of Du Bridge and Brown (1) except for changes in the connections to the control grid. The photoelectric cell acted essentially as a grid leak, having a resistance which was a function of the light intensity on the cell. An increased light intensity lowered this resistance, giving a less negative grid potential and a correspondingly larger plate current. This effect was counteracted by applying a higher negative potential to R_4 by means of the potentiometer. Thus light intensities were measured in terms of potentiometer readings.

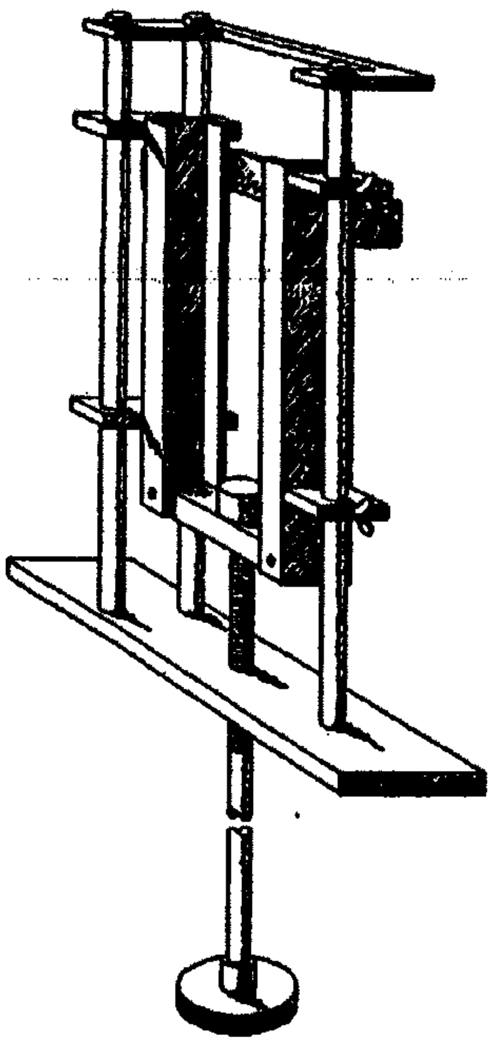

FIG. 2. Diagram of cell holder

The amplifier and photoelectric cell were carefully shielded. The battery unit, consisting of two 6-volt, 120-ampere hour storage batteries, was contained in a lead-lined box. A heavy, air-tight iron shield enclosed the amplifying tube and the resistance R_8. The grid lead to the photoelectric cell was supported in a 1-in. brass tube by three sulfur insulators. All shielding was connected by short wire leads to a common ground.

Since the theory of this type of circuit is fully discussed by Du Bridge and Brown (1), only a brief description of the method of adjustment will be given.

(1) Connect the battery and adjust the filament current to about 90 milliamperes by means of R_6. Allow the tube to warm up at this current for an hour or more.

(2) With the potentiometer set at zero voltage and with no light on the photoelectric cell, adjust R_1 to bring the galvanometer deflection to zero. Have the galvanometer connected so that the reading decreases (i.e., moves to the left) with a decrease in plate current.

(3) Change the filament current slowly by adjusting R_6 in such a direction that the galvanometer deflection is decreased. It should pass through a rather flat minimum. If it goes off the end of the scale before the minimum is reached, bring it back near the center by readjusting R_1.

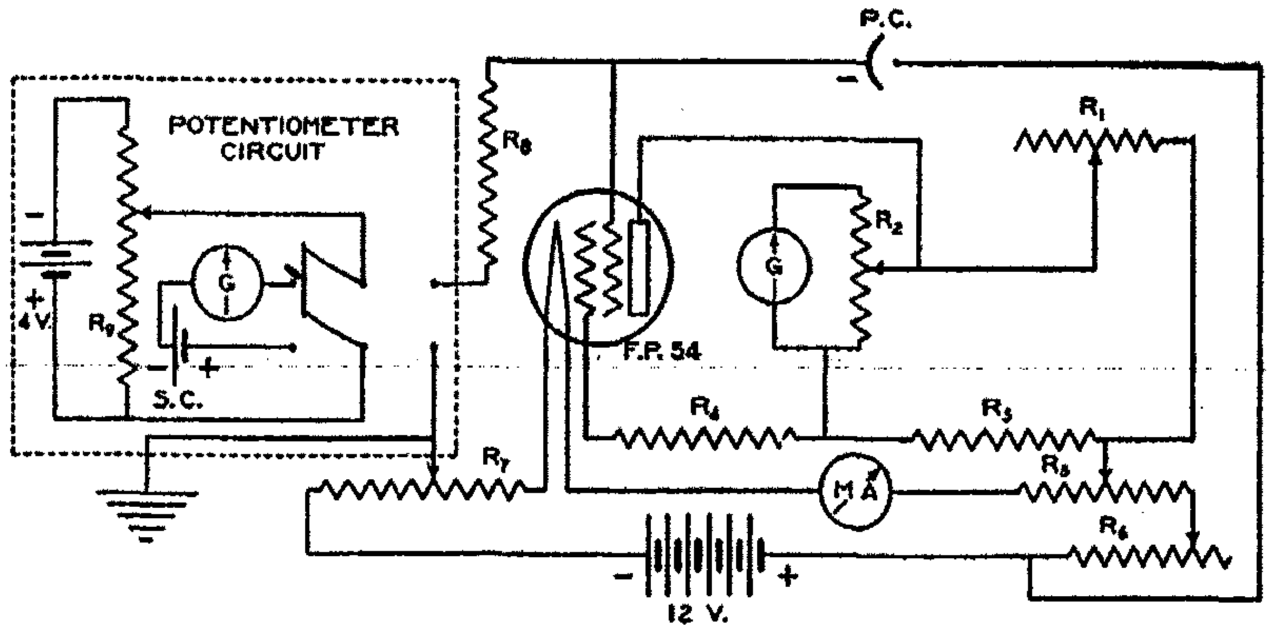

FIG. 3. Diagram of photometer circuit

P. C.	Visitron 71A photoelectric cell
S. C.	Standard cell
R_1	10,000-ohm radio rheostat with 50-ohm rheostat in series for fine adjustment
R_2	Ayrten shunt for galvanometer
R_3	2000-ohm fixed resistance
R_4	10,000-ohm fixed resistance
R_5 and R_7	50-ohm voltage dividers with movable taps
R_6	50-ohm radio rheostat
R_8	100-megohm fixed resistance
R_9	L. & N. potentiometer

(4) If the value of the filament current at the minimum differs from the rated value for the tube by more than 2 milliamperes, shift the tap on R_5 and repeat the adjustment. With the galvanometer at maximum sensitivity, make a final adjustment to the minimum by changing R_6 and bring the galvanometer deflection to zero with R_1.

(5) The position of the tap on R_5 should be such that the plate is 6 volts positive to the negative end of the filament. If the plate voltage differs more than 0.5 volt from this value, shift the tap on R_7 or change the value of R_4 and repeat the adjustment. The adjustment of the taps on R_5 and R_7 will not need to be changed except when changing tubes.

The amplifier unit proved to be very satisfactory, and was practically devoid of any fluctuations or drift. The current drain on the batteries was small, and it was found to be more satisfactory to leave it turned on continuously except when the battery was being charged.

The light source was operated from a separate battery, and it was necessary to turn it on for an hour or more before the light intensity became sufficiently constant for quantitative measurements.

EXPERIMENTAL METHOD

The diffusion equation was tested by studying the diffusion of methylene blue in gelatin gels.

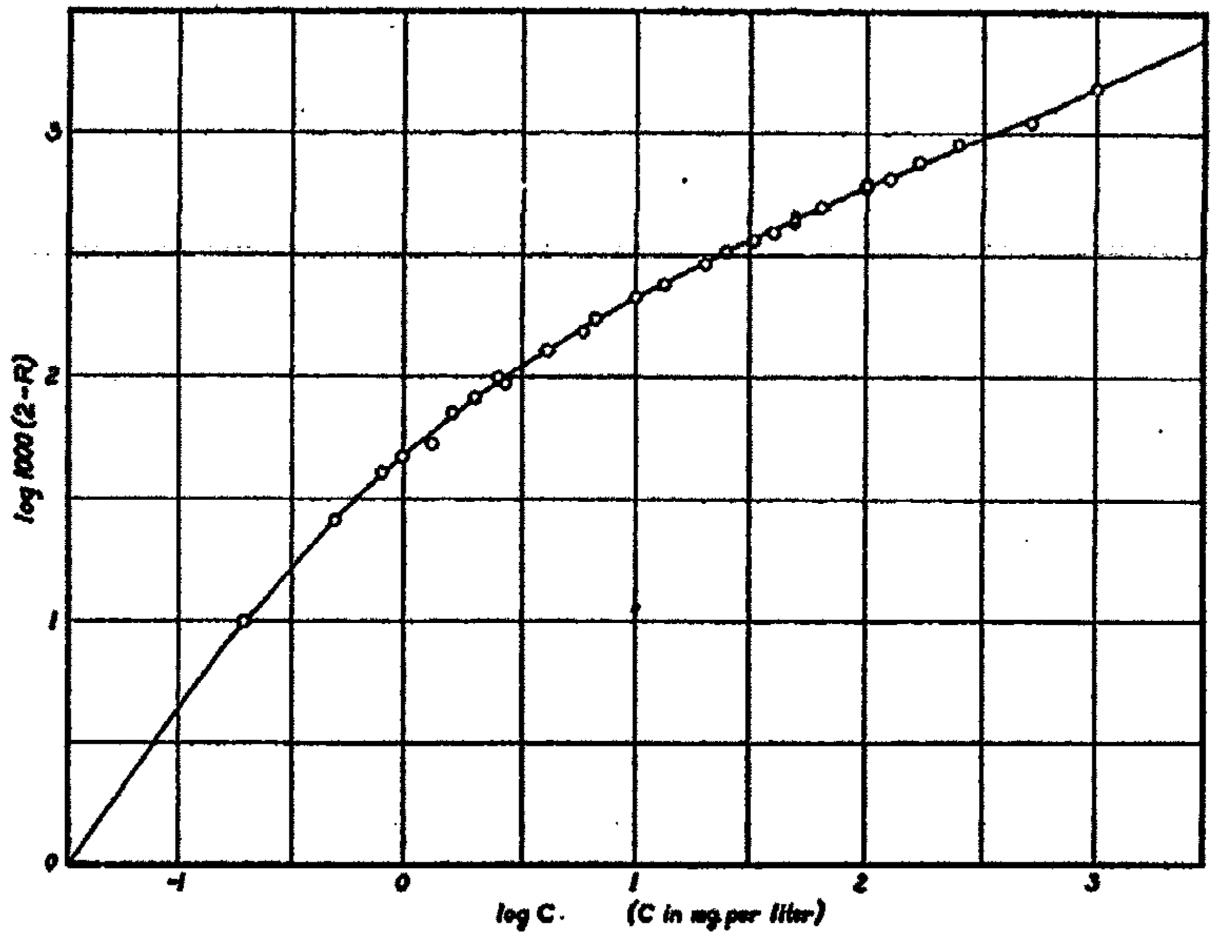

FIG. 4. Calibration curve for diffusion apparatus

Eastman (ash-free) gelatin was dissolved by stirring at 40° to 50°C. to give a 5 per cent solution. The clear solution was poured into the diffusion cell and allowed to set at 25°C., care being taken to prevent evaporation from the surface of the gel. After the gel had set for several hours the zero distance reading was taken by reading the height of the cell at the point where the meniscus of the gel just reflected the light beam off the slit in the photoelectric cell housing.

The diffusing solution was then poured on top of the gel at zero time. The solution contained 1.0 g. of methylene blue per liter of water solution, and the concentration was kept constant throughout the measurements by the continuous addition of fresh solution as the excess volume was drawn off by gentle suction.

To operate the measuring circuit, the resistance R_6 was adjusted to minimum galvanometer deflection and R_1 was adjusted so that the galvanometer at maximum sensitivity gave a reading near the center of the scale. This adjustment was made with the potentiometer set at zero and with the light source cut off from the photoelectric cell by means of a shutter which was operated from outside the bath. By this means a reference position of the galvanometer was established. The potentiometer was then set at 2 volts, the shutter was opened, and the intensity of the light source was adjusted until the original reading of the galvanometer was obtained with the light passing through the clear gel in the diffusion cell. Care was taken during this adjustment to prevent large deflections which might change the reference position by twisting the suspension of the galvanometer.

After these adjustments had been made, the potentiometer was set at definite readings and the cell was moved downward until the original galvanometer reading was obtained for each potentiometer setting. The cell height readings and the corresponding potentiometer readings (R) were recorded. The concentrations corresponding to the different potentiometer readings were obtained from the calibration curve (figure 4).

The calibration curve was obtained by finding the potentiometer readings for known concentrations of methylene blue in water, the intensity of the light source being adjusted to a potentiometer reading of 2 volts with pure water in the diffusion cell. The calibration curve was tested by analyzing gels containing known concentrations of methylene blue, and was found to be satisfactory.

RESULTS AND DISCUSSION

In previous work (2) the following diffusion equation was derived

$$m = m_0 e^{-\frac{X^2}{4Dt}} \qquad (1)$$

where m is the concentration at any distance, X, from the point where the diffusion started, t is the time in seconds during which the diffusion process has been taking place, D is the diffusion coefficient in cm.^{2} per second, and m_0 is a constant which is equal to the concentration at zero distance.

Taking the logarithm of both sides of equation 1, equation 2 is obtained.

$$\log m_0 - \log m = \frac{X^2}{2.3026 \times 4 \times Dt} \qquad (2)$$

Thus at any given time,

$$\sqrt{\log m_0 - \log m} = kX = k(X_r - A) \qquad (3)$$

where

$$k = \sqrt{\frac{1}{9.2104\,Dt}} \qquad (4)$$

In equation 3, X_r was taken as the distance measured by means of the cathetometer and A was any constant error in the reading of zero distance. Such an error might have resulted from the influence of the curvature of the meniscus on the effective zero distance in the diffusion process, or from the method used to make the zero reading. However, at any given time a plot of $\sqrt{\log m_0 - \log m}$ against X_r was a straight line. K was the slope of the straight line and gave D by equation 4, and A was the intercept on the X_r axis. Figure 5 shows the results of a representative series of measurements at different times. A large number of such measurements gave a value of -0.030 cm. for A, and a mean value of 1.635×10^{-6} cm.^{2} per second for the diffusion coefficient.

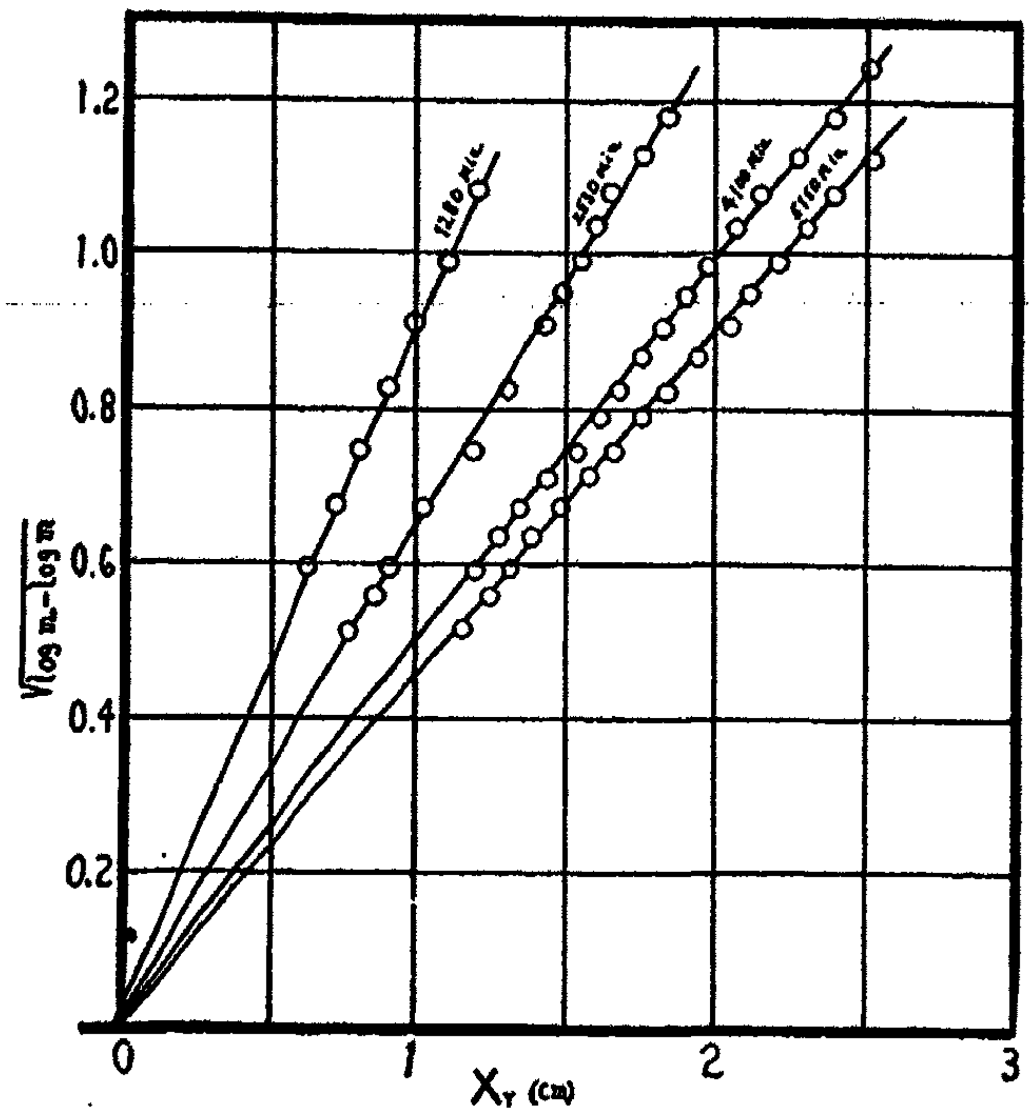

FIG. 5. Experimental verification of equation 3 for different values of t

The greater part of the errors in these measurements resulted from variations in the optical properties of the diffusion cell and the gels. The error involved in assuming t constant over the period of time required (about fifteen minutes) to make a set of readings was negligible after the first twelve hours. This time error was further minimized by taking the time as that when the lower concentrations were being measured, since in this region $\left(\frac{\partial X}{\partial t}\right)_m \left(= \frac{X}{2t}\right)$ was greatest. If the exact value of X could be determined with certainty, these errors could be eliminated to a large extent by keeping X constant and expressing $\log m_0 - \log m$ as a linear function of $1/t$.

In figure 6 the measured values of the concentration have been plotted against the corresponding values of $X_r + 0.030$ cm. for a series of measurements at different times. The measurements could not be extended to values of X_r less than 0.5 cm. on account of the disturbing effect of light reflected by the meniscus of the gel. The solid curves in this figure show the concentration values given by equation 1, using $m_0 = 1000$ mg. per liter and $D = 1.635 \times 10^{-6}$ cm.^{2} per second.

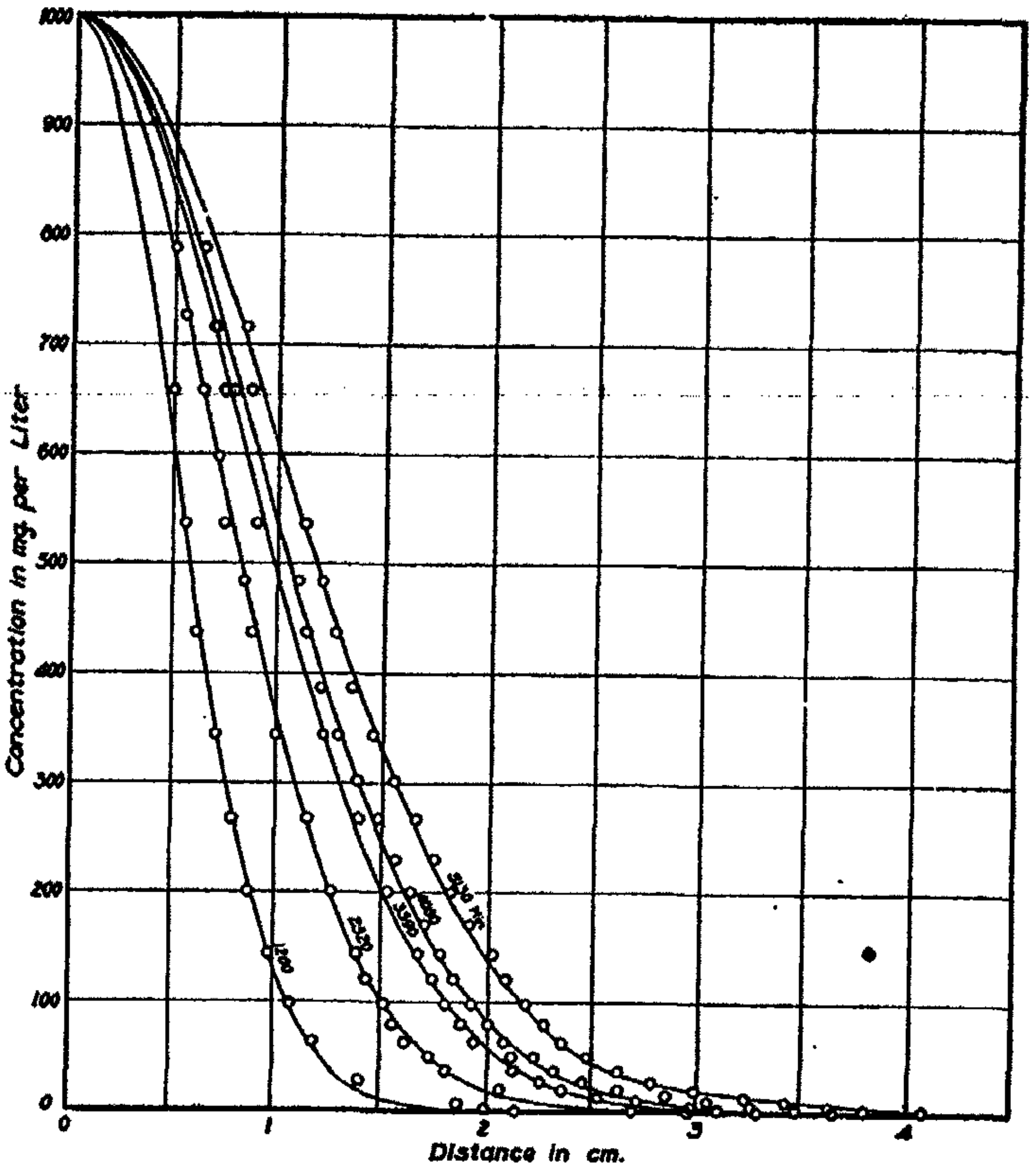

FIG. 6. Comparison of calculated concentrations with measured values at different times

It should be pointed out that all of the theoretical concentration-distance curves are determined by a single exact measurement of m at any known value of X and t. Thus the diffusion equation not only permits accurate interpolation between two known concentrations at a given time, but also leads to equally correct values when extrapolated to other times in the diffusion process.

SUMMARY

1. A new and accurate photometric apparatus for the analysis of thin sections of colored solutions has been devised and applied to measurements of the diffusion of methylene blue.

2. The relation $m = m_0 e^{\frac{-X^2}{4Dt}}$ is shown to be in agreement with the results of experimental measurements.

3. The diffusion coefficient of methylene blue in 5 per cent gelatin gels at 25°C. is 1.635×10^{-6} cm.^{2} per second.

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THE PHYSICAL CHEMISTRY OF FLOTATION. IX

THE ADSORPTION OF XANTHATES BY ACTIVATED CARBON AND GRAPHITE AND ITS RELATION TO THE THEORY OF FLOTATION

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The adsorption of xanthates by graphite has been considered in a previous communication (7). However, a correspondent has suggested to us that he attributes the adsorption of the collector to the presence of impurities in the graphite, and that he considers that pure graphite would not adsorb xanthates. In support of this view he states that experiments have shown that the purer the graphite, the less xanthate it consumes. Though it is true that xanthate is consumed by iron minerals, which are present in most specimens of native graphite, these observations do not necessarily imply that graphite itself does not adsorb a small amount of xanthate. Perfectly pure graphite cannot be obtained easily, and if one had to await finding a suitable specimen the question might remain open for a long time. If, however, it can be shown that ash-free activated carbon adsorbs xanthate, the graphite problem becomes of secondary importance. For it will then be established that xanthate can be adsorbed at a solid surface without the formation of metallic xanthates. The tests to be described prove that sugar charcoal adsorbs both amyl and ethyl xanthates and that their adsorption has a profound influence on its flotation. The significance of these results for the theory of flotation has already been considered (7).

Balfour, Riley, and Robinson (1) have shown that sugar charcoal contains hydrogen that cannot be expelled by heating. To some extent it is therefore a hydrocarbon, and it is believed that the hydrogen atoms are situated between flat layers of carbon atoms such as occur in graphite. The authors suggest that this hydrogen is available for exchange adsorption reactions; our observation that potassium ions are adsorbed is therefore readily accounted for. The authors claim, moreover, that other ions and atoms may penetrate between the layers of the carbon atoms; assuming that oxygen has done so, it would be possible for hydroxyl ions to be produced by exchange adsorption with xanthate ions.

Investigations by Bartell and Miller (2) and by Frumkin (3) have shown that sugar charcoal, activated by heating in oxygen, can adsorb organic and inorganic acids but not inorganic bases. Frumkin considers that the charcoal behaves as a gas electrode; any oxygen contained by the charcoal can be displaced by anions, hydroxyl ions entering the solution.

Our results for potassium xanthates are similar to those obtained by Miller (5) for potassium benzoate and potassium salicylate; both anions and cations are adsorbed and at the same time the alkalinity of the solution increases. Table 1 shows that with sugar charcoal more xanthate than potassium is adsorbed; the difference, however, is almost quantitatively accounted for by the amount of alkali liberated, the sum of alkali and potassium being 98 and 94 per cent of the xanthate adsorbed in two independent tests. This would be expected if each potassium ion adsorbed were replaced by a hydrogen ion and each xanthate ion adsorbed were replaced by a hydroxyl ion. With graphite the alkali liberated is approximately equivalent to the xanthate adsorbed, little or no potassium being adsorbed. However, we have been unable to establish whether the rise in pH value that accompanies xanthate adsorption is due to simultaneous adsorption of hydrogen ions (possibly as xanthic acid) or to exchange adsorption with oxygen or hydroxyl ions.

TABLE 1

Adsorption of amyl xanthate by sugar charcoal and graphite

MATERIAL	WEIGHT	CONCENTRATION OF AMYL XANTHATE	VOLUME OF SOLUTION	TIME OF CONTACT	pH VALUE		XANTHATE ADSORBED	ALKALI LIBERATED*	POTASSIUM ADSORBED*
					Initial	End			
	grams	*mg. per liter*	*ml.*	*minutes*			*per cent*		
Sugar charcoal....	4.0	500	50	30	6.7	7.5	86		
	4.0	500	50	60			94	21	
	4.0	500	50	100	6.7	7.9	96	23	
Sugar charcoal....	3.9	1000	60	60	6.7	7.7	61.2	17.5	81
	4.0	1000	60	60	6.7	7.9	64.5	16	78
Graphite..........	4.0	1000	60	60	6.7	10.4	71	93	Nil
	4.0	1000	60	60	6.7	11.3	46	106	Nil

* These are calculated as molecular percentages of the xanthate adsorbed.

Time was not available to make a complete study of the adsorption of xanthates on activated carbon. Thus we did not determine the equilibria reached nor the rate at which they are established. We have not determined whether the hydrogen content of the activated carbon has any influence on the relative amounts of xanthate and potassium adsorbed, nor whether the apparently greater activity of the carbon prepared by the sulfuric acid process is a reproducible phenomenon or merely one of those unexplained anachronisms mentioned by McBain and Sessions (4). A careful study of xanthate adsorption by standardized charcoal of uniform particle size would throw light on the adsorption process. Xanthates, being readily prepared and purified, easily estimated, soluble in water, and strongly adsorbed, are eminently suitable for the study of adsorption.

EXPERIMENTAL METHODS

Preparation of sugar charcoal

Sugar that had been recrystallized by addition of alcohol to a strong aqueous solution was carbonized in small portions by heating, and after grinding to approximately 60-mesh size was ignited for fifteen minutes at 900°C. in silica vessels in an electric muffle furnace. A slightly more active charcoal was prepared by carbonizing sugar with strong sulfuric acid, washing free from acid, drying at about 120°C., grinding to approximately 60 mesh, and finally igniting for fifteen minutes at 900°C. All samples of the charcoal were ash-free.

The graphite was hand-picked to remove as much pyrite as possible, but it was by no means ash-free. After grinding, it was heated for 20 minutes at 900°C. before use. The major impurity was iron oxide.

Methods of analysis

Xanthate was estimated by titration against $N/1000$ iodine. With the amount of xanthate usually employed (about 50 mg.) the error of the method did not exceed 0.5 per cent. Potassium was estimated by a modification of the cobaltinitrite method (6): for 5 mg. of K_2O the average error was about 1 per cent. The amount of hydroxyl and/or carbonate liberated simultaneously with the adsorption of xanthate was determined by a titration against $N/100$ hydrochloric acid to an end point of $\mathrm{pH} = 4.5$. Xanthic acids are strong acids, consequently the presence of xanthates does not influence the titration of carbonate; furthermore, xanthic acid itself does not decompose rapidly if the acidity is not greater than $\mathrm{pH} = 4.5$. pH values were determined by means of the Hellige comparator.

Method of testing

The ground carbon or graphite was shaken at frequent intervals over the time specified for the test, with the required volume of solution. The solution was then filtered and separate portions of the filtrate used for the estimation of xanthate, alkali, and potassium.

EXPERIMENTAL RESULTS

Table 1 summarizes the results obtained when using neutral solutions of amyl xanthate. Charcoal carbonized by the ignition process was employed.

Graphite that has been heated previously in hydrochloric acid and then heated to 900°C. did not liberate much alkali, but it did not adsorb more than 13 per cent of the amount of potassium to make up the difference. The result is unexplained.

Since alkali is apparently liberated during the adsorption process the influence of added alkali on the adsorption of ethyl xanthate was determined. The results are summarized in table 2.

Charcoal prepared by the sulfuric acid method was more active than that prepared by the ignition method. In 30 minutes contact with 30 cc. of a 1000 mg. per liter solution of ethyl xanthate 1 g. of the first mentioned charcoal adsorbed 53 per cent of the xanthate, whereas the latter adsorbed only 34 per cent.

Corresponding to our previous observation (7) that cyanide is without influence on the flotation of graphite, we now find that 50 mg. per liter of sodium cyanide has no marked influence on the amount of ethyl xanthate adsorbed by sugar charcoal. (Since cyanide reacts with iodine, although not as rapidly as does the xanthate, the titrations could merely prove that if cyanide is adsorbed by charcoal it takes the place of an equivalent amount of xanthate. Since the cyanide was not completely adsorbed and the amount of xanthate adsorbed was greatly in excess of the cyanide present, any adsorption of cyanide was relatively unimportant.)

TABLE 2

Influence of alkali on adsorption of ethyl xanthate by sugar charcoal

WEIGHT OF CHARCOAL	CONCENTRATION OF ETHYL XANTHATE	VOLUME OF SOLUTION	TIME OF CONTACT	pH VALUE		XANTHATE ADSORBED
				Initial	Final	
grams	*mg. per liter*	*ml.*	*minutes*			*per cent*
2	1000	30	90	6.5	7.9	58
2	1000	30	90		9.1	54
1	100	40	60	6.5	7.4	68
1	100	40	60	12.0	12.0	51
1	20	40	90	6.5	6.5	92
1	20	40	90	12.0	12.0	61

The flotation properties of charcoal prepared by the sulfuric acid process are interesting. Despite the subsequent heat treatment the material adsorbed a considerable amount of gas, and when the material was immersed in water this gas was apparently displaced by water. During the liberation of the gas the carbon particles were floated to the surface where the bubbles immediately collapsed and the particles dropped to the bottom. This liberation of gas continued for about ten minutés; thereafter the carbon showed no tendency to float. Amyl xanthate was then a very effective collector; ethyl xanthate however was only a weak collector, even at a concentration of 1 g. per liter. Treatment of the carbon with copper sulfate did not increase the flotation of the carbon by ethyl xanthate if the copper sulfate solution were removed before adding the xanthate. Copper sulfate and ethyl xanthate together caused good flotation, but this was probably due to the formation of dixanthogen, which is a good collector for sugar carbon. The presence of silver nitrate did not increase the flotation of carbon by ethyl xanthate; dixanthogen is not formed in the reaction between these two compounds.

SUMMARY

The adsorption of xanthates by sugar charcoal has been studied, and an attempt has been made to interpret it in terms of exchange adsorption reactions. Some potassium ion is adsorbed simultaneously with the xanthate ion. Alkali is liberated corresponding to the difference between the xanthate and potassium ions adsorbed. Addition of alkali decreases the amount of xanthate adsorbed in a given time. Cyanide is without marked effect. With graphite the xanthate ions abstracted and the alkali liberated are approximately equivalent, little or no potassium being abstracted. A sample of sugar charcoal prepared by carbonizing sugar with sulfuric acid was more active than a sample prepared by heat carbonization. The xanthates are flotation collectors for sugar charcoal. It is concluded that the flotation of graphite by xanthates is not due to any metallic impurities contained therein.

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THE OXIDATION OF CHROMOUS TO CHROMIC SULFATE[1]

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I. THE REACTION BETWEEN CHROMOUS SULFATE AND SULFURIC ACID

While investigating the autoxidation of chromous sulfate it was found by the authors that in the presence of metallic silver a solution of this compound undergoes oxidation with the liberation of hydrogen. This paper deals with certain conditions which influence this reaction.

Reagents and method

The chromous sulfate was prepared by the electrolytic reduction of chromic sulfate as described by Asmanov (1). The salt was precipitated by alcohol and washed by ether, these operations being carried out in an atmosphere of hydrogen. A necessary precaution in the preparation of the salt is the removal of moisture, as well as dissolved oxygen and peroxides, from the ether used in washing. The chromous sulfate pentahydrate obtained by this method was 93 per cent pure, the impurity consisting of the chromic salt. By sealing the salt in tubes under an atmosphere of nitrogen, it was possible to keep it for weeks at room temperature without any oxidation. This shows that under these conditions there is no appreciable reaction between the chromous salt and the water of hydration.

"Molecular" silver prepared by the method described by Gomberg (3) was used as the catalyst. It was thoroughly mixed, thus providing a product which gave samples of uniform surface.

The method of measuring the rate at which the reaction proceeded has been described by the senior author (2). The chromous sulfate was weighed into glass capsules which were suspended in the necks of special reaction flasks which contained 25 cc. of water and the substance whose effect was to be studied. The flask was placed in a thermostated shaking device and connected to water-jacketed burets in which the evolved hydrogen was measured. The starting of the shaker dropped the capsule containing the chromous sulfate into the flask, and after the salt was dis-

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solved the volume of hydrogen evolved was measured at various time intervals. Since the reaction must be carried out in the absence of oxygen, the air in the flask and the buret was replaced by pure nitrogen. All measurements, unless otherwise stated, were carried out at 25°C.

THE EFFECT OF SHAKING

The agitation of the solution prevents supersaturation of the hydrogen, keeps the silver dispersed, and brings the catalyst into contact with fresh portions of the chromous sulfate, thereby making constant the time necessary for a chromous ion to reach a point at which it will be adsorbed by the silver. In reactions which occur at an interface the shaking efficiency is of utmost importance. When stannous chloride solutions are oxidized by shaking with air, for example, a point is reached at which more vigorous shaking is without effect on the rate of oxidation (5). On the other hand, cuprous chloride solutions when shaken with air show increased speed of oxidation as the shaking of the solution is increased (2).

TABLE 1

Data of a typical run

Time (in minutes)........	10	20	30	40	50	60	70	80	90	100
Mg. of H_2......	0.100	0.188	0.274	0.366	0.458	0.551	0.652	0.754	0.861	0.968
$K \times 10^3$.......	10.0	9.4	9.1	9.2	9.2	9.2	9.3	9.4	9.6	9.7

Total volume of hydrogen = 43.4 cc. (3.36 mg.)
K = mg. of hydrogen/time in minutes.

To determine the effect of shaking, experiments were carried out in which the speed of the particular shaker used was varied from 590 to 1162 and then increased to 1780 "shakes per minute." The corresponding values for the half-life of the chromous sulfate solution agree within experimental error, showing that a maximum shaking efficiency had been reached.

The data of a typical run are given in table 1. The solution contained 0.4 g. $CrSO_4 \cdot 5H_2O$, 0.1 g. Ag, and 1.5 g. $Cr_2(SO_4)_3 \cdot 5H_2O$ in 25 cc. of 0.9 *N* sulfuric acid. This will be referred to hereafter as the "standard solution." The sulfuric acid and chromic sulfate were added because the former is a reactant, the latter is a product and, as will be shown later, each compound has a definite effect upon the speed of the reaction. By adding an excess of sulfuric acid and chromic sulfate to the solution, however, the changes in concentration due to the reaction are so small that the effect on the velocity of the reaction may be disregarded. For the first part of this reaction the values of *K* correspond to zero order. The average is 9.4. In a duplicate run the value 9.36 was obtained. In general duplicate experiments did not vary more than 5 per cent. The zero order holds only for about the first half of the reaction when the concentration of chromous sulfate is sufficiently great to saturate the surface of the catalyst.

Effect of chromic sulfate

This substance acts as a negative catalyst. The data in table 2 were obtained with the standard solution, using 0.5 g. of silver.

The constancy of the data in the last line of table 2 shows that the retarding effect of the chromic ions is directly proportional to the increase in chromic-ion concentration until the higher concentration of the salt is reached. This effect can be explained by the adsorption of chromic ions by the silver.

To test this point the conductances of dilute solutions of chromic sulfate were measured before and after the addition of 0.5 g. of molecular silver. The increase in resistance after shaking with silver showed that some of the salt had been adsorbed. Since the data are of a qualitative nature only, they are not given. With the higher concentrations used the surface of the silver became so saturated that the silver was practically without effect as a catalyst.

TABLE 2

Data obtained with the standard solution

$Cr_2(SO_4)_3 \cdot 5H_2O$ (in grams)	0	0.25	0.75	1.00	1.25	1.50	2.00	3.00
Half-life (in minutes)	5.4	9.5	16.0	19.5	24.8	28.2	38.3	74.2
$\frac{\text{Increase in half-life}}{Cr_2(SO_4)_3 \cdot 5H_2O \text{ (in grams)}}$		16.4	14.1	14.1	15.5	15.2	16.4	22.9

TABLE 3

The effect of increase in acid concentration

H_2SO_4 (normality)	0.904	1.97	2.92	3.94
Half-life (in minutes)	92.4	63.3	47.0	30.1
H_0 (acidity function)	0.31	−0.11	−0.41	−0.70

Effect of acid concentration

To find the effect of increase in acid concentration experiments were carried out in which the acid concentration was increased to about 4 *N*. The results are listed in table 3. The standard solution was used.

At higher concentrations the speed of the reaction is approximately in direct proportion to the normality of the acid. With hydrochloric acid the same relationship was found to exist, the ratio of the half-life being about 10 to 6 for equivalent solutions of hydrochloric acid and sulfuric acid.

When the acidity functions of the sulfuric acid (H_0 above) as determined by Hammett and Deyrup (4) are plotted against the half-life, a linear relationship is obtained. The effect of the acid, consequently, is to increase the speed of the reaction in direct proportion to the acidity function.

In the above experiments the reactions were zero order. With very dilute solutions of sulfuric acid, when the relative concentrations of chromous and hydrogen ions had the value 2 to 1, second-order reaction constants were obtained.

Temperature effect

With the standard solution the velocity was measured at 25°, 30°, and 35°C. The values of K in cc. per minute for these temperatures were 0.139, 0.124, and 0.109, giving a temperature coefficient of 1.27. This indicates that the effect of temperature change is largely an effect on the rate of diffusion.

TABLE 4

Data obtained using standard solution with varying amounts of silver

Silver (in grams)	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Half-life (in minutes)	92	68.5	45.5	36.2	28.2	26.5	19.5
$\frac{\text{Silver (in grams)}}{\text{Reciprocal of half-life}}$	9.2	13.7	13.7	14.5	14.1	15.9	13.7

TABLE 5

Increase in adsorption with increasing atomic weight

SOLUTION	RESISTANCE	RESISTANCE WITH SILVER	DIFFERENCE
	ohms		
0.001 N LiI	1050	1067	16
0.001 N NaI	801	827	26
0.001 N KI	810	915	105
0.001 N RbI	792	898	106

Effect of silver

The data obtained using the standard solution with varying amounts of silver follow in table 4. When the concentration of the silver is plotted against the reciprocal of the half-life a straight line is obtained, as evidenced by the constancy of the values of the last line in table 4. Within the limits of these concentrations the velocity of the reaction is directly proportional to the concentration of the silver. These data furnish additional confirmation of the efficiency of the shaking of the solution.

The effect of various salts

Using the standard solution with 0.5 g. of silver results for quarter-life periods were obtained with normal solutions of the following halides: potassium chloride, 14.2 min.; potassium bromide, 105 min.; potassium iodide, immeasurably slow. The quarter-life in the absence of these salts was 14.1 min. The quarter-life period was used here because of the slowness of the reaction. When the conductances of these solutions (0.001 *N*) were measured before and after shaking 100 cc. with 0.5 g. of silver, the following data were obtained: potassium chloride, practically no change; potassium bromide, resistance change from 815 to 842; potassium iodide, resistance change from 810 to 915. These measurements show that the effects of these salts may again be ascribed to adsorption. While no attempt has been made to study the nature of the adsorption, the data in table 5 are of interest as showing that with both anions and cations the adsorption tends to increase with increasing atomic weight.

It was of interest to compare the effect of other sulfates with that of the chromic sulfate. Normal solutions of sodium sulfate, magnesium sulfate, and aluminum sulfate gave half-life values of 13, 9.1, and 17.8 min., respectively, when the standard solutions containing 0.5 g. of silver were used. Without these salts the half-life is 7 min. The slight effect of these salts parallels their lack of adsorption, as evidenced by practically unchanged conductance before and after shaking with silver.

Summary

A solution of chromous sulfate in the absence of air is oxidized very slowly at ordinary temperatures. Finely divided silver increases the rate very slightly. The addition of hydrogen ions in the form of sulfuric acid also causes a slight increase in the rate of oxidation.

With silver and sulfuric acid together the reaction takes place rapidly.

The presence of chromic ions retards the rate of oxidation.

The speed of reaction is directly proportional to the acidity function of the solution, even when the concentration of the acid is forty times as great as the chromous-ion concentration.

In this reaction a chromous ion gives an electron to a hydrogen ion, and the latter is evolved in the form of molecular hydrogen. It seems probable that the chromous ions are adsorbed by the "molecular silver" and that they react with the hydrogen ions in solution. Increasing the hydrogen-ion concentration results in more impacts per unit of time. If the assumption is made that the surface of the silver is continually saturated with chromous ions the zero order of reaction would be explained, inasmuch as the sulfuric acid is present in such a high concentration that it undergoes no appreciable change during the reaction. It seems probable then that the adsorbed chromous ions react with the hydrogen ions in the solution rather than with adsorbed hydrogen ions, an assumption that is supported by the linear relationship between acid concentration and reaction velocity.

The existence of a complex resulting as the product of an equilibrium reaction between chromous sulfate and sulfuric acid must not be overlooked. Such a compound might be more readily oxidized than the chromous sulfate, just as H_2SnCl_4 is more rapidly oxidized than $SnCl_2$. The existence of such a complex is quite in accordance with many of the results of this study.

Here, as in many other reactions of this kind, the lack of information concerning the nature of adsorption and the laws which govern the formation and behavior of adsorption compounds makes it impossible to do more than speculate concerning the mechanism of this reaction.

II. THE AUTOXIDATION OF CHROMOUS SULFATE

For the study of the autoxidation of chromous sulfate by oxygen gas the apparatus used was similar to that described in section I, the only change being the use of an atmosphere of pure oxygen instead of nitrogen over the chromous sulfate solutions. When this solution was shaken the oxygen was used up, and the rate of oxidation could be followed by measuring the rate of disappearance of the oxygen, the method being similar to that used in the study of the autoxidation of stannous chloride (2).

Inhibitors

The reaction between oxygen and chromous sulfate was found to be practically instantaneous. In an attempt to find any similarity between this reaction and the autoxidation of stannous chloride, a number of compounds which inhibit the latter reaction were investigated from the standpoint of inhibiting the chromous sulfate oxidation.

Small amounts of the following compounds when dissolved in the chromous sulfate solution were found to be without effect: tartaric acid, acetanilide, succinic acid, thiourea, chromic chloride, ethanol, benzene, toluene, aniline, trinitrotoluene, picric acid, *p*-toluidine, *p*-aminophenol, pyrogallol, pyridine, *n*-butyl alcohol, iodobenzene, glycine, potassium cyanide, ammonium chloride, and acetaldehyde. Many of these compounds, especially those containing nitro groups, were extremely potent as inhibitors of the stannous chloride reaction (5). It should be noted that these nitro compounds were in general reduced by the chromous sulfate. The presence of sufficient water to dissolve the chromous sulfate seems to be essential to its rapid oxidation. In a few experiments the solid chromous sulfate was added to such liquids as acetone, formic acid, acetic acid, and ethanol. The salt is practically insoluble in these reagents, and in this state undergoes practically no oxidation.

Coupled oxidation

In the autoxidation of acid solutions of stannous chloride (5), the presence of allyl alcohol causes the absorption of an excess of oxygen, owing to the induced oxidation of the latter by a peroxide intermediate. The autoxidation of chromous sulfate caused no coupled oxidation with allyl alcohol nor with sodium arsenite, sodium sulfite, or ferrous sulfate. It was found, however, that while a neutral aqueous solution of stannous chloride absorbs oxygen very slowly (0.1 cc. per hour), coupled oxidation of the stannous chloride occurs in the presence of chromous sulfate. The coupled oxidation was complete within two minutes. This oxidation is not due to the chromic sulfate formed, for this compound has no effect on the speed of the autoxidation of the stannous chloride. Using equimolecular amounts of chromous sulfate and stannous chloride, all of the chromous sulfate was oxidized and about 52 per cent of the stannous chloride. The amount of coupled oxidation depends upon the relative amounts of stannous chloride and chromous sulfate. It increased with the amount of chromous sulfate until 95 per cent of the stannous chloride was oxidized.

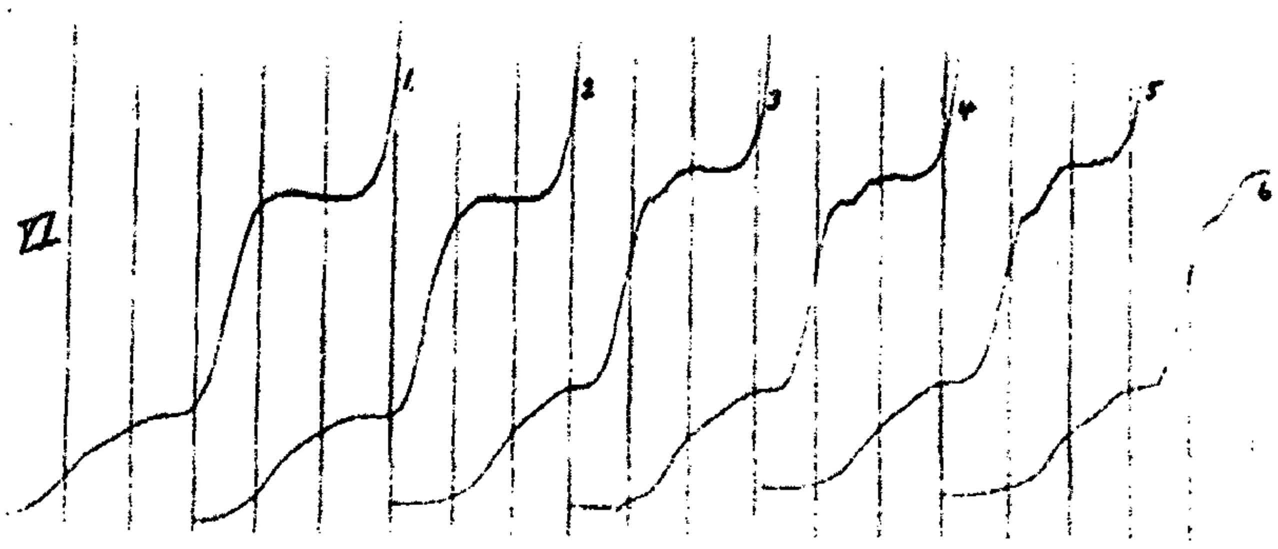

FIG. 1. Polarogram of chromous sulfate and chromic sulfate

The use of oxygen instead of air increased the amount of coupled oxidation. An increase of the oxygen pressure to 2 atmospheres increased the amount of stannous chloride oxidized by 20 per cent. The amount of coupled oxidation thus appears to be dependent on the amount of chromous sulfate and dissolved oxygen in solution.

Exposure to ultra-violet rays from a mercury arc light had no effect on the amount of coupled oxidation.

These results are best explained by the peroxide theory of autoxidation; this postulates the formation of a very reactive intermediate peroxide which causes the coupled oxidation of certain oxidizable substances.

Several polarograms of chromic and chromous sulfates were made on the polarograph, using 0.001 N solutions of the salts and a supporting electrolyte concentration of 0.05 N ammonium sulfate. A typical polarogram of chromic sulfate is shown by curves 1 and 2 in figure 1, which are similar to those obtained by Prajzler (6). The first break indicates the reduction of chromic ion to chromous ion and the second the reduction of chromous ion to chromium. When successive amounts of oxygen were blown through a chromous sulfate solution, as represented in curves 3 and 4, and 5 and 6, a third break in the curve was found. This third break indicates the presence of another compound with a higher oxidation–reduction potential. It can not be stated definitely that this compound is a peroxide, but thermodynamically it has an oxidation–reduction potential of the right order of magnitude.

Summary

1. The effect of a number of organic and inorganic compounds on the oxidation of chromous sulfate by oxygen has been studied.

2. Stannous chloride was the only substance whose oxidation could be induced by the autoxidation of chromous sulfate.

3. Evidence has been found for the formation of a peroxide intermediate in the autoxidation of chromous sulfate.

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THE VISCOSITY OF SOLS MADE FROM X-IRRADIATED AGAR

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INTRODUCTION

While investigating a problem concerned with the killing by x-rays of *Bacillus subtilis* spores on the surface of an agar medium, Blank and Kersten (1) observed that, if dry agar was given a sufficient dose, a medium subsequently made from it would not jell as well as a control made from unirradiated agar. In this paper a more detailed study of the effect has been made by comparing the viscosity of sols made from agar which had received various dosages of x-radiation.

EXPERIMENTAL

The x-rays were supplied by a copper target gas x-ray tube (2) operated at 40 peak kv. and 10 ma. The window of the x-ray tube was made of thin aluminum and Cellophane, so that the most intense part of the radiation passing through it had a wave length of 1.54 A.U. Powdered agar was irradiated in the cavity of a drop-culture microscope slide, placed about 3 cm. from the focal spot of the x-ray tube. After being irradiated, each sample was mixed and divided into several parts, each containing 0.2 g. These were placed in flasks to which 250 cc. of distilled water was added. Control samples were made in exactly the same way, except that unirradiated agar was used. One flask containing the control agar, one containing agar irradiated for 15 minutes, one containing agar irradiated for 1 hour and 15 minutes, and one containing agar irradiated for 3 hours and 15 minutes were simultaneously placed in a saline bath, and held at about 105° C. for 2 hours. They were then all removed at the same time, and allowed to cool to room temperature. The time elapsed after a sample had reached room temperature was termed its "age." The viscosity of each sample was measured at intervals by permitting 5 cc. of it to flow through an Ostwald viscosimeter. The entire experiment was repeated several times. The results plotted in figure 1 show that the viscosity of all of the samples increased with their age, but that the viscosity of all of the irradiated samples remained less than that of the control. Before each measurement the viscosimeter was rinsed with distilled water, and regarded as clean when 5 cc. of distilled water at room temperature required approximately 76 seconds to flow.

To determine whether or not the dry agar "recovered" from the effects of the irradiation, samples were irradiated for the same length of time, and allowed to stand in the laboratory for periods ranging from 13 minutes to seventeen days, and then carried through the procedure mentioned above. The curves are shown in figure 2 to be so nearly coincident that one concludes that the effect of the irradiation endures for at least seventeen days.

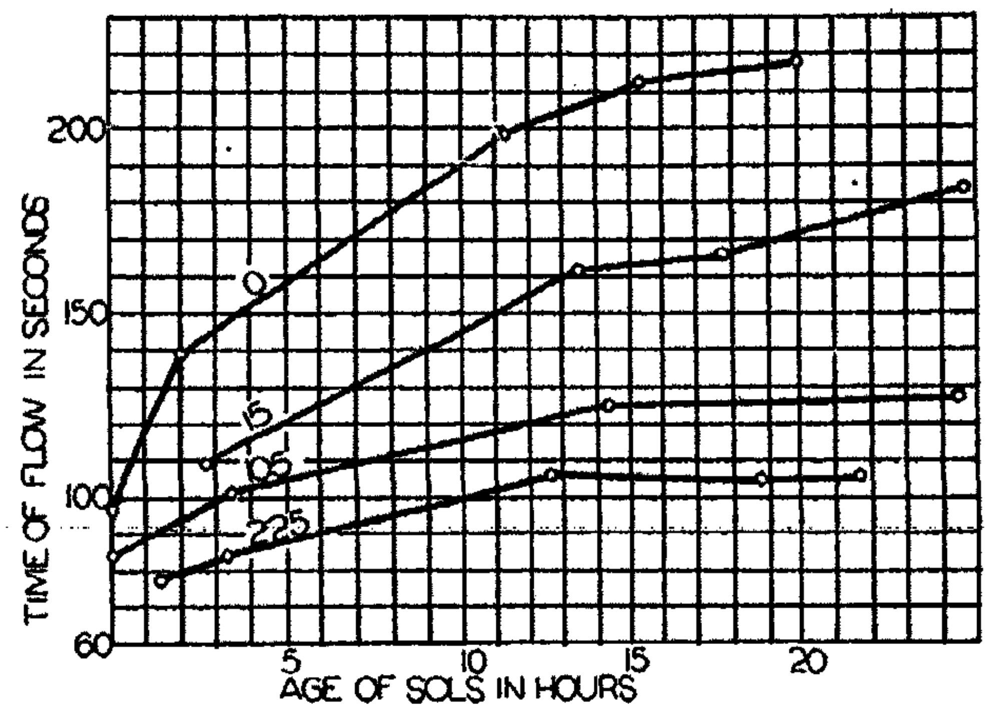

Fig. 1. Variation of viscosity with age. The numbers next to each graph show the number of minutes that the agar had been irradiated.

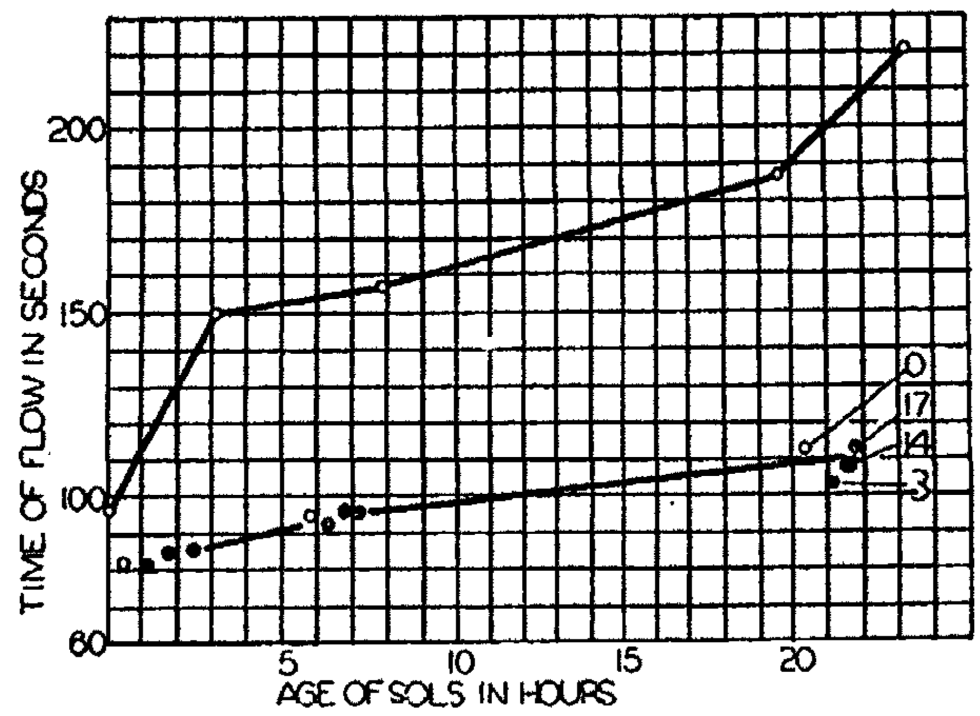

Fig. 2. Variation of viscosity with age. The upper graph is that for unirradiated agar. The numbers next to the lower graph show the time of the "recovery" of the agar in days.

To determine whether or not the small amount of heat coming through the window of the x-ray tube with the x-rays caused the change, a thermocouple was placed in a sample of agar being irradiated, and the temperature found to rise only a few degrees above room temperature. A sample of agar heated in an oven at a higher temperature, and for a longer period, than any used in the x-ray experiments gave a viscosity curve identical with those of control samples. The effect cannot then be attributed to heat alone.

The pH of sols made from irradiated agar was found to be slightly less than that for sols made from unirradiated agar. Measurements were made with indicators and with the quinhydrone electrode.

CONCLUSIONS

1. Irradiation of dry agar decreases the viscosity of the resulting sol.
2. There is no appreciable "recovery" of the dry agar from the effects of irradiation, at least within seventeen days.
3. The effect on the agar is not due to heat emanating from the target of the x-ray tube.
4. Irradiation of the dry agar slightly decreases the pH of the resulting sol.

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FURTHER STUDIES ON THE KINETICS OF THE COLORING OF GLASS BY X-RAYS

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It was shown recently (2) that the rate of coloring which is produced in glass by x-rays can be represented, within the limits of experimental error, by a simple equation, which in turn is consistent with a very simple mechanism. The results of an experimental study of some of the assumptions made in the earlier work, as well as a new and more accurate series of measurements on the rate of coloring, are presented in this paper.

DISTRIBUTION OF COLORED MATERIAL IN THICK PLATES

It was assumed in the earlier work that the colored substance was not concentrated at the surfaces of the glass plates (which were approximately 4 mm. thick) but was uniformly distributed throughout the plate. To test this assumption, a pile of eight thin Pyrex glass plates was irradiated, under conditions similar to those previously described (2), for twenty-eight hours. Neither the order nor the position of the plates was disturbed during the irradiation; consequently the radiation which reached the bottom plate had to pass through the other seven plates. The relative transparency (I/I_0) for light of λ4000 A.U. was determined for each of the plates.[2] These measurements are summarized in table 1.

If Beer's law applies, the quantity $\frac{1}{l} \log \frac{I_0}{I}$ is directly proportional to the concentration of the colored substance in each plate. In all of the rate measurements, plates approximately 4 mm. thick were used. Therefore the maximum difference in concentration which could exist in these plates would be approximately 10 per cent. Moreover, since the same face was not directed toward the x-ray tube during the entire period of radiation of each plate, it is probable that the maximum difference in concentration existing in these plates was less than 5 per cent. Any effect which this relatively small inhomogeneity may have had on the results is undoubtedly

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[2] The spectrophotometer used was the same as that previously described.

less than the error of measurement. It should also be noted that those glass samples which were protected by copper filters were subjected to harder and more homogeneous x-rays, and were, therefore, even more homogeneously colored.

TABLE 1

Measurements of the distribution of colored material in a thick plate

PLATE NUMBER	$\frac{I}{I_0}$	THICKNESS OF PLATE l	$\frac{1}{l}\log\frac{I_0}{I}$
		mm.	
1 (top)	0.620	1.005	0.207
2	0.619	1.015	0.206
3	0.635	1.030	0.192
4	0.646	1.000	0.190
5	0.645	1.020	0.187
6	0.680	0.995	0.169
7	0.680	0.990	0.170
8 (bottom)	0.705	1.000	0.152

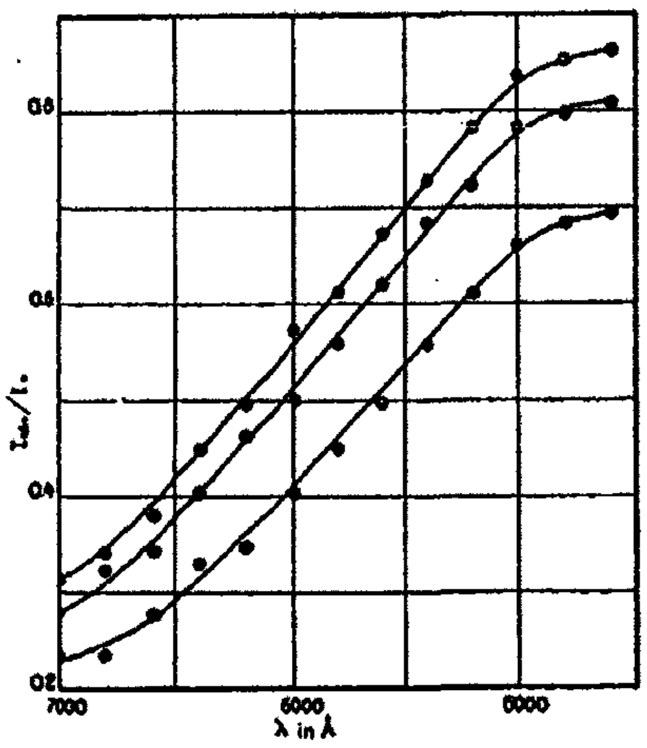

FIG. 1. Relative absorption as a function of wave length

SPECTRAL DISTRIBUTION OF ABSORPTION

The earlier measurements (2) on the spectral distribution of color were consistent with the postulate that "the color is due to one substance and Beer's law applies to the absorption of monochromatic light of all wave lengths studied." As a further test of this postulate, a spectrophotometric analysis was made of three samples of Pyrex glass (samples A, B, and C of the rate experiments) after they had been exposed for 233 hours to x-rays having relative intensities of 1.000, 0.453, and 0.253, respectively. The results of these measurements are summarized in figure 1, where the absorption of light, $I_{abs.}/I_0$, is plotted against wave length in A.U. In figure 1 the three samples appear to have the same distribution of color. However a more rigid test may be applied by plotting the quantity (2)

$$\log \log (I_0/I)_\lambda - \log \log (I_0/I)_{\lambda,\ \text{reference}}$$

against the intensity of the x-rays, I_x. Inspection of such a plot shows that the quantity is, within the limits of experimental error, the same for samples A and B for all wave lengths used. It is possible that there is some real variation when the quantity for C (the sample exposed to the least intense x-rays) is compared to that for A and B; however, if such a variation exists it is no greater than the erratic errors of the measurements. We may conclude, therefore, that our present more accurate measurements are in agreement with those previously published (2) in supporting the postulate stated at the beginning of this section.

RATE OF COLORING

The experiments were performed as follows: Four samples of glass, each about 1 in. square and 4.2 mm. thick, were cut from the same plate of Pyrex glass. Three of the samples were placed in small copper boxes at distances from the target of the x-ray tube of 34.0, 50.5, and 67.5 cm., respectively. The tube was operated at 30 ma. and a peak voltage of 200 kv. The x-rays which reached the samples passed through a small window in the lead protection drum of the tube stand. The sides of the copper boxes which faced the tube were 0.2 mm. thick; the other sides were 1.0 mm. thick. As in the earlier experiments (2) the irradiation was not continuous, but occurred during the routine treatment of patients in the Cancer Institute of the Minnesota General Hospital. From time to time the samples were removed and their absorptions of light of wave lengths 4800 and 6800 A.U. were determined with a Bausch and Lomb spectrophotometer, using the fourth (unirradiated) sample as a standard. The measurements were continued until the samples had received 1168 hours of irradiation, in contrast to the 60 hours of radiation given the samples in the earlier experiments (2). The results are summarized in figures 2 and 3, where the experimental values of $\log I_0/I$ (which is proportional to the concentration of the colored substance) are plotted as points (circles, etc.) against the time of irradiation in hours. It is apparent that, contrary to the assumption made in our earlier work (2), the saturation color is a function of the intensity of the irradiation.

A kinetic interpretation, which is consistent with the new results but retains the essentials of our former theory (2), may be stated as follows. The initial rate of formation of the colored substance is proportional to the product of the concentration $(M - C)$ of some substance, which can be transformed into the colored material, and the intensity (I_x) of the absorbed x-rays. Saturation is reached when this rate is counterbalanced

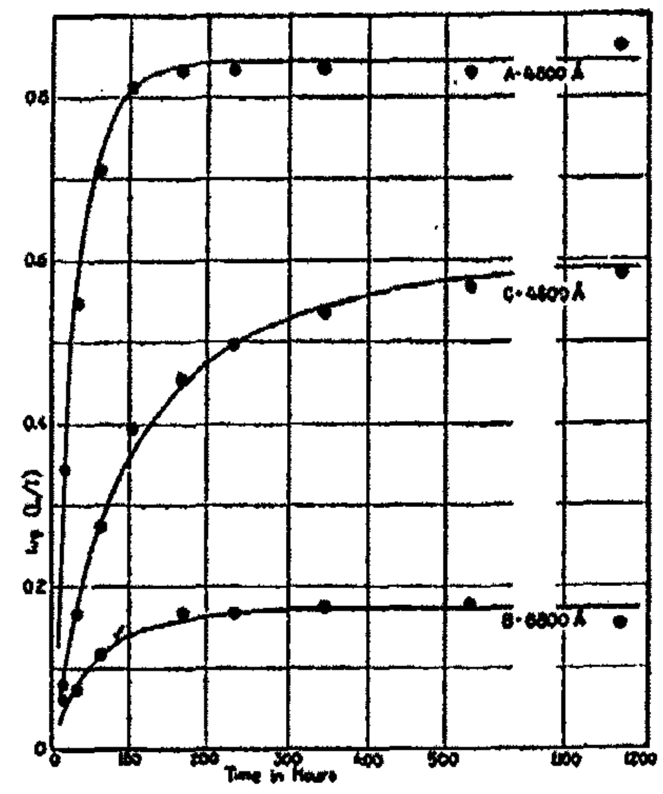

FIG. 2. Rate of coloring

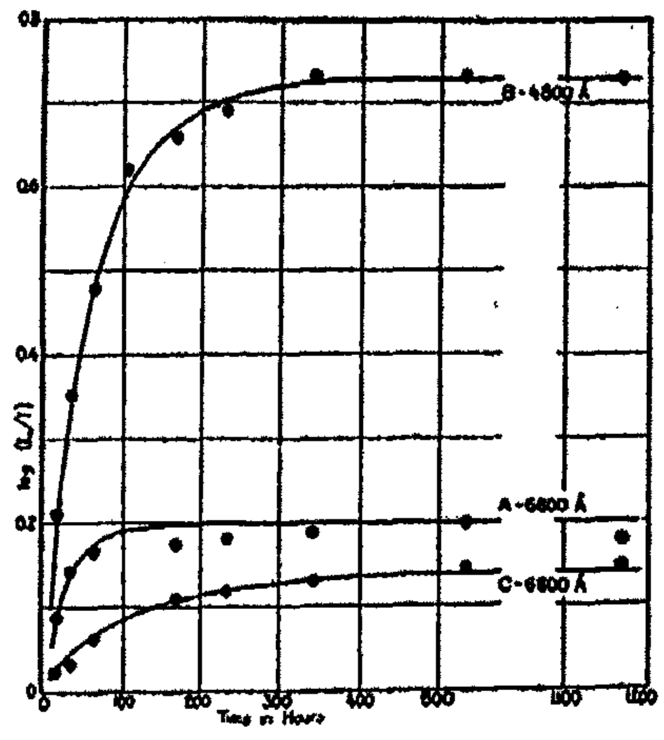

FIG. 3. Rate of coloring

by thermal fading and by a second process which is induced by x-rays. The thermal rate is of the first order in respect to the colored substance. The rate of the induced fading is proportional to the product of the concentrations (C) of the colored substance and the intensity of the absorbed x-rays. The total rate of formation of the colored substance is given by the relation

$$\begin{aligned}\frac{dC}{dt} &= k_m I_x(M - C) - k_c I_x C - k''C \\ &= kI_x - k'I_xC - k''C \qquad (1)\end{aligned}$$

where[3] $k = k_m M$ and $k' = k_m + k_c$. Upon integration and substitution of Beer's law, we may write

$$\log \frac{I_0}{I} = \frac{\gamma}{\beta}(1 - e^{-\beta t}) \qquad (2)$$

where[4]

$$\begin{aligned}\gamma &= kI_x\,al \\ \beta &= k'I_x + k''\end{aligned}$$

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[3] It should be noted that, while k and k' are expressed in reciprocal hours, k'' is expressed in terms of an arbitrary time unit. This is necessary since the reaction steps corresponding to k and k' occur only during the (intermittent) periods of irradiation, while the thermal process occurs continuously. Strictly speaking, equation 1 represents the total reaction as an approximation, which becomes more accurate as the ratio of the individual periods to the total time becomes small.

[4] As in the previous paper (2), a is the Beer's law coefficient of the colored substance and l is the thickness of the glass.

Equation 2 is in fairly good agreement with the experimental data, but the differences between observed and computed values of log I_0/I exhibit some systematic departures which are apparently larger than the experimental error.

While better agreement might be obtained by modifying the equation in any of a variety of ways, a simple and interesting method is to generalize the mechanism underlying equation 1, as follows:[5] The x-rays produce not merely one colored substance (at a concentration C) but rather a whole series of colored substances (at concentrations C_1, C_2;C—$_n$). While all of these substance have the same Beer's law coefficient for visible light of any given wave length, they have different probabilities of reverting to the uncolored state. If we neglect the possibility that they may be converted directly from one to another colored form, we may write

$$\frac{dC_i}{dt} = k_i I_x - k_i' I_x C_i - k_i'' C_i \tag{3}$$

Furthermore, since

$$\sum_i alC_i = alC$$

it follows that

$$\log \frac{I_0}{I} = \sum_i \frac{\gamma_i}{\beta_i} (1 - e^{-\beta_i t}) \tag{4}$$

where

$$\gamma_i = alk_i I_x \tag{5}$$

and

$$\beta_i = k_i' I_x + k_i'' \tag{6}$$

It is obviously futile to attempt to apply equation 4 to the experimental data without first imposing some limitation on the number of terms or on the relative values of k_1, k_2, etc. Since no general theory has been developed to guide us in this choice, let us make the following simplifying assumptions. The colored substance exists in only two forms, and one of these is thermally stable. The value of k_i' is the same for both substances. Therefore

$$\beta_1 = k' I_x + k_1'' \tag{7}$$

$$\beta_2 = k' I_x \tag{8}$$

[5] This generalized mechanism has the additional advantage that it clearly indicates the parallelism between these measurements on the rate of coloring of glass and the extensive measurements on the decay of luminescence of "phosphors" (1).

and

$$\log \frac{I_0}{I} = \frac{\gamma_1\beta_2 + \gamma_2\beta_1}{\beta_1\beta_2} - \frac{\gamma_1}{\beta_1}e^{-\beta_1 t} - \frac{\gamma_2}{\beta_2}e^{-\beta_2 t} \qquad (9)$$

This equation may be adjusted to fit the experimental data quite accurately, as is illustrated in figures 2 and 3. The points (circles, etc.) represent the experimental measurements; the curves are plots of equation 9, using empirical values for the several constants. The curves for $(I_0/I)_{6800\text{ A.U.}}$ were obtained by multiplying the corresponding values (for each sample) of $(I_0/I)_{4800\text{ A.U.}}$ by the factor 0.237. This factor is the ratio of the Beer's law coefficients for λ6800 A.U. and λ4800 A.U.

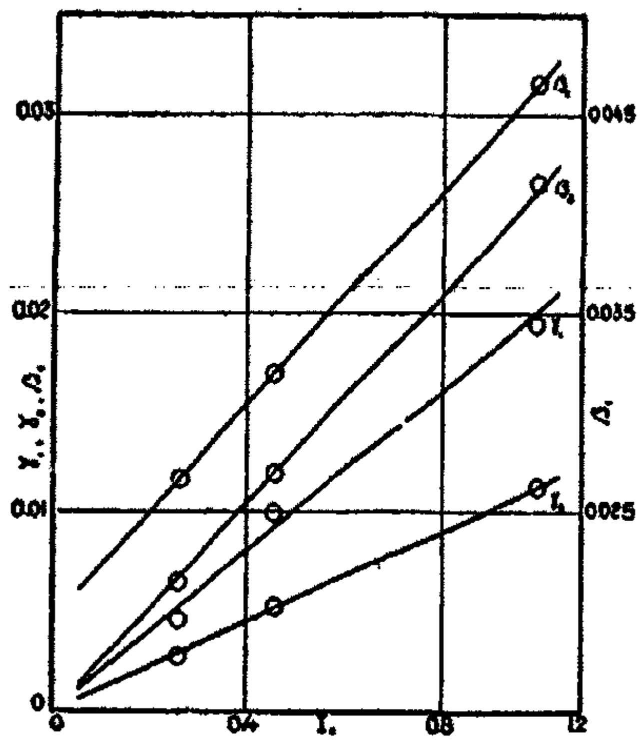

FIG. 4. Relation between the empirical constants and the intensity of the absorbed x-rays.

$$\frac{(\gamma_1/\beta_1)_{6800\text{ A.U.}}}{(\gamma_1/\beta_1)_{4800\text{ A.U.}}} = \frac{(\gamma_2/\beta_2)_{6800\text{ A.U.}}}{(\gamma_2/\beta_2)_{4800\text{ A.U.}}} = \frac{a_{6800\text{ A.U.}}}{a_{4800\text{ A.U.}}} = 0.237$$

To demonstrate that the experimental results are consistent with the limited form of the theory presented here, it is necessary to show, first, that equation 9 can be adjusted to each set of data, and second, that the empirical values of γ_i and β_i used satisfy equations 5, 7, and 8. These three equations require that the several constants be linear functions of the intensity of the absorbed x-rays. γ_1, γ_2, and β_2 should lie on straight lines passing through the origin, while β_1 should lie on a line parallel to and above that representing β_2. Figure 4 illustrates that these conditions are satisfied. The values of the rate constants for the several reaction steps (k_1, k_2, k_1', etc.) may be read directly from figure 4. However, the special theory (represented by equation 9) is by no means the only way in which the general theory (represented by equation 4) may be adjusted to fit the data, and therefore we must conclude that the values of these rate constants have little theoretical significance. It should be pointed out that Przibram has developed (3) a theory for the coloring of rock salt by β-rays, which in several respects is similar to that presented here. It is very probable that a suitable modification of his equation could be adjusted to present data on glass coloring. Further development of the theory must await more accurate and extensive measurements. An accurate study of the thermal rate of fading of glass colored by x-rays would be particularly useful.

SUMMARY

A new experimental study of the kinetics of the coloring of glass by x-rays is presented, and a general theory of the process is suggested and adjusted to the measurements. In the present study, emphasis is placed upon the relation between the saturation color and the intensity of the absorbed x-rays, the homogeneity of color in thick plates, and the effect of intensity of x-rays on the spectral distribution of color.

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AN INVESTIGATION OF THE RATIO OF ELECTROSMOTIC MOBILITY ALONG A FLAT SURFACE TO ELECTROPHORETIC MOBILITY OF PARTICLES OF ULTRAMICROSCOPIC SIZE

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Recent work (1, 4, 11) with particles of microscopic dimensions in dispersing media of proper electrolyte concentration has led to the verification of the correctness of the factor, $1/4\pi$, in the Smoluchowski equation,

$$V = \frac{\zeta_p DX}{4\pi\eta}$$

for particle mobility. The significance of the individual terms is well known. White, Monaghan, and Urban (11) have shown, however, that the equation is not adequate when electrolyte concentration is very low. The Smoluchowski equation,

$$U = \frac{\zeta_0 DX}{4\pi\eta}$$

for electrosmotic mobility is accepted as correct. The validity of the V-equation for the treatment of ultramicroscopic particles (radius of lower order of magnitude) is unknown. Further, the rôle of electrolyte as a factor influencing the ratio of electrosmotic mobility, U, to electrophoretic mobility, V, of micelles of this size is a matter of conjecture.

The present investigation was undertaken to test this same factor with these smaller particles and at the same time to note whether radius has any effect on mobility. It was proposed to do this by determining the ratio, U/V, of electrosmotic mobility of liquid along a fixed relatively flat surface to electrophoretic mobility of particles of the desired size. If this ratio is unity the factor $1/4\pi$ in the V-equation is correct and the radius of the particle has no effect. The theory relating to such an attack has been discussed thoroughly in the above references, as well as in articles by Henry (9), Kemp (10), and others. The system must be such that both particle and plane exhibit the same chemical and physical surface. Hazel and King (8) have shown that particles of ferric oxide in a dilute gelatin sol take on the properties of the gelatin. Abramson and Freundlich (6) and several others (5, 11) have shown the same for glass. Ayres and

Sorum (3) determined the radius of colloidal ferric oxide, assuming a sphere, to be about 37 × 10^{-7} cm., and it is assumed that the radius of the gelatin agglomerates is of the order of 10^{-7} cm. The size in the latter case depends upon the pH of the medium. Thus the proper system may be obtained by using an unbuffered ferric oxide–gelatin mixture in a Mattson-type electrophoresis cell made of Pyrex glass. It should be pointed out that this method of approach depends upon the assumption that gelatin adsorbed at a solid–liquid interface presents a smooth exterior and that the radius of the resulting interface is largely determined by the radius of the adsorbing material and not by the gelatin, as was suggested by Abramson (2). If the gelatin imparted to the surface its own effective radius, the ratio, U/V, would of necessity be unity. This follows since the constant factor in the U-equation was arrived at by assuming an extremely large radius. If the radius is not large and is the same as that of the particle, the mobility ratio is the ratio of two equations having all terms identical, and the constant factor in each might be either $1/6\pi$ or $1/4\pi$. The ratio would shed no light on this point.

Before proceeding with the determination of the mobility ratio, it seemed advisable to test the hydrodynamic equations and predictions for the behavior of suspended particles and dispersing medium in a closed capillary tube or cylindrical electrophoresis cell under the influence of an applied electromotive force. Up to the present, no tests of the theory seem to have been made with the use of ultramicroscopic particles.

EXPERIMENTAL

The electrophoresis cell was of the type described by Hazel and Ayres (7). It had an inside radius of 1.076 mm. The distance between electrodes was 11.75 cm. The applied potential was usually 6 to 10 volts per centimeter.

The ultramicroscope was the same as described by these same investigators. It was, however, modified so that ready adjustment and focus could be made at any depth in the cell. The cell was clamped rigidly upon a stage that had the solid center removed to permit the passage of light from below into the lens. If the eyepiece were removed and the eye held in its place, the cell could be easily centered by means of the horizontally adjustable stage. The microscope lens was adjusted to a desired depth by means of a calibrated screw. The whole microscope part could be raised or lowered to the proper position in the light beam from the arc lamp by means of another lift screw. The technique in making observations was the same as used previously (7).

The sols were prepared as described by Hazel and King (8). The gelatin concentration was 0.034 per cent instead of 0.04 per cent.

A glass electrode was used for the determination of the pH. All determinations were made after the sols were mixed and just before or simultaneously with the mobility observations.

Curves 1 and 2 of figure 1 and the curve in figure 2 illustrate the type of results obtained by plotting observed mobility, $V_{obs.}$, against per cent of diameter from the top of the cell. Curve 1 is for a sol on the acid side of the isoelectric point at pH 3.83. Curve 2 is for the same sol with 10^{-3} molar potassium chloride present. The isoelectric point of the gelatin used in obtaining the data in figure 1 was 4.3. For all of the rest of the work reported here a new sample having an isoelectric point of 4.73 was used. Figure 2 gives the results of a typical experiment on the alkaline side of the isoelectric point. It is noted that the mobility in this case changes sign, and that there is a large velocity gradient near the depth at which the stationary liquid layer exists. This probably serves to magnify mobility measurement errors due to slight errors in focusing. The symmetrical nature of the curves at the top is fair indication that proper focus had been attained. According to the theory, the mean mobility in the cell or the average value obtained from the mobility–depth curve should be equal to the true electrophoretic mobility, V, which is the mobility measured at the depth 0.147 of the diameter from the top. According to Abramson (1), this mean value is more readily obtained if $V_{obs.}$ is plotted against (a^2), the square of the distance from the position of observation to the axis of the cell, whence a straight line results. The value of V is given by the expression

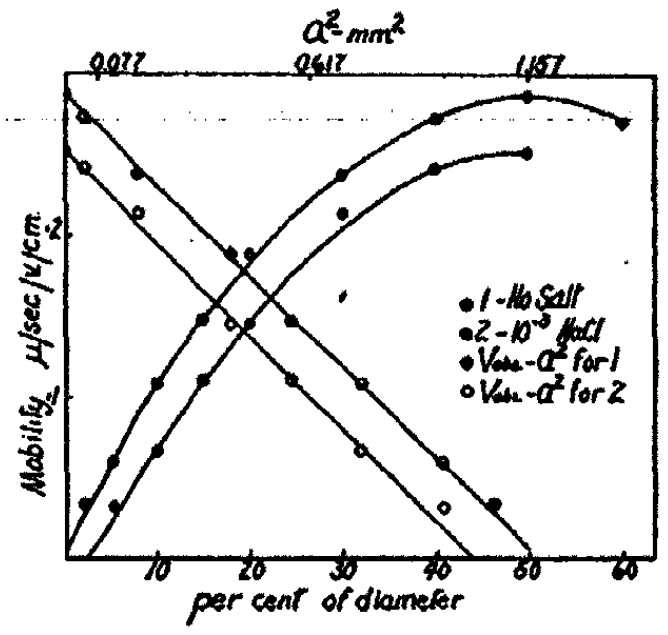

FIG. 1

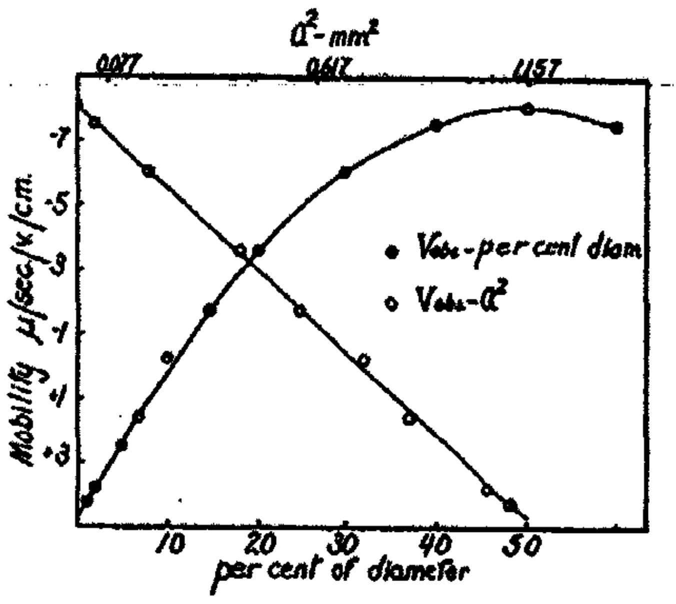

FIG. 2

FIG. 1. Mobility–depth curves. pH = 3.83
FIG. 2. Mobility–depth curve. pH = 5.7

$$V = \frac{1}{r^2}\int_0^r V_{obs.}\, d(a^2)$$

where r is the radius of the cell. The value of the integral is obtained from the area under the straight line. The $V_{obs.} - a^2$ lines are put on the same graphs for comparison. Table 1 gives the values of $V_{obs.}$ at the 0.147 depth and those calculated from the areas under the above lines. The agreement is found to be good.

The observed particle mobility is equal to the sum of the true mobility of the particle and of the mobility of the liquid as shown by the expression $V_{obs.} = V + V_w$, where V_w is the mobility of the water at the depth of observation. At the center of the cell $V_{obs.} = V + U$. By making observations at the 0.147 and 0.50 levels, the values of both V and U may be obtained since $U = V_{0.5} - V$. It also is true that $U = V + V_0$, where V_0 is the mobility observed right at the cell wall. This latter method of obtaining U has been said to give poor results, because the particles experience interference with their motion along the wall. During the course of the present investigation, in which over two hundred values of U and V were determined, it happened that in nine cases observations were made at the zero, 0.147, and 0.50 levels. Table 2 gives the results of calculating U by the two methods. Of the nine, six of them show excel-

TABLE 1

Calculated and observed values of electrophoretic mobility

	ELECTROPHORETIC MOBILITY	
	Calculated	Observed
	μ/sec./v./cm.	*μ/sec./v./cm.*
Curve 1, figure 1	+1.46	+1.46
Curve 2, figure 1	+1.07	+1.06
Curve 2, figure 2	−1.70	−1.70

TABLE 2

Comparing U calculated by two methods as indicated

$V_{0.5} - V$	$V_0 + V$
μ/sec./v./cm.	*μ/sec./v./cm.*
−6.54	−6.57
6.13	5.58
6.33	6.35
5.90	6.05
2.10	1.78
4.11	4.00
5.57	5.55
3.93	3.99
6.85	5.95

lent agreement, while lack of agreement is pronounced in only one experiment. The experiments were not performed for the purpose of making this comparison. In all other instances U was determined by the first method.

Early in the investigation it became apparent that U and V varied differently with a change in pH with the sols containing 0.34 g. of gelatin per liter. This was especially manifest on the alkaline side of the isoelectric point and at higher concentrations of hydrogen ions on the acid side. This behavior was unexpected, as it was thought that the ratio of U to V would be near either 1 or 1.5. White et al. (11) make the statement that the ratio is independent of pH. The curves in figure 3 show this variation more clearly. The V–pH curve agrees well with one by Hazel and King (8). It is important that both curves cross the horizontal axis at the same point. This indicates that gelatin adsorbed on glass and on ferric oxide has the same isoelectric point of 4.73, and that, at least at this pH, the glass wall was covered so that it presented the same surface as the ferric oxide–gelatin particles.

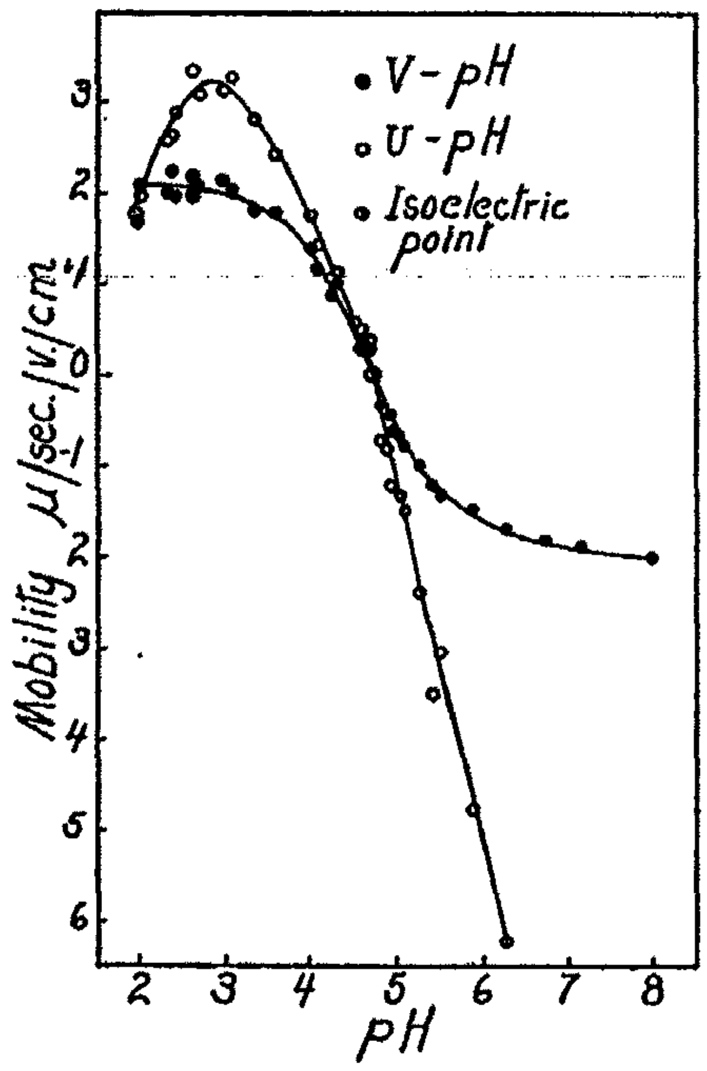

Fig. 3. Mobility-pH curves

When U/V was not near 1, the addition of electrolyte caused the ratio to approach this value. The change came about as a result of a rapid decrease in *U* and only a slight decrease in *V*. Table 3 shows the effect of salts on the alkaline side, and table 4 shows a similar effect at a pH where the maximum occurs on the acid side. In table 4 the *U*/*V* ratios are slightly higher than those recorded in figure 3, as are also the individual values of *U* and *V*. The higher *U* and *V* values were due to a temperature effect which could not be controlled. All of the data in figure 3 were obtained when room temperature was near 22°C. The work with which table 4 is concerned was done in the spring, when room temperature was

TABLE 3

Variation of V, U, and U/V with electrolyte concentration

ELECTROLYTE CONCENTRATION	NUMBER OF RUNS AVERAGED	*V*	*U*	*U/V*	pH
moles per liter		*μ/sec./v./cm.*	*μ/sec./v./cm.*		
H_2O	3	−1.78	−6.67	3.74	6.03
KCl 10^{-4}	2	1.74	4.56	2.63	6.00
10^{-3}	2	1.30	1.75	1.34	6.05
10^{-2}	2	0.82	0.94	1.15	6.03
$BaCl_2$ 0.5×10^{-4}	1	1.39	2.29	1.65	6.00
10^{-4}	1	1.34	1.70	1.30	6.00
10^{-3}	3	0.72	0.85	1.18	6.05
0.5×10^{-2}	2	0.41	0.38	0.93	6.05
K_2SO_4, 0.5×10^{-3}	1	1.44	1.83	1.27	6.00

TABLE 4

Variation of V, U, and U/V with electrolyte concentration at a pH near 3

ELECTROLYTE CONCENTRATION	NUMBER OF RUNS AVERAGED	*V*	*U*	*U/V*	pH
moles per liter		*μ/sec./v./cm.*	*μ/sec./v./cm.*		
H_2O	7	+2.47	+3.94	1.60	2.99
KCl 10^{-3}	4	2.15	3.25	1.51	2.99
10^{-2}	5	1.58	1.90	1.20	2.99
K_2SO_4 10^{-4}	1	2.09	3.24	1.55	3.00
0.5×10^{-3}	1	1.75	2.28	1.30	3.00
10^{-3}	2	1.46	2.03	1.39	3.00
10^{-2}	3	0.94	1.03	1.09	2.98
$BaCl_2$, 0.5×10^{-3}	1	2.35	2.87	1.22	3.00

between 25° and 27°C. Several experiments were performed to test this point. The cell was insulated with rubber tubing, and samples of sol were cooled to different temperatures and run through the cell for some time. Velocity measurements were then made. The temperature inside the cell rapidly rose to that of the room, so that only a few observations could be made, and consequently the data obtained were not definitely reliable. The experiments, however, indicated a temperature coefficient of about 7 per cent for a 5-degree temperature increase insofar as V was concerned. It was not possible to determine whether or not U varied in the same way as did V. Further investigation along this line would be desirable.

In neither table 3 nor table 4 did the addition of 10^{-2} moles of potassium chloride per liter cause the ratio to become exactly 1. In both cases slight but definite particle motion was discernible at the cell wall. The use of more concentrated solutions caused considerable electrolysis. Table 5 illustrates the effect of electrolyte at a pH where U/V is already near 1. Table 5 also demonstrates the reproducibility obtained.

TABLE 5

Variation in V, U, and U/V with potassium chloride concentration with sols at pH 4.16

ELECTROLYTE CONCENTRATION		V	U	U/V
	moles per liter	*μ/sec./v./cm.*	*μ/sec./v./cm.*	
H_2O		1.19	1.13	0.95
		1.12	1.12	1.00
		1.08	1.08	1.00
		1.13	1.19	1.06
KCl	10^{-3}	0.72	0.60	0.84
		0.74	0.71	0.96
	10^{-2}	0.46	0.44	0.96
		0.47	0.50	0.96

White and Monaghan[12] report that amounts of added potassium chloride of the order of 10^{-5} moles per liter at first increased the zeta potential and thus the mobility of particles, and that larger amounts decreased it. They did not note this in their first paper (11). An attempt was made to observe this phenomenon with our sols. Pure dialyzed ferric oxide, diluted in the usual way with redistilled water, was added to the usual amount of gelatin in redistilled water. With no acid, base, or electrolyte added, the resulting pH was very close to 5. The mobility of the water and particles was determined in this sol. Then the mobility was measured in sols to which small amounts of potassium chloride had been added and, within the limits of experimental error, no increase in mobility resulted.

No change in pH could be detected after addition of the salt. The same results were obtained with sols very near the isoelectric point on the acid side. Abramson (1) has reasoned that no increase should be expected in the case of proteins.

The results of experiments to determine the effect of gelatin concentration on the values of V, U, and U/V are given in table 6. The pH was 5.8. In one case no gelatin was used. Ferric oxide sol was diluted to the concentration used in the gelatin–ferric oxide sols and a pH of 6 resulted. V was found to be $+3.34$ and U was $+1.21$. This shows how strongly ferric oxide is attracted to glass. In the event of no adsorption U should have been about -10. Another experiment at a pH near 4, in which a more concentrated ferric oxide sol was used, showed that U had become positive enough to make U/V equal 0.9. Further investigation along this line might prove interesting. It opens the possibility of studying the U/V ratio with surfaces other than protein.

TABLE 6

The effect of gelatin concentration on the values U, V, and U/V

GELATIN	V	U	U/V
per cent	*μ/sec./v./cm.*	*μ/sec./v./cm.*	
0.017	−1.64	−5.55	3.38
0.043	1.66	4.11	2.46
0.085	1.53	2.10	1.37
0.170	1.45	1.51	1.04
0.340	1.22	1.21	0.99
0.770	0.97	0.98	1.01

The very large change in electrosmotic mobility might indicate that the glass wall was not covered at the lower dilutions. However, this is not in accord with the findings of Abramson and Freundlich (6), Dummet and Bowden (5), and White et al. (11), who report the wall to be covered with gelatin at concentrations of gelatin lower than any used in table 6. It was felt that the large surface of the ferric oxide present might have reduced the effective gelatin concentration below the amount found necessary by the above investigators, or that sufficient time had not been allowed for equilibrium to be established at the wall. Experiments showed, however, that the use of only one-fiftieth as much ferric oxide, which was just enough to give a faint yellow color to the sol mixture, gave values of U and V and of the ratio almost identical with those previously obtained. The allowance of 100 minutes for the establishment of equilibrium instead of the usual 15 or 20 minutes caused no change in the measured values.

The curves in figure 4 show the results of experiments, with sols on the alkaline side of the isoelectric point, to determine the effect of pH on the amount of gelatin necessary to coat the glass wall. The complete data for U and V are given in table 7. Abramson and Freundlich (6) have performed similar experiments in the presence of $M/50$ acetate buffers, and have interpreted the curves to mean that complete coating is attained at a concentration of gelatin where the curves begin to flatten out. They found that 0.1 g. of gelatin per liter was sufficient at a pH of 6.6 to 7.5. The above curves demonstrate that about 2 g. per liter is necessary on the basis of the criterion mentioned. They also show that as the pH increases the amount of gelatin necessary to cover the glass increases. Curve 4 in figure 4 probably explains the difference between these observations and those of the other investigators mentioned. The addition of a small amount of sodium chloride, 10^{-3} moles per liter, caused the glass to become coated even at the smallest concentration of gelatin used. Thus the amount of gelatin necessary in the presence of $M/50$ buffer salt would also be much less. White and coworkers used no buffers but worked only with isoelectric gelatin. Table 7 shows that the ferric oxide particles were covered at all of the concentrations used.

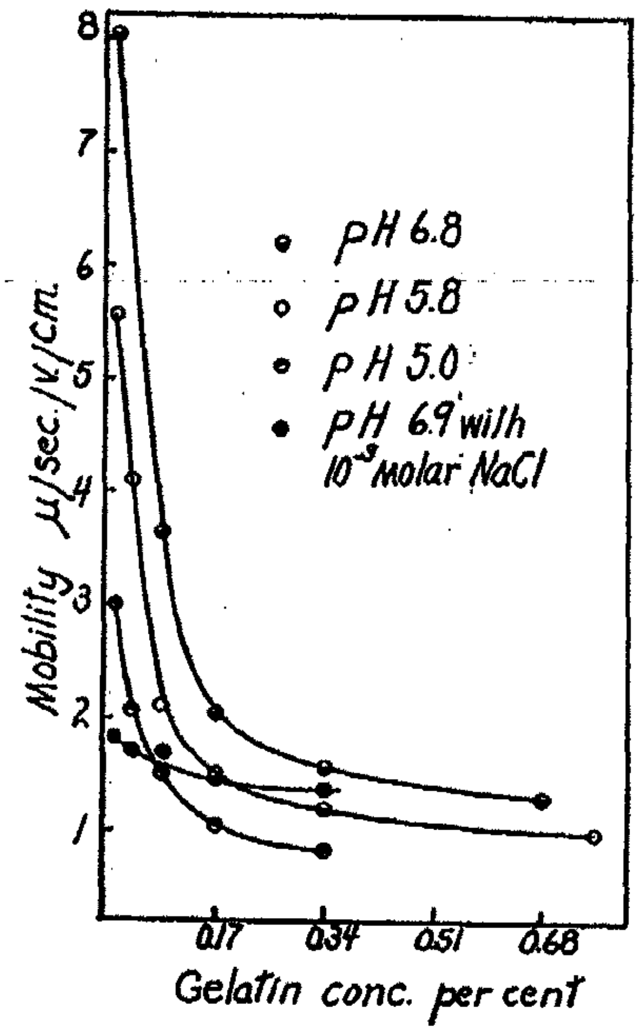

FIG. 4. Showing the effect of gelatin concentration and pH on U. Alkaline side of isoelectric point.

These results explain the nature of the U–pH curve in figure 3. As the pH increases, a given small concentration of gelatin becomes less and less effective in covering a glass surface. The large values of *U* are probably due to partially bare glass. They also explain the abnormal effect of salts on *U* as shown in table 3. The addition of electrolyte allows the small amount of gelatin to cover the wall more effectively. This might take place as a result of either or both of the following effects. The gelatin aggregates are dispersed by the electrolyte, thus giving a greater effective concentration, or the negative charges on the wall and on the gelatin particles are both reduced, making it possible for increased adsorption of the protein at a given concentration, since the forces of repulsion are reduced.

TABLE 7

Showing the effect of gelatin concentration on mobility on the alkaline side of the isoelectric point

GELATIN	*V*	*U*	*U/V*
pH = 6.8			
per cent	*μ/sec./v./cm.*	*μ/sec./v./cm.*	
0.017	−2.01	−8.04	4.02
0.043	2.00	3.64	1.82
0.085	1.83	2.04	1.12
0.170	1.50	1.55	1.04
0.680	1.33	1.29	0.98
pH = 6.9; with 10^{-3} molar NaCl			
0.017	−1.55	−1.82	1.18
0.043	1.60	1.71	1.07
0.085	1.56	1.69	1.08
0.170	1.51	1.46	0.97
0.340	1.39	1.35	0.97
pH = 5.0			
0.017	−1.12	−3.00	2.68
0.043	1.16	2.07	1.78
0.085	1.11	1.50	1.35
0.170	1.13	1.03	0.91
0.340	0.89	0.82	0.91

The data plotted in figure 5 illustrate the effect of gelatin concentration and pH on sols on the acid side of the isoelectric point. In these curves both *U* and *V* are plotted. The results are consistent with the maximum in the *U*–pH curve in figure 3. It is observed that increased gelatin concentration eliminates this maximum. Other experiments have amply demonstrated this. The wall must be completely coated at the lowest concentration of protein used. If this were not so, an increase in the mobility would have resulted with an increase in the amount of gelatin, since the glass surface is negative and the gelatin is positive. The use of ferric oxide in these systems makes it impossible to study the concentration region where U is negative and finally becomes positive. The decreasein the mobility shown in the curves is due to decreased dielectric constant, increased viscosity, and increased ionic strength in the medium. The behavior exhibited in the U–pH curve in figure 3 on the acid side seems entirely anomalous. The variation from V can not be explained by insufficient covering, nor can it be rationalized by assuming a polarization of the particles which should give them a lower mobility than exhibited along a plain surface. However, since this maximum is removed by electrolyte addition or by increasing the concentration of gelatin, it was concluded that identical surfaces were not presented on particle and wall until this latter had been done.

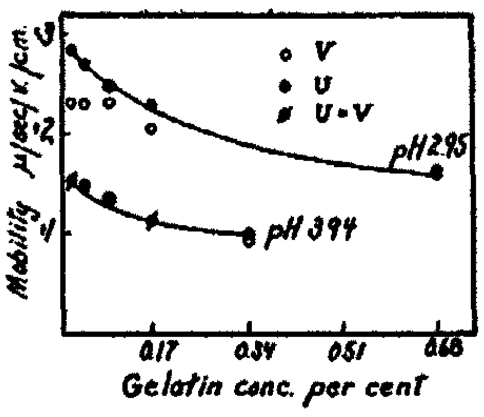

FIG. 5. Showing the effect of gelatin concentration and pH on U and V. Acid side of isoelectric point.

It has been shown that the U–pH and V–pH curves become identical when sufficient gelatin is used, i.e., $U/V = 1$ and is independent of pH, and that the ratio is independent of electrolyte concentration under the same conditions. Since under the proper conditions this ratio is 1, and since with particles as small as those used electrolyte up to 10^{-3} molar should not remove the effects, as it does with larger particles (11), it was concluded that the factor $1/4\pi$ in the Smoluchowski equation for electrophoresis is correct. Furthermore, the radius of curvature can have no effect on mobility.

SUMMARY

1. The hydrodynamic theory for electrophoresis has been tested with the use of ultramicroscopic particles, and has been found to hold.

2. The ratio of electrosmotic to electrophoretic mobility has been investigated with the use of these smaller particles. The system used was an unbuffered gelatin–ferric oxide mixture in a Mattson-type electrophore-

sis cell of Pyrex glass. When the gelatin concentration was below about 2 g. per liter, electrolyte and pH had a profound influence on this ratio. When the gelatin concentration was above this value, the ratio was unity and independent of electrolyte or pH.

3. It was concluded that to get surfaces that were identical, other than at the isoelectric point, and in the absence of electrolyte, about 2 g. of gelatin per liter was necessary.

4. Since the ratio was unity when identical surfaces were obtained, it was concluded that the factor $1/4\pi$ in the Smoluchowski equation for electrophoresis is correct and that the radius of the particle has no effect on mobility.

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THE USE OF MOBILITY DATA IN DETERMINING THE COMPOSITION OF COLLOIDAL MICELLES

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In a recent publication (2) by J. W. McBain and W. McClatchie Thomas, the fraction of free chloride ion in a ferric oxychloride hydrosol was calculated by assuming that ultrafiltration effected a separation of the free hydrochloric acid in the colloidal system. Sufficient data, however, are presented in that paper to evaluate the fraction of free chloride ion without this assumption by making use of the difference of mobility existing between the chloride constituent in crystalloidal form and in the micelle. The method of calculation which follows is applicable also to colloidal solutions with one or more kinds of "contra" ions, as is the case when a salt is added to a "pure" hydrosol.

If a colloidal solution be electrolyzed in a Hittorf transference apparatus the concentration change at an electrode chamber in terms of the mobility of the bound and unbound portions of a particular constituent may be derived as follows: Consider the region in the transference apparatus where the sol remains unaltered during the electrolysis. Let the area of the cross section of this region be called A. Then the number of grams of micellar constituent passing A in t seconds is equal to AV_1xt, where V_1 is the velocity of the micelle and x is the number of grams (per cubic centimeter) of the constituent in the micelle. The number of grams of crystalloidal constituent passing A in the same interval is $AV_2(M - x)t$, where V_2 is the velocity of the crystalloidal fraction which has the original concentration of $(m - x)$ grams per cubic centimeter. Thus at an electrode chamber the total *change*, Δ, of the quantity of the constituent whose original concentration was m grams per cubic centimeter is

$$\Delta = At\,[V_1x + V_2(m - x)] \tag{1}$$

Replacing A by I/KE, where I is the current, K the specific conductivity of the original sol, and E the potential gradient, we get

$$\Delta = \frac{It}{KE}\,[V_1x + V_2(m - x)] \tag{2}$$

Setting E equal to unity, V_1 and V_2 may be replaced by their respective mobilities U_1 and U_2. Thus

$$\Delta = \frac{It}{K}[U_1x + U_2(m - x)] \tag{3}$$

Taking the particular case of their sol No. 13 (2), the data for which are given in table 1, one obtains by the use of equation 3 the value of 4.07×10^{-3} equivalents per liter of free chloride ion, which differs from the result given by McBain and Thomas by 57 per cent.

It is to be noted that all quantities used in equation 3 to evaluate the concentration of free chloride ion were determined experimentally except the value for the mobility of the free chloride ion, U_2, in which case the limiting mobility 7.91×10^{-4} was used. Although these colloidal oxide micelles are viewed generally as giant multivalent ions, the use of the limiting mobility for their contra ions may be justified to some extent by the consideration that the interionic forces resulting from these micelles are more like that of a 1-1 salt. This can be seen from the result that for every faraday of free charge, there are associated more than 200 chemical equivalents of iron. Furthermore, there is evidence from another source (4) that six groups (consisting of H_2O, OH, Cl) surround each iron atom in the form of a complex of the Werner type, thus making the distance between like charges on the micelle 10 or more Ångström units.

TABLE 1

Description of "ferric hydroxide" sol No. 13, as given by McBain and Thomas (2)

Concentration of Fe in equivalents per liter	0.912*
Concentration of Cl in equivalents per liter	0.04405*
C_{H^+}	6.3×10^{-5}
Specific conductivity in mhos	5.70×10^{-4}
Hittorf number for Fe	70.3†
Hittorf number for Cl (not chloride ion only)	−2.51
Mobility of Fe in cm. per second per volt per centimeter	4.52×10^{-4}
Mobility of Cl^-	7.91×10^{-4}

* See reference 3.

† Unlike the Hittorf number for Cl, the Hittorf number for Fe can furnish the mobility of the micelle, since this element exists entirely within the micelle. This is confirmed by the fact that McBain and Thomas found that both the Hittorf transference and the moving-boundary method gave the same values for the mobility of the micelle.

The calculated specific conductivity of sol No. 13, on the basis that there exist 4.07×10^{-3} equivalents per liter of negative charge balanced by the positive charge on the micelles and hydrogen ions,[1] each ion moving with

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[1] The contribution of the hydrogen ions to the conductivity of the sol is 4 per cent.

its respective mobility, is 5.1×10^{-4} mhos. This value does not consider the contribution that the conductivity may receive from the contamination of the sol by the dialyzing membrane (Cellophane) in which the sol was kept for several weeks. The contribution from this source may be set equal to 0.2×10^{-4} mho,[2] giving finally a calculated conductivity of 5.3×10^{-4} as compared with the observed value of 5.7×10^{-4}.

The difference of 7 per cent between these two figures does not in any way indicate the correctness of the value used for the mobility of the free chloride ion, but rather it shows the validity of the experimental measurements, particularly the transference number for chloride and the mobility of the colloidal particle.

SUMMARY

It has been shown that the fraction of a constituent that is unbound may be determined in a colloidal solution by means of mobility data without including the usual procedure of ultrafiltration and its concomitant assumption.

The author is grateful to Prof. A. W. Thomas for his suggestions in connection with this work.

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[2] This correction is derived from the fact that ultrafiltrate of sol No. 13, which had passed rapidly through a Cellophane membrane, had a conductivity of 0.3×10^{-4} mho and only one fourth of this conductivity could be attributed to the presence of hydrochloric acid (see reference 1).

HOMOLOGY AND ISOMERISM IN LONG-CHAIN COMPOUNDS. I

A THERMOCHEMICAL STUDY OF THE n-ALKYL ESTERS DERIVED FROM THE MONOETHYLENIC MONOCARBOXYLIC ACIDS IN C_{18}

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INTRODUCTION

A decade ago a preliminary study was attempted of the relative stability of oleic and elaidic acids and of their methyl esters from a comparison of the energy contents of the best samples of these substances which were available at the time (1).

With regard to the acids it was found that the heat of combustion of oleic acid was higher than that of elaidic acid by a much larger amount than could be accounted for merely by the difference between the states of aggregation of the two acids before combustion. This observation, when taken in conjunction with Stohmann's rule, led to the conclusion that, in agreement with observations derived from other fields, oleic acid should be regarded as the *cis*-form and elaidic acid as the *trans*-form of the same chemical structure.

With regard to the methyl esters, however, the sole pair to be investigated at the time, the differences between the heats of combustion were so small (1 part in 10,000 only) as to be within the limits of the experimental error for the calorimetric measurements (1 in 10,000 also) and well within these limits for the extent of the purification process for these substances. No definite conclusion could therefore be drawn as to the relative stability of these two esters.

It is with a view to the removal of this ambiguity that the work to be described in the following pages has been attempted. Instead, however, of limiting the comparison to the methyl esters only, the ethyl, *n*-propyl, and *n*-butyl esters have been examined as well.

CONTROL OF THE PURITY

All the esters considered in this paper are liquids at ordinary temperature; the elaidates remain so down to the region of the melting point of ice and the oleates down to some 20°C. lower. The melting point and the setting point are therefore not very useful for testing the purity of these substances, the more so that the values of these constants are not known, at least with any degree of exactness, from the literature. The same remark applies, though to a lesser extent, to oleic acid itself. As for elaidic acid, the *International Critical Tables* give values as far apart as 44° and 51°C. From our own experience, it is the former of these which is in the immediate neighborhood of the true value for the setting point, but as it changes only slowly with further purification, its usefulness is extremely limited as a criterion of purity.

When, however, the elaidic acid is obtained from samples of oleic acid which have been previously freed from polyethylenic impurities (as was shown to be possible in a previous paper on the purification of oleic acid (2)), the determination of the iodine value gives a true indication of the extent of the purification, without any ambiguity. The purification of elaidic acid was actually carried on until the iodine value was raised to the theoretical value for that substance and went no further. As an additional control of the purity, the heat of combustion of a large number of different fractions was determined; only small variations were found for that constant, except for the early tail fractions, which were therefore rejected for the preparation of the esters. The purity of the elaidates and oleates was also controlled by comparison of the observed with the theoretical iodine values, under the same conditions of non-ambiguity.

DISCUSSION

In order to facilitate the discussion of the results detailed in table 1, the molecular heats of combustion of the various esters have been calculated and collected in table 2. The value of the energy increment (represented by ΔCH_2 in the table) when passing from one member of the series to the next higher homolog has also been calculated. The corresponding values observed for the series of the alcohols which were used in building up the two series of esters have been added for the sake of comparison. (For the difference between the methyl and ethyl alcohols, the latest value, namely that of Rossini (4) has been taken, while for the other alcohols, the values of Richards (3) were selected.) Finally the heat of transformation for each member of the *cis*-series to the corresponding member of the *trans*-series has been reported.

The first striking fact is the complete parallelism between the series of energy increments for the elaidates and for the parent alcohols; it indicates that the replacement of the hydrogen atom of the alcohol by the heavy radical $CH_3(CH_2)_7:(CH_2)_7CO$— has not deeply altered the structural relationships inside the liquid molecule. On the other hand, the nearly perfect constancy of the increment between the second and fifth members of the elaidate series and of the alcohol series provides a strong argument in favor of the additive character of the molecular heat of combustion of organic liquids whose molecules possess a large number of carbon atoms, as is the case for the elaidates, or whose terminal groups are not endowed with strong residual affinities, as is the case for the alcohols.

In the case of the oleates, however, such regularities are not apparent, though they possess the same number of carbon atoms as the corresponding elaidates. This difference in behavior might be explained by one of the following alternatives:

(*1*). While the successive elaidates were all prepared from the same pure sample of elaidic acid (iodine number = 89.9), the various oleates were derived from different samples of oleic acid (iodine number about 0.3 to 0.4 unit lower than the theoretical), none of which was quite as pure as the elaidic acid, and amongst which there may therefore have been slight discrepancies between the energy contents. In order to investigate that possibility, a new series of oleates was built up, starting now each time from the same sample of oleic acid (iodine number = 88.9). Though this new sample was, like the earlier ones, quite free from polyethenoid acids, it contained a slightly higher proportion of saturated impurities, so that the values obtained for the heats of combustion of the derived esters cannot be strictly compared with those of table 2; but the value for the energy increment per CH_2 is naturally more accurate in this than in the earlier case. The values of the successive increments actually observed with these new samples of esters were as follows:

	Methyl oleate Ethyl oleate	Ethyl oleate n-Propyl oleate	n-Propyl oleate n-Butyl oleate	
ΔCH_2 in kg-cal	152.5	155.5	155.1	for oleates
as against	153.0	155.8	156.0	for alcohols
and	153 2	155.8	155.9	for elaidates

The agreement is therefore much better than before.

(*2*). Another reason that may be put forward in order to explain the differences between the energy increments of the various esters depends on their mode of preparation. Indeed, while the members of the first series of oleates were all obtained by fractional distillation, on the contrary not a single one of the second series of oleates or of the elaidates was submitted to such treatment. As a consequence, the older oleates may have been obtained in a slightly different thermodynamic state than the later ones, this difference being made apparent through the irregularities observed in the values for the energy increment.

(*3*). A third possibility that should not be overlooked is that the state of association of the earlier samples of ethyl oleate (which had been distilled and burnt directly afterwards) may not have been the same as

TABLE 1

Isothermal heat of combustion per gram (in vacuo), under constant volume and at the constant temperature of 20°C. (in cal._{15}*)*

SUBSTANCE (TH. I. N.) AND [WATER EQUIVALENT]	IODINE NO.	FRACTION	OXYGEN	WEIGHT IN GRAMS (*in vacuo*)	RISE OF TEMPERATURE (OBSERVED)	CORRECTIONS IN TEN-THOUSANDTHS FOR		RISE OF TEMPERATURE (CORR.)	CORRECTION IN CALORIES FOR		HEAT OF COMBUSTION PER GRAM (ISOTHERMAL)	MEAN
						col.	stirr.		HNO_3	cott		
Methyl oleate (th. 85.7) [4276.9]	85.3	2	K	1.1558	2.5779	0	53	2.5906	1.4	14.6	9574.4	9575.8
	85.3	3	—	1.1552	2.5769	−1	46	2.5902	1.5	15.4	9577.2	
	85.5	4	—	1.1552	2.5781	0	60	2.5901	3.3	15.4	9575.2	
	85.5	5	—	1.1533	2.5728	0	51	2.5857	1.7	15.4	9576.1	
	85.6	6	—	1.1567	2.5795	−1	45	2.5929	1.1	14.8	9575.5	
	84.7	7	—	1.1554	2.5771	0	46	2.5905	2.4	14.6	9576.5	
Ethyl oleate I (th. 81.8) [4274.8]	82.2	2	G	0.8887	2.0003	0	56	2.0087	15.7	14.2	9630.5	9632.5
	82.4	3	—	0.8853	1.9930	+2	54	2.0017	15.5	11.4	9637.2	
	82.2	4	—	0.8900	2.0021	−3	46	2.0112	15.5	13.8	9629.1	
	82.4	5	—	0.8887	1.9985	0	33	2.0092	15.3	13.8	9633.9	
	82.0	6	—	0.8855	1.9921	+1	42	2.0019	16.5	14.2	9631.6	
	82.0	3A	—	0.8850	1.9910	−1	44	2.0004	16.2	12.2	9632.5	
Ethyl oleate I.A [4275.3]	81.7	3	M	0.8883	1.9962	−2	64	2.0036	2.3	8.4	9630.3	9629.2
	81.8	4	—	0.8862	1.9904	−2	64	1.9978	2.4	8.4	9625.1	
	81.8	4	—	0.8872	1.9927	0	70	1.9997	1.8	9.4	9627.1	
	81.7	5	—	0.8888	1.9978	−1	64	2.0053	2.4	7.8	9633.0	
	81.8	6	—	0.8877	1.9957	−2	70	2.0025	2.0	9.4	9630.7	
Ethyl oleate I.B	81.5	2	M	0.8856	1.9898	−3	65	1.9969	2.1	8.6	9630 9	9630.8
	81.6	3	—	0.8876	1.9939	−3	62	2.0014	2.4	8.6	9630.5	
	81.7	4	—	0.8858	1.9904	−1	64	1.9979	2.6	9.0	9631.9	
	81.7	5	—	0.8845	1.9871	−3	61	1.9946	2.4	9.8	9630.0	

Propyl oleate (th. 78.3)	78.0	3	M	0.8831	1.9983	0	59	2.0064	2.4	9.4	9702.8	9701.6
	78.0	3	—	0.8828	1.9975	+1	64	2.0052	2.5	8.2	9701.6	
	77.8	4	—	0.8843	2.0022	0	74	2.0088	2.2	9.4	9701.5	
	77.8	5	—	0.8836	2.0001	−1	69	2.0071	2.2	10.2	9700.0	
Butyl oleate (th. 75.0) [4273.6]	74.7	2	J	0.8716	1.9894	+3	57	1.9979	16.9	13.4	9763.3	9761.5
	75.1	3	—	0.8722	1.9909	+3	64	1.9987	16.8	13.8	9760.1	
	75.3	4	—	0.8733	1.9935	+3	61	2.0016	16.2	13.8	9762.7	
	75.3	5	—	0.8716	1.9889	+3	60	1.9971	16.9	14.2	9758.4	
	74.7	2A	—	0.8718	1.9876	+2	31	1.9886	17.0	14.6	9763.0	
Methyl elaidate (th. 85.7) [4273.3]	85.6		R	0.9005	2.0141	−1	76	2.0205	2.8	12.2	9573.9	9570.3
	—		—	0.8951	1.9998	+1	63	2.0076	3.2	11.0	9570.9	
	—		—	0.8960	2.0025	−2	65	2.0098	3.5	9.8	9572.7	
	—		—	0.8952	1.9998	−2	61	2.0075	4.4	9.8	9569.4	
	—		—	0.8922	1.9925	−2	60	2.0002	2.9	9.8	9568.2	
	—		—	0.8944	1.9992	−3	75	2.0054	4.9	9.4	9567.8	
	—		—	0.8920	1.9933	+1	68	2.0005	2.9	11.8	9569.4	
Ethyl elaidate (th. 81.8)	81.6		R	0.8879	1.9962	0	60	2.0042	3.5	11.0	9631.7	9632.1
	—		—	0.8849	1.9896	0	63	1.9972	2.2	10.6	9632.4	
	—		—	0.8887	1.9986	0	68	2.0058	3.3	11.4	9630.5	
	—		—	0.8877	1.9969	−1	65	2.0043	3.3	11.8	9633.7	
n-Propyl elaidate (th. 78.3) [4273.4]	78.1		T	0.8817	1.9983	−4	41	2.0037	2.3	12.2	9696.3	9697.0
	—		—	0.8831	1.9976	−3	44	2.0068	1.9	12.2	9696.3	
	—		—	0.8852	2.0023	0	41	2.0122	2.3	12.6	9698.4	
n-Butyl elaidate (th. 75.0)	74.5		R	0.8776	1.9983	0	62	2.0060	2.9	11.4	9754.6	9756.7
	—		—	0.8875	1.9981	−1	58	2.0062	2.6	11.4	9756.6	
	—		—	0.8781	2.0009	+1	72	2.0078	2.4	11.4	9757.8	
	—		—	0.8769	1.9973	+1	62	2.0052	3.7	11.4	9756.9	

A corrective term, approximately equal to 0.014°C., has been added per 2.000°C. of temperature rise.

for the corresponding ethyl elaidate, which had not been distilled at all! One should indeed remember in this connection that there has often been observed a striking anomaly between the methyl and the ethyl members of homologous series, and that such anomalies may possibly be of quite different degree for the elaidates and for the oleates, as is emphasized further here by the change of sign of the heat of transformation between the ethyl members of the two ester series. For the other pairs of esters, the heat of transformation has not only the same sign, but it seems to have very nearly the same value, namely 1.6 ± 0.1; this shows a very striking constancy, considering the great difficulty of obtaining pure samples and the fact that the samples of oleic acid used for the building of the first series of oleates were all different.

TABLE 2

Isothermal molecular heat of combustion (in vacuo) under constant volume and at the constant temperature of 20°C.

ESTER	MOLECULAR WEIGHT	MOLECULAR HEAT OF COMBUSTION	ΔCH_2	MOLECULAR HEAT OF TRANSFORMATION
Methyl oleate	296.28	2837.2		+1.5
			151.0	
Ethyl oleate	310.30	2988.2		−0.7
			158.0	
n-Propyl oleate	324.31	3146.2		+1.5
			156.1	
n-Butyl oleate	338.33	3302.3		+1.7
n-Amyl oleate	352.36			
Methyl elaidate	296.28	2835.7		
			153.2	
Ethyl elaidate	310.30	2988.9		
			155.8	
n-Propyl elaidate	324.31	3144.7		
			155.9	
n-Butyl elaidate	338.33	3300.6		
			155.9	
n-Amyl elaidate	352.36	3456.5		
Methyl alcohol				
			153.0	
Ethyl alcohol				
			155.8	
n-Propyl alcohol				
			156.0	
n-Butyl alcohol				
			156.1	
n-Amyl alcohol				

All the regularities exhibited in table 2 should be considered as supplying a strong, though indirect, proof of the amount of trustworthiness that may be accorded to the values tabulated.

SUMMARY

1. The isothermal heat of combustion of the four lower members of the alkyl oleate series was found to have the following values:

	g-cal.$_{15}$ per gram	*kg.-cal.$_{15}$ per mole*
Methyl oleate	9575.8	2837.2
Ethyl oleate	9630.0	2988.2
Propyl oleate	9701.6	3146.2
Butyl oleate	9761.5	3302.3

2. The isothermal heat of combustion of the five lower members of the alkyl elaidate series was found to have the following values:

	g-cal.$_{15}$ per gram	*kg-cal.$_{15}$ per mole*
Methyl elaidate	9570.3	2835.7
Ethyl elaidate	9632.1	2988.9
Propyl elaidate	9697.0	3144.7
Butyl elaidate	9756.7	3300.6
Amyl elaidate	9810.2	3456.5

3. While the energy increment per addition of a CH_2 group was found to be remarkably constant for the liquid elaidates and practically equal to that for the corresponding parent alcohols, it was, to say the least, less constant for the corresponding oleates. Several possible reasons were indicated for interpreting this apparent anomaly.

4. The heat of transformation of each of the oleates into the corresponding elaidate was shown to be very nearly constant for three out of the four members available for comparison; in the case of the fourth, the ethyl member, it changed sign.

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THE EFFECT OF BETAINE ON THE CONDUCTIVITY OF SODIUM HYDROXIDE SOLUTIONS[1]

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According to Bjerrum (1) betaine exists in solution as the zwitterion $(CH_3)_3\overset{+}{N}\cdot CH_2CO_2^-$. In fairly concentrated solutions, therefore, betaine should lower the equivalent conductivity of an electrolyte by contributing to the ionic strength. Since the acid $(CH_3)_3\overset{+}{N}\cdot CH_2COOH$ is not a strong electrolyte (6), such studies can only be made in basic solution. In the experiments to be described, the effect on the conductivity of adding various amounts of betaine to sodium hydroxide solutions was measured.

The apparatus (figure 1), of Pyrex glass, is similar to one used by Brønsted and Nielsen (2, 4). The capacity of the cell in the apparatus of figure 1 is small compared to that of the reservoir. This, together with the three-way stopcock and capillary (to avoid trapping of liquid), made possible the withdrawal and measurement of a considerable number of samples from the reservoir. An atmosphere of carbon dioxide-free air, saturated with water at the temperature of the measurements, was maintained by making connections at the openings shown. The reservoir was paraffined. Advantages of this apparatus have been discussed previously (2, 4).

A Jones bridge (3) with oscillator and amplifier, all built by Leeds and Northrup Co., was used for the measurements. The thermostat bath, of distilled water, was maintained at 25°C. ±0.002°.

Betaine monohydrate was prepared from the hydrochloride by the method of Stolzenberg (5), and also by treating the hydrochloride with silver oxide. In each case the product was twice recrystallized from absolute alcohol. It was found to remain dry when stored over 60 per cent sulfuric acid. It dissolved completely to give a clear solution which showed no tests for the inorganic ions involved in the preparation. Tests for traces of organic acids could not easily be made, but the fact that the two preparations gave the same results in the experiments was taken as evidence of purity.

Standard sodium hydroxide solutions were prepared from the saturated solution and "conductivity water," and stored with the usual precautions.

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[1] Contribution from the Chemical Laboratory of the University of Minnesota.

The paraffin had been washed with hot, dilute sodium hydroxide, then thoroughly washed with hot distilled water and dried by heating.

PROCEDURE

A measured volume of sodium hydroxide solution of known concentration was put into the paraffined reservoir, the entire apparatus being of course first flushed out with the carbon dioxide-free air. Some of the solution was then run into the cell to a definite height above the electrodes, and the resistance measured. This was then withdrawn from the cell into a buret, and a weighed amount of betaine added to the remaining solution through the side opening in the reservoir. During the addition of the betaine, a slow stream of the carbon dioxide-free air bubbled through the solution, while a faster stream entered at the top. A sample was then again run into the cell. A number of additions of betaine were made in each run. Occasionally this procedure was carried out without the addition of betaine, as a check on the purity of the air. The solutions that were run into the cell were not returned to the reservoir, for fear of the effect of the glass and electrodes.

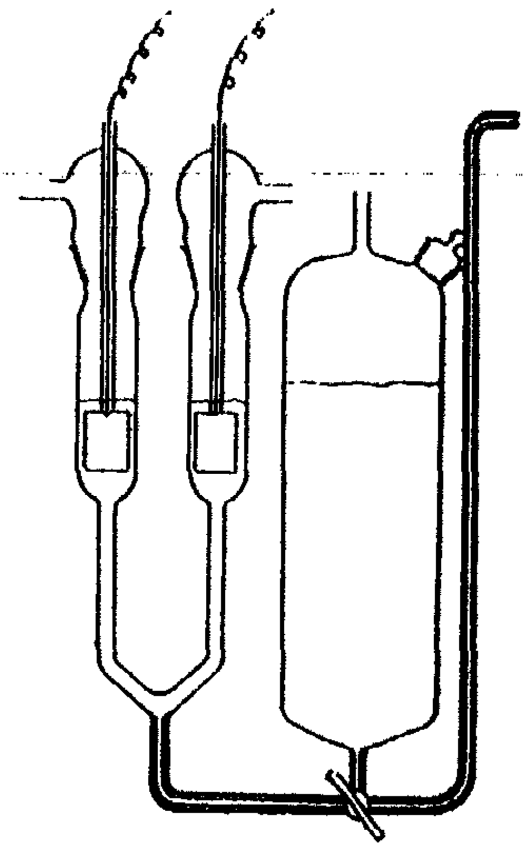

FIG. 1. The apparatus

In order to calculate the exact normality of sodium hydroxide and betaine for each measurement, the partial molal (or specific) volume of the betaine must be known. By means of a dilatometer, the partial specific volume was found to be nearly constant at 0.85 (±0.01) over the range of concentrations of betaine and sodium hydroxide used in the conductance measurements.

TABLE 1

Effect of betaine on the equivalent conductivity of sodium hydroxide solutions at 25°C.

INITIAL CONCENTRATION OF NaOH	CONCENTRATION OF BETAINE	DILUTION	TOTAL CONCENTRATION	EQUIVALENT CONDUCTIVITY OF NaOH
moles per liter	*moles per liter*	*per cent*	*moles per liter*	
0.05			0.0500	(224.00)
	0.0015	0.02	0.0515	224.00
	0.0087	0.10	0.0586	224.00
	0.0204	0.23	0.0703	223.59
	0.0325	0.37	0.0822	223.06
	0.0587	0.67	0.1084	222.38
0.1			0.1000	(218.20)
	0.0050	0.06	0.1050	218.01
	0.0085	0.10	0.1084	217.92
	0.0127	0.15	0.1126	217.70
	0.0269	0.31	0.1266	217.33
	0.0483	0.55	0.1477	216.65
0.1[*]			0.1000	(218.20)
	0.0021	0.02	0.1021	218.17
	0.0064	0.07	0.1063	218.11
	0.0146	0.17	0.1144	217.87
	0.0354	0.41	0.1350	217.32
0.2			0.2000	(210.00)
	0.0012	0.01	0.2012	210.07
	0.0121	0.14	0.2118	209.75
	0.0265	0.30	0.2259	209.29
	0.0402	0.46	0.2393	208.83
	0.0575	0.66	0.2562	208.32
0.5			0.5000	(195.00)
	0.0023	0.03	0.5022	194.59
	0.0060	0.07	0.5057	195 04
	0.0148	0.17	0.5140	194.60
	0.0291	0.34	0.5274	194 60
	0.0445	0.51	0.5420	194.28
	0.0703	0.81	0.5663	193.73
1.0			(1.0000)	(176.00)
	0.0021	0.02	1.0019	175.96
	0.0060	0.07	1.0053	175.88
	0.0130	0.15	1.0115	175.72
	0.0238	0.27	1.0211	175.50
	0.0409	0.47	1.0362	175.08
	0.0593	0.68	1.0561	174.86

[*] This run was made with betaine prepared by the use of silver oxide.

RESULTS

The results are tabulated in table 1 and plotted in figure 2. Concentrations are in moles per liter of solution. The last column gives the equivalent conductivity of the sodium hydroxide as calculated from its concentration (corrected for dilution) and the resistance of the solution. The results have been multiplied by a factor which gives the value taken from the *International Critical Tables* (by extrapolation in the case of the two most concentrated solutions, with the aid of the more complete data at 18°C.), for the initial concentration of sodium hydroxide in each run. The first column gives the concentration of the betaine, the second the per cent increase in volume (dilution of the sodium hydroxide) due to the betaine, and the third the total concentration of the two solutes. Runs were also made with 0.005 N and 0.02 N sodium hydroxide, but no appreciable increase in the resistance of the solutions was observed on addition of betaine, probably due in part to "hydrolysis" of the betaine.

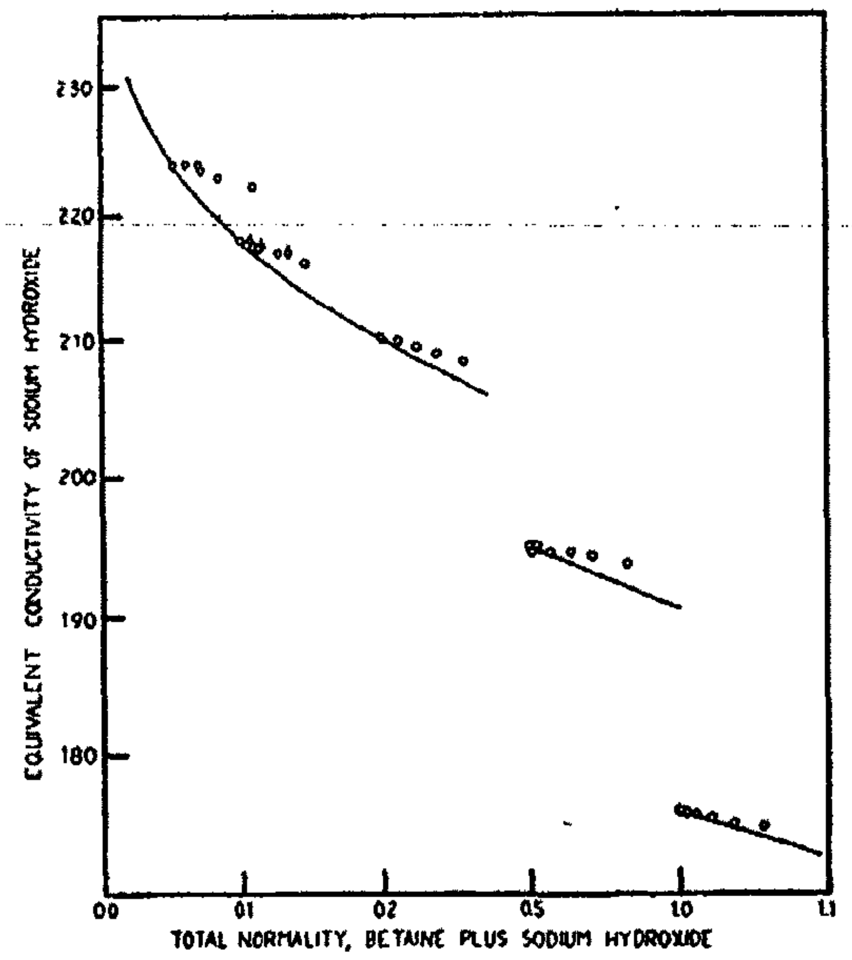

FIG. 2. Effect of betaine on the equivalent conductivities of sodium hydroxide solutions.

In figure 2 a curve has been drawn through the values taken from the *International Critical Tables*. Apparently the effect of the addition of betaine is only about half that produced when the ionic strength is increased by the addition of an equimolal quantity of sodium hydroxide. There are, of course, a number of factors which cause electrolytes of similar valence types to differ in regard to the effect of concentration on equivalent conductivity in the range studied. The fact, however, that the "zwitterion" has no conductivity of its own may, it seems, be a basis for an explanation of the magnitude of the observed effect. It is hoped that further study with, for instance, solutions containing neutral salts in addition to a strong base, will prove enlightening.

SUMMARY

The effect of small amounts of betaine on the equivalent conductivities of sodium hydroxide solutions of several concentrations, up to 1 *N*, was studied.

The observed effect, at concentrations from 0.05 *N* to 1 *N*, was only about half that produced when the ionic strength is increased by the addition of an equimolal quantity of sodium hydroxide.

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THE DIELECTRIC PROPERTIES OF WATER-DIELECTRIC INTERPHASES

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When a dielectric dispersed in water is placed in an electrical field a part of the current passes through the system at the interphases and these become polarized, as shown under certain conditions by the occurrence of electrochemical reactions (1, 3). For this reason the dielectric properties of such systems are generally different from what would be expected from the contributions of the single phases, on the basis, for example, of the Clausius-Massotti-Maxwell theorem, for the particular case of a suspension of spherical particles. This influence of the interphases is especially pronounced when measurement is made with direct current or with alternating current of low frequency, in which case the dielectric properties may be radically different from those of either of the components, as measured in the bulk.

Recent measurements by Fricke and Curtis (11, 12) of the dielectric constant and electric conductance of suspensions show this influence of the interphases clearly; there is a rapid increase of the dielectric constant and a decrease of the conductance as the frequency decreases, the change in both being approximately as powers of the frequency. The high dielectric constant often found for colloidal solutions is undoubtedly also of this origin (6, 11, 14, 15, 16, 20, 21). This property was first observed by Errera on colloidal vanadium pentoxide (6), and explained by him as due to electric moments of the colloidal particles.

In spite of the importance of these interphasial properties for the dielectric characteristics of a number of important systems, such as living cells (5, 9), soil (7, 23, 24), and many of the insulating (hygroscopic) materials used in the electrical industry (paper, fabrics, rubber) (19, 25), experimental data suitable for reaching an understanding of their nature are largely lacking. The present study is based upon alternating current measurements of the dielectric constant and electric conductance of suspensions, particularly those with particles of spherical form.

The measurements were made with a Wheatstone bridge by a substitution method which is based upon the comparison of the suspension with a potassium chloride solution. The solutions were measured in cells constructed as shown in figure 1. The cells are of Pyrex glass, cylindrical, and with one platinum electrode sealed into one end, while the other electrode is movable and mounted on a micrometer screw reading to an accuracy of 0.002 mm. The purpose of the design is to make it possible to correct for electrode polarization by measuring at different electrode distances.

In making the measurements two similar cells are used, one containing the suspension and the other a potassium chloride solution of approximately the same specific resistance. The cell with the suspension (the measuring cell) is placed in the bridge, and equilibrium established by varying a resistance box and a condenser in one of the other arms of the bridge. The measuring cell is now replaced by the comparison cell and equilibrium reëstablished for resistance, by varying the electrode distance, and for capacitance by varying a condenser (the measuring condenser) in parallel with the cell. The resistance of the comparison cell is thereafter measured by substitution against a resistance box, this measurement being made at low frequency.

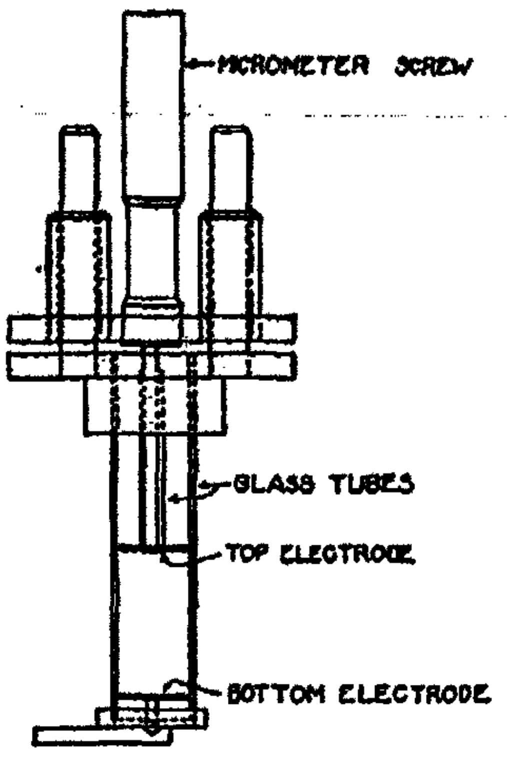

FIG. 1. Electrolytic cell

The following terms are used: The complex admittance $1/Z$ is given by

$$1/Z = 1/R + j\omega C$$

where R (ohms) and C (f) are termed resistance and capacitance of the suspension. The specific values of R and C are termed the resistivity

R (ohms-cm.) and capacity C (f-cm.$^{-1}$), respectively, and the conductivity σ and the dielectric constant ϵ are determined by

$$\sigma = 1/R \tag{1}$$

$$\epsilon = 36\pi C \times 10^{11} \tag{2}$$

Neglecting for the present the influence of electrode polarization, the capacitance of the electrolytic cell is the sum of two parts, of which one, C_1, is the capacitance of the solution in the cell, and the other, C_2, the capacitance derived from the space outside the solution. The value of C_1 is

$$C_1 = \epsilon \cdot 10/(36\pi \cdot K) \cdot \mu\mu\text{f}$$

where K is the cell constant determined as the ratio of the resistance, measured with a standard potassium chloride solution in the cell, to the specific resistance of this solution. For the experimental conditions used here the value of C_2 can with sufficient accuracy be taken as independent of the solution, and therefore C_2 cancels out in the comparison between the two cells when the comparison is made with equal electrode distances.

The dielectric constant, ϵ, of the unknown solution consequently is determined by

$$\epsilon \cdot 10/(36\pi \cdot K) = (\epsilon_0 \cdot 10/36\pi \cdot K) + C' + C''$$

where K is the cell constant for the measuring cell, C' is the difference in readings on the measuring condenser (in $\mu\mu$f), and ϵ_0 is the dielectric constant of the potassium chloride solution, which in the present measurements can be taken as equal to that of water. The value of C'' is the change in the capacitance of the comparison cell as the electrode distance is changed from that used in the measurement to that used in the measuring cell. The values of C'' are obtained by a calibration in which the measuring and comparison cells are compared with potassium chloride solutions in both. The concentration of the solution in the measuring cell is kept constant, while the concentration of the solution in the comparison cell is changed to give electrode distances over the desired range.

One difficulty encountered in this work is that the dielectric constant and particularly the conductance are not perfectly reproducible for suspensions because of settling, and for colloids apparently because of changes in their internal structure. For this reason, relative values of ϵ and σ, referred to those obtained at some standard frequency, can be obtained with much greater accuracy than can their absolute values. Under the best conditions such relative values can be measured with an accuracy of one part in 100,000 for σ and of 0.1 for ϵ, and so perfectly satisfactory frequency curves for σ and ϵ can be obtained, although the absolute values of σ and ϵ are not reproducible with this accuracy.

The inductance of the measuring condenser was shown to be negligible by comparing it against a specially built fixed condenser, consisting of two plates clamped close together and attached directly across the binding posts to the electrolytic cell; this condenser has a very much smaller inductance than the measuring condenser. The comparison of the two condensers showed no frequency dependence over the range of frequencies used. The capacity of the fixed condenser was 50 $\mu\mu$f, which is as large a capacity as is ever used at the highest frequency.

The influence of electrode polarization is eliminated by making measurements at two different electrode distances. After completing the measurements at the greater distance, the electrodes are brought together to a suitable closer distance and measurements taken at such frequencies for which the electrode polarization is appreciable. In order to take into consideration any slight change in the electrode polarization during these two sets of measurements, the electrodes are thereafter brought back to the original distance and the measurements at the low frequencies repeated. When the electrodes are moved, a slight change may occur in the absolute values of ϵ and σ. This error is eliminated by measuring the rates of change of ϵ and σ with frequency, rather than their absolute values.

The electrode polarization acts as a capacity (C_p) and a resistance (R_p) in series with each other and with the cell. In the present measurements $1/C_p\omega$ is always small compared to the resistance of the cell, which is the condition under which the formulae now to be given can be used. Designate by ΔC_1 and ΔR_1 the non-corrected values for the difference in capacitance and resistance of the suspension, at the two successive frequencies ω and 2ω, and for the greater electrode distance. Similarly, for the smaller electrode distance, ΔC_2 and ΔR_2. Furthermore, designate by ΔC^p and ΔR^p those parts of ΔC and ΔR which are due to the electrode polarization, and by ΔC^s and ΔR^s the true values of these two quantities. The following equalities hold:

$$\Delta C_1 = \Delta C_1^p + \Delta C_1^s$$

$$\Delta C_2 = \Delta C_1^p \, (R_1^s/R_2^s)^2 + \Delta C_1^s \, (C_2^s/C_1^s)$$

giving

$$\Delta C_1^s = \frac{\Delta C_1 - \Delta C_2 \, (R_2^s/R_1^s)^2}{1 - (C_2^s/C_1^s) \, (R_2^s/R_1^s)^2} \tag{3}$$

$$\Delta R_1 = \Delta R_1^p + \Delta R_1^s$$

$$\Delta R_1 = \Delta R_1^p + \Delta R_1^s \, (R_2^s/R_1^s)$$

$$\Delta R_1^s = \frac{\Delta R_1 - \Delta R_2}{1 - (R_2^s/R_1^s)} \tag{4}$$

The ratios C_2°/C_1° and R_2°/R_1° are obtained as the values of C_2/C_1 and R_2/R_1 at such a high frequency that the electrode polarization is negligible. Owing to settling, in coarser suspensions these ratios may deviate somewhat from the ratio of the cell constants.

In order to decrease the polarization, the electrodes are electrolytically covered with platinum black, from a 3 per cent platinum chloride solution containing 0.025 per cent of lead acetate. With palladium black the polarization may be still further reduced, but the greater constancy of the platinum black makes it more satisfactory.

Most of the work has been carried out with two types of cell, of which one has a cross-sectional area of 1.0 cm.² and a length of 20 cm., and the other an area of 2.9 cm.² and a length of 5 cm. In a few measurements we have used a third pair of cells, the cross-sectional area of which is 10 cm.² and the length 20 cm. Before using any pair of cells they were compared, at all frequencies, with potassium chloride solutions in both.

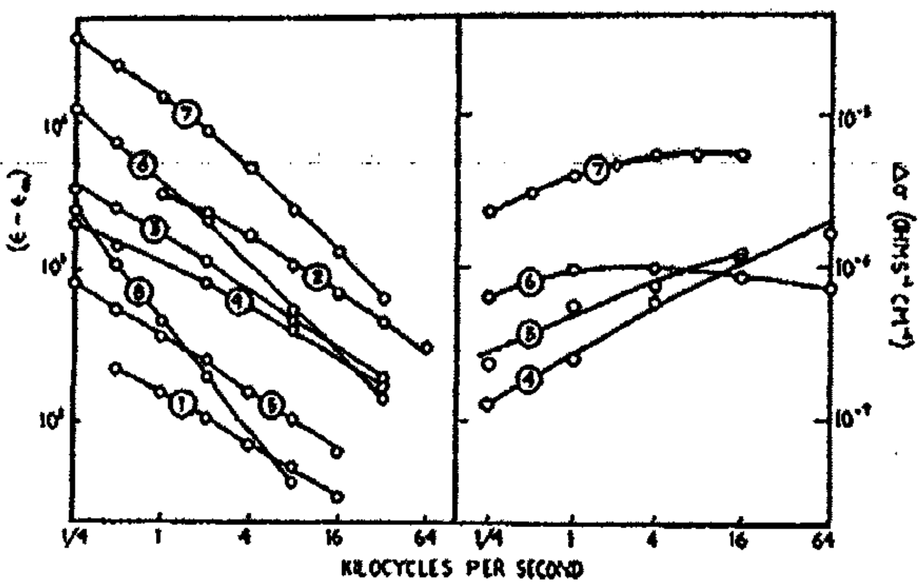

FIG. 2. Logarithmic graphs of $(\epsilon - \epsilon_\infty)$ and $\Delta\sigma$ for various suspensions. Curve 1, 33 per cent cream (natural); curve 2, 12 per cent homogenized cream (commercial brand); curve 3, 3 × latex (63 per cent); curve 4, 25 per cent mineral oil (diameter 0.5μ) in 2 per cent oleic acid + 1 per cent triethanolamine; curve 5, 20 per cent rouge (diameter 2μ) in 1.5 per cent isoelectric gelatin; curve 6, 45 per cent kaolin (diameter 0.5μ) in 0.0005 M KCl; curve 7, 45 per cent kaolin (diameter 0.5μ) in 0.5 per cent sodium oleate; curve 8, 5 per cent cellulose in water.

The measurements were usually made with the cells in air in a room kept at the constant temperature of 21.4°C. In some cases, when a steadier temperature was desired, the cells were kept in an oil bath.

Data obtained for a variety of suspensions are shown in figure 2. The figure contains logarithmic graphs against the frequency of the quantities $(\epsilon - \epsilon_\infty)$ and $\Delta\sigma$. The value ϵ_∞ is the nearly constant value of ϵ obtained at high frequencies and can be taken to represent the contribution of the suspending and suspended phases to the dielectric constant, the value of $(\epsilon - \epsilon_\infty)$ therefore representing the contribution of the interphases. The value $\Delta\sigma(\omega) = \sigma(2\omega) - \sigma(\omega)$ represents the change in σ resulting from a twofold increase in the frequency. The change of σ with the frequency is small and has not been measured for all systems. The values of $(\epsilon - \epsilon_\infty)$ and $\Delta\sigma$ usually vary approximately as powers of the frequency, although this is not so apparent in the particular measurements shown in figure 2. The exponent for $(\epsilon - \epsilon_\infty)$ is negative and is usually near -1. The difference between the two exponents is approximately equal to 1. The theoretical reason for this relation will be given below.

For comparison, we have shown in figure 3 a series of dielectric measurements on soil, which were made by Smith-Rose (23). The moisture content of this soil was 25 per cent. In passing we may remark that the rapid increase in the conductance of soils observed at frequencies above 1000 kc. per second can also be accounted for as due to the influence of the interphases (12).

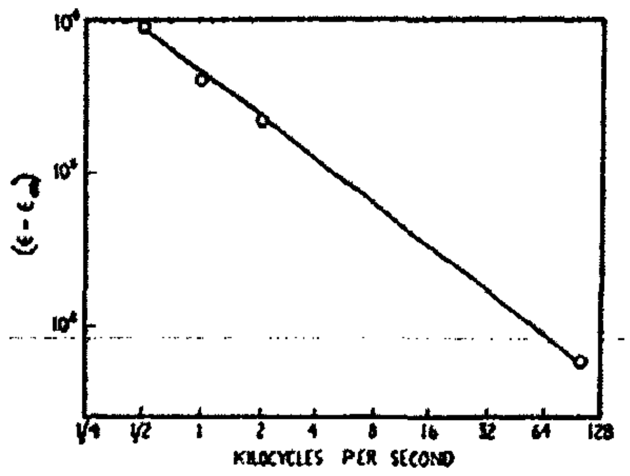

FIG. 3. Values of $(\epsilon - \epsilon_\infty)$ for soil, moisture content 25 per cent. [From Smith-Rose (23).]

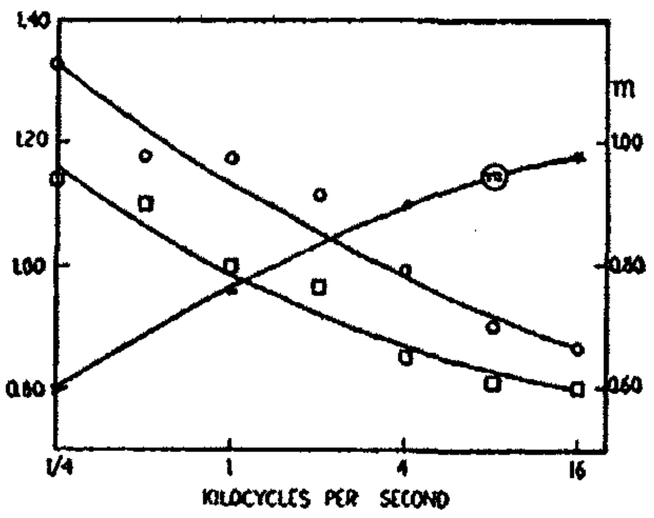

FIG. 4. Test of formula (5) for 45 per cent kaolin in 0.5 per cent sodium oleate (values of σ, ϵ, and m from figure 2). The left ordinates represent the values of $[(\sigma_2 - \sigma_1)/(\epsilon_1 - \epsilon_2)\omega] \times 10^{12}$(□) and $(10/36\pi)[(2^{1-m} - 1)\tan(m\pi/2)/(1 - 2^{-m})]$(○).

The values of $\Delta(\epsilon - \epsilon_\infty)/\Delta\omega$ and of $\Delta\sigma/\Delta\omega$ obtained for any particular system are theoretically interrelated (10, 22). The relation is generally of a complicated form but becomes simple when $(\epsilon - \epsilon_\infty)$ varies as a power of the frequency (10). Let us first consider this special case. Represent the complex impedance of the system by

$$Z = R' + 1/jC'\omega$$

and assume

$$C' = C_0'\omega^{-m}$$

The following equality holds (equation 6, reference 10)

$$C'\omega R' = \tan(m\pi/2)$$

Introducing C and R (as defined above) instead of C' and R', we obtain

$$C = C'/[1 + (C'\omega R')^2] = C_0'\omega^{-m}\cos^2(m\pi/2)$$

and

$$1/R = 1/R' \cdot [(C'\omega R')^2/1 + (C'\omega R')^2] = C_0'\omega^{(1-m)}\sin(m\pi/2)\cos(m\pi/2)$$

Designate by R_1, C_1 and R_2, C_2 the values of R and C at the consecutive frequencies ω and 2ω respectively, and we obtain

$$C_1 - C_2 = C_0'\omega^{-m}(1 - 2^{-m})\cos^2(m\pi/2)$$
$$1/R_1 - 1/R_2 = (C_0'\omega^{(1-m)})(1 - 2^{(1-m)})\sin(m\pi/2)\cos(m\pi/2)$$
$$(1/R_1 - 1/R_2)/(C_1 - C_2)\omega = (1 - 2^{(1-m)})\tan(m\pi/2)/(1 - 2^{-m})$$

Introduce $(\epsilon - \epsilon_\infty)$ and σ instead of C and R:

$$1/R = \sigma$$
$$\mathrm{C} = [(\epsilon - \epsilon_\infty)(10/36\pi)] \times 10^{-12}$$

and we obtain (5)

$$[(\sigma_2 - \sigma_1)/(\epsilon_1 - \epsilon_2)\omega] \times 10^{12} = (10/36\pi)[(2^{(1-m)} - 1)\tan(m\pi/2)]/(1 - 2^{-m})$$

This formula was derived with the assumption that $(\epsilon - \epsilon_\infty)$ varies as a power of the frequency, $(\epsilon - \epsilon_\infty) \sim \omega^{-m}$. Since the right-hand side of equation 5 is independent of the frequency, it follows that $\Delta\sigma = \sigma_2 - \sigma_1$ also varies as a power of the frequency with an exponent equal to $(1 - m)$. The difference between the exponents equals 1, as remarked upon above.

The variation of the observed values of $(\epsilon - \epsilon_\infty)$ is only approximately as a power of the frequency, but we can test equation 5 by using for each particular value of ω, as the corresponding value of m, that given by the slope of the logarithmic graph for $(\epsilon - \epsilon_\infty)$ between the frequencies ω and 2ω. The agreement hereby obtained is usually quite good, the difference between the experimental values of $[(\sigma_2 - \sigma_1)/(\epsilon_1 - \epsilon_2)\omega] \times 10^{12}$ and those given by the right-hand side of equation 5 being seldom in excess of 10 per cent. A typical case is shown in figure 4.

The following experiments were carried out to determine the dependence of $(\epsilon - \epsilon_\infty)$ on the size of the suspended particles of a suspension. Powdered Pyrex glass was separated into three different size groups by sedimentation, the average particle diameters being 80, 20, and 2.5μ, respectively, and suspensions were prepared from each in 0.005 *M* potassium chloride. The measurements were made on the settled suspensions, the values of $(\epsilon - \epsilon_\infty)$ as functions of the frequency being given in figure 5. The graphs are parallel and the distances between them are $\Delta_1 = 0.50$ and $\Delta_2 = 0.95$, respectively. These values are within the experimental accuracy equal to the values log (80/20) = 0.60 and log (20/2.5) = 0.90, respectively, showing that $(\epsilon - \epsilon_\infty)$ varies inversely as the particle diameter.

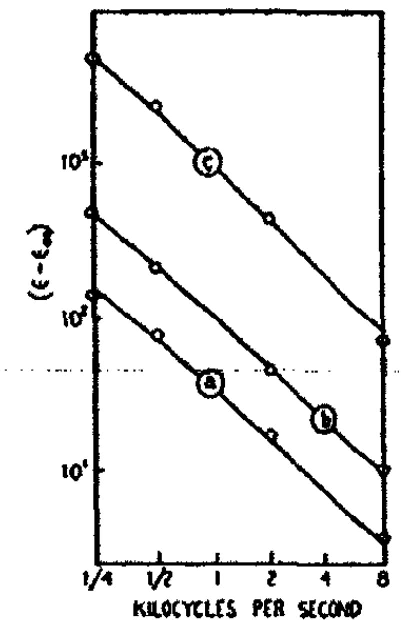

FIG. 5. Values of $(\epsilon - \epsilon_\infty)$ for suspensions of Pyrex of different particles diameter. (a) 80μ; (b) 20μ; (c) 2.5μ

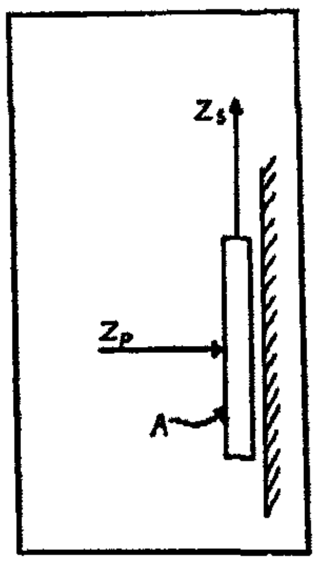

FIG. 6

Consider a unit element *A* of interphase (figure 6) and represent the complex admittance of this element in the direction parallel to the interphase as $1/Z_s = \sigma_s + jC_s\omega$, where σ_s is referred to as the surface conductivity and C_s as the surface capacity. The value of σ_s is to represent the total conductance at the interphase including the conductance due to the ionic atmosphere present in the aqueous phase close to the interphase. In general the complete representation of the dielectric properties of *A* requires the addition of $1/Z_p$ as the complex admittance in the direction perpendicular to the interphase, this admittance representing the occurrence of electrolytic polarization resulting from the flow of current between the aqueous phase and the interphase. The simplest explanation of the finding that $(\epsilon - \epsilon_\infty)$ varies inversely as the particle diameter is that $1/Z_p$ is so high that its influence is negligible, under the conditions of these experiments. Assuming this to be the case, we shall now proceed to calculate σ_s and C_s in terms of σ and $(\epsilon - \epsilon_\infty)$, limiting ourselves for the present to the case of a suspension of spherical particles.

The suspended particle itself is assumed to have a negligible conductance and dielectric constant, and the presence of surface admittance is introduced by surrounding each particle with a concentric region of thickness Δa, the specific complex admittance of which is given by

$$(1/\Delta a)\ (\sigma_s + jC_s\omega)$$

The admittance of the suspension and suspending fluid are $1/Z = \sigma + jC\omega$ and $1/Z_1 = \sigma_1 + jC_1\omega$, respectively. For a suspension of this type, but for which the different phases are characterized by conductances alone, Maxwell (18) has derived the formula

$$\frac{(\sigma/\sigma_1) - 1}{(\sigma/\sigma_1) + 2} = \frac{(\bar{\sigma}_2/\sigma_1) - 1}{(\bar{\sigma}_2/\sigma_1) + 2} \tag{6}$$

where σ and σ_1 are the conductivities of the suspension and the suspending fluid, respectively, and $\bar{\sigma}_2$ is given by

$$\bar{\sigma}_2 = \frac{(2\sigma_3 + \sigma_2)(a + \Delta a)^3 - 2(\sigma_3 - \sigma_2)\, a^3}{(2\sigma_3 + \sigma_2)(a + \Delta a)^3 + (\sigma_3 - \sigma_2)\, a^3}$$

The values σ_2 and σ_3 are the conductivities of the sphere and the surface region, respectively. Taking $\sigma_2 = 0$ and assuming for the present that $\Delta a/a$ is small, we obtain

$$\bar{\sigma}_2 = 2\sigma_3\, \Delta a/a \tag{7}$$

We introduce now the complex admittances, as defined above, instead of conductances in equations 6 and 7 and obtain:

$$\frac{(\sigma + jC\omega)/(\sigma_1 + jC_1\omega) - 1}{(\sigma + jC\omega)/(\sigma_1 + jC_1\omega) + 2} = \frac{(2/a)(\sigma_s + jC_s\omega)/(\sigma_1 + jC_1\omega) - 1}{(2/a)(\sigma_s + jC_s\omega)/(\sigma_1 + jC_1\omega) + 2} \tag{8}$$

We derive from equation 8:

$$C - C_\infty = \frac{(18C_s/a)\rho}{[(\rho + 2) + (2\sigma_s/a\sigma_1)(1 - \rho)]^2 + [(1 - \rho)(2C_s\omega/a\sigma_1)]^2} \tag{9}$$

$$\sigma = \sigma_1 \cdot \frac{[2(1-\rho) + (2\sigma_s/a\sigma_1)(1+2\rho)][(\rho+2) + (2\sigma_s/a\sigma_1)(1-\rho)] + (1-\rho)(1+2\rho)(2C_s\omega/a\sigma_1)^2}{[(\rho+2) + (2\sigma_s/a\sigma_1)(1-\rho)]^2 + [(1-\rho)(2C_s\omega/a\sigma_1)]^2} \quad (10)$$

where C_∞ is the capacity of the suspension for $C_s = 0$.

Usually $C_s\omega$ is so small (compared with $a\sigma_1$) that the terms containing $(2C_s\omega/a\sigma_1)^2$ can be neglected, in which case we obtain

$$C - C_\infty = \frac{(18C_s/a)\cdot\rho}{[(\rho+2) + (2\sigma_s/a\sigma_1)(1-\rho)]^2} \quad (11)$$

$$\sigma = \sigma_1 \cdot \frac{2(1-\rho) + (2\sigma_s/a\sigma_1)(1+2\rho)}{(\rho+2) + (2\sigma_s/a\sigma_1)(1-\rho)} \quad (12)$$

Introducing dielectric constants instead of capacities we obtain from equations 11 and 12:

$$\epsilon - \epsilon_\infty = (36\pi/10)\,\frac{(18/a)\rho C_s}{[(\rho+2) + (2\sigma_s/a\sigma_1)(1-\rho)]^2}\,{}^{*} \quad (13)$$

$$C_s = (10/36\pi)\,\frac{(a/18)[(\rho+2) + (2\sigma_s/a\sigma_1)(1-\rho)]^2}{\rho}\cdot(\epsilon - \epsilon_\infty) \quad (14)$$

$$\sigma_s = (a/2)\,\frac{(\sigma/\sigma_1)(\rho+2) - 2(1-\rho)}{(1+2\rho) - (\sigma/\sigma_1)(1-\rho)}\cdot\sigma_1 \quad (15)$$

In figure 7 the values of $(\epsilon - \epsilon_\infty)$ (from equation 13) are plotted against ρ, for different values of $\alpha = 2\sigma_s/a\sigma_1$, taking as unity the value of $(\epsilon - \epsilon_\infty)$ for $\rho = 1$. $[(\epsilon - \epsilon_\infty)_{\rho=1} = 72\pi\cdot C_s/10a)]$.

We may now return to the experiments in which the relation of $(\epsilon - \epsilon_\infty)$ to particle diameter was determined. The conductivity of the suspending fluid (0.005 M potassium chloride) was $\sigma_1 = 0.00067$ ohms^{-1}. The value of σ_s for Pyrex glass in 0.005 M potassium chloride is approximately $\sigma_s = 1.5 \times 10^{-9}$ (13). The diameter of the smallest particles used was $2a = 2.5 \times 10^{-4}$ cm., giving $\alpha = (2/1.25 \times 10^{-4})(1.5 \times 10^{-9}/0.7 \times 10^{-3}) \sim 0.03$, while for the larger particles α is still smaller. For such small values of α, equation 13 is approximately

$$\epsilon - \epsilon_\infty = [(36\pi)/10]\,[(18\rho C_s/a)/(\rho+2)^2] \quad (16)$$

showing that $(\epsilon - \epsilon_\infty)$ varies inversely as the particle diameter $2a$, in accordance with the experimental result.

For highly dispersed systems, according to equation 13, $(\epsilon - \epsilon_\infty)$ decreases with decreasing particle size, if we can assume C_s and σ_s to be independent of the size. When ρ is small, $(\epsilon - \epsilon_\infty)$ reaches its maximal

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* In equations 13 and 14 C_s is given in $\mu\mu$f.

value for $\alpha = (2/a)(\sigma_s/\sigma_1) = 2$, or $2a = 2\sigma_s/\sigma_1$. For example, for $\sigma_1 = 10^{-4}$ ohms^{-1} and $\sigma_s = 0.5 \times 10^{-9}$ ohms^{-1}, the maximal value of $(\epsilon_1 - \epsilon_\infty)$ is reached for $2a = 0.1\mu$.

The dependence of $(\epsilon - \epsilon_\infty)$ on ρ has been determined experimentally for glass and for kaolin in various suspending fluids. At the higher volume concentrations, the rise of $(\epsilon - \epsilon_\infty)$ with ρ is generally found to be slower than that given by equation 13. To some extent this is due to the non-spherical particle form of the suspensions used, but the chief reason may be the occurrence of aggregation. In heavy suspensions $(\epsilon - \epsilon_\infty)$ may even decrease with increasing ρ. Representative data are shown in figure 8, in which the theoretical course of the curves, calculated from equation 13, is shown by the broken lines.

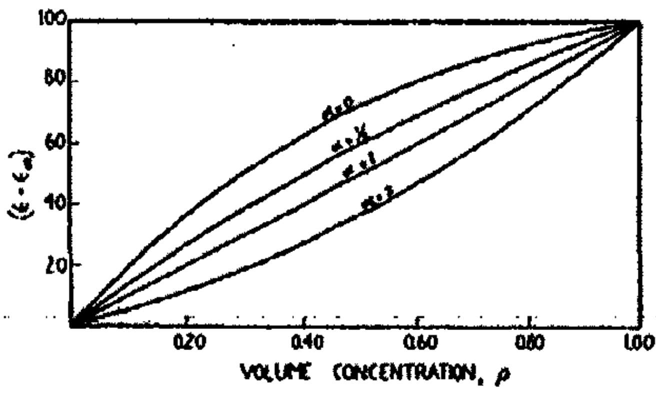

FIG. 7. Representation of $(\epsilon - \epsilon_\infty)$ as a function of ρ, for different values of $\alpha = 2\sigma_s/a\sigma_1$

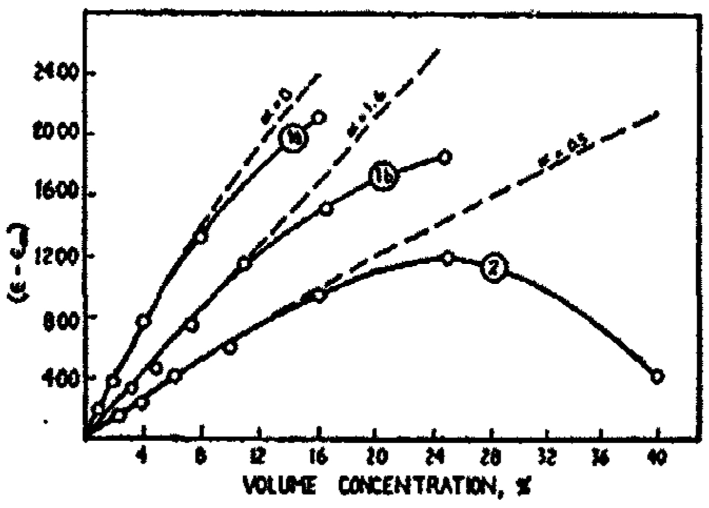

FIG. 8. Measurements of $(\epsilon - \epsilon_\infty)$ for different volume concentrations of suspensions of (*1*) kaolin (diameter 0.5μ) in (a) 1 per cent sodium oleate, (b) 0.00005 *M* sodium carbonate; and (*2*) Pyrex (diameter 1.0μ) in 0.00005 *M* sodium carbonate. Frequency: 2 kc. per second. The broken curves are calculated from equation (13).

The surface conductance is, to an important extent, derived from the ionic atmosphere present in the suspending fluid close to the interphase; this part (σ_s') of the surface conductance can be calculated when the electrokinetic potential is known (4, 13), and thus it is possible to obtain that part (σ_s'') of the surface conductance which is derived from the interphase itself. We shall refer to σ_s'' as the interphasial conductance and to $\sigma_s'' + jC_s\omega$ as the interphasial admittance.

The interphasial admittance for Pyrex in solutions of potassium chloride was determined by measurements on suspensions of Pyrex spherules of diameter 1.7μ; the volume concentration was $\rho = 0.21$ and the potassium chloride concentration was varied between 0.0001 and 0.004 *M*. The results obtained at 0.50 kc. per second are given in table 1, the values of σ_s and C_s being calculated from equations 14 and 15. Further details as to the experimental procedure will be found in the reference given (13). The values of C_s as well as of σ_s'' appear to be independent of the salt concentration, their averages being respectively $C_s = 0.005$ $\mu\mu f$ and $\sigma_s'' = 0.2 \times 10^{-9}$ ohms^{-1} at 0.50 kc. per second. The values of C_s and σ_s'' as functions of the frequency are given in figure 9. The interphasial conductivity σ_s'' can, at the most, represent only in part a true conductance current at the interphase. From the fact that C_s decreases with increasing frequency it follows (10) that the polarization of the interphase is associated with an energy loss and this loss would be measured as a conductance. Because of the rapid variation of C_s with the frequency (approximately as ω^{-1}), this conductance would be expected to be many times greater than the admittance $C_s\omega$ and may completely account for the observed interphasial conductance.

TABLE 1

Dielectric data for suspensions of Pyrex spherules in solutions of potassium chloride

$\rho = 0.21$; $2a = 1.7\mu$; frequency 0.50 kc. per second

SUSPENDING FLUID						
Millimoles per liter KCl	Conductivity σ_1	$\epsilon - \epsilon_\infty$	σ_s	σ_s'	σ_s''	C_s
	ohms^{-1} cm.$^{-1}$		*ohms^{-1}*	*ohms^{-1}*	*ohms^{-1}*	*$\mu\mu f$*
0.123	17.1×10^{-6}	443	0.38×10^{-9}	0.18×10^{-9}	0.20×10^{-9}	0.60×10^{-2}
0.31	43.0×10^{-6}	445	0.53×10^{-9}	0.29×10^{-9}	0.24×10^{-9}	0.52×10^{-2}
0.53	73.0×10^{-6}	456	0.59×10^{-9}	0.40×10^{-9}	0.19×10^{-9}	0.50×10^{-2}
1.87	254×10^{-6}	530	0.82×10^{-9}	0.69×10^{-9}	0.13×10^{-9}	0.53×10^{-2}
3.67	494×10^{-6}	561	1.33×10^{-9}	0.91×10^{-9}	0.42×10^{-9}	0.57×10^{-2}

In several other cases we have determined the effect of adding potassium chloride to the suspending fluid of suspensions, increasing the electric conductance up to one-hundredfold, and have found C_s to remain wholly or nearly unchanged. It may be assumed that changes would occur under conditions where the electrolyte is adsorbed at the interphase and this deserves further study. What is immediately important is the fact that these experiments give added evidence that C_s originates at the dielectric side of the interphase. That C_s is greatly sensitive to the presence of surface-active molecules, such as soap, is shown by the data in figure 2. There is some indication (14, 15) that C_s is dependent upon the electric charge on the interphase, C_s being generally smallest when the charge is zero. The following experiments may be cited in support of this. Powdered Pyrex glass was suspended ($\rho = 0.23$) in three different solutions of 1 per cent gelatin at pH = 3.0, 4.9, and 7.0, respectively, the solution at pH = 4.9 being prepared from isoelectric gelatin, and the other two solutions by adding hydrochloric acid and sodium hydroxide, respectively, to the isoelectric solution. The results are shown in figure 10. The dielectric constant is smallest for the isoelectric solution, but is still very high. The influence of the charge on the dielectric constant may, of course, be an indirect one, owing to an increased aggregation of the suspended particles in the isoelectric solution. In this connection it may be worth remarking upon a certain similarity between the dielectric properties of interphases and those of solid dielectrics. The dielectric constant

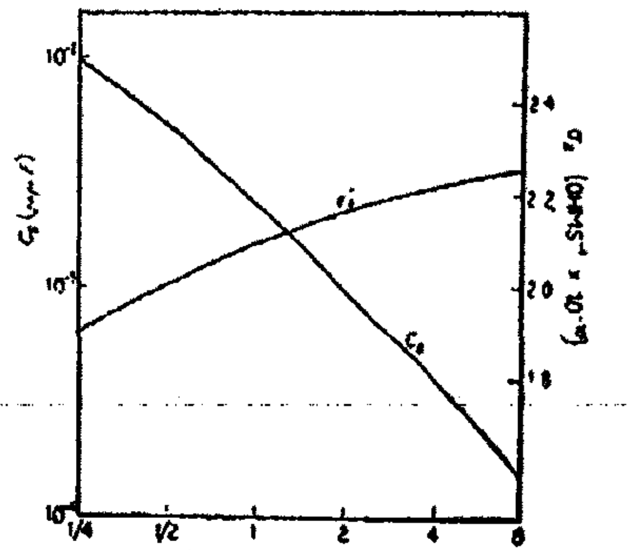

FIG. 9. The interphasial conductivity (σ_s'') and capacity (C_s) for Pyrex glass in solutions of potassium chloride.

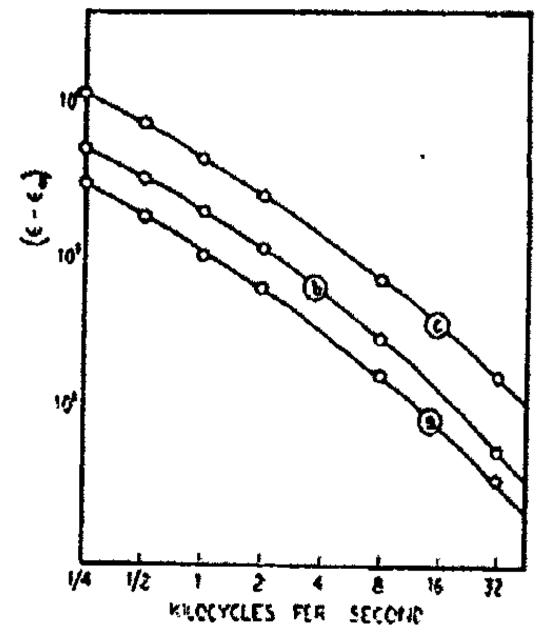

FIG. 10. Values of ($\epsilon - \epsilon_\infty$) for suspensions of kaolin in 1.5 per cent gelatin for different pH values. (a) pH = 4.9; (b) pH = 2.78; (c) pH = 7.72.

of solid dielectrics also generally increases rapidly at low frequencies and approximately as a power of the frequency, the exponent, however, being smaller than usually found for interphases.[1] This is particularly interesting, since it is generally accepted that this rise in the dielectric constant of solid dielectrics is due to the presence of loosely bound ions which can be transferred over considerable distances (as compared with molecular dimensions) under the influence of an electric stress. The establishment of a direct relation between the dielectric properties of the interphases and their degree of electrification thus becomes important in strengthening the view suggested by the above considerations as to the origin of these properties, and we expect to make a more careful study of this subject later.

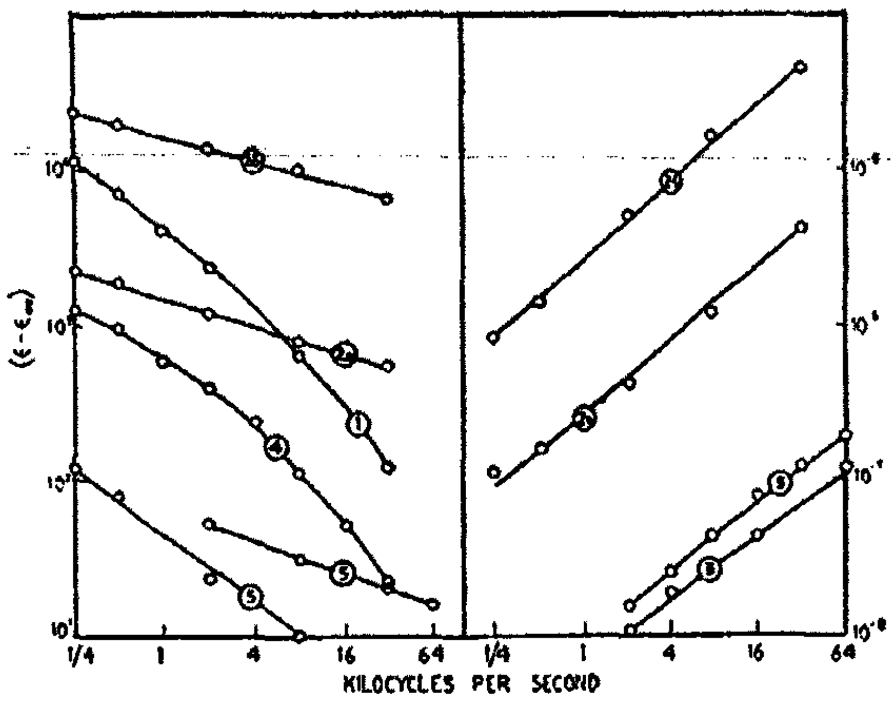

FIG. 11. Values of $(\epsilon - \epsilon_\infty)$ and $\Delta\sigma$ for various colloidal solutions. Curve 1, 2 per cent Fe_2O_3 (17); curve 2, 1 per cent V_2O_5 (2), (a) freshly prepared; (b) 3 months old; curve 3, 1 per cent Al_2O_3 (8); curve 4, 0.5 per cent soap (commercial); curve 5, 5 per cent soluble potato starch.

We could probably learn a good deal about the origin of the dielectric properties of interphases if we could determine the variation of the interphasial admittance with the size of the suspended particles, as this is reduced towards molecular dimensions. Data which we have obtained for a number of colloidal solutions are interesting from this point of view. Besides the solutions shown in figure 11, measurements have also been made on solutions of gum arabic (5 per cent) and isoelectric gelatin (1.5 per cent), both of which showed dielectric properties only slightly different from those of water.

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[1] It is generally found that the anomalous charging current of solid dielectrics varies according to $i \sim t^{-m}$ (t, time), where m is around 0.80. From this it follows theoretically that the dielectric constant, as determined by alternating current measurement, varies inversely as a power of the frequency with an exponent equal to $1 - m$.

From the data it is clear that the dielectric constant of colloidal solutions generally decreases as the degree of dispersion increases. It is not possible, however, to conclude from this that the interphasial capacitance itself decreases with decreasing particle size, because the value of $2\sigma_s/a\sigma_1$ in equation 13 would generally be high, and the dielectric constant would therefore decrease with decreasing particle size, even though the interphasial capacitance itself remained constant. Until the value of $2\sigma_s/a\sigma_1$ can be determined it is therefore not possible to proceed further in the interpretation of the data. Another complicating factor may be an appreciable electrolytic polarization of the interphases, which would cause a decrease of the dielectric constant to an increasing extent as the dispersion increases. Nevertheless it appears likely, on general grounds, that the interphasial dielectric properties are developed only at interphases composed of a great number of molecules, and that this is the chief reason for the disappearance of these properties in solutions of molecular dispersion. If this were true, dielectric studies should be of considerable value in solutions intermediate between colloidal and molecular dispersion. The high dielectric constants in starch and soap as compared with the small value in gum arabic may be remarked upon in this connection.

The results for colloidal vanadium pentoxide are of particular interest because of Errera's original work with this colloid (6). The solution was prepared according to Biltz (2), and measurements were made immediately after preparation and three months later. The dielectric constant increases with aging, as already found by Errera, but the form of the frequency curve for $(\epsilon - \epsilon_\infty)$ remains unchanged. This increase of dielectric constant with aging is probably due to a decrease in dispersion.

SUMMARY

The dielectric properties of dielectrics dispersed in water are derived from the interphases to an important extent, a fact essential to the dielectric behavior of a number of important systems, such as living cells, soil, and insulators of the hygroscopic type, such as paper and fabrics. These interphasial dielectric properties have been studied by alternating current measurements of the dielectric constant and electric conductance of suspensions, including a study of the dependence of these quantities upon the frequency of the alternating current, the volume concentration of the suspension, the size of the suspended particles, and the characteristics of the interphase and of the suspending fluid. The measurements were made over a frequency range of 0.25 to 2000 kc. per second by a substitution method based upon the comparison of the suspension with a potassium chloride solution. The most important error is electrode polarization, which was eliminated by making measurements at different electrode distances in electrolytic cells especially designed for this purpose.

A unit element of interphase should generally be characterized by two

complex admittances, for the directions parallel to, and perpendicular to, the interphase, respectively. The influence of the latter is found to be negligible for the suspensions studied, and the former is expressed as $\sigma_s'' + jC_s\omega$, where σ_s'' is termed the interphasial conductivity (σ_s'' does not include the conductivity of the ionic atmosphere in the aqueous phase) and C_s the interphasial capacity. The theory is given for calculating σ_s'' and C_s from observable quantities, for the case of a suspension of spherules.

The value of C_s increases and σ_s'' decreases as the frequency is decreased, $\Delta C_s/\Delta\omega$ and $\Delta\sigma_s''/\Delta\omega$ varying approximately as powers of the frequency. They are connected by a theoretical relation which has been derived under simplifying assumptions and found to be in satisfactory agreement with the experimental results. The values of σ_s'' and C_s show no dependence upon the ionic strength of the aqueous phase, but are very sensitive to the presence of surface-active substances; there is some indication that they depend upon the electric charge of the interphase, being generally smallest when the interphase is uncharged. For Pyrex glass in potassium chloride we find $\sigma_s'' = 0.2 \times 10^{-9}$ ohm^{-1} and $C_s = 0.005$ μμf at 0.50 kc. per second, independent of the potassium chloride concentration between 0.0001 and 0.003 *M*.

The high dielectric constants observed for colloid solutions, first discovered by Errera for vanadium pentoxide, appear generally to be due to the interphasial capacitance. Data for a number of colloidal solutions are given and the importance of these measurements in colloidal studies is pointed out, particularly with reference to the disappearance of the interphasial properties in systems of molecular dispersion.

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THE ELECTRON DIFFRACTION INVESTIGATION OF THE FLUOROCHLOROMETHANES

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The structures of the fluorine compounds of the non-metallic elements are of special interest because many of them exhibit abnormal interatomic distances. The investigation of the structures of the fluorochloromethanes has shown that the abnormalities observed in the values of the interatomic distances may be related to the chemical properties of these substances. These relations have been published as a part of the recent Symposium on Molecular Structure held at Princeton University (2). In the present paper the structural investigation is described for these compounds, including methyl fluoride, difluoromethane, fluorochloromethane, difluorochloromethane, fluorodichloromethane, difluorodichloromethane, and fluorotrichloromethane.

Methyl fluoride was prepared by heating a dry mixture of potassium methyl sulfate and potassium fluoride. The gas evolved was bubbled slowly through an alkaline solution, dried, and then fractionated to remove any traces of methyl ether. Vapor pressure measurements on various fractions indicated that the sample was homogeneous and had about the right boiling point, −78°C.

Difluoromethane, fluorodichloromethane, and difluorodichloromethane were furnished by Mr. Thomas Midgley, Jr., and Dr. A. L. Henne of the Midgley Foundation in Columbus, Ohio. Fluorochloromethane, difluorochloromethane, and fluorotrichloromethane were supplied through the courtesy of Kinetic Chemicals, Inc., Wilmington, Delaware. Each of these substances was fractionated by repeated vacuum distillations in which the first and last portions were discarded at each stage. A sample was taken for the electron diffraction experiments when the vapor pressure changed by only a few millimeters during the course of a single distillation. Since the preparation of these compounds consists in the substitution of fluorine for chlorine or bromine, the separation by fractionation is very good because of the 40° to 50° differences in the boiling points of the substances involved.

[1] Contribution No. 578.

The samples were used as liquids, each at a temperature where the vapor pressure was from 100 to 300 mm.

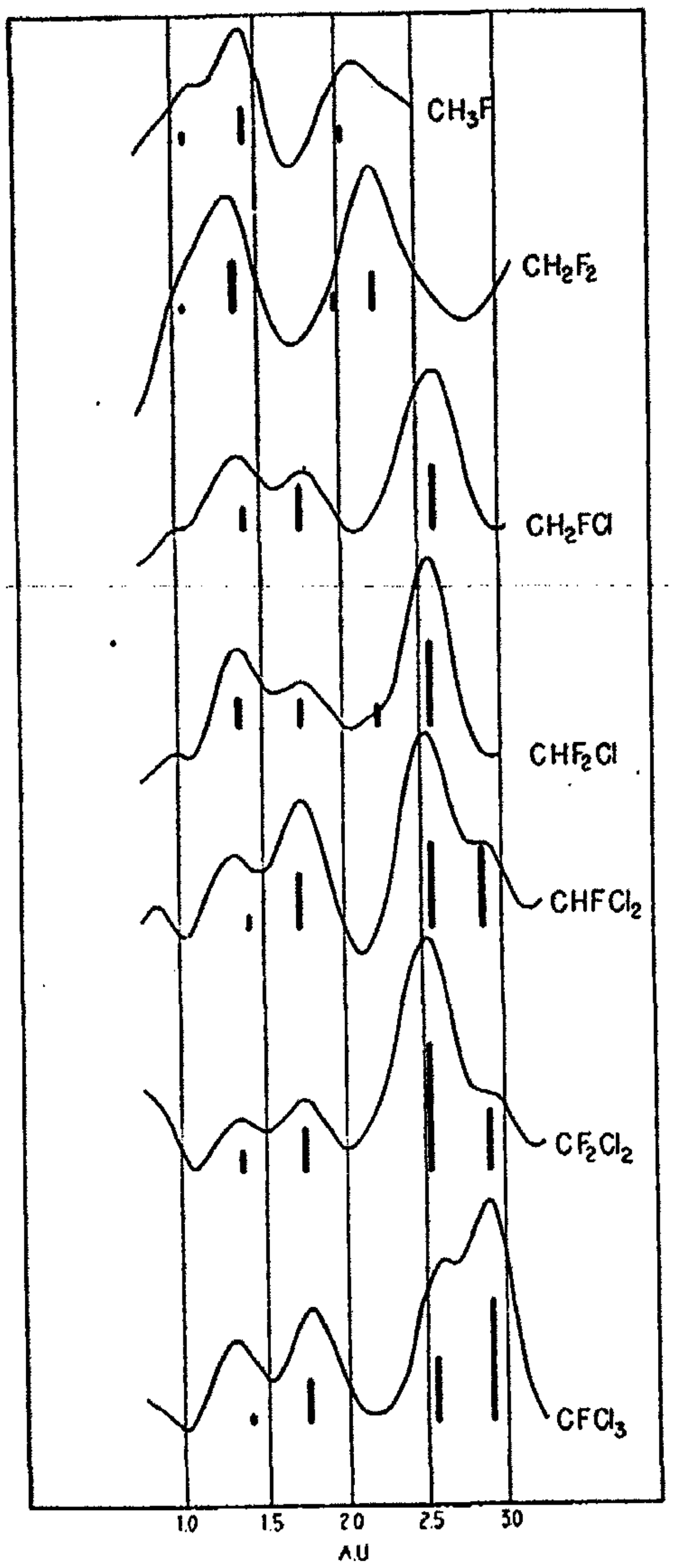

FIG. 1. Radial distribution curves for the fluorochloromethanes. The arrows show the values of the interatomic distances as determined with the aid of theoretical intensity curves.

The details of the electron diffraction method of investigating gas molecules have been given elsewhere (1). In these experiments the electron wave length was always 0.0611 A.U. and the camera distance was 10.85 cm. From ten to twenty photographs were taken of each substance. The averages of the visually measured diameters of the maxima and minima on from six to nine of the best negatives are tabulated for each compound as "observed s" values, where s is 4π ($\sin \theta/2)/\lambda$, θ is the total scattering angle, and λ is the electron wave length. The estimated intensities given in the tables under the column heading I were combined with the observed s values to give the radial distribution curves (4) shown in figure 1. The position of the highest maximum in each curve represents the value of the corresponding interatomic distance to within 0.02 A.U.; the other points may be somewhat less reliable. The positions of the arrows mark the values of the interatomic distances as determined by comparison of the photographs with theoretical intensity curves, and their heights show the relative contributions of the various interatomic separations within a given molecule.

The comparison with the photographs of theoretical intensity curves for various molecular models is also given in the tables. The "calculated s" values represent the positions of the maxima and minima on the curves shown in the figures. The ratios of calculated and observed s values are multiplied by the distances assumed for the molecular models to give the observed distances at the foot of the columns of ratios. The assumed distances for the carbon-hydrogen bonds were always 1.06 A.U., and the hydrogen-carbon-hydrogen bond angles were 109°28′.

The final values for the interatomic distances and the angles depend upon the choice among the molecular models. The basis for this choice and the result in each case are given in the following paragraphs. In general the agreement between the qualitative appearance of the photographs and of the theoretical intensity curves is very good, so that the appearance of the photographs may be inferred from the curves and the estimated relative intensities.

Methyl fluoride

The two curves (figure 2) calculated for methyl fluoride correspond to models with carbon-fluorine distances of 1.36 A.U. (model I) and 1.41 A.U. (model II), respectively. In the quantitative comparisons of table 1 both curves lead to very nearly the same observed distance, and the final value for the C–F distance is 1.42 ± 0.02 A.U. This is supported by the radial distribution result, 1.41 A.U.

Difluoromethane

The three models of difluoromethane correspond to F–C–F bond angles of 109°28′, 112°, and 115°, respectively, with assumed C–F distances of 1.36 A.U. Model III is unsatisfactory because its curve (figure 2) shows a

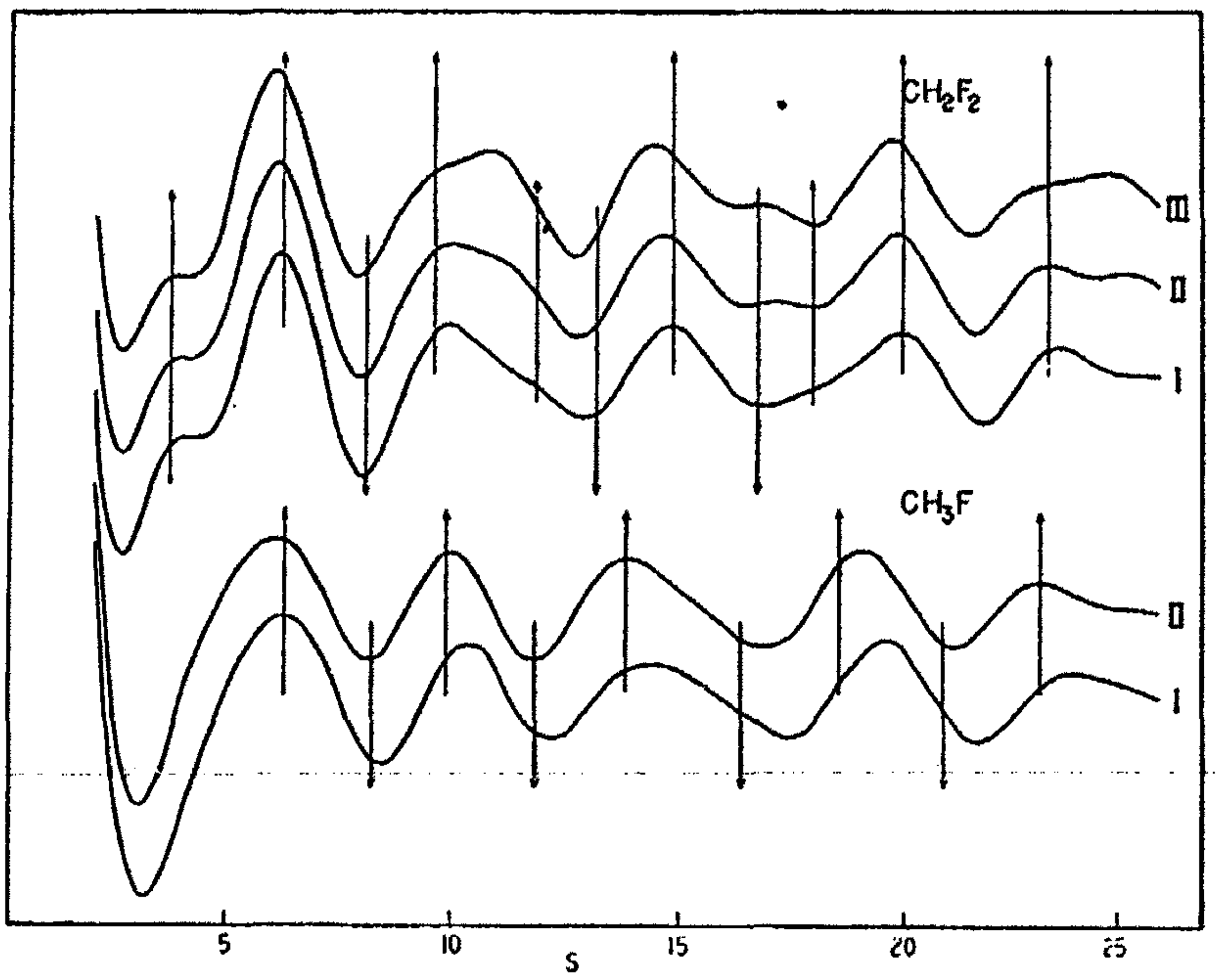

FIG. 2. Theoretical intensity curves for methyl fluoride and difluoromethane. In this and the following figures the positions of the maxima and minima measured on the photographs are shown by the arrows.

TABLE 1

Methyl fluoride

MAXIMUM	MINIMUM	I	OBSERVED VALUES OF s	CALCULATED VALUES OF s	s_{II}/s
				s_{II}	
1		5	6.31	6.12	0.970
	2		8.21	8.17	0.995
2		5	9.87	9.97	1.010
	3		11.87	11.85	0.998
3		3	13.91	13.91	1.000
	4		16.41	16.90	1.030
4		2	18.64	19.14	1.027
	5		20.96	21.18	1.010
5		1	23.29	23.20	0.996
Average					1.004
Average deviation					0.014
C-F					1.416

Final value: C-F = 1.42 ± 0.02 A.U.

small maximum at $s = 16.6$ where a minimum is observed on the photographs. Moreover, the asymmetric maximum near $s = 10$ has the shape indicated in curves I or II rather than that of curve III. These two features of the photographs are best represented by a curve nearer to I than II, and the probably correct value for the bond angles of 110° ±1°.

In the calculation of the bond distances (table 2) values from the third maximum and its shelf and the maximum numbered 5a are unreliable because of the St. John effect, which produces a shift in their measured positions on the photographs. The final value averaged from the remaining six points is C–F = 1.36 ±0.02 A.U. The bond distance in this compound is definitely 0.05 or 0.06 A.U. shorter than in methyl fluoride.

TABLE 2

Methylene fluoride

MAXIMUM	MINIMUM	I	OBSERVED VALUES OF s	CALCULATED VALUES OF s	s_I/s
				s_I	
1		4	(3.66)		
	2		(4.63)		
2		20	6.24	6.20	0.994
	3		8.06	8.03	0.996
3		6	(9.57)	9.89	St. John effect
3a		2	11.85		St. John effect
	4		13.33	12.93	
4		6	14.86	14.83	0.998
	5		16.73	16.78	1.003
5a		1	18.1		St. John effect
5		2	20.0	19.98	1.00
6		1	23.4	23.68	1.01
Average					1.000
Average deviation					0.004
C–F					1.360
F–F					2.220
∠ F–C–F					109°28′

Final values: C–F = 1.36 ± 0.02 A.U.; ∠ F–C–F = 110° ± 1°

Fluorochloromethane

In the photographs of fluorochloromethane the fifth maximum has about one-third the intensity of the fourth and about half that of the sixth. Inspection of the curves for this compound in figure 3 shows that this fact eliminates model IV, in which the assumed distances were C–F = 1.42 A.U. and C–Cl = 1.73 A.U. and the angle F–C–Cl = 110°.

In models I and II the tetrahedral angle 109°28′ was assumed with

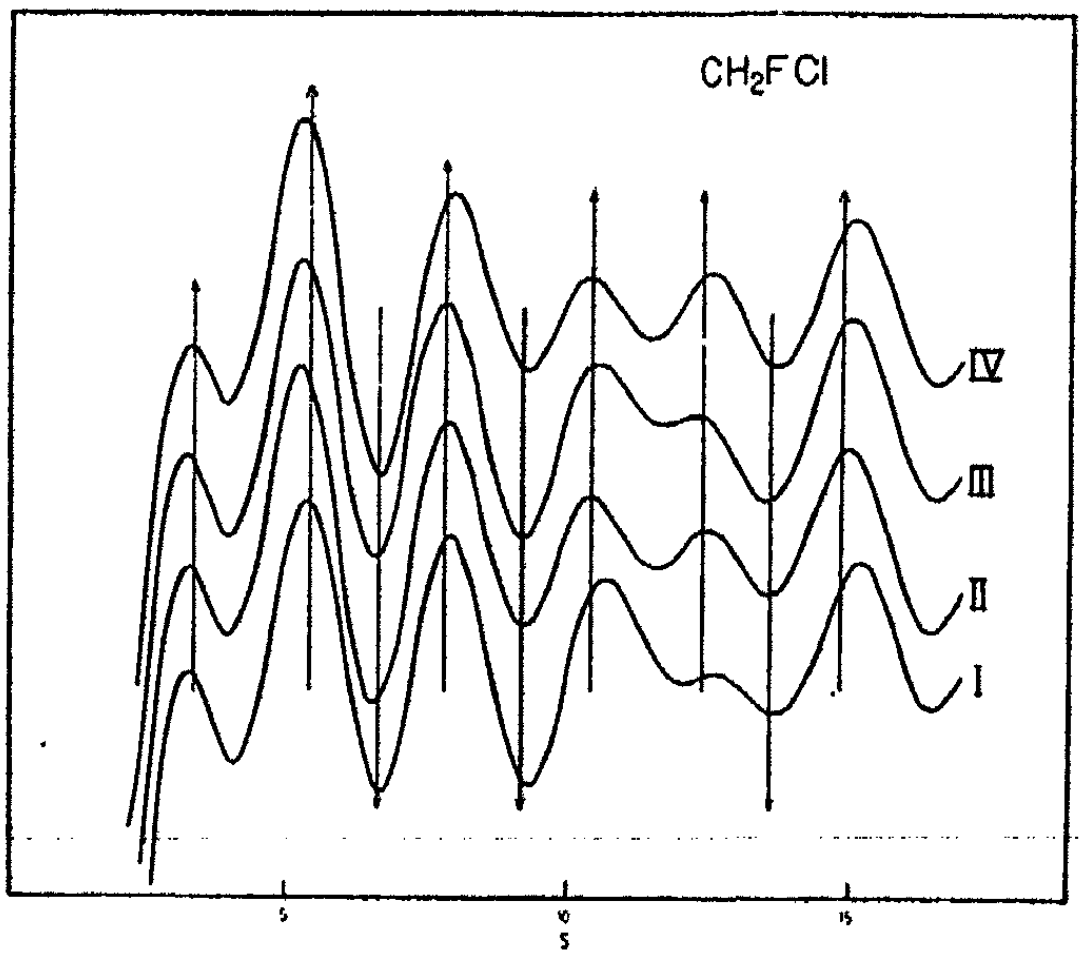

FIG. 3. Theoretical intensity curves for fluorochloromethane

TABLE 3

Fluorochloromethane

MAXIMUM	MINIMUM	I	OBSERVED VALUES OF s	CALCULATED VALUES OF s	s_{II}/s
				s_{II}	
1		3	(3.27)		
	2		(4.12)		
2		10	5.44	5.28	0.971
	3		6.88	6.55	0.981
3		8	7.85	7.92	1.010
	4		9.19	9.24	1.005
4		6	10.43	10.45	1.002
5		2	12.39	12.48	1.007
	6		13.62	13.61	0.999
6		4	14.82	14.96	1.009
Average					0.998
Average deviation					0.011
Cl-F					2.595
C-Cl					1.756
C-F					1.417
∠F-C-Cl					109°28′

Final values: Cl-F = 2.59 ± 0.03 A.U.; C-Cl = 1.76 ± 0.02 A.U.; C-F = 1.40 ± 0.03 A.U., ∠F-C-Cl = 110° ± 2°

carbon–fluorine distances of 1.36 and 1.42 A.U., respectively. Model III has an assumed carbon–fluorine distance of 1.36 A.U. and a bond angle of 112°. For all three the carbon–chlorine distance is 1.76 A.U. The Cl–F distance is 2.59 ± 0.03 A.U. The next most important term, carbon–chlorine, varies only a little and the C–Cl distance is fixed at 1.76 ±0.02 A.U. The C–F distance and the bond angle cannot be directly determined within a range of about 3 per cent. The angles of 110° and 112° observed in difluoro- and dichloro-methane, respectively, together with the evidence from fluorotrichloromethane that the chlorine–fluorine repulsion is appreciably less than that of chlorine–chlorine (for these atoms attached to the same carbon atom) support a value of 110° ±2° for the F–C–Cl angle in fluorochloromethane. The corresponding C–F distance is 1.40 A.U. with an uncertainty of ±0.03 A.U.

TABLE 4

Difluorochloromethane

MAXIMUM	MINIMUM	I	OBSERVED VALUES OF s	CALCULATED VALUES OF s	s_{III}/s
				s_{III}	
1		3	(3.50)	3.22	
	2		(4.44)	4.26	
2		10	5.57	5.54	0.995
	3		6.82	6.87	1.007
3		8	7.97	8.05	1.010
	4		9.25	9.22	0.997
4		8	10.43	10.51	1.008
	5		11.67	11.73	1.005
5		3	12.79	12.65	0.989
	6		14.06	13.77	0.979
6		6	15.23	15.23	1.000
	7		16.63	16.65	1.001
7		2	17.90	17.88	0.999
8		2	20.34	20.06	0.986
Average					0.998
Average deviation					0.007
Cl–F					2.554
C–F					1.357
C–Cl					1.726
∠ F–C–F					111°
∠ F–C–Cl					111°

Final values: Cl–F = 2.56 ± 0.03 A.U.; C–F = 1.36 ± 0.03 A.U.; C–Cl = 1.73 ± 0.03 A.U.; ∠ Cl–C–F = ∠ F–C–F = 110½° ± 1°

In fluorochloromethane the carbon–chlorine bond distance is not appreciably different from the values observed in the chloromethanes. The carbon-fluorine distance is less certain, but it is definitely not as short as in difluoromethane and tetrafluoromethane.

Difluorochloromethane

Four models were tried for difluorochloromethane which would test for possible shortening in either the carbon-fluorine or the carbon-chlorine bonds or both. The assumed distances and angles upon which the calculated s values in table 4 are based are the following: model I, C–F = 1.36, C–Cl = 1.76, ∠ F–C–F = 109°28′; model II, C–F = 1.42, C–Cl = 1.76, ∠ F–C–F = 109°28′; model III, C–F = 1.36, C–Cl = 1.73, ∠ F–C–F = 111°; model IV, C–F = 1.36, C–Cl = 1.70, ∠ F–C–F = 112°. In view of the results on difluoromethane and fluorochloromethane the F–C–F and F–C–Cl angles are probably equal to within a degree and their equality was assumed here. The four curves in figure 4 all show good qualitative agreement with the photographs, and although the observed relative intensities are best reproduced in curve III, the differences among the curves are not striking.

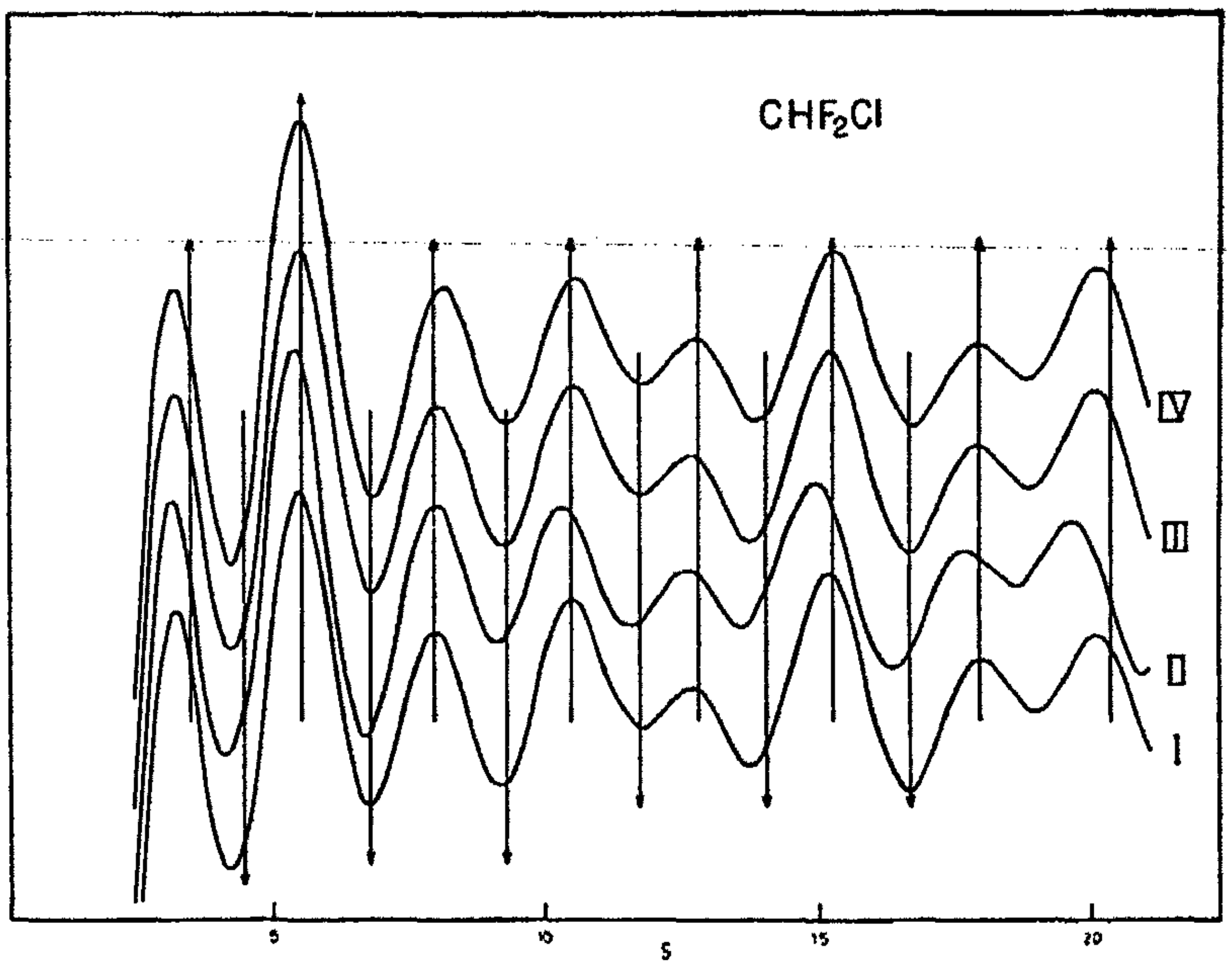

FIG. 4. Theoretical intensity curves for difluorochloromethane

The chlorine-fluorine separation, which gives rise to the strongest interference term, is fixed by all four models as well as by the radial distribution curve at 2.56 ±0.03 A.U. The evaluation of other interatomic distances is facilitated by an assumption regarding the bond angles. From the results obtained for related molecules it is very probable that in this molecule also the F-C-F and F-C-Cl bond angles are close to 110° or 111°. With this assumption the photographs definitely require that the C-F and C-Cl distances be less than the single-bond values. The radial distribution curve (with peaks at 1.36 A.U. and 1.75 A.U.) indicates that the shortening is greater for C-F than for C-Cl. Considering also the data of table 4, we are accordingly led to the following model for difluorochloromethane: C-F = 1.36 ± 0.03 A.U., C-Cl = 1.73 ±0.03 A.U., Cl-F = 2.56 ±0.03 A.U., ∠ F-C-Cl = ∠F-C-F = 110½° ±1°.

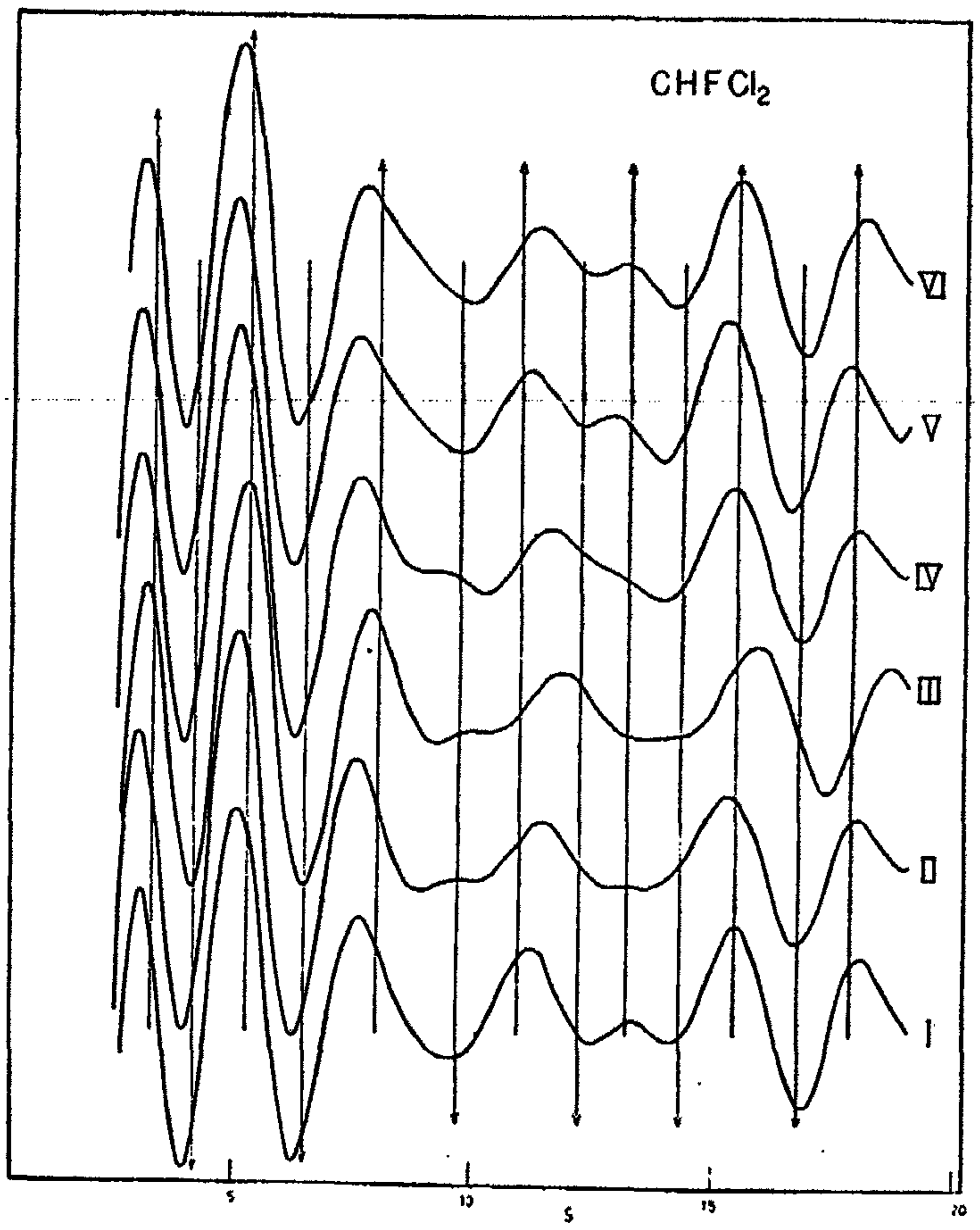

FIG. 5. Theoretical intensity curves for fluorodichloromethane

Fluorodichloromethane

Curves were calculated for six models of fluorodichloromethane. The bond distances and angles used were the following: model I, C-F = 1.36, C-Cl = 1.76, ∠ Cl-C-Cl = ∠ F-C-Cl = 109°28′; model II, C-F = 1.41, C–Cl = 1.76, ∠ Cl–C–Cl = ∠ F–C–Cl = 109°28′; model III, C–F = 1.36, C–Cl = 1.70, Cl–C–Cl = F–C–Cl = 109°28′; model IV, C–F = 1.41, C–Cl = 1.73, ∠ Cl–C–Cl = 112°, F–C–Cl = 111°; model V, C–F = 1.41, C–Cl = 1.76, ∠ Cl–C–Cl = 112°, ∠ F–C–Cl = 110°; model VI, C–F = 1.41, C–Cl = 1.73, ∠ Cl–C–Cl = 112°, ∠ F–C–Cl = 108°40′. Of these, models II, III, and IV are eliminated by the fact that their curves (figure 5) fail to show the fifth maximum observed on the photographs. Model I is not satisfactory because the Cl–C–Cl angle should very probably be larger than the regular tetrahedral value, as it is observed to be in dichloro-, trichloro-, and fluorotrichloro-methane. Models V and VI agree in their results for the more important distances: Cl–F = 2.56 ±0.03 A.U.; Cl–Cl = 2.87 ±0.03 A.U.; and C–Cl = 1.73 ±0.03 A.U. Model VI was devised as a modification of model V which would give better agreement between the assumed and the observed distances; the 0.5 per cent smaller

TABLE 5

Fluorodichloromethane

MAXIMUM	MINIMUM	I	OBSERVED VALUES OF s	CALCULATED VALUES OF s	s_{VI}/s
				s_{VI}	
1		3	(3.19)	2.95	
	2		(4.13)	3.86	
2		10	5.27	5.05	0.995
	3		6.55	6.37	0.972
3		10	8.05	7.77	0.965
	4		9.71	9.97	1.026
4		8	10.97	11.35	1.035
	5		12.24	12.50	1.022
5		2	13.25	13.20	0.997
	6		14.38	14.10	0.987
6		5	15.46	15.50	1.002
	7		16.73	16.84	1.006
7		2	17.83	18.06	1.014
Average					1.002
Average deviation					0.017
Cl–F					2.565
Cl–Cl					2.875
C–Cl					1.734
C–F					1.413
∠ Cl–C–Cl					112°
∠ F–C–Cl					108°40′

Final values: Cl–F = 2.56 ± 0.03 A.U.; Cl–Cl = 2.87 ± 0.03 A.U.;
C–Cl = 1.73 ± 0.04 A.U.; C–F = 1.41 ± 0.03 A.U.;
∠Cl–C–Cl = 112° ± 2°; ∠ F–C–Cl = 109° ± 2°

deviations in the average for model VI indicate that model VI is probably better than model V. The C–F distance accordingly is 1.41 ±0.03 A.U., the range of the estimated probable error allowing a possible decrease in this value to 1.39 A.U., as found for model V. The corresponding F–C–Cl angle is 109° ±2°.

The results for fluorodichloromethane show that in this case the carbon–fluorine bond is not appreciably shortened, but that there may be a small shortening in the carbon–chlorine bond.

TABLE 6

Difluorodichloromethane

MAXIMUM	MINIMUM	I	OBSERVED VALUES OF s	CALCULATED VALUES OF s	s_{VI}/s
				s_{VI}	
1		10	(3.20)	3.05	
	2		(4.19)	4.06	
2		15	5.44	5.32	0.978
	3		6.77	6.71	0.991
3		12	8.16	8.14	0.998
	4		9.57	9.55	0.998
4		10	10.80	10.91	1.010
	5		12.04	12.12	1.007
5		5	13.15	13.15	1.000
	6		14.34	14.25	0.994
6		10	15.48	15.54	1.004
	7		16.79	16.85	1.004
7		3	17.77	18.11	1.019
Average					1.000
Average deviation					0.008
Cl–F					2.520
Cl–Cl					2.900
C–Cl					1.730
C–F					1.360
∠ ClCCl					113°44′
∠ FCF					108°50′

Final values: Cl–F = 2.52 ± 0.02 A.U.; Cl–Cl = 2.90 ± 0.03 A.U.;
C–Cl = 1.74 ± 0.03 A.U.; C–F = 1.35 ± 0.03 A.U.;
∠ Cl–C–Cl = 113° ± 2°; ∠ F–C–F = 109° ± 2°

Difluorodichloromethane

The six models for difluorodichloromethane were calculated with the following assumed distances and angles: model I, C–F = 1.36, C–Cl = 1.76, ∠ Cl–C–Cl = ∠F–C–F = 109°28′; model II, C–F = 1.36, C–Cl = 1.76, Cl–C–Cl = 112°, ∠F–C–F = 117°; model III, C–F = 1.41, C–Cl = 1.76, ∠Cl–C–Cl = ∠ F–C–F = 109°28′; model IV, C–F = 1.36, C–Cl =

1.73, ∠ Cl–C–Cl = ∠F–C–F = 109°28′; model V, C–F = 1.33, C–Cl = 1.76, ∠ Cl–C–Cl = 111°, ∠ F–C–F = 112°; model VI, C–F = 1.36, C–Cl = 1.73, ∠ Cl–C–Cl = 113°44′, ∠ F–C–F = 108°50′.

Model II, with the very large F–C–F angle, 117°, was arranged to have the same bond distances as model I and at the same time to have the value 2.52 A.U. for the important Cl–F distance which was fixed by the radial distribution curve. This model is undoubtedly incorrect, since all of the existing evidence indicates that the F–C–F angle should be considerably smaller than 117° and indeed smaller than the Cl–C–Cl angle. Models I, III, and IV are unsatisfactory, because in the curve for each (figure 6) the fifth maximum is considerably less prominent than in the photographs. Moreover, their respective values for the ratios of calculated and observed *s* values show deviations which are significantly larger than those for models V and VI. The curves for these two models are both in good qualitative agreement with the photographs.

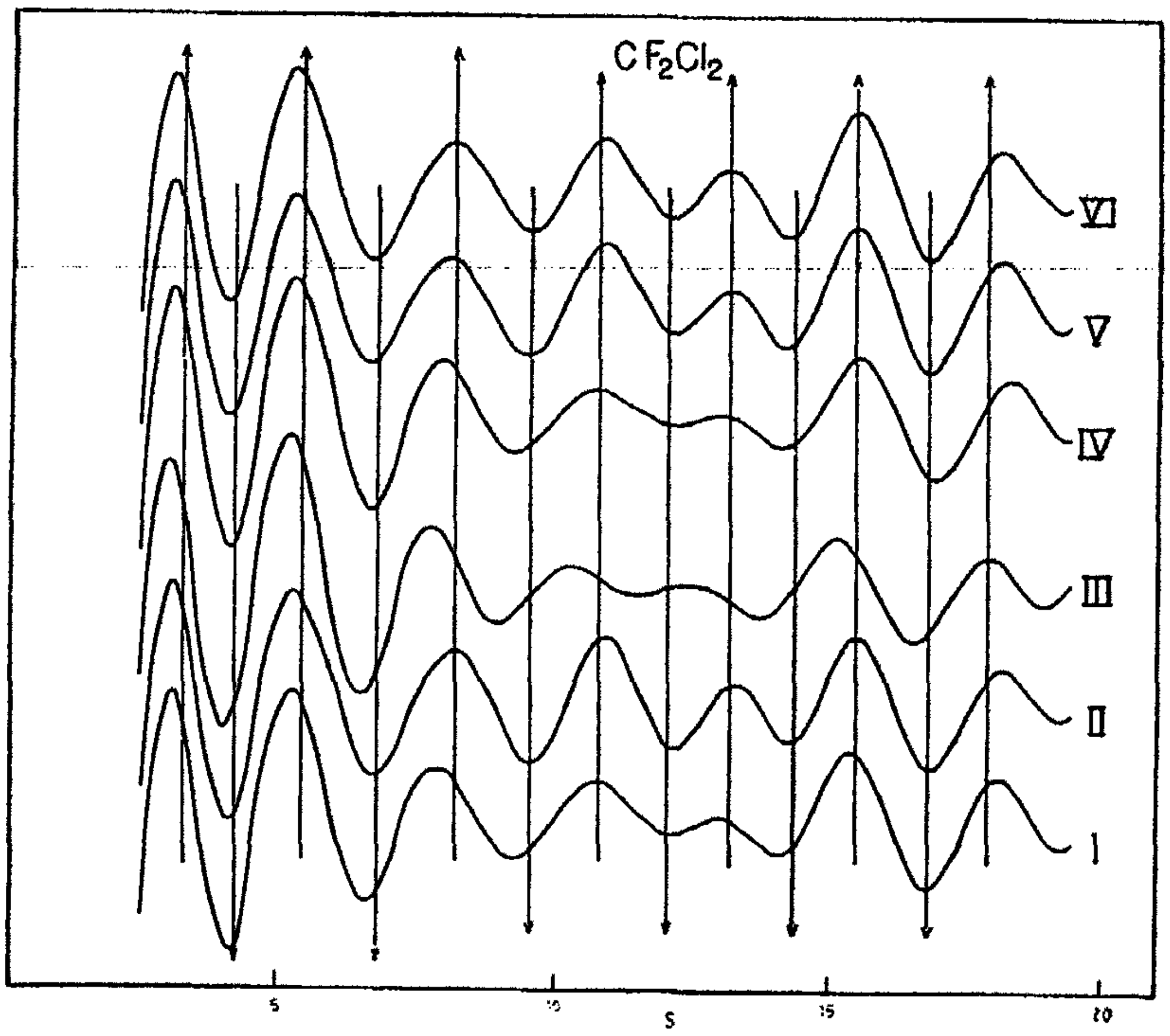

FIG. 6. Theoretical intensity curves for difluorodichloromethane

The Cl–F and Cl–Cl distances are reliably determined to have the respective values 2.52 ±0.02 A.U. and 2.90 ± 0.03 A.U. The C–F and C–Cl distances each differ by 0.03 A.U. in the results of models V and VI and the final values chosen are intermediate, namely, C–F = 1.35 ±0.03 A.U. and C–Cl = 1.74 ±0.03 A.U.

In difluorodichloromethane the carbon–fluorine bond has the shortened distance observed in some of the foregoing compounds, and the carbon–chlorine bond appears to be shortened by a smaller amount.

Fluorotrichloromethane

The diffraction pattern of fluorotrichloromethane has the regular appearance of the one for carbon tetrachloride, with the fifth and seventh maxima each stronger than the one preceding it. Ten rings were measured on these photographs. The models considered were fixed by the following parameters: model I, C–F = 1.36, C–Cl = 1.76, ∠ Cl–C–Cl = 109°28′; model II, C–F = 1.42, C–Cl = 1.76, ∠ Cl–C–Cl = 109°28′; model III, C–F = 1.36, C–Cl = 1.76, ∠ Cl–C–Cl = 111½°; model IV, C–F = 1.42, C–Cl = 1.76, Cl–C–Cl = 111½.°

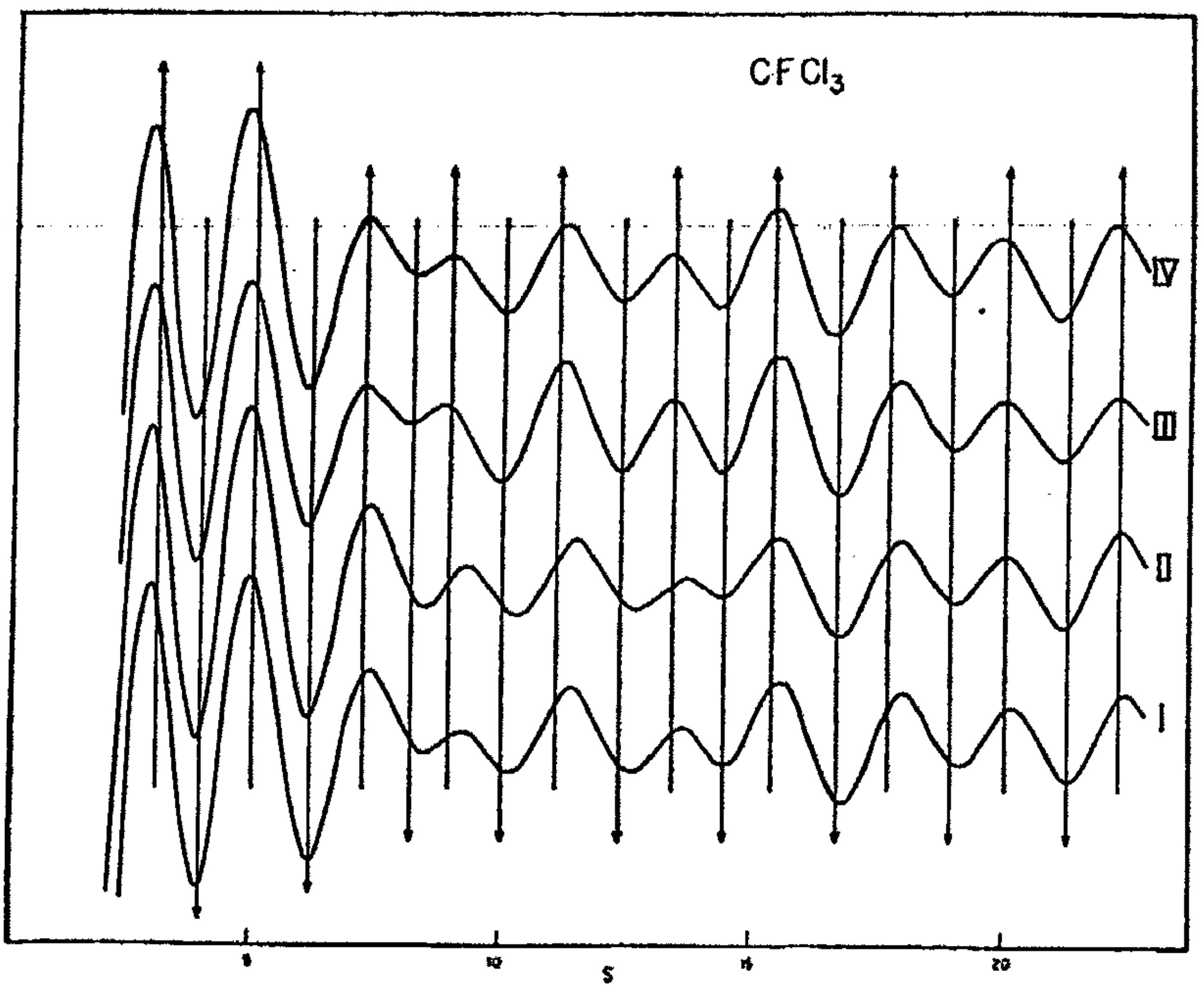

FIG. 7. Theoretical intensity curves for fluorotrichloromethane

The comparison with observed *s* values with all of the models leads to a chlorine–chlorine separation of 2.91 ±0.03 A.U. The corresponding distance in carbon tetrachloride is 2.87 A.U. and in chloroform 2.93 A.U.; the bond angles are 109°28′ and 112°, respectively. It is very probable that the ClCCl angle is no greater in fluorotrichloromethane than in chloroform and that the C–Cl distance is not greater than in the chloromethanes, 1.76 A.U. These assumptions, together with the observed Cl–Cl separation, fix the ClCCl angle at 111½ °± ½° and the C–Cl distance at 1.76 ±0.02 A.U. The fluorine atom cannot be located to within several hundredths of an Ångström unit because its scattering power is so much less than that of the three chlorine atoms. The position of the chlorine–fluorine peak in the radial distribution curve supports a carbon–fluorine bond distance of not less than 1.40 A.U. Accordingly this distance is reported with a large probable error, ±0.04 A.U.

TABLE 7

Fluorotrichloromethane

MAXIMUM	MINIMUM	I	OBSERVED VALUES OF s	CALCULATED VALUES OF s	s_{IV}/s
				s_{IV}	
1		8	2.97		
	2		3.91		
2		20	5.03	4.92	0.978
	3		6.21	6.14	0.989
3		15	7.30	7.32	1.002
	4		8.16	8.30	1.017
4		5	8.97	9.00	1.004
	5		10.04	10.07	1.003
5		12	11.08	11.26	1.016
	6		12.33	12.35	1.002
6		4	13.34	13.31	0.998
	7		14.43	14.29	0.990
7		12	15.44	15.44	1.000
	8		16.72	16.65	0.996
8		6	17.72	17.85	1.007
	9		18.95	18.89	0.997
9		2	20.04	19.91	0.994
	10		21.28	21.06	0.990
10		1	22.32	22.28	0.998
Average					0.999
Average deviation					0.007
Cl–Cl					2.907
Cl–F					2.577
C–Cl					1.758
∠ ClCCl					111½°
∠ FCCl					107½°

Final values: Cl–Cl = 2.91 ± 0.03 A.U.; Cl–F = 2.56 ± 0.04 A.U.;
C–Cl = 1.76 ± 0.02 A.U.; C–F = 1.40 ± 0.04 A.U.;
∠ Cl–C–Cl = 111½° ± 1°

In fluorotrichloromethane the carbon–chlorine bonds are not shortened,

TABLE 8

Structures of the fluorine and chlorine derivatives of methane

SUBSTANCE	C-F	C-Cl	F-F	Cl-Cl	Cl-F	∠ F-C-F	∠ Cl-C-Cl	∠ F-C-Cl
CH_3F	1.42 ± 0.02							
CH_3Cl		1.77 ± 0.02						
CH_2F_2	1.36 ± 0.02		2.23 ± 0.03			110° ± 1°		
CH_2FCl	1.40 ± 0.03	1.76 ± 0.02			2.59 ± 0.03			110° ± 2°
CH_2Cl_2		1.77 ± 0.02		2.93 ± 0.02			112° ± 2°	
CHF_2Cl	1.36 ± 0.03	1.73 ± 0.03	2.24 ± 0.04		2.56 ± 0.03	110½° ± 1°		110½° ± 1°
$CHFCl_2$	1.41 ± 0.03	1.73 ± 0.04		2.87 ± 0.03	2.56 ± 0.03		112° ± 2°	109° ± 2°
$CHCl_3$		1.77 ± 0.02		2.93 ± 0.02			112° ± 2°	
CF_4	1.36 ± 0.02		2.22 ± 0.03			109°28′		
CF_2Cl_2	1.35 ± 0.03	1.74 ± 0.03	2.21 ± 0.03	2.90 ± 0.03	2.52 ± 0.02	109° ± 2°	113° ± 2°	110° ± 2°
$CFCl_3$	1.40 ± 0.04	1.76 ± 0.02		2.91 ± 0.03	2.56 ± 0.04		111½° ± 1°	107½° ± 1°
CCl_4		1.755 ± 0.005		2.87 ± 0.02			109°28′	

and although the carbon–fluorine bond distance cannot be accurately determined it is apparently not much shorter than in methyl fluoride.

SUMMARY OF RESULTS

The results of the measurements on the foregoing compounds are collected in table 8, together with those previously obtained for the chloromethanes (5) and for carbon tetrafluoride (3). The relative certainty of the observed values for the various interatomic distances is indicated by the estimated probable errors.

The tabulated values for the bond angles show that in general the chlorine–carbon–chlorine angle is larger than the chlorine–carbon–fluorine angle, which in turn is larger than the fluorine–carbon–fluorine angle. The high electronegativity of fluorine apparently has little effect on the angles between carbon–fluorine bonds.

The fluorine compounds listed in table 8 apparently fall into two groups: those having carbon–fluorine bond distances close to the value 1.41 A.U., and those having distances close to the value 1.36 A.U. In the first group are methyl fluoride, fluorochloromethane, fluorodichloromethane, and probably also fluorotrichloromethane. In the second group are difluoromethane, tetrafluoromethane, difluorodichloromethane, and difluorochloromethane. The significance of this distinction in the carbon–fluorine bond distances and the close analogy with the variations in the chemical properties of these compounds have been explained in the previous discussion (2) in the light of a suggested theory of the chemical reactivity of carbon compounds containing fluorine.

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(4) Pauling, L., and Brockway, L. O.: J. Am. Chem. Soc. **57**, 2684 (1935).
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NEW BOOKS

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 23: Ammonium. Lieferung 1. 26 x 17 cm.; pp. 1-242. Berlin: Verlag Chemie, 1936. Price: 28 RM.

The present volume of the great treatise deals with the occurrence (minerals) of ammonium, the free radical, the ion, analysis, compounds with hydrogen and oxygen (the system NH_3-H_2O), nitrogen (including oxy-salts), fluorine, chlorine (including oxy-salts), bromine, and iodine. The section on the free radical is rather brief. Among the descriptions of the salts that on ammonium nitrate is noteworthy, the different modifications and its modes of decomposition being well covered. The manufacture of ammonium salts is to be dealt with in another volume. The present volume is one of considerable interest from many points of view, and the subject has been dealt with in an admirable manner.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 4: Stickstoff. Lieferung 4. 26 x 17 cm.; pp. 855-1038. Berlin: Verlag Chemie, 1936. Price: 25.15 RM.

With the publication of the present section the volume on nitrogen and its compounds is completed. The Editor is to be congratulated on having seen through the whole volume in a commendably short time and on the high standard of the work. The present section deals with compounds of very considerable interest: nitroxyl, hydroxylamine, nitro- and nitroso-hydroxylamine, nitramide, nitrosamide, hyponitrous, nitrous, nitric, pernitrous, and pernitric acids, and some doubtful compounds. The section on nitric acid deals with its action on metals and with the absorption of nitrous gases.

J. R. PARTINGTON.

Glastechnische Fabrikationsfehler. By H. JEBSEN-MARWEDEL. 28 x 20 cm.; 295 pp.; 441 figs.; one colored plate. Published under the auspices of the Deutsche Glastechnische Gesellschaft. Berlin: Julius Springer, 1936. Price: paper covers, 45 RM.; bound, 48.60 RM.; less 25 per cent in England and less a further 20 per cent to members of the D.G.G.

The subject of the defects in glass and glassware arising during the course of manufacture is dealt with in a comprehensive and very competent manner such as one has come to expect from an author who has made valuable original contributions to our knowledge of glass-making processes. The subject matter is divided into nine chapters, each with numerous sections. Chapter I. *General.* Glass production in Germany; graphic representation of data about defects during production; comparative degrees of homogeneity in various types of commercial glass; interconnection of several causes of defects; technical field of multicomponent systems from which glasses are derived. Chapter II. *Defects in the Glass Mass.* Cords, veins and strings in glass, their various origins. Chapter III. *Gases in Glass.* Bubbles and seed. Chemical reactions in glassmaking leading to gas evolution. Solution in and extraction of gases from glass. Refining processes. Chapter IV. *Solid Inclusions in Glass.* Stones of various kinds derived from raw materials and refractory materials. Corrosion and solution of refractory materials. Chapter V. *Crystals in Glass.* Devitrification. Chapter VI. *The Color Tint of Glasses.* Variation in color tint due to displacement of equilibrium between ferrous and ferric iron through furnace and other conditions. Theory and practice of decolorizing glass. Chapter VII. *Defects Arising in Production.* Deformation and misshaping of articles of glassware from various causes. Chapter VIII. *Defects in the Surface of the Glass.* Reaction and corrosion phenomena due to action of gases, fumes, moisture, etc. Chapter IX. *Cracks and Crizzles in Glass.* (Internal Stresses, Fracture.) Brittleness and its definition. Tensile and compressive forces in unannealed glass. The annealing of glass. Fracture systems in glass. Glass cutting.

The above outline of the contents gives but slight indication of the thoroughness of the treatment of the subject. The book consists of no mere collection of empirical facts; in every case there is endeavor to relate the various types of defects and their practical origin to scientific principles. The text in fact contains some 660 references to original literature. The section on the tint in glass, and particularly on the theory of decolorizing, has been done in a more satisfying way than in any previous textbook on the subject.

The book is very well printed and, despite a few errors in the spelling of foreign—particularly English—names, it does not appear to contain any serious errors. The diagrams are good and the numerous photographic reproductions reach a high standard.

The price of the book, especially to English and American readers, is high, but all things considered the volume is very well worth the money. It is, indeed, in the reviewer's opinion, indispensable to all glass technologists; and many workers in physical chemistry and physics may find by perusal of this work dealing with glass numerous instances of phenomena which arise in substances of high viscosity.

W. E. S. TURNER.

The Scientist in Action: A Scientific Study of His Methods. By WILLIAM H. GEORGE. 21.5 x 14 cm.; 355 pp. London: Williams & Norgate, Ltd., 1936. Price: 10 s. 6d.

Probably most scientists have never read a book on scientific method, and think they would gain nothing by doing so. Well, it depends upon the book, but in this case gain should certainly result for many: in pleasure, in the fuller realization of what they are doing, and in the stimulus to further thought. And it is not unlikely that many would be surprised to discover their lack of scientific method outside their professional researches. Even concerning these researches Dr. George stresses the fact that a scientific worker is human but cannot escape being part of his apparatus: "in interpreting the results of research it becomes necessary to examine to what extent they depend upon the human factor." The influence of the human factor is carefully discussed.

A deterrent to the reading of books on scientific method is often their "dryness." But here Dr. George's astonishingly wide knowledge of all kinds of subjects, from ancient to ultra-modern, is combined with much humor, yet thorough earnestness and care, to give his theses illustrations which are always pleasantly interesting, and often, as Kai Lung would say, "gravity removing."

Chapter XI is certainly controversial, as Dr. George points out, but the facts brought forward are arresting, to say the least.

Not only professional scientists, but all interested in the meaning of science and its connection with civilization, should be able to read this book with ease, profit, and delight.

L. F. GILBERT.

Elementary Physical Chemistry. By HUGH S. TAYLOR and H. AUSTIN TAYLOR. Second edition. 22 x 15 cm.; ix + 664 pp.; 112 figs. New York: D. Van Nostrand Co., Inc., 1937. Price: $3.75.

The first-edition of this book, published in 1927 and well known to all teachers and students of physical chemistry, was "adapted from the two-volume *Treatise on Physical Chemistry* which appeared under the author's editorship." . . . A need had "been felt in several quarters for a single volume of a more elementary nature which should follow the general lines of development in the larger treatise, without, however, its detail."

The present second edition, written under the joint authorship of Professor Hugh S. Taylor and his brother, Professor H. Austin Taylor, says of itself:

"The main lines of development that have been achieved by research in physical chemistry during the ten years which have elapsed since the first issue of this elementary exposition of the subject are concerned with problems of atomic and molecular structure and their general bearing upon the field of reaction kinetics.

"The more intimate knowledge of the energies of atomic systems resulting from spectroscopy, the newer techniques for the elucidation of structure of molecules, and the keener theoretical analysis of the problems of molecular energies have, together with the isolation, in pure form, of isotopes and derived isotopic compounds, given considerable impetus to new efforts towards the elucidation of problems of mechanism and velocity in chemical processes. This is true not only of thermal processes but also of reactions produced through the agency of outside sources of radiation."

"The present volume attempts to adjust the content of the elementary course in physical chemistry to these changes. . . . It recognizes that much of the content of the classical course in physical chemistry is now to be found in modern courses of general chemistry, at least in the more advanced presentations of this subject. It assumes that physical chemists should no longer ignore this state of affairs and, consequently, should incorporate into their courses an elementary presentation of those aspects of the subject which will enable the student to sense some of the present vivid progress in the science."

A doubt arises in the mind of the reviewer as to the justification of assuming that the student in our average or even better than average general chemistry courses absorbs much background in physical chemistry; and even if so, whether it is not highly desirable to develop the topical material in an elementary treatment of physical chemistry in very easy stages. Also, if the authors of our textbooks of physical chemistry could forget their dignity and find it possible to strike a much less formal note, their writings would assuredly be far more readable and useful to the student struggling to understand what it is all about. One also wonders why our various authors do not develop explicitly, in their books, some of the simpler aspects of the theory of probability, with its extraordinarily powerful and enlightening approach to the problems of physical chemistry.

On the whole, the present book by the Taylor brothers is a most excellent job. It is well written, its expositions are reasonably clear, the emphasis is fair and just, and the subject matter very well chosen indeed. The contents are as follows: I, The Atomic Concept of Matter; II, Energy in Chemical Systems; III, The Gaseous State, I; IV, The Atomic Concept of Energy—Energy Quanta; V, The Gaseous State, II · VI, The States of Aggregation. II, The Liquid State; VII, The Crystalline State; VIII, Velocity and Mechanism of Gaseous Reactions; IX, The Direction of Chemical Change; X, Solutions; XI, Homogeneous Equilibrium; XII, Heterogeneous Equilibrium; XIII, Electrical Conductance and Ionization; XIV, Ionic Equilibria, I. Weak Electrolytes; XV, Ionic Equilibria, II. Strong Electrolytes; XVI, Photochemistry; XVII, Colloid Chemistry; Appendix I, II, III; Author Index; Subject Index.

This text not only presents a well-reasoned treatment of the main elements of classical physical chemistry but, as it seems to the reviewer, offers the best handle, among the list of available introductory textbooks of physical chemistry, by which the student may take hold of the newer developments in the field.

Edward Mack, Jr.

Ions in Solution. By R. W. Gurney. 206 pp.; 44 figs. Cambridge: The University Press. New York: The MacMillan Company, 1936.

I have seldom read a scientific book with greater pleasure and interest than I experienced in going through this small volume by Dr. Gurney. I can heartily recommend it to the attention of my fellow physical chemists. From the most modern point of view, Dr. Gurney discusses such topics as solvation energy, the interactions of gas ions among themselves and with a metal electrode, the properties of ions in a solvent and their deposition on electrodes, the formation of double layers at phase boundaries, the electromotive force of cells, the properties of an assembly of dipoles, the conditions restricting the coëxistence of ions in a solvent, the electrochemical series, and many other phenomena of great importance to the physicist and chemist. The treatment adopted by Dr. Gurney employs only the simplest mathematics but by frequent use of diagrams (particularly potential-energy diagrams) the author is able to give to the reader an illuminating account of the phenomena under consideration. The book should be of great interest to all physical chemists and especially to all students of electrochemistry.

Dr. Gurney announces that the ideas and methods outlined in the present book will be elaborated in a second volume. The appearance of the second volume will be awaited with great interest.

F. H. MacDougall.

Reagent Chemicals and Standards with Methods of Assaying and Testing Them. By Joseph Rosin. 530 pp. New York: D. Van Nostrand Company, Inc., 1937. Price: $6.00.

A book of this nature should be of value to anyone who makes use of chemicals. Various examples could be quoted from the literature showing that the results of some physicochemical researches were invalidated by the fact that the authors worked with impure chemicals.

One of the outstanding features of the book is that the maximum limits of impurities as indicated by the tests are specified. These tests conform, as a rule, to the requirements of "reagent chemicals," and are of much more importance than the assays given in many cases. If barium nitrate (p. 71) should contain, for example, less than 0.2 per cent impurities its assay should be at least 99.8 per cent. The minimum assay given is 99 per cent, and the difference may be interpreted as due to the presence of water (for which a separate test could be made) or to inaccuracies in the quantitative procedure described. In testing reagent chemicals such assays are of much less value than the tests for impurities, unless a highly refined analytical procedure is employed.

A short description of the various chemicals is given. It would be of value to add simple tests of identification as well.

In general the tests are adequate, although one might in certain cases prefer simpler procedures. Calcium carbonate, for example, can be tested simply for alkalies by direct sensitive reactions for potassium and sodium. The assay for glycine can be simplified by making use of the formaldehyde reaction. In examining the primary standard silver nitrate, a test for included water should be given.

These few suggestions, to which more could be added, do not detract from the value of the book, which we should like to see in the hands of all chemists who wish to rely upon the purity of their chemicals.

I. M. KOLTHOFF.

A Commentary on the Scientific Writings of J. Willard Gibbs. Vol. I, Thermodynamics. xxiii + 742 pp. *Vol. II, Theoretical Physics.* xx + 605 pp. Edited by F. G. Donnan and Arthur Haas. New Haven: Yale University Press, 1936. Price: $10.00.

"These volumes," in the words of the editors, "have been prepared with a twofold purpose,—to honor the memory of J. Willard Gibbs, and to meet what is believed to be a real need. They are designed to aid and supplement a careful study of the original text of Gibbs' writings and not, in any sense, to make such a study unnecessary."

Volume I contains an outline of Gibbs' lectures on "Thermodynamics" by E. B. Wilson, a presentation (pp. 61–180) of the "General Thermodynamic System" of Gibbs by J. A. V. Butler, "Osmotic and Membrane Equilibria, including Electrochemical Systems" by E. A. Guggenheim, a paper on various thermodynamic potentials by E. A. Milne, "The Phase Rule and Heterogeneous Equilibrium" by G. W. Morey, "Graphic Representation of Equilibria in Binary Systems by Means of the Zeta Function" by F. A. H. Schreinemakers, "Equilibrium under the Influence of Gravity" by D. H. Andrews, "Equations of Ideal Gases and Gas Mixtures" by F. G. Keyes, "The Thermodynamics of Strained Elastic Solids" (pp. 395–504) and "Surfaces of Discontinuity" (pp. 505–708) by James Rice, and finally "The General Properties of a Perfect Electrochemical Apparatus" by H. S. Harned.

Volume II consists of the "Thermodynamic Principles as Extended and Perfected by Gibbs" (pp. 1–58) by A. Haas, "Application of Gibbs' Method to Modern Problems of Thermodynamics" by Paul S. Epstein, "Gibbs' Contributions to the Theory of Light" by Leigh Page, "The Contributions of Gibbs to Vector Analysis" by E. B. Wilson, "Gibbs and the Statistical Conception of Physics" by A. Haas, "The Chief Results of Gibbs' Statistical Mechanics" by A. Haas, "Special Commentary on Gibbs' Statistical Mechanics" by A. Haas, "Critical Appreciation of Gibbs' Statistical Mechanics" by Paul S. Epstein, "Gibbs' Methods in Quantum Statistics" by Paul S. Epstein, and "Commentary on Gibbs' Papers on Dynamics" by A. Haas.

There is a good deal of repetition in the various papers on thermodynamics and in those on statistical mechanics. This repetition was more or less unavoidable; in fact, it may serve the useful purpose of making the ideas of Gibbs more readily understood. In any case the two volumes contain a wealth of material sufficient to rejoice the heart and mind of the discerning chemist or physicist. In several papers (notably those by Epstein) the presentation goes beyond that of Gibbs and takes into account the latest developments.

The only serious error that I have noticed occurs on page 22 in Volume II, in the paper by A. Haas on the thermodynamic principles of Gibbs. The chemical potential of a component of a phase is quite correctly defined as the partial derivative of the energy with respect to the mass of this component, the masses of the remaining components, the total volume, and the total entropy being kept constant. However, it is then erroneously stated that the condition that the total entropy shall be constant is equivalent to the condition that the process considered (viz. an increase in the mass of a certain component of a phase by the addition of some of this substance) shall be carried out adiabatically.

F. H. MACDOUGALL.

Hydroxyde und Oxydhydrate. By R. FRICKE and G. F. HÜTTIG, with the coöperation of H. Zocher and H. Saechtling. 640 pp. Leipzig: Akademische Verlagsgesellschaft, m.b.H., 1937.

This volume constitutes Part IX of the *Handbuch der allgemeinen Chemie* edited by Paul Walden. Every worker interested in the physical and chemical properties of oxides, hydroxides, and their hydrous products will welcome the publication of this monograph. The literature in this field is extremely extensive and full of contradictory statements. Fricke and Hüttig, both of whom have contributed so much to the subject, have succeeded in writing a critical and systematic review with full consideration of the world literature.

Particular emphasis is laid on the structural relationships between, and physicochemical properties of, the metal oxides, hydroxides, and hydrous products. Not all the properties are discussed in an exhaustive way, but a multitude of references to the literature, Gmelin Kraut, and, regarding the colloid chemical properties, to Weiser's *The Hydrous Oxides and Hydroxides* enable the reader to find more complete sources of information.

The book is divided into a special part (502 pages) and a general part. In the former the properties of the individual metal oxides and hydroxides are given, including a highly successful chapter on the system SiO_2-H_2O by Zocher of almost 100 pages, and a chapter on the rare earths and the platinum metals by Saechtling and Zocher. The general part comprises chapters on x-ray analysis with detailed discussion regarding the perfection of the crystal lattices, aging (unfortunately, not much has been said about thermal treatment, although a summary of Hüttig's own work would have been very valuable), aqueous vapor pressure, kinetics of dehydration, thermochemical data showing the different energy contents of oxides and hydroxides as a function of the degree of perfection of the lattices, magnetic susceptibility, and dielectric constants.

The book will be of great use in defining a compound as an oxide hydrate, hydrous oxide, hydroxide, hydroxide hydrate, or hydrous hydroxide. The detailed table of contents with the subject and author index are helpful in finding the wealth of information offered in this book. The print and appearance are excellent. Chemists owe a debt of gratitude to the authors for their painstaking work of collecting all the important data on this subject into one volume.

I. M. KOLTHOFF.

Relativity Theory of Protons and Electrons. By A. S. EDDINGTON.

This unusual book contains a review and "summing up" of the theory which Professor Eddington has been developing for the last several years in an effort to bridge the gap between the theory of relativity and quantum mechanics. In reviewing a book of this type, in which there is such a departure from customary theory and notation, it is only possible to sketch the highlights of what the reader may expect to find there. This is *not* a textbook, either of relativity theory or of quantum mechanics. Consequently the reader must be already well grounded in both of the theories and their associated mathematics, and must expect that the main emphasis will be on the author's ideas about their relationships.

With this word of warning, we may turn to a brief discussion of the book itself. The first portion is devoted to the study of the complete set of sixteen anticommuting operators built up from the four Dirac operators as basis. This leads to the introduction of a 16-space and of a calculus of vectors and tensors in this space. This forms the first part of the mathematical bridge between relativity and quantum mechanics.

Apart from this purely mathematical theory the most interesting portions of the book are the discussions of the author's ideas on the composition of two or more simple systems to form a complex system, the Pauli exclusion principle, and the sharp distinction between "internal" and "external" wave functions. These must be studied to understand the basis for the startling results which the author has predicted from his theory: the value of 1/137 for the fine structure constant, the mass ratio of the proton and electron, etc. The sophisticated reader will undoubtedly find here many things with which he will want to disagree, but the reviewer believes that if he approaches the theory at all sympathetically he will also find much that is stimulating and provocative of further thought.

E. L. HILL.

Applied Chemistry for Engineers. By A. F. H. WARD. 19 x 12 cm.; xi and 127 pp. London: Longmans, Green and Co., 1936. Price: 5s.

The writing of an easily understandable book on applied chemistry for engineers is no easy task. The present book is intended, the author tells us in his preface, to provide a practical course in applied chemistry for students of mechanical, municipal, or electrical engineering in technical colleges and universities. As an alternative, its use is suggested to students of pure chemistry needing an introduction to applied chemistry. The book may appeal more to the latter. The method of instruction adopted is theoretical description followed by experiment to be performed; general references to textbooks or pamphlets are added at the end of each part. Almost half the volume is allotted to water, domestic and industrial, its analysis and treatment. This branch of the subject is dealt with in detail; alternative and latest methods are given with, in some cases, literature references.

The difficult problem of metal corrosion, including a consideration of overvoltage and the passive state, occupies the next thirty-odd pages, the electrochemical theory only of corrosion being considered.

The rest of the text of the volume is concerned with coal and oil. In contrast to the section on water, the information is scanty, in the case of coal only proximate analysis being mentioned, and no calorific determination in the case either of coal or of oil.

Some mistakes occur, for instance, an obvious misprint in the equation on p. 56, the high value of the Faraday (p. 73), and the description of methyl orange as a weak acid indicator (p. 116). However, the book as a whole serves a useful purpose, and a future edition might be extended with advantage.

W. H. PATTERSON.

Elektronentheorie der Metalle. By H. FRÖHLICH. 22 x 14 cm.; vii and 386 pp. Berlin: Julius Springer, 1936. Price: 27 RM.; cloth-covered, 28.80 RM.

Dr. Fröhlich gives an exhaustive and detailed account of the modern electron theory of metals. The mathematical physicist will find the book full of useful information; in particular the chapters on the optical properties of metals are worth mentioning. This group of problems, to which the author himself made valuable contributions, is particularly clearly exposed. The book appeals also to experimentalists who want to acquaint themselves with the theory, and only the elements of wave mechanics are assumed to be known to the reader. But Dr. Fröhlich wants the full attention of his reader, and a superficial glance at the book may not lead to much benefit. This holds particularly for an English reader, who may be scared by the double difficulty of rather involved German constructions expressing involved arguments with many afterthoughts. He will, however, be rewarded for his patience by much interesting information, and a very detailed list of references opens the way for further studies. The book represents a fair summary of the present position.

The number of slight slips or misunderstandings which have crept in is, considering the involved subject, remarkably small.

R. Peierls.

Gmelins Handbuch der anorganischen Chemie. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 36: Gallium. 26 x 18 cm.; pp. xviii + 100. Berlin: Verlag Chemie, 1936. Price: 13.87 RM.

Previous to 1915 gallium was so rare as to be of little general interest. It was then found to occur in zinc distillation residues, and more recently it has been extracted from Mansfeld copper residues. Metallic gallium has been used for thermometer filling, since it is easily superfused and has a high boiling point. Gallium vapor-discharge lamps show some promise, and gallium compounds have been used as catalysts and in medicine. A comprehensive survey of the chemistry of gallium from the modern standpoint is provided by the present volume, which deals also with the physics of the metal and its compounds. The doubtful compounds are clearly distinguished from those whose existence is well established, and this critical attitude is one of the most valuable features of the handbook as a whole.

J. R. Partington.

Gmelins Handbuch der anorganischen Chemie. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 37: Indium. 26 x 18 cm.; pp. xviii + 116. Berlin: Verlag Chemie, 1936. Price: 15.75 RM.

The uses of indium so far proposed include alloys with tin and gallium for high temperature thermometers, plating or alloying with silver, dental amalgams, and in the form of compounds for coloring glasses and in medicine. A drawback to its applications is its great rarity and high price. Indium occurs in most zinc blendes and in some other minerals and in metallurgical products. It is found in marked amount (0.01 per cent) in tin and in some rare tin ores. The present volume deals very comprehensively with the occurrence, extraction, and purification of indium, the various sources being covered exhaustively from the point of view of the literature. The properties of the metal are fully discussed, including the nuclear transformations of the atom and the spectra. The analytical chemistry of indium is dealt with. Indium alloys are described, with phase rule diagrams. The compounds of indium are described. The existence of a gaseous hydride is considered improbable and only the oxides In_2O, InO, and In_2O_3 are regarded as individuals. The halogen compounds include the three chlorides, $InCl$, $InCl_2$, and $InCl_3$. Other compounds are the sulfides and sulfates and the interesting acetylacetonate, $In(C_5H_7O_2)_3$. The volume contains a very thorough review of the literature and some previously unpublished communications. It constitutes a valuable monograph on indium.

J. R. Partington.

Gmelins Handbuch der anorganischen Chemie. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 59: Eisen. Teil D. Magnetische und elektrische Eigenschaften der legierten Werkstoffe. 26 x 18 cm.; pp. xviii + 466. Berlin: Verlag Chemie, 1936. Price: 57.75 RM.

The present volume extends the series already published on iron by a very full and up-to-date account of the magnetic and electrical properties of ferrous alloys, many of which are of great technical importance. It is richly provided with tables and curves. Some sections which may be singled out for special mention are those dealing with silicon-iron, silicon-carbon steels, chromium and molybdenum steels, nickel steels ("permalloy"), cobalt steels, and the modern cobalt-nickel steels ("perminvar"). Some of these are closely associated with modern permanent magnet construction and cable transmission. In all cases the magnetic and electric properties are discussed according to a definite plan, so that it is easy to find what is required from the table of contents. The literature used extends far beyond chemical journals, and the volume is one which will be of great service not only to chemists and physicists but also to electrical engineers and metallurgists. At the head of each of the larger sections is a general bibliography including books and review articles, and the literature throughout is truly international, American and Japanese workers being well represented. The subject is critically treated and attention is often drawn to errors detected in the literature used. The curves have also often been redrawn in a more useful form. At the end is a general survey of the whole subject, especially from the point of view of technical uses, and a brief summary of the alloy systems in a series of tables.

J. R. PARTINGTON.

Chemiker-Taschenbuch. Ein Hilfsbuch für Chemiker, Physiker, Mineralogen, Hüttenmänner, Industrielle, Mediziner und Pharmazeuten. Als Chemiker-Kalender begründet von R. BIEDERMANN, fortgeführt von W. A. ROTH, herausgegeben von I. KOPPEL. 58 Auflage in drei Teilen. 15 x 9 cm.; iv + 495 + vi + 616 pp. Berlin: Julius Springer, 1937.

The *Chemiker-Kalender*, which now appears under a new name in one volume, is too well known to require detailed description. It contains a full series of tables of the properties of inorganic and organic compounds, sections on analysis, accounts of the latest developments in chemistry, including atomic structure, and concise but comprehensive monographs on a variety of subjects, including the important parts of physical chemistry. Among the new additions are sections on vapor pressures of condensed gases and organic liquids, dielectric constants, and latent heats of fusion. Each section is written by a specialist. The book is one which should be in every chemical laboratory, for it could almost take the place of a whole library. The book, which is very handy in size and unusually well printed in very small but extremely clear type, will appeal to physical chemists, since it not only covers the field of older discoveries but also takes in very modern developments, both in descriptive articles and in critical collections of numerical data.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 23: Ammonium. Lieferung 2. Verbindungen bis Ammonium und Kalium. Hydrazonium. Hydroxylammonium. 26 x 18 cm.; pp. xviii + 243-602. Berlin: Verlag Chemie, 1936. Price: 44.25 RM.

This volume continues the chemistry of ammonium and includes compounds (also oxy-salts) with sulfur, selenium, tellurium, boron, carbon, cyanogen compounds, formate, acetate, oxalate, and tartrate, compounds with silicon, phosphorus, arsenic, antimony, bismuth, lithium, sodium, and potassium, and the technical production of ammonia and ammonium salts. At the end are sections on salts of hydrazine and hydroxylamine. The treatment on the purely chemical side is on the whole entirely satisfactory, although the technically important question of the oxidation of ammonium sulfite and that of the conversion of ammonium carbamate into urea could with advantage have been dealt with in greater detail. The excuse that technical details are incompatible with the scope of the work will not hold, since in other volumes dealing with metals great attention has been paid to this side of the subject, and some are for all purposes treatises on metallurgy. The discussion of the sulfates includes an account of the double salts of ammonium sulfate and ammonium nitrate, and a summary of the researches on the explosive properties of Leunasaltpeter after the disastrous explosion at Oppau. It appears that the salt can be exploded by violent detonation, the explosibility falling rapidly with increase of cubic density.

The section on the technical production of ammonium salts is too brief, occupying only ten pages, although it is perhaps the best short survey available. It is true that ammonia synthesis has been fully dealt with in a previous volume and that the authors give some reasons for the very brief treatment, yet the reviewer feels that many readers will be disappointed by the sketchy character of the text, as compared with the exhaustive detail given in other volumes on purely physical properties of little chemical interest. For example, although the recovery of by-product ammonia is treated, there is no mention of the very important question of purification, particularly from pyridine. The reviewer thinks attention should be drawn to this tendency to limit the purely chemical side at the expense of the physicochemical, or even of pure physics, and to express the opinion that it is not advantageous to the work. He has, before expressing this opinion, read the justification given by the authors for their procedure.

J. R. PARTINGTON.

Enzyme Chemistry. By HENRY TAUBER. 15 x 23 cm.; xii + 241 pp.; 28 figs. New York: John Wiley and Sons, Inc., 1937. Price: $3.00.

The fact that most physical chemists are interested in the phenomena of catalysis and that enzymes are probably the most important catalysts known to the chemist justifies a brief review of this volume in a journal devoted to physical chemistry.

The author defines enzymes as "catalysts which are produced by the living cell, but whose action is independent of the living cell, and which are destroyed if their solutions are heated long enough." He adds that there are two other classes of biochemical catalysts which he does not classify as enzymes. In one class he places those "catalysts produced by the living cell, active *in vitro* as well as *in vivo*, their activity, however, depending upon the unimpaired cell. They are destroyed on heating and their activity ceases on mechanical destruction of the cell. Examples: the catalyst affecting the synthesis of urea in the liver, and the dehydrogenetic function of certain bacteria."

In the third class he places those "catalysts elaborated by the living cell, their action being independent of the living cell. They are not destroyed when their solutions are heated. Examples: glutathione, ascorbic acid."

In the preface the author frankly states that he makes no claims to have exhaustively dealt with the subject of enzyme chemistry or to have duplicated material available in earlier monographs. Instead he desires to present some of the more recent advances in the field. In this respect the reviewer feels that he has been very successful and that the prospective reader may safely purchase this volume; by perusing it he will become familiar with the direction of modern thought in explaining enzyme phenomena and with what has been achieved in the chemistry of enzyme reactions.

The volume is divided into eleven chapters, as follows: Introduction and General Considerations; Esterases; Proteolytic Enzymes and Peptidases; Amidases; Carbohydrases; Catalase; Oxidizing Enzymes; The Flavin Oxidation System; The Zymase Complex and Alcoholic Fermentation; Carbonic Anhydrase; and Luciferase. Complete citations, including titles of papers, are given to 796 literature sources. The text, in conjunction with these references, makes the volume well adapted for an advanced course in enzyme chemistry, supplemented, of course, with other material which the lecturer would provide. For those whose fields lie outside of enzyme chemistry it affords an excellent prospective of recent trends and advances in the subject.

ROSS AIKEN GORTNER.

Praktische Einführung in die physikalische Chemie. Erster Teil: Moleküle und Kräfte. By KARL LOTHAR WOLF and HANS-GEORG TRIESCHMANN. 22 x 14 cm.; viii + 114 pp. Braunschweig: Vieweg & Sohn, 1937. Price: unbound, 4.50 M.

This introduction to practical physical chemistry, of which the present volume forms the first part, is planned for the future advance of the science. A wide interpretation is given to chemistry. The text is divided into theory, exercises based thereon, partial experiments (being either short tests or allusions to fuller investigations for which references are given to well-known textbooks), and actual work to be carried out. The experiments in the last category, of which there are forty-four, include, in addition to the usual routine of practical physical chemistry, the determination of the characteristics of a valve, the photography of Raman spectra, extinction coefficients, para- and dia-magnetism, and measurement of the viscosity of gases. Thus the treatment of the subject is novel and opens up new ground; it would bewilder the average student who used it as a start for his work, but it should prove interesting and serviceable to those with more mature knowledge.

W. H. PATTERSON.

Katalytische Umsetzungen in homogenen und enzymatischen Systemen. By W. FRANKENBURGER. 444 pp. Leipzig: Akademische Verlagsgesellschaft, m.b.H., 1937. Price: 36 RM.

A little more than a hundred years ago Berzelius (1835) introduced the word "catalysis" and defined a catalyst as a substance which affects the rate of a reaction without occurring in the stoichiometric equation. It is a tribute to Berzelius' vision that this definition, presented at a time when nothing was known of the kinetics and mechanism of catalytic reactions, still holds at present.

Frankenburger's book reviews our past and present knowledge of homogeneous and microheterogeneous catalysis. It includes an introduction of 55 pages, in which, after a short historical development, a modern review of reaction kinetics is given. Homogeneous catalysis (in gaseous and liquid phases) constitutes the main bulk of the book, and the last 100 pages are devoted to enzymatic reactions which are of primary importance in biology.

Considering the wide field covered, the book is of interest not only to chemists, but also to biologists. The book is outstanding regarding the kinetics of the various reactions, which are presented in a modern fashion and can be understood by readers who have no mathematical background. A great number of catalytic reactions are discussed in detail, and numerous references to the literature are found. On the other hand, one misses a comprehensive treatment of our present views of certain particular subjects. Acid-base catalysis (100 pages), for example, cannot be well understood without a modern picture of acidity and basicity in general, and particularly of the medium effect. In this part one also looks in vain for a discussion of Hammett's "acidity function" and its usefulness in the kinetic analysis of various acid-base catalyses. In the discussion of oxidation-reduction catalysis no mention is made of a selection on the basis of free energy relations of substances which may have a catalytic effect.

In spite of these limitations the book is strongly recommended to those interested in catalysis from the chemical or biological viewpoint.

I. M. KOLTHOFF.

Vakuumspektroskopie. By H. Bomke. 22 x 14 cm.; x + 248 pp. Leipzig: J. A. Barth, 1937. Price: 17.70 RM.; bound, 19 RM.

Although the vacuum spectrograph has played a very important part in problems of analysis of both atomic and molecular spectra, Lyman's *Spectroscopy of the Extreme Ultra-violet* is the only book that has hitherto dealt exclusively with this subject. When the second edition of that well-known monograph appeared in 1928, the region first penetrated to 1250 A.U. by Schumann with a fluorite spectrograph had been extended to about 500 A.U. by Lyman and to 136 A.U. by Millikan and Bowen with concave gratings at normal incidence. At that time, too, Thibaud and Hoag had used gratings (plane and concave, respectively) at grazing incidence, an arrangement which had previously been used by A. H. Compton for x-rays only, and which has advantages over the normal-incidence mounting in regard to compactness, intensity, and dispersion; they did not succeed, however, in reaching Millikan's 136 A.U. limit. Working from the soft x-ray side and using glass gratings (plane and concave, respectively) at grazing incidence, Thibaud and Osgood had extended the upper limit of wave-length measurements, and Osgood's observations had closed the gap between x-ray and optical wave lengths. It is since the appearance of Lyman's second edition, however, that the most rapid progress has been made. In 1929 Ericson and Edlén, working in Siegbahn's laboratory at Uppsala, announced their first results on the measurement and interpretation of very short wave lengths emitted by highly ionized light atoms. Since then grazing-incidence grating technique has been further improved, and the apparent optical limit is now about 30 A.U. (Edlén, 1936).

Bomke's connected account of all this work is welcome; no worker in the extreme ultra-violet can afford to be without it. About one half of the book describes the instruments and methods employed, and most of the other half deals with the results obtained. The treatment of atomic spectra is fuller and much better than that of molecular spectra. The tables include Edlén's standard wave lengths between 1371 and 160 A.U., and the ground states and ionization potentials of all the atomic emitters; the latter table will be found particularly useful, but could be set out in a rather more compact and instructive form involving less printing of spectroscopic notation. Not the least valuable feature of the book is a list of 626 references.

W. Jevons.

Anschauliche Quantentheorie. By P. Jordan. 24 x 17 cm.; xii + 320 pp. Berlin: J. Springer, 1936. Price: 12 RM.

This book is an important contribution to the literature, coming as it does from such a well-known worker on various aspects of the quantum theory. It may perhaps be doubted, in spite of its fundamental importance, if it is the kind of book which is likely to attract the attention of the average physical chemist.

It is a very different type of work from that of Pauling and Wilson, for example, where a successful effort was recently made to transmit to the experimental chemist and physicist the technique involved in the working out of applications of the theory.

Dr. Jordan's book is concerned much more with the skeleton, the bones, and sinews of the quantum theory itself than with its applications. His book is divided into five chapters, the first of which contains a very clear account of the fundamental experiments of quantum physics. This is followed by an equally clear theoretical analysis of these experiments; Schrödinger's equation is not in fact dealt with until page 110. The third chapter is rather hard going and deals with quantum and wave mechanics in some detail; this part of the book involves discussion of matrices and statistical transformation theory. The fourth chapter is concerned with many-body problems and elementary particles. Finally there is a somewhat philosophical chapter on the relation between atoms and organisms.

To those with the necessary mathematical and physical background this will certainly prove a most interesting book.

In view of the title the average reader may perhaps be pardoned for thinking that Dr. Jordan's perceptions are more than usually acute.

J. T. RANDALL.

Blätter für Geschichte der Technik. Herausgegeben von Österreichen Forschungsinstitut für Geschichte der Technik. Heft 3. 25 x 18 cm.; 101 pp.; one plate. Vienna: Julius Springer, 1936. Price: 3.60 RM.

This number contains a biography of the inventor of the Kaplan turbine, an account of the Welsbach exhibition in Vienna in 1936, a bibliography of the history of Austrian industrial firms, and other matter.

J. R. PARTINGTON.

Thermodynamic Theory of Affinity. By TH. DE DONDER and PIERRE VAN RYSSELBERGHE. xx + 141 pp.; 4 fig. Stanford University, California: Stanford University Press, 1936. Price: $3.00.

We quote from the preface: "In presenting to the English-speaking physical chemists the thermodynamic theory of affinity, we are convinced that this synthetic work will be of definite usefulness to them. The systematic application of the various concepts upon which the theory is based (degree of advancement of the reaction, uncompensated heat, affinity considered as a function of the instantaneous state of the system, etc.) should not only result in greater formal clarity in the discussion and interpretation of experimental results but should also lead to new developments in fields where a particularly accurate thermodynamic treatment is required."

The reviewer does not believe that the high hopes expressed by the authors will be completely fulfilled; he can, however, recommend the book to the attention of advanced students of thermodynamics.

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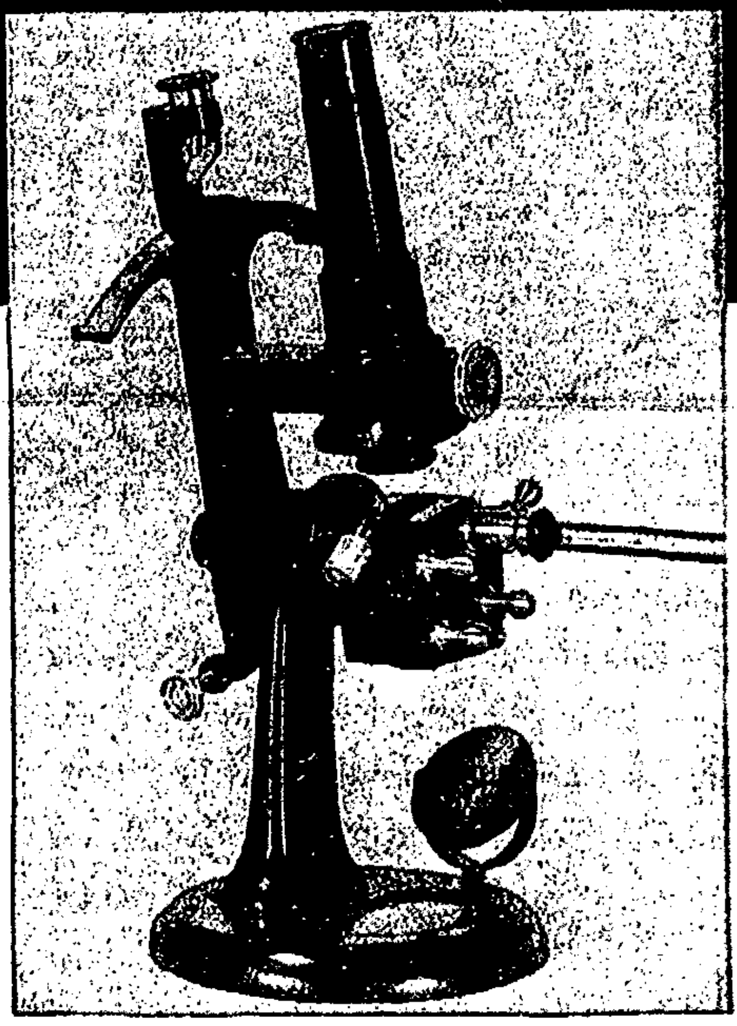

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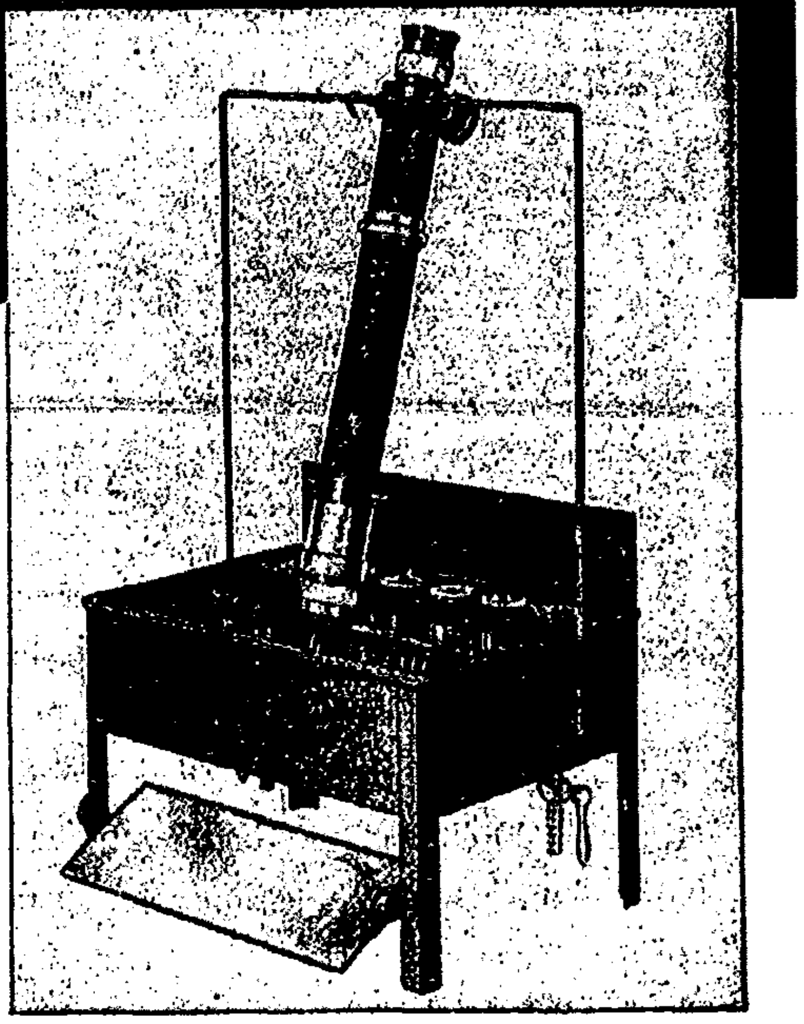

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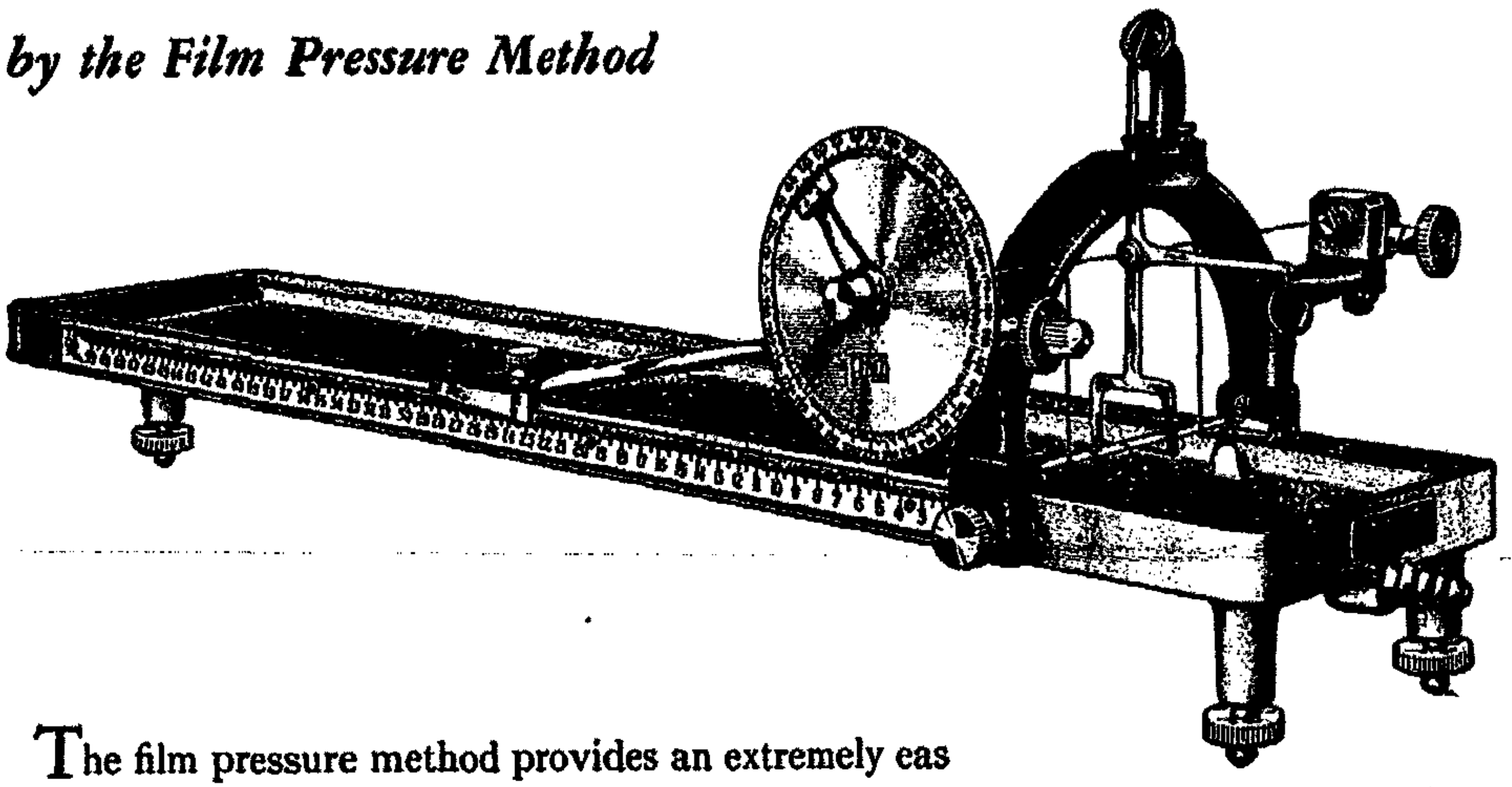

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AN X-RAY DIFFRACTION STUDY OF THE ACTION OF LIQUID AMMONIA ON CELLULOSE AND ITS DERIVATIVES

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Department of Chemistry, University of Illinois, Urbana, Illinois

Received February 20, 1937

INTRODUCTION

The mercerizing action of sodium hydroxide on cellulose has been long known. Hess and coworkers (15, 24, 11, 13, 26), Schramek (22, 23), and others (18, 4, 5, 17, 20, 21) have studied in detail the addition compounds of cellulose and sodium hydroxide; even a 9 per cent solution will form an addition compound. In contrast to the vast amount of work which appears on the action of sodium hydroxide there is none on the action of ammonium hydroxide, and only two papers have appeared as yet on the action of liquid ammonia on cellulose.

Trogus and Hess (25) have studied the action of hydrazine, ethylenediamine, and tetramethylenediamine on cellulose. Apparently a compound is formed in each case, as the x-ray pattern goes through the same transition as in acetylation, where the reaction is of the micellar heterogeneous type and the pattern of the reaction product does not show until half of the material is acetylated. This same type was found with the diamines, and a pure pattern obtained when the ratio of diamine to glucose residue was 1:1. On treating these reaction products with water the original materials, native or mercerized cellulose, were obtained. According to Katz (14), such swelling would be called permutoid-intramicellar swelling combined with compound formation between swelling agent and cellulose.

Barry, Peterson, and King (2) found the same type of swelling in cellulose by the use of liquid ammonia. Though they found maximum swelling when the ratio of NH_3 to C_6 groups was 1:1, the ammonia evaporated immediately on removal of the fibers from the liquid ammonia bath unless a thin protective coating was used, i.e., light paraffin oil. If the ammonia complex was immediately put into water, dilute acetic acid, or ammonium hydroxide, native cellulose was regenerated, but if mercerized cellulose was used as starting material the regenerated product gave an x-ray diagram too diffuse to permit interpretation.

If the ammonia was allowed to evaporate spontaneously or on heating,

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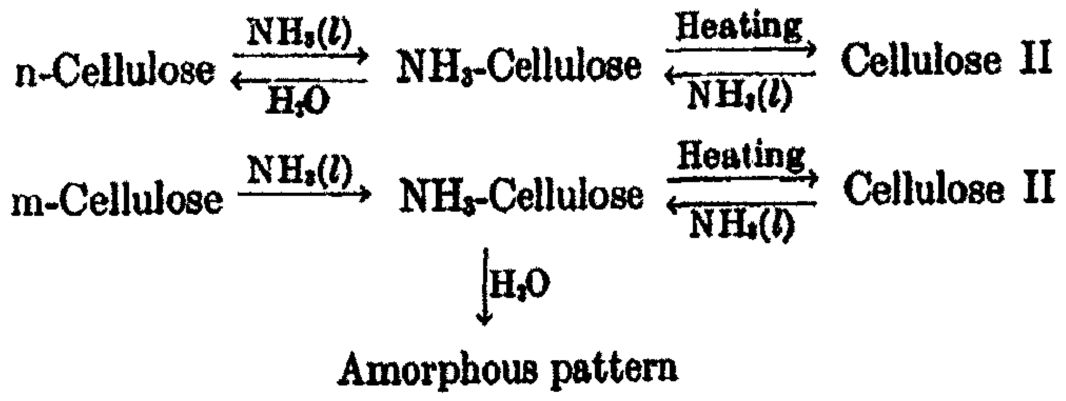
[1] *Textile Foundation Fellow.*

a third x-ray pattern was obtained. At first glance it looked much like that of mercerized cellulose, but further study showed that only one diffraction spot appeared for 002 and 10$\bar{1}$ planes. This material, which they designated as cellulose II, could also be obtained from mercerized cellulose. Though the patterns were identical the materials were not, as the reverse process gave different products. A summary of the course of reaction is:



$$\text{n-Cellulose} \underset{H_2O}{\overset{NH_3(l)}{\rightleftarrows}} NH_3\text{-Cellulose} \underset{NH_3(l)}{\overset{\text{Heating}}{\rightleftarrows}} \text{Cellulose II}$$

$$\begin{tikzcd} \text{m-Cellulose} \arrow[r, "NH_3(l)"] & NH_3\text{-Cellulose} \arrow[r, shift left, "\text{Heating}"] \arrow[d, "H_2O"] & \text{Cellulose II} \arrow[l, shift left, "NH_3(l)"] \\ & \text{Amorphous pattern} & \end{tikzcd}$$

These authors also determined the space lattice of both the complex and the new modification, cellulose II. The main differences are: (1) the angle β from 84° in native and 62° in mercerized cellulose changed to 53.5° in the complex and 58° in cellulose II, and the interplanar distance of 101 planes changed from 6.28 A. U. in native and 7.7 A. U. for mercerized cellulose to 8.88 A. U. in the complex and 7.9 A. U. in the new modification.

Hess and Trogus (12) immediately published a note on the work that they had already done on the action of liquid ammonia on cellulose. They found no appreciable swelling, in contrast with the work of Barry, Peterson, and King (2), who noticed considerable swelling. On distilling the ammonia, the fibers were identical in appearance with the original, but the x-ray pattern compared favorably with Barry's swollen ammonia-cellulose. If the new modification, which Hess and Trogus designated as cellulose III, was treated with concentrated aqueous ammonia the pattern they obtained was identical with that of mercerized cellulose, with the exception that the 101 planes had a value of 8.90 A. U. instead of 7.4 A. U. If cellulose III was treated with methanol, a pattern was obtained which matched Barry's cellulose II. In no case were they able to get the original material from cellulose III.

In view of these many obviously contradictory statements, it was decided to repeat all of the above work. If the ammonia is so easily lost, there ought not to be any compound formation, and also it should be possible to follow the change in the interplanar distance of the 101 planes as the ammonia evaporates. If both native and mercerized cellulose give the same ammonia complex and the same new modification, then on retracing the steps only one product should be obtained from the complex.

If the new modification is as stable as the above authors believe, then its reactions with various chemicals should be examined. Will it give the mercerized form on treatment with 20 per cent sodium hydroxide? Will it give the same acetates on treatment with the usual acetylating agents? Is it more susceptible to intramicellar swelling than native and mercerized cellulose, as Hess and Trogus claim? Can mercerized cellulose be converted to native cellulose through these intermediates?

EXPERIMENTAL

A Philips Metalix, copper target, x-ray tube was used operating at 28 kv. and 25 ma. For patterns of the ammonia complex a specimen-to-plate distance of 3 cm. and an exposure time of one hour were used. For the study of the reactions of the third modification, which we shall call cellulose III in agreement with Hess and Trogus, a specimen-to-plate distance of 5 cm. and exposure times of three to five hours were used. The x-ray beam was defined by a pinhole system of 0.030-in. and 0.025-in. pinholes, 6 cm. apart.

Samples of native and mercerized cellulose (with x-ray patterns shown in figures 1 and 2) in the form of bundles of ramie and cotton were immersed in liquid ammonia at a temperature of −75°C. for varying lengths of time On removal from the liquid ammonia they were immediately placed in paraffin oil cooled to a very viscous state by the use of liquid air. After a few minutes the bundle of fibers was removed, and the excess paraffin oil removed by the use of filter paper. These samples were immediately x-rayed (figure 3). The fibers increased in diameter about threefold immediately after immersion in the liquid ammonia. When the sample was ready for x-raying it had about normal size, since much of the ammonia escaped in spite of the paraffin oil. Samples were taken from one hour to ten months after treatment, in order to study the effect of time on this reaction if it is such.

Other samples treated with liquid ammonia in the same manner were not treated with paraffin oil, but were allowed to stand in air for a few minutes and then immediately x-rayed.

Still other samples were removed from the liquid ammonia and immediately placed in water, dilute and concentrated acetic acid, and concentrated ammonium hydroxide (28 per cent); after a few minutes they were removed, dried, and subjected to x-ray analysis.

Samples of cellulose III were boiled with water for three to fifteen hours, treated with glacial acetic acid for twenty-four hours, treated with concentrated aqueous ammonia for several days, dried at 105°C. for two weeks, allowed to stand in air for a year, treated with chloroform, treated with 20 per cent sodium hydroxide for fifteen minutes, washed, and dried; after these varied treatments the samples were then x-rayed.

Cellulose III was acetylated at 55°C. and 100°C. by the method of Hess and Trogus (10, 8, 9, 27, 7), using acetic anhydride and sulfuric acid as a catalyst. Benzene was used at the lower temperature as a diluent, and toluene at the higher temperature. The acetates were obtained in the form of the original fibers in most cases, although serious disintegration had already taken place in most of the samples at higher temperatures. The

Fig. 1

Fig. 2

Fig. 1. Diffraction pattern for native ramie. Copper radiation. Specimen-to-plate distance, 3 cm.

Fig. 2. Diffraction pattern for mercerized ramie dried under tension

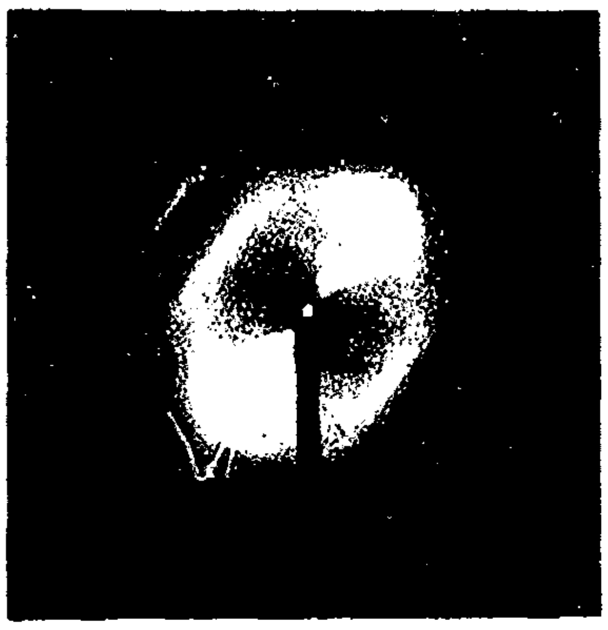


Fig. 3

Fig. 4

Fig. 3. Diffraction pattern for ammonia-cellulose

Fig. 4. Diffraction pattern for cellulose III

following materials were acetylated: native cellulose, mercerized cellulose, and cellulose III from both native and mercerized cellulose. Samples were taken from time to time during the course of the reaction for x-ray study, and also analyzed for acetic acid content by the following method, which is a modification of most of the methods reported in the literature (16, 3, 1, 19, 6): A 0.5-g. sample of the dried purified fibers was suspended in 25 cc. of alcohol and an excess of standard sodium hydroxide (50 cc. of 0.15 *N* solution) was added and the mixture allowed to stand overnight at 35°C. An excess of standard acid was added with a drop or two of phenolphthalein solution, and allowed to stand several hours after the pink color had disappeared from the fibers. The solution was then poured off and titrated. The fibers were washed thoroughly, and the washings were added to the solution to be titrated.

X-ray patterns were taken of the saponified fibers to determine the modification of cellulose present.

Samples of commercial cellulose triacetate and cellulose "triester" (monobutyl diacetate) were treated with liquid ammonia for a week. During this time the solution slowly formed a thick gel, after which the ammonia was allowed to evaporate and the residue extracted with water. The residues were then x-rayed. Samples of the gel were also x-rayed before the evaporation of the gel and also after evaporation of the ammonia.

DISCUSSION OF RESULTS

X-ray patterns showed that it was necessary to have some kind of a protective coating in order to keep the ammonia in the fiber. Collodion did not help, and a small cell with mica windows gave no better results. When cold paraffin oil (–70°C.) was used, most of the ammonia escaped at once and the cross-sectional diameter decreased to almost the original size, but appreciable swelling of the 101 plane was found in the x-ray pattern. Table 1 gives a comparison of the patterns obtained in this work with that of Barry, Peterson, and King (2). It will be noticed at once that in general most of the spacings agree, but the most striking difference is in the value of the 101 plane, which Barry and coworkers listed as 8.88, while in this work a value of 10.3 A. U. was found. Exposures of five to twelve hours were used by Barry, Peterson, and King (2), while in this work only an hour was necessary to get a good pattern, and three hours gave a pattern in which the very weakest interferences could be measured.

With the idea in mind that a sample could lose enough ammonia during such long exposures, a series of patterns were taken on the same sample after different lengths of time. Table 2 shows the progressive change in 101 planar distance as the ammonia evaporated.

From table 1 it is seen that Barry and his coworkers obtained only a value of 8.9 A. U. when their exposures were of the order of ten hours. Table 1 also shows that maximum swelling did not take place at a concentration such that the ratio of NH_3 to C_6 group was 1:1, but that the entire process was continuous and only a case of intermicellar swelling. Mercerized cellulose, treated in the same manner with ammonia, gave a pattern identical with that from native cellulose.

TABLE 1

Ammonia-cellulose

INTERFERENCE	BARRY AND COWORKERS		THIS WORK	
	A. U.	Intensity	A. U.	Intensity
A_1	8.86	vs	10.3	s
A_2	4.473	ms		
A_3	4.467	vvs	4.57	s
A_4	4.049	vs	3.83	w
A_5	3.27	vw	3.10	w
A_6			2.48	ww
A_7	2.247	w	2.28	w
I_1	4.12	vw		
I_2	2.383	vw	2.50	ww
II_0	5.141	s	5.15*	s
	5.158	ms		
II_1	4.50	vw	4.51	w
II_2	3.38	ms	3.37	ms
II_3	3.17	w		
III_0			3.37	ms
III_1	3.225	ms	3.27	ms
III_2	2.673	vw	2.70	w
IV_0	2.545	m	2.54	ms
IV_1			2.26	w
V_0			2.02	w

* Used as standard to determine accurately the specimen-to-plate distance.

TABLE 2

Progressive change in 101 planar distance as the ammonia evaporated

TIME	INTERPLANAR DISTANCE IN ÅNGSTRÖM UNITS	
	101 Plane	$10\bar{1}$ and 002 Planes
Immediately	10.3	4.57
After 3 hours	9.8	4.53
After 8 hours	8.85	4.47
After 21 hours	8.06	4.42
After 45 hours	7.70	4.40
Cellulose III	7.55	4.30

If the swollen ammonia-cellulose from native cellulose was immediately placed in concentrated aqueous ammonia the pattern obtained was that of native cellulose, which is in agreement with the results of Barry and coworkers and in opposition to those of Hess and Trogus, who found no such reversion. If mercerized cellulose was the original material the reversion was not so complete,—the pattern showing a combination of about 70 per cent hydrate and 30 per cent cellulose III, as determined from relative intensities of the superposed interferences. Barry and coworkers obtained a pattern too diffuse to measure.

If the ammonia-swollen native cellulose was treated with water immediately a pattern was obtained which consisted of equal amounts of native cellulose and cellulose III, while if mercerized cellulose was used the somewhat ill-defined pattern was that of cellulose III. If, instead of water, dilute acetic acid was used the reversion was even less: native, 30 per cent; cellulose III, 70 per cent; and hydrate, 0 per cent; cellulose III, 100 per cent. Barry and his coworkers found complete reversion in the case of native cellulose, even in the case of dilute acetic acid, dilute ammonia, and water. Hess and Trogus found no reversion in any case.

If no protective coating for the fibers was used the pattern was essentially that of cellulose III with the interplanar distance of the 101 planes about 8.0 A. U., showing that a small amount of ammonia had been retained. On further standing or heating in an oven at 105°C. cellulose III was obtained (figure 4). Mercerized cellulose gave the same pattern after this treatment.

Table 3 gives a comparison of the data of Barry and his coworkers (2), of Hess and Trogus (12), and of the present work.

On treating cellulose III from native cellulose with concentrated aqueous ammonia for twelve hours, the x-ray pattern showed about 40 per cent native and 60 per cent cellulose III. If the original material was mercerized cellulose, there was practically no reversion.

After boiling cellulose III from both sources in water for fifteen hours some reversion took place, the patterns indicating, respectively, 40 per cent native cellulose and 60 per cent cellulose III, and 10 per cent mercerized cellulose and 90 per cent cellulose III. When these samples were further treated with aqueous ammonia, the reversion was increased about 5 to 10 per cent. If cellulose III was treated with glacial acetic acid, no changes could be detected on the x-ray pattern. Barry, Peterson, and King found no changes whatsoever on treating cellulose III with dilute acetic acid or concentrated ammonium hydroxide, or on baking it at 105°C.

When cellulose III was treated with 20 per cent sodium hydroxide (mercerizing strength) for fifteen minutes and then the sodium hydroxide was completely washed out, the pattern obtained was that of mercerized cellulose. This definitely shows that cellulose III is a metastable form, as is native cellulose.

From a study of the acetylation of cellulose III, it was found that the acetate produced was identical with that obtained from native and mercerized cellulose. The most important factors influencing the rate of acetylation are the amount of swelling prior to acetylation and the amount of catalyst used. If the fibers were not pretreated for several days with water or acetic acid, acetylation did not proceed. If a very small amount of sulfuric acid was used as a catalyst, the reaction did not proceed to completion.

The course of acetylation was followed in every case and all the curves were similar.

TABLE 3

Cellulose III

INTERFERENCE	BARRY AND COWORKERS		HESS AND TROGUS		THIS WORK	
	"d"	*Intensity*	"d"	*Intensity*	"d"	*Intensity*
A_1	7.55	s	8.90	s	7.48	s
A_2	4.30	vvs	4.45	vs	4.31	vs
A_4	3.78	vw	4.17	ms		
A_5	3.40	m				
A_6	2.89	w				
A_7	2.48	vw				
A_8	2.24	vw			2.25	vw
I_1	3.99	vw				
I_2	3.23	vw				
I_3	2.73	vw				
I_4	2.45	m			2.38	vvw
II_0	5.14	vs			5.15*	s
II_1	4.43	s			4.47	ms
II_2	4.28	s				
II_3	3.33	vw			3.34	w
II_4	3.03	vw				
II_5	2.84	vvw				
III_1	3.17	ms			3.26	ms
III_2	2.68	mw			2.59	w
III_3	2.55	vw				
III_4	2.06	vw			2.25	vw
IV_0					2.54	w
IV_1	2.43	vw				
IV_2	2.21	vw			2.25	vw
V_0						

* *Used as standard to determine accurately the specimen-to-plate distance.*

The main difficulty in analyzing the acetate fibers for acetic acid content was the fact that the fibers held the excess sodium hydroxide very tenaciously, but this was eliminated by adding an excess of acid and allowing to stand for a few hours. The acid was very easy to wash out. With the strength of alkali used it was necessary to have alcohol present and to maintain the material at a temperature above 30°C. for complete saponification.

Two forms of acetates were produced, which are the low- and high-temperature forms, respectively. These modifications are dependent not on the original cellulose but on the diluent and the temperature of the acetylation process. On saponification with $0.1N$ alcoholic sodium hydroxide the low-temperature form yielded a rather diffuse native cellulose pattern with the A_3 and A_4 interferences of equal intensity, showing that there has been some mercerizing effect. The high-temperature form or acetate II on saponification always gave the mercerized structure. These facts are all in agreement with the vast amount of work done in this field by Hess and coworkers (10, 8, 9, 27, 7).

If the acetates were treated with liquid ammonia a clear solution was obtained which gelled on standing for several days. A pattern of this gel agrees very well with ammonia-swollen cellulose. On evaporation of the ammonia, cellulose III was obtained. Therefore the acetate had been saponified by the liquid ammonia.

SUMMARY

1. An x-ray pattern of cellulose swollen with liquid ammonia was obtained.
2. The increase in size of the 101 interplanar distance was much greater than reported by previous workers.
3. A study of the decrease in size of the 101 plane was made as the ammonia evaporated.
4. The swollen ammonia-native cellulose may be completely reverted to native cellulose by treatment with concentrated aqueous ammonia. The swollen ammonia-mercerized cellulose was only 70 per cent reverted.
5. Slow evaporation of ammonia from the swollen cellulose gave a new modification of cellulose,—cellulose III.
6. The action of heat, dilute and concentrated ammonia, acetic acid, and boiling water on cellulose III was studied. The material derived from native cellulose was easier to revert to its original state than that derived from mercerized cellulose.
7. Sodium hydroxide of mercerizing strength converted cellulose III from both sources to mercerized cellulose.
8. A study was made of the acetylation of cellulose III.
9. Commercial cellulose acetates are saponified by liquid ammonia.

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THERMODYNAMIC CONDITIONS AND EFFICIENCIES OF THE COUPLING OF CHEMICAL REACTIONS

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I. INTRODUCTION: GENERAL CONSIDERATIONS AND FORMULAS

In 1931 Burk (3) published in this journal a very interesting discussion of the thermodynamics of coupled reactions in biological systems. This fundamental subject has also been treated by several other authors. Very complete references can be found in the reviews published by Wilson and Peterson (8) and by Borsook (1).

In the present paper we wish to show how a considerable amount of elegance and clarity can be introduced into this subject through the use of the thermodynamic method recently expounded by De Donder and Van Rysselberghe (4), and how certain principles which have been suggested by Burk (3) and others can be exactly formulated.

We are dealing with irreversible simultaneous reactions for which the first and the second law of thermodynamics give us definite conditions valid for any infinitesimally small period of time dt. The differential dt is always positive:

$$dt > 0 \qquad (1)$$

Let us consider a system in which two simultaneous reactions are taking place:

$$0 = \sum_{\gamma} \nu_{\gamma 1} M_{\gamma} \qquad (2.1)$$

$$0 = \sum_{\gamma} \nu_{\gamma 2} M_{\gamma} \qquad (2.2)$$

The ν_{γ}'s are the stoichiometric coefficients of the various reactants and products; the M_{γ}'s their molecular masses. The ν_{γ}'s are positive for products, negative for reactants. Some of the components γ may appear in both reactions, but we may extend the summations to all chemical species present in the system by assigning the value zero to the coefficients ν_{γ} of the components which do not react.

Example: The reactions by which nitrate ion is reduced to ammonium ion by the alga *Chlorella* (5) can be represented by

$$\begin{cases} NO_3^- + 2H^+ + H_2O \rightarrow NH_4^+ + 2O_2 \\ \frac{1}{6}C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O \end{cases}$$

The only component appearing in both reactions is O_2, for which we have:

$$\nu_{O_2,1} = 2 \qquad \nu_{O_2,2} = -1$$

We also have:

$$\nu_{NO_3^-,1} = -1 \qquad \nu_{NO_3^-,2} = 0, \quad \text{etc.}$$

We consider the system as *closed.* It consists, therefore, of the total volume containing all the components taking part in the reactions (source of oxygen, which also contains the carbon dioxide produced, etc.).

During the time dt we have, according to the first law of thermodynamics,

$$dQ = dE + pdV \tag{3}$$

and, according to the second law,

$$dQ = TdS - dQ' \tag{4}$$

with

$$dQ' \geq 0 \tag{5}$$

dQ is the heat received, dE the increase in energy, p the external pressure, dV the increase in volume, dS the increase in entropy, and dQ' the uncompensated heat.

The affinities A_1 and A_2 of reactions 2.1 and 2.2 are defined by

$$A_1 = -\left(\frac{\partial G}{\partial \xi_1}\right)_{p,T} \qquad A_2 = -\left(\frac{\partial G}{\partial \xi_2}\right)_{p,T} \tag{6}$$

G being the total thermodynamic potential or free energy of the system, and ξ_1 and ξ_2 the degrees of advancement of the two reactions. We have

$$d\xi_1 = \frac{dn_{\gamma 1}}{\nu_{\gamma 1}} \qquad d\xi_2 = \frac{dn_{\gamma 2}}{\nu_{\gamma 2}} \tag{7}$$

and

$$dn_\gamma = \nu_{\gamma 1} d\xi_1 + \nu_{\gamma 2} d\xi_2 \tag{8}$$

dn_γ being the increase in the total number of moles of component γ. We have (4)

$$dQ' = A_1 d\xi_1 + A_2 d\xi_2 \geq 0 \tag{9}$$

Dividing by $dt > 0$ we get

$$\frac{dQ'}{dt} = A_1 \frac{d\xi_1}{dt} + A_2 \frac{d\xi_2}{dt} \geq 0 \tag{10}$$

Introducing the reaction velocities

$$\mathrm{v}_1 = \frac{d\xi_1}{dt} \qquad \mathrm{v}_2 = \frac{d\xi_2}{dt} \tag{11}$$

and placing

$$P = \frac{dQ'}{dt} \tag{12}$$

we obtain

$$P = A_1 \mathrm{v}_1 + A_2 \mathrm{v}_2 \geq 0 \tag{13}$$

The quantity P is the *power* of the system.

For a finite period of time Δt we have

$$Q' = \int_0^{\Delta t} (A_1 \mathrm{v}_1 + A_2 \mathrm{v}_2)\, dt \geq 0 \tag{14}$$

or

$$Q' = \int_0^{\xi_1} A_1 d\xi_1 + \int_0^{\xi_2} A_2 d\xi_2 \geq 0 \tag{15}$$

In biological systems the states may usually be regarded as constant over rather long periods of time. The affinities A_1 and A_2 being functions of the state are, therefore, also constant and formula 15 may be written

$$Q' = A_1 \xi_1 + A_2 \xi_2 \geq 0 \tag{16}$$

II. THERMODYNAMICS OF COUPLED REACTIONS: EXACT FORMULATION OF BURK'S "MACHINE EFFICIENCY" (THERMODYNAMIC EFFICIENCY)

Let us imagine that for some particular state of a system in which the above reactions are taking place we have

$$A_1 < 0,\ A_2 > 0,\ \mathrm{v}_2 > 0 \tag{17}$$

Formula 13 gives us

$$\mathrm{v}_1 \leq -\frac{A_2}{A_1} \mathrm{v}_2 \tag{18}$$

Division by $A_1 < 0$ requires the change in the sign of the inequality. The upper limit of v_1 is positive. We thus see that reaction 1 can take place in its unnatural direction with a velocity which cannot exceed the value $-\frac{A_2}{A_1}v_2$.

If we consider a long period of time for which the inequalities in 17 hold, we deduce from formula 16 that

$$\xi_1 \leq -\frac{A_2}{A_1}\xi_2 \tag{19}$$

Reactions 1 and 2 are independent, but we could also represent the chemical transformations taking place in the system by means of any two linear combinations of reactions 1 and 2. The corresponding affinities and the variables ξ would be similarly combined. Which set of reactions should one adopt?

In the study of biological systems the following choice is advisable: The *coupling* reaction describes the metabolism of the system, i.e., the combustion with oxygen of a certain metabolite. It should be written in such a manner that the reaction velocity is positive. This will be reaction 2 of our discussion. The *coupled* reaction should be written in such a manner that its velocity be positive and that the metabolite of the coupling reaction be neither a reactant nor a product.

Example: The combustion of hydrogen with simultaneous reduction of carbon dioxide by *Bacillus pycnoticus*, studied experimentally by Ruhland (5) and theoretically by Burk (3), is described by the following independent reactions:

$$\begin{cases} CO_2 + 0.931H_2O \rightarrow \frac{1}{6}C_6H_{12\times 0.931}O_6 + \frac{1.931}{2}O_2 \\ 2H_2 + O_2 \rightarrow 2H_2O \end{cases}$$

Hydrogen plays here the part of a metabolite; reaction 1 is written in such a manner that hydrogen does not appear in it. This system could also have been described by means of the following two sets of reactions

$$\begin{cases} 1.931H_2 + CO_2 \rightarrow \frac{1}{6}C_6H_{12\times 0.931}O_6 + H_2O \\ \frac{1}{6}C_6H_{12\times 0.931}O_6 + \frac{1.931}{2}O_2 \rightarrow CO_2 + 0.931H_2O \end{cases}$$

$$\begin{cases} CO_2 + 0.931H_2O \rightarrow \frac{1}{6}C_6H_{12\times 0.931}O_6 + \frac{1.931}{2}O_2 \\ \frac{1}{6}C_6H_{12\times 0.931}O_6 + \frac{1.931}{2}O_2 \rightarrow CO_2 + 0.931H_2O \end{cases}$$

in which the carbohydrate plays the part of the metabolite but also appears in reaction 1. Another possibility is the following:

$$\begin{cases} 1.931H_2 + CO_2 \rightarrow \frac{1}{6}C_6H_{12\times 0.931}O_6 + H_2O \\ 2H_2 + O_2 \rightarrow 2H_2O \end{cases}$$

Here again the metabolite H_2 appears in both reactions. The velocities of all these reactions are positive, and the affinity of reaction 1 is negative in each set.

If we had adopted the set

$$\begin{cases} 2H_2 + O_2 \rightarrow 2H_2O \\ \frac{1}{6}C_6H_{12\times 0.931}O_6 + \frac{1.931}{2}O_2 \rightarrow CO_2 + 0.931H_2O \end{cases}$$

the velocity of the second reaction would be negative, the affinity of the first one positive, and the set is seen to be equivalent to the first one above.

Adopting then the first set of reactions as the most suitable for a thermodynamic discussion, we get from Burk's data:

$$A_1\xi_1 = A_1\Delta n_c = -105{,}140 \times \Delta n_c$$

in which Δn_c represents the number of moles of $\frac{1}{6}$ $C_6H_{12\times 0.931}O_6$ synthesized, and

$$A_2\xi_2 = A_2\frac{\Delta n_{H_2}}{2} = 108{,}460 \times \frac{\Delta n_{H_2}}{2}$$

in which Δn_{H_2} represents the number of moles of H_2 consumed.

The absolute value of the ratio $\frac{A_1\xi_1}{A_2\xi_2}$ is what Burk calls the *machine efficiency*. It is important to realize that a significant efficiency can only be obtained if the reactions are written according to definite rules such as those adopted above.

In the present case one has

$$\frac{\xi_1}{\xi_2} = 0.231 \qquad \left|\frac{A_1}{A_2}\right| = 0.969$$

The "machine efficiency" is thus

$$\eta = -\frac{A_1\xi_1}{A_2\xi_2} = 0.224$$

An efficiency of 1.000 would correspond to a total Q' equal to zero. Further on we suggest replacing the term *machine efficiency* by *thermodynamic efficiency*.

III. STOICHIOMETRY OF COUPLED REACTIONS: EXACT FORMULATION OF BURK'S "SECOND-LAW EFFICIENCY" (STOICHIOMETRIC EFFICIENCY)

It seems fairly certain that coupling of a reaction with negative affinity by a reaction with positive affinity is possible only if at least one reactant or product is common to both reactions. Let i be this component. If i is produced in the coupled reaction, the condition for the maintenance of the coupling is that i be consumed in the coupling reaction. *Vice versa*, if i is consumed in the coupled reaction, it should be produced in the coupling reaction. In the case of *Bacillus pycnoticus*, oxygen is liberated in reaction 1 and consumed in reaction 2. This is also the case in the reduction of nitrate to ammonium by *Chlorella*.

In the synthesis of urea by liver tissues (2) carbon dioxide is produced in reaction 2 and absorbed in reaction 1:

$$\begin{cases} 2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O \\ \frac{1}{6}C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O \end{cases}$$

The transfer of energy from the coupling to the coupled reaction is then actually occurring through this common component.

According to a principle proposed by Burk (3) the amount of free energy or, better, of uncompensated heat Q' provided by reaction 2 which can actually be used by reaction 1 is given in our theory by

$$Q'_{2,1} = A_2\xi_1 \left|\frac{\nu_{i1}}{\nu_{i2}}\right| > 0 \tag{20}$$

in which ν_{i1} and ν_{i2} are the stoichiometric coefficients of the common component i in reactions 1 and 2. The uncompensated heat for reaction 1 is

$$Q'_1 = A_1\xi_1 > 0 \tag{21}$$

Burk's principle is then formulated as follows:

$$Q'' = A_1\xi_1 + A_2\xi_1 \left|\frac{\nu_{i1}}{\nu_{i2}}\right| \geq 0 \tag{22}$$

or, since ξ_1 is positive,

$$\left|\frac{A_1}{A_2}\right| \leq \left|\frac{\nu_{i1}}{\nu_{i2}}\right| \tag{23}$$

Coupling of reaction 1 with negative affinity A_1 by reaction 2 with positive affinity A_2 is thus possible only if the inequality in 23 is satisfied. If $\left|\frac{A_1}{A_2}\right|$ and $\left|\frac{\nu_{i1}}{\nu_{i2}}\right|$ happen to be equal, we have

$$Q'_1 + Q'_{2,1} = 0 \tag{24}$$

According to Burk we then have perfect reversibility, because the portion of Q'_1 which can be utilized by reaction 1 is actually entirely utilized. Such a coincidence occurs in the case of *Bacillus pycnoticus* for which we have:

$$\left|\frac{A_1}{A_2}\right| = 0.969 \qquad \left|\frac{\nu_{i1}}{\nu_{i2}}\right| = \frac{1.931}{2} = 0.966$$

The *second-law efficiency* introduced by Burk is defined as follows:

$$\eta = \left|\frac{A_1\nu_{i2}}{A_2\nu_{i1}}\right|$$

For *Bacillus pycnoticus* we have

$$\eta = \frac{0.969}{0.966} = 1.003$$

The total Q' is obviously larger than or equal to $Q'_1 + Q'_{2,1}$:

$$Q' \geq Q'_1 + Q'_{2,1} \tag{25}$$

or

$$A_1\xi_1 + A_2\xi_2 \geq A_1\xi_1 + A_2\xi_1\left|\frac{\nu_{i1}}{\nu_{i2}}\right| \tag{26}$$

We have, therefore, since ξ_2, ξ_1, and A_2 are positive:

$$\frac{\xi_2}{\xi_1} \geq \left|\frac{\nu_{i1}}{\nu_{i2}}\right| \tag{27}$$

Now, according to Burk's principle, coupling can only occur if

$$\left|\frac{A_1}{A_2}\right| \leq \left|\frac{\nu_{i1}}{\nu_{i2}}\right| \tag{28}$$

If coupling occurs, its extent is limited by condition 19:

$$\left|\frac{A_1}{A_2}\right| \leq \frac{\xi_2}{\xi_1} \tag{29}$$

The two conditions of occurrence and extent can be combined as follows:

$$\left|\frac{A_1}{A_2}\right| \leq \left|\frac{\nu_{i1}}{\nu_{i2}}\right| \leq \frac{\xi_2}{\xi_1} \tag{30}$$

In general only the inequality signs will hold:

$$\left|\frac{A_1}{A_2}\right| < \left|\frac{\nu_{i1}}{\nu_{i2}}\right| < \frac{\xi_2}{\xi_1} \tag{31}$$

Introducing the *machine efficiency* or *thermodynamic efficiency*

$$\eta' = \left|\frac{A_1\xi_1}{A_2\xi_2}\right| \tag{32}$$

and the *second-law efficiency* (Burk)

$$\eta'' = \left|\frac{A_1\nu_{i2}}{A_2\nu_{i1}}\right| \tag{33}$$

we may also write

$$\eta' < \eta'' < 1 \tag{34}$$

The portion

$$\eta' < 1 \qquad \text{or} \qquad \left|\frac{A_1}{A_2}\right| < \frac{\xi_2}{\xi_1} \tag{35}$$

of this general statement is a direct consequence of the second law and is unquestionable, since it is highly probable that the second law always applies to biological systems. The portion

$$\eta'' < 1 \qquad \text{or} \qquad \left|\frac{A_1}{A_2}\right| < \left|\frac{\nu_{i1}}{\nu_{i2}}\right| \tag{36}$$

of expression 34 is very plausible, and experimental data so far obtained agree with this principle. Disagreement with it, however, would in no way imply disagreement with the second law. It would merely require some other explanation for the mechanism of transfer of energy from coupling to coupled reaction. The efficiency η' is the real second-law efficiency and we would suggest calling it *thermodynamic efficiency*. For the efficiency η'' we would suggest the name *stoichiometric efficiency*. This latter efficiency is independent of the degrees of advancement ξ_1 and ξ_2 or of the reaction velocities $\mathbf{v}_1$ and $\mathbf{v}_2$, while the efficiency η' directly depends on these quantities.

Our discussion has been limited to cases such that one single reaction is coupled by the coupling reaction. Let us consider a case for which, besides reaction 1, there is some other coupled reaction, perhaps unknown. Burk's so-called second-law efficiency would then be computed as follows:

Let Δn_i be the algebraic value of the increase in the number of moles of the common component i during the finite period of time Δt. The amount of component i produced by the coupling reaction 2 is equal to $\nu_{i2}\xi_2$. The amount produced by the coupled reaction 1 and the other coupled reaction is then (all values are algebraic)

$$\Delta n_i - \nu_{i2}\xi_2 = \Delta n_i' \tag{37}$$

The portion of $\Delta n_i'$ corresponding actually to reaction 1 alone is $\nu_{i1}\xi_1$. The efficiency considered by Burk for a case of this sort is given by the formula

$$\eta''' = \left|\frac{A_1\nu_{i2}}{A_2\nu_{i1}}\right| \frac{\nu_{i1}\xi_1}{\Delta n_i'} = \left|\frac{A_1\nu_{i2}}{A_2\nu_{i1}}\right| \frac{\nu_{i1}\xi_1}{\Delta n_i - \nu_{i2}\xi_2} \tag{38}$$

The value of ξ_1 is deduced from the increase in the number of moles of any component appearing in reaction 1 alone (the ammonium ion in the case of *Chlorella* (3, 7)). One easily sees that formula 38 reduces to formula 33 when reaction 1 is the only one coupled by reaction 2. We have, indeed, in such a case,

$$\Delta n_i - \nu_{i2}\xi_2 = \nu_{i1}\xi_1 \tag{39}$$

and

$$\eta''' = \left|\frac{A_1\nu_{i2}}{A_2\nu_{i1}}\right| \tag{40}$$

Even when formula 38 should be applied we prefer to call η''' the *stoichiometric efficiency.*

The efficiency η''' defined by formula 38 has as an upper limit η'' defined by formula 33. This upper limit is actually reached when reaction 1 is the only one coupled by reaction 2.

We believe that very interesting developments could be obtained in this field by studying instantaneous properties starting from our equation 9 to equations 13 and 18. The power P might very well be a periodic function of time, oscillating between zero and a maximum value. Considerations involving finite periods of time and finite increments ξ_1, ξ_2, rather than the instantaneous velocities $\frac{d\xi_1}{dt}, \frac{d\xi_2}{dt}$, may actually hide some important intimate properties of living matter. We have published considerations of this type elsewhere (6). The main object of the present communication was to put in simple mathematical form the interesting ideas of Burk and other authors.

SUMMARY

1. Thermodynamic properties of systems in which simultaneous reactions are taking place are briefly reviewed.

2. The thermodynamic conditions for the coupling of a reaction with negative affinity by a reaction with positive affinity are established. Rules are proposed for the choice of independent reactions in the case of biological systems. The *machine efficiency* (Burk), which we prefer to call *thermodynamic efficiency*, is formulated.

3. The stoichiometric condition for the coupling (Burk) is expressed in simple mathematical form.

The *second-law efficiency* (Burk), which we prefer to call *stoichiometric efficiency*, is formulated.

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THE SYSTEM AMMONIA–SELENIC ACID–WATER AT 30°C.

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Relatively few studies of the solubility of selenates in selenic acid appear to have been made. Several acid selenates have been isolated, but no systematic study of their formation has been reported. Macalpine and Sayce (3) investigated the system $CuSeO_4$–H_2SeO_4–H_2O. The hydrates $CuSeO_4 \cdot H_2O$ and $CuSeO_4 \cdot 5H_2O$ were indicated, but there was no evidence for the formation of acid salts. Friend (1) determined the solubility of neodymium selenate in dilute solutions of selenic acid. Meyer (4) determined the solubility of Tl_2O_3 in sulfuric acid solutions and in selenic acid solutions. Similar solubility relationships in the two acids were found.

In order to obtain further information relative to the formation of acid selenates and to compare the solubility of selenates in selenic acid solutions with the solubility of sulfates in sulfuric acid solutions, it has been proposed to study ternary systems of the type selenate–selenic acid–water. This data would also be useful in a consideration of the crystallization of selenates from solution.

As far as the author is aware there are no data available on the system ammonia–selenic acid–water other than that normal ammonium selenate ($(NH_4)_2SeO_4$) is known, as well as ammonium hydroselenate (NH_4HSeO_4). Tutton (7) has determined the solubility of the normal selenate in water, but the solubility in selenic acid solutions has not been determined. Ammonium hydroselenate was prepared by Topsöe (6) by the addition of an excess of selenic acid to aqueous ammonia. The hydroselenates of potassium and sodium have been prepared similarly.

EXPERIMENTAL

Preparation and purification of materials

Selenic acid was prepared by a method previously described (2). The acid was recrystallized to a melting point of approximately 56°C. It gave no test for the presence of selenite. Ammonium selenate was prepared by neutralizing selenic acid with ammonia. The solution was concentrated, and the salt recrystallized twice.

Apparatus and method of procedure

Ammonium selenate was dissolved in solutions of selenic acid of various concentrations. To prepare a saturated solution, ammonium selenate was dissolved in a mixture of selenic acid and water at a temperature of approximately 70°C. On the basis of preliminary experiments, the proportions were so regulated that a considerable quantity of solid would be obtained when the solution was cooled to 30°C. The tubes containing the solutions were then placed in an electrically controlled thermostat which was maintained at a temperature of 30°C. ± 0.05°. It was necessary in some cases to seed the solution with the proper phase to cause crystallization of solid. The solutions were kept in the thermostat with frequent agitation until equilibrium had been established. This required only a few days time for the more dilute selenic acid solutions, but a somewhat longer period for the viscous and more concentrated acid solutions. It was found that all solutions reached equilibrium with the solid phase within two weeks time. By means of a centrifuge, the crystals of the solid phase were obtained in the bottom of the tube in a compact form.

Methods of analysis

After equilibrium had been established, samples of the solution were pipetted off and weighed. After draining the excess of solution from the solid phase, the crystals were transferred to a weighing bottle and weighed. This method of procedure was very satisfactory for analysis of the solid phase obtained in the more dilute acid solutions. In the solutions containing more than 50 per cent selenic acid, the wet residue was filtered rapidly through a small weighed Gooch crucible, the filtering device being kept at a temperature of approximately 30°C. A small amount of suction was used in the very concentrated solutions to free the solid phase from as much of the adhering solution as possible. This gave quite satisfactory results. The Gooch crucible with the solid residue was weighed, after which the solid was dissolved in water, and the solution filtered. The samples of solid and solution were each diluted to 100 cc., and 20-cc. aliquots were taken for analysis. All analyses were made in duplicate.

The selenic acid was determined by titration with standard alkali, using *p*-nitrophenol as an indicator. This indicator was found to be very satisfactory for the titration of the acid, giving a sharp and distinct color change at the end point. The ammonium selenate was determined by distilling the ammonia from an alkaline solution into standard acid solution. The excess acid was determined by titration with standard alkali. The compositions of the solid phases in equilibrium with the solutions were determined graphically by the method proposed by Schreinemakers (7). The results of all analyses are given in table 1 and represented graphically in figure 1.

Three solid phases may exist in equilibrium with solutions of selenic acid at 30°C. From 0 to 10.8 per cent selenic acid, the solid phase in equilibrium with the solution is $(NH_4)_2SeO_4$; from 10.8 to 28.1 per cent selenic acid the solid phase is $3(NH_4)_2SeO_4 \cdot H_2SeO_4$; and from 42.5 to 67.4 per cent selenic acid the solid phase is NH_4HSeO_4. The first and third compounds are known, but the compound $3(NH_4)_2SeO_4 \cdot H_2SeO_4$ has not been reported, as far as the author is aware. The latter compound crystallizes in small needles. A similar compound of $(NH_4)_2SO_4$ and H_2SO_4 of the composition $3(NH_4)_2SO_4 \cdot H_2SO_4$ has been reported (8). Solubility data from the system $(NH_4)_2SO_4$–H_2SO_4–H_2O at 30°C. (8) have been plotted in figure 1 (broken line curve). The solubility of the ammonium sulfate follows rather closely the solubility of ammonium selenate, particularly in acid concentrations of more than 20 per cent.

TABLE 1

The system $(NH_4)_2SeO_4$–H_2SeO_4–H_2O at 30°C.

SOLUTION		RESIDUE		SOLID PHASE
$(NH_4)_2SeO_4$	H_2SeO_4	$(NH_4)_2SeO_4$	H_2SeO_4	
weight per cent	*weight per cent*	*weight per cent*	*weight per cent*	
55.12	0.0			$(NH_4)_2SeO_4$
53.82	3.56	75.98	1.67	$(NH_4)_2SeO_4$
53.03	5.39	89.75	1.47	$(NH_4)_2SeO_4$
53.22	9.08	78.38	3.49	$(NH_4)_2SeO_4$
54.40	10.75	66.47	7.84	$(NH_4)_2SeO_4$
53.11	12.73	82.12	8.77	
50.48	14.88	71.65	19.61	$3(NH_4)_2SeO_4 \cdot H_2SeO_4$
48.40	19.24	71.10	22.18	$3(NH_4)_2SeO_4 \cdot H_2SeO_4$
46.36	24.18	73.40	22.80	$3(NH_4)_2SeO_4 \cdot H_2SeO_4$
45.49	28.08	52.31	26.80	$3(NH_4)_2SeO_4 \cdot H_2SeO_4$
43.92	34.13	60.53	31.40	
44.74	34.52			
34.41	42.50	54.76	45.10	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
24.13	50.53	48.08	46.32	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
23.41	50.77	47.88	46.19	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
20.04	55.26			
18.47	58.61	46.94	48.54	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
17.27	60.74	43.07	49.96	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
17.40	61.08	45.57	48.85	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
17.20	63.28	46.95	49.73	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
23.79	67.38	43.38	52.82	$(NH_4)_2SeO_4 \cdot H_2SeO_4$
29.72	66.23	46.85	50.51	$(NH_4)_2SeO_4 \cdot H_2SeO_4$

It may be concluded from table 1 that ammonium selenate may be crystallized from solutions in which the concentration of selenic acid is less than 10.8 per cent. Crystallization of ammonium hydroselenate may be made from solutions in which the concentration of selenic acid is greater than 42.5 per cent.

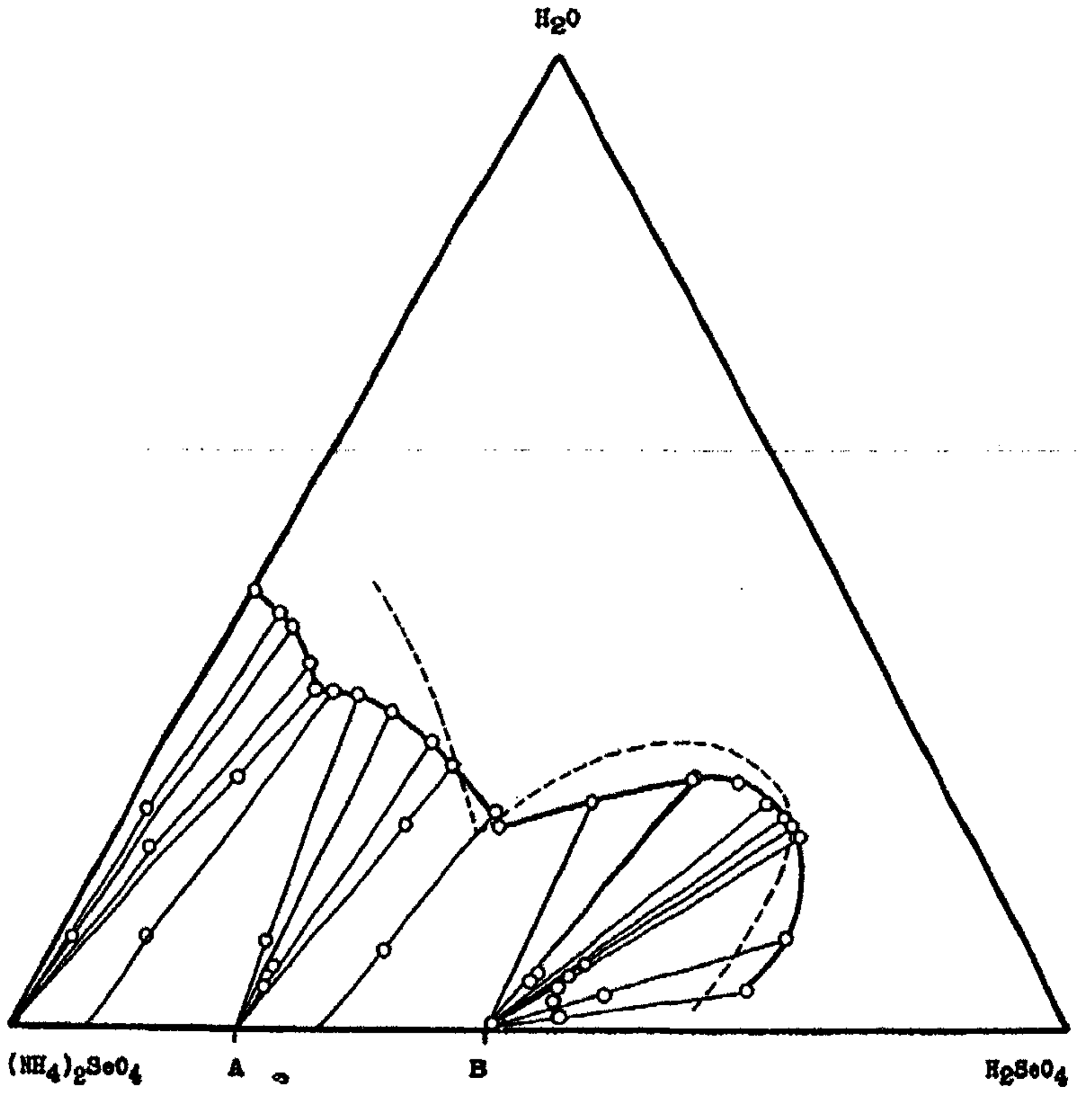

Fig. 1. Solubility relationships in the system $(NH_4)_2SeO_4$–H_2SeO_4–H_2O at 30°C. The compositions of the two acid salts are represented on the diagram by A and B. A has the composition $3(NH_4)_2SeO_4 \cdot H_2SeO_4$ and B the composition $(NH_4)_2SeO_4 \cdot H_2SeO_4$. The broken line curve represents the solubility of $(NH_4)_2SO_4$ in solutions of H_2SO_4 at 30°C. (taken from data of van Dorp (8)).

SUMMARY

1. The solubility relations in the system ammonia–selenic acid–water have been investigated at 30°C.
2. The existence of the compound $3(NH_4)_2SeO_4 \cdot H_2SeO_4$ has been shown.
3. The solubility of ammonium selenate in solutions of selenic acid is of approximately the same order as the solubility of ammonium sulfate in solutions of sulfuric acid.

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ELECTROMETRIC TITRATION OF SELENATES

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The study of certain ternary systems involving selenic acid and selenates suggested the desirability of a method by which free selenic acid and selenates could be rapidly and accurately determined in a mixture of the salt and acid. As far as the authors are aware, no attempts have been made to estimate selenates electrometrically. The purpose of this investigation was to apply electrometric methods to these determinations.

Although selenic acid has long been recognized as a strong acid and has been treated as such in titrations with bases, no study of potentiometric titrations appears to have been made. Macalpine and Sayce (5) titrated selenic acid with sodium hydroxide, using methyl orange as an indicator, in the study of the ternary system copper selenate–selenic acid–water. One of the authors (2) titrated the free acid with sodium hydroxide, using *p*-nitrophenol as indicator, in the study of the system ammonia–selenic acid–water.

An attempt was made to estimate total selenate in solution by titration with lead nitrate solution, using a lead electrode in contact with the solution. Owing to chemical action an encrustation was soon formed on the lead electrode, and values obtained were erratic.

Kolthoff (4) has made use of a ferrocyanide–ferricyanide electrode for the direct titration of sulfates. He has pointed out that "if we have a mixture of ferricyanide and lead ferrocyanide in contact with platinum, the system behaves both as a lead and as a ferrocyanide electrode." Since lead selenate is of the same order of solubility as lead sulfate, it was proposed to apply the above principle, if possible, to the estimation of selenates.

EXPERIMENTAL

Preparation and purification of materials

The preparation of selenic acid has previously been described (3). The acid was twice recrystallized and gave a melting point of approximately 56°C. It gave no test for selenite with sulfur dioxide. Solutions of various concentrations of the acid were prepared, and their strength determined by titration with standard alkali. This standardization was checked by determination of available oxygen by the method described by Scott (7).

Ammonium and magnesium selenates were prepared by neutralization reactions. The recrystallized salts were used for preparation of solutions.

Lead ferrocyanide was prepared from lead acetate solution and potassium ferrocyanide. The precipitate was washed several times with distilled water. The solid was then kept covered with distilled water until used. It was found that, if the latter procedure was followed, the solid remained finely divided and when added to the solution being titrated came to equilibrium rapidly with the ferricyanide in solution. Solid lead ferrocyanide which had been dried functioned satisfactorily, but came to equilibrium very slowly. Other reagents used were of C.P. quality or better.

Apparatus and method of procedure

A glass electrode of the type described by McInnes and Dole (6) was used to measure hydrogen-ion concentrations. The electrode was standardized with standard buffer solutions.

The ferrocyanide–ferricyanide electrode (4) was formed by introducing a bright platinum wire into the solution to which had been added a few small crystals of potassium ferricyanide and enough solid lead ferrocyanide to form a saturated solution. A normal calomel electrode served as the reference electrode.

The voltage measurements were made by means of a Leeds and Northrup student potentiometer in conjunction with a modification of the thermionic amplifier described by Gelbach and Compton (1). The measuring circuit is shown diagrammatically in figure 1.

The apparatus was adjusted by substituting a low-range milliammeter for the galvanometer G_2, and by varying the grid bias on the 222 tube by means of potentiometer R_1, until optimum sensitivity was obtained. By means of the variable resistor R_5 the current flowing through the milliammeter was reduced to zero, after which the galvanometer was reconnected and final adjustment made for zero deflection.

The potentiometer, P, was standardized in the usual manner against the standard cell, E_6. These adjustments having been made, the apparatus was then ready for operation.

The titrating cell containing the glass and calomel electrodes was connected at X, and switches S_1 and S_2 were thrown so as to connect the titrating cell and potentiometer into the grid circuit with the potentiometer voltage opposing that of the titrating cell. The potentiometer was then adjusted until the two voltages became equal, being indicated by a null reading on the galvanometer.

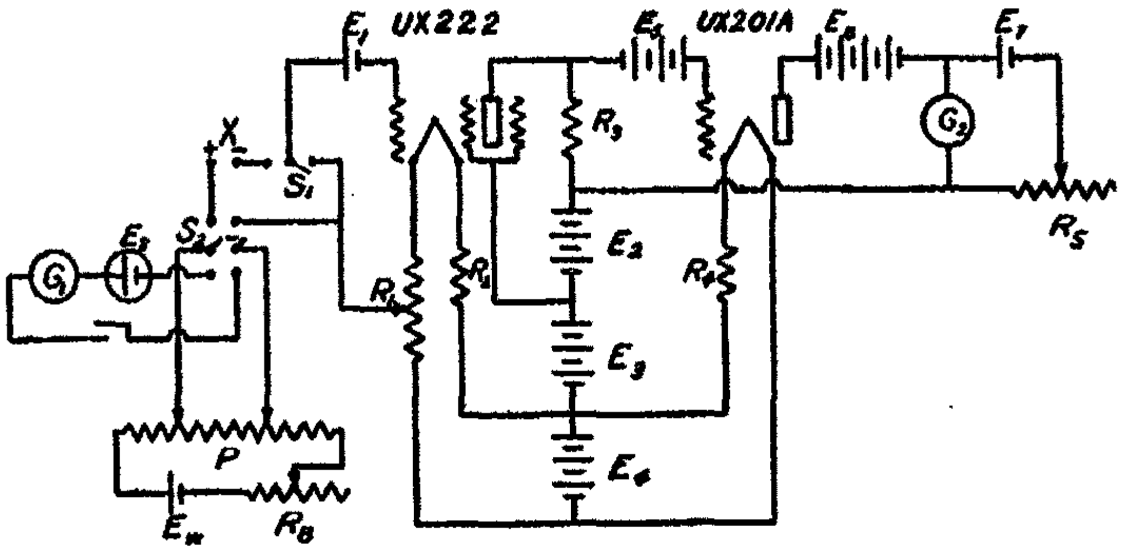

Fig. 1. The measuring circuit

E_1 and E_7	1.5 volts
E_2, E_3, and E_5	22.5 volts
E_4	6 volts
E_6	90 volts
E_s	Weston standard cell
E_w	2 volts
R_1	15-ohm potentiometer
R_2	6-ohm resistor
R_3	0.25-megohm resistor
R_4	4-ohm resistor
R_5	1000-ohm rheostat
R_8	300-ohm rheostat
S_1	single pole double throw switch
S_2	double pole double throw switch
G_1 and G_2	L and N portable galvanometers

TABLE 1

Solutions of selenates titrated with 0.09912 M lead nitrate using a ferrocyanide–ferricyanide electrode

SELENATES IN SOLUTION	CONCENTRATION	VOLUME TAKEN FOR ANALYSIS	VOLUME OF 0.09912 *M* $Pb(NO_3)_2$	THEORETICAL FOR REACTION
		cc.	cc.	cc.
H_2SeO_4	0.01004 *M*	25	2.56	2.53
H_2SeO_4	0.05020 *M*	25	12.70	12.65
H_2SeO_4	0.1004 *M*	10	10.14	10.13
H_2SeO_4	0.1004 *M*	25	25.21	25.32
H_2SeO_4	0.3818 *M*	5	19.32	19.27
$(NH_4)_2SeO_4$	0.3066 g. in solution		17.22	17.30
$(NH_4)_2SeO_4 + H_2SeO_4$	0.3066 g. $(NH_4)_2SeO_4$ + 0.1456 g. H_2SeO_4		27.50	27.43
$MgSeO_4 + H_2SeO_4$	0.0428 g. $MgSeO_4$ + 0.00136 g. H_2SeO_4		2.62	2.62
$MgSeO_4 + H_2SeO_4$	0.0341 g. $MgSeO_4$ + 0.0078 g. H_2SeO_4		2.60	2.59

Titration of selenic acid

Samples of standard selenic acid of several concentrations were titrated potentiometrically. It was found that the end point was determinable within 0.05 cc. The titration curve was typically that of a strong electrolyte.

Titration of selenates

Solutions containing soluble selenates and mixtures of selenates and free selenic acid were titrated using the ferrocyanide–ferricyanide electrode (4). It was found that the titrations could be carried out more satisfactorily in alcoholic solution, the initial concentration being approximately 75 per cent alcohol. Results obtained in aqueous solutions were not reproducible. A mechanically driven stirrer was used during the addition of the lead nitrate titrating solution. As the end point was approached a period of three to five minutes was required after each addition of titrating solution in order to obtain a steady voltage reading, requiring on the average about thirty minutes for each titration. In table 1 a summarization is given of a number of typical analyses; in figure 2 corresponding titration curves are shown. The effect of foreign salts on the titrations has not as yet been determined.

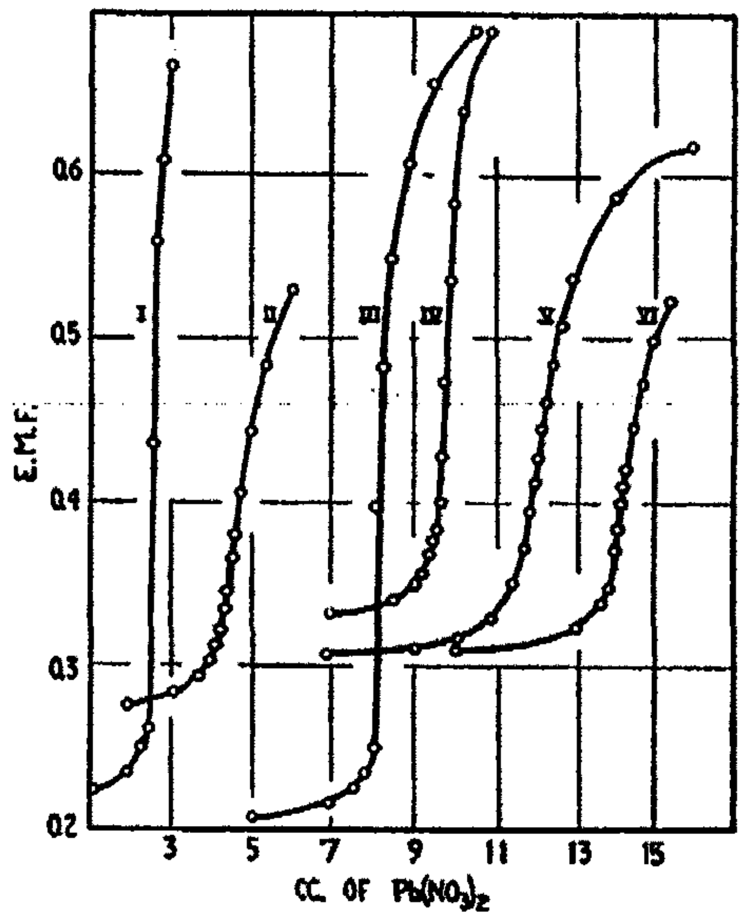

FIG. 2. Titration of selenate solutions with 0.09912 *M* lead nitrate, using ferrocyanide-ferricyanide electrode.

I 0.0428 g. $MgSeO_4$ + 0.00136 g. H_2SeO_4 + 25 cc. H_2O + 75 cc. alcohol.

II 0.3066 g. $(NH_4)_2SeO_4$ + 0.1456 g. H_2SeO_4 + 25 cc. H_2O + 75 cc. alcohol. Add 23 to the cc. of lead nitrate scale.

III 0.3066 g. $(NH_4)_2SeO_4$ + 25 cc. H_2O + 75 cc. alcohol. Add 9 to cc. of lead nitrate scale.

IV 25 cc. of 0.0502 *M* H_2SeO_4 + 75 cc. alcohol. Add 3 to cc. of lead nitrate scale.

V 25 cc. of 0.1004 *M* H_2SeO_4 + 75 cc. alcohol. Add 13 to cc. of lead nitrate scale.

VI 5 cc. of 0.3818 *M* H_2SeO_4 + 20 cc. H_2O + 75 cc. alcohol. Add 5 to cc. of lead nitrate scale.

SUMMARY

1. Potentiometric titrations of selenic acid were made using a glass-calomel electrode system; the end point was determinable within 0.05 cc.

2. Selenate determinations were made in solutions of selenic acid and mixtures of the acid and its salts, using a ferrocyanide–ferricyanide electrode. Results were very reproducible.

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A RELAY-FREE MERCURY VAPOR TRIODE CONTROL FOR A CONSTANT-TEMPERATURE WATER BATH

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Most of the temperature-controlling devices for water baths in use at the present time in chemical laboratories have, somewhere in the assembly, a relay which operates on a very small current and permits the passage of a comparatively heavy current through the heating coils of the bath. As long as the points in the relay never stick, these devices work very satisfactorily.

While the construction of supersensitive relays has been brought to a very high point of excellence, one failure in the operation of the relay may have serious consequences, and the elimination of such a part in the controlling device is something to be desired. In the assembly about to be described, the current passing through the thermoregulator points is reduced to approximately 2 milliamperes. Because of the elimination of the relay and the reduction in thermoregulator current, the regulator is trouble-free.

The authors make no claim for originality in the use of the gas-filled triode in controlling temperatures (1), but recommend this circuit for its simplicity and reliability.

Transformers are not necessary in this circuit and, with the exception of the gas-filled triode tube, all parts are easily obtainable at almost any radio store and for a very nominal sum.

Since the tube is the heart of this controlling device, the principles involved in its operation will be briefly discussed. The R.C.A.-91 mercury vapor triode tube requires a positive grid voltage with respect to the cathode, of 6 to 9 volts to start the tube operating, with 115 volts R.M.S. on the plate. No supplementary battery is needed to supply a negative bias, since the tube will not fire when the grid is at zero voltage in respect to the cathode of the tube. The reader will see from the circuit shown in figure 1, that the positive bias for starting the tube is supplied by the drop across the cathode heater. Since the voltage is far greater than that necessary for this service, the tube is protected against a dangerous grid current surge by the limiting resistor R_2. The tube will fire on each positive half-cycle so long as the thermoregulator remains open. When the thermoregulator contacts close, the drop introduced across the 50,000-ohm resistor R_2 is so great that the tube is no longer supplied with a positive bias great enough to make it fire. The resistance R_1 serves to reduce the current further through the thermoregulator contacts. R_3 is used to adjust the filament voltage of the tube.

Either a lamp or a variable resistor, or both, placed in the position in the circuit marked "lamp" should have its values adjusted until the length of time that the tube is operating is approximately equal to the time that the tube is "off". If a low wattage lamp is used, the light will dim when the tube "fires" and will glow at full brilliance when the tube is "off".

In actual operation, the tube will pass current through the heating coils as long as the thermoregulator points remain open. When the temperature of the water bath reaches the required temperature as determined by the setting of the thermoregulator, the contacts will close and the tube will cease to conduct. While the tube is not conducting, the only current supplied to the heating coils is that supplied through the lamp.

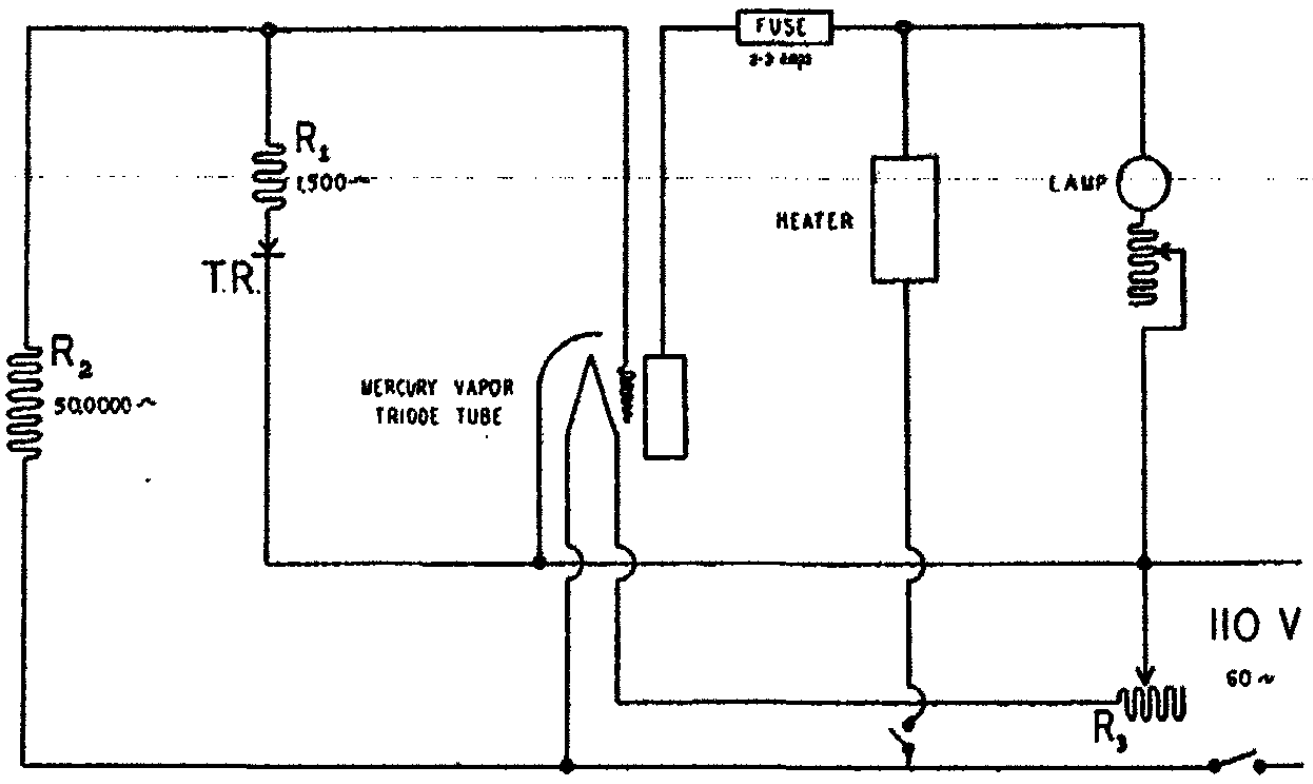

FIG. 1. The circuit

During the operating time of the tube, the heating coils receive current from both the lamp circuit and the tube-plate circuit.

The temperature of a water bath of a capacity of 30 to 50 liters can be very easily controlled with this device by using heating coils of the type drawing 250 watts in 110-volt service. The thermoregulator may be set at 25°C., the temperature frequently used in experimental work. Close observations on an open bath so controlled in this laboratory have shown that temperatures in the neighborhood of 25°C. may be held to ±0.005°C.

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THE IDENTIFICATION OF OPAQUE SOLIDS BY SELECTIVE IRIDESCENT FILMING. I

OPTICS

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In previous articles (20, 21) the discovery was announced of a means of staining characteristically some sulfide minerals by reaction with a suitable aqueous solution. Further work (22, 47) in this field has shown that the development of characteristic, brilliant colors on normally white, gray, or even on colored sulfide minerals is not peculiar to a few sulfide minerals, but is susceptible of development into a general method for the systematic identification of opaque solids.

The method consists in coating a plane surface of each opaque substance with a virtually transparent thin film of such physical properties that interference of the rays reflected from the top of the film and from the bottom of the film takes place for some particular wave lengths of the visible spectrum. Thus, a polished surface consisting of several different phases acquires films that display in white light substantially the same color whereever substance A occurs, while displaying characteristically different colors where substances B, C, D, etc., occur.

There is nothing new in the development of uniform iridescent colors at the surface of solids. The phenomenon has been extensively investigated, in particular by Evans and his associates (12 to 17), Tammann and his associates (48 to 54), and also by others (1, 27, 29, 30, 33, 40, 55, 57) in what concerns the action of oxygen, hydrogen sulfide, and halogens on metals. In fact, Tammann has touched on the phenomenon in what concerns the action of oxygen on sulfides at elevated temperatures (50).

Use of iridescent filming was proposed by Koerber (28) as a means for the determination of silicon in iron–silicon alloys, the interference color obtained, after reaction for a given time, depending upon the amount of silicon in solid solution in the iron.

Observations were also recorded by Leo (32) concerning the natural occurrence of iridescent faces on crystals, and concerning the artificial preparation of interference colors on polished sections of sulfide minerals.

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[1] Research Professor of Mineral Dressing.

It would seem that Leo had in mind in 1911 a method analogous to that which has been developed at Montana School of Mines. This is indicated, for example, by the subtitle of Leo's book. Careful reading of the book, however, shows that he sought a method of producing a *permanent* end-color, something which is constitutionally incompatible with interference colors; it appears also that Leo rejected treatments which gave various colors in succession, as surface films become thicker and thicker.

In view of the apparently general applicability of the phenomenon of selective iridescent filming to determinative microscopy, a search of the literature was made to find out what had been done in a theoretical way concerning the optics of these films. This search was disappointing. Most recent investigators have been content with a general statement of the problem for a *thin film included between layers of the same substance.* Older investigators have examined the same problem in some detail, particularly Newton (37), Wertheim (56), and Rollett (43). No one apparently has analyzed the general problem of a thin film between layers of dissimilar substances, although an experimental spectrophotometric study was made by Constable (7, 8, 9). The object of this article is partly to fill this gap, and at the same time to pave the way for a clear understanding of the experimental phenomena to be detailed in subsequent articles.

The interference between the light reflected from the top of the film and that reflected from the bottom involves both a qualitative and a quantitative requirement. The qualitative requirement is that the rays which are to interfere must differ in phase by some fraction of a wave. The quantitative requirement is that the intensity of the net ray resulting from the interfering components must differ sufficiently as between one visible wave length and another, or else, even if interference takes place qualitatively, it will not be quantitatively perceptible to the eye.

Let n_A be the index of refraction of the medium adjoining the filmed mineral, n_F that of the film, and n_M that of the mineral. Consider further that

$$n_A < n_F < n_M \qquad \text{(I)}$$

This will be the general case in dealing with polished opaque solids, such as sulfide minerals, viewed by reflected light.

INTERFERENCE BY SINGLE REFLECTION

In figure 1 is represented the interference between the ray reflected at the top of the film AQB (reflection order 0) and the ray reflected once at the bottom of the film, $A'M'P'QB$, (reflection order 1). The time required to traverse $M'T'$ and SQ is the same, since $M'S$ and $T'Q$, drawn perpendicular to AQ and $M'P'$, are the wave fronts of the incident and refracted light. Hence, the interfering rays differ in path by $T'P' + P'Q$, which equals

$T'W'$ or $2t \cos r$, in which t is the thickness and r the angle of refraction. If λ is the wave length of the light (considered, for the present, as being monochromatic), interference, qualitatively speaking, occurs if

$$\left.\begin{aligned} 2n_F \cdot t \cos r &= m \frac{\lambda}{2} \\ \text{or,} \qquad t &= m \frac{\lambda}{4n_F} \cdot \frac{1}{\cos r} \end{aligned}\right\} \qquad \text{(II)}$$

in which m is an odd integer.

This is correct in view of the assumption $n_A < n_F < n_M$, as such an assumption (42) necessitates reflection with a phase retardation of $\lambda/2$ at

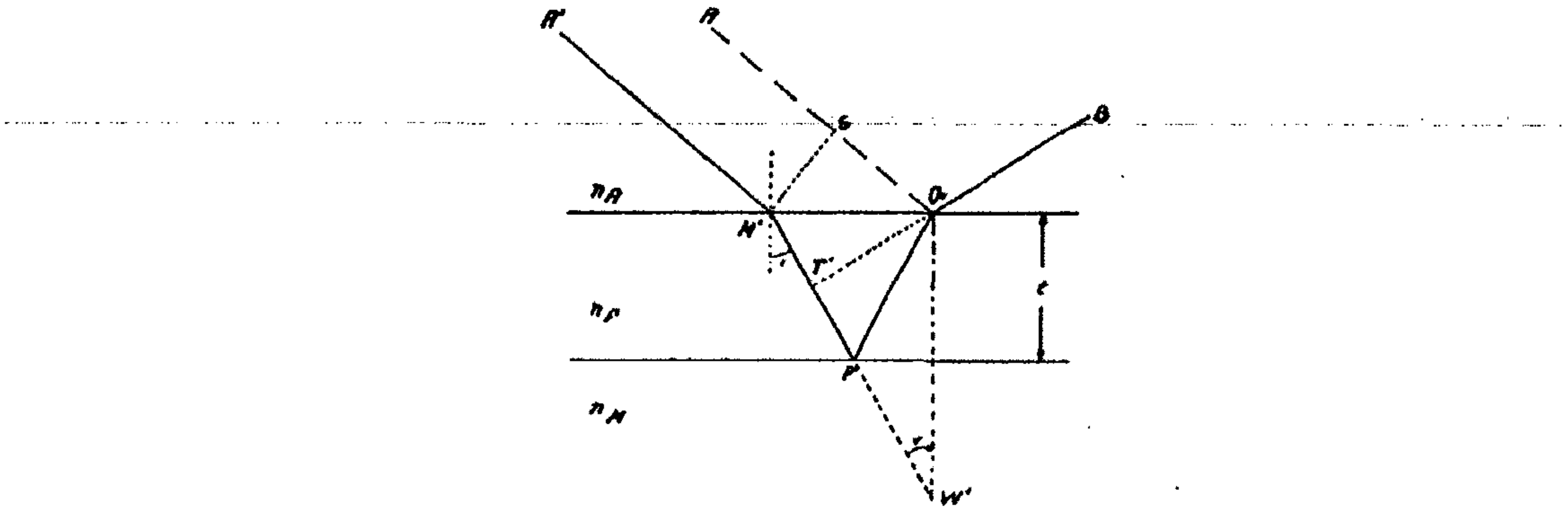

FIG. 1. Zero- and first-order reflections at a filmed surface

both interfaces. A phase retardation of $\lambda/2$ occurs in any event upon reflection at a metallic surface (62).

INTERFERENCE BY MULTIPLE REFLECTION

Interference, however, is not limited to the interaction of reflections of the zero and first orders. Consider the reflection of the p order involving light that has been reflected p times at the film–substratum interface and light that is being reflected for the first time at the air–film interface. Reflection within and at the top of the film does not involve a phase retardation, since $n_F > n_A$, but each of the reflections at the bottom of the film requires a phase retardation of $\lambda/2$, since $n_F < n_M$; also, the zero-order reflection requires a phase retardation of $\lambda/2$. The path difference between the reflection of the zero order and that of the p order is p times the path difference between the reflections of zero and first orders or,

$$p \cdot 2t \cos r$$

Hence the retardation of the reflection of p order is

$$p \cdot 2n_F \cdot t \cdot \cos r + (p - 1)\frac{\lambda}{2}$$

If interference takes place between reflections of the zero and first orders, then

$$2n_F \cdot t \cdot \cos r = m\frac{\lambda}{2}$$

and the retardation of the reflection of p order as compared to that of zero order is

$$pm\frac{\lambda}{2} + (p - 1)\frac{\lambda}{2}$$

or,

$$\frac{\lambda}{2}p(m + 1) - \frac{\lambda}{2}$$

Since m is odd, the term $p(m + 1)$ must be even and the retardation can be expressed as

$$L\lambda - \frac{\lambda}{2}$$

in which L is an integer.

It follows that if interference occurs between the reflections of the zero and first orders, all the other reflections team up with the reflection of the first order, working against the reflection of the zero order.

QUANTITATIVE ESTIMATION OF INTERFERENCE

In order to arrive at a quantitative estimation of the extent to which this interference will be perceived, it is necessary to consider the indices of refraction of the transparent media and the reflectivity of the plane opaque solid. Let (58) the amplitude of the incident ray be unity, b and c be fractions which describe the amplitude of the ray reflected from the upper film surface (zero order) and of the first refracted ray. Let k^2 be the reflectivity of the plane opaque solid in contact with the film. As shown in figure 2, the ray reflected at the bottom of the film has amplitude ck. This is based on the well-known relationship that the intensity of illumination with monochromatic light is directly as the square of the amplitude of the light. The ray refracted from the film into the medium A, above it (reflection order 1), has the amplitude cfk; that reflected back into the film, cbk, etc. After substitution of $1 - b^2$ for cf (46), the amplitudes of the various reflections $b_0, b_1, b_2 \ldots b_p$ are as follows, in relation to amplitude of unity for the incident ray:

$$\begin{aligned} b_0 &= b \\ b_1 &= (1 - b^2)k \\ b_2 &= (1 - b^2)kbk \\ b_3 &= (1 - b^2)b^2k^3 \\ b_4 &= (1 - b^2)b^3k^4 \\ b_p &= (1 - b^2)b^{p-1}k^p \end{aligned} \qquad \text{(III)}$$

It has already been pointed out that if the reflections of the zero and first orders interfere, the reflections of all other orders team up with the reflection of first order. The amplitude of the net reflection is then $b_0 - (b_1 + b_2 + b_3 + \ \ldots\ + b_p)$.

On the contrary, if the thickness of the film is such that reflections of the zero and first orders differ by a full wave, b_2 will lag behind b_1 by $\frac{3}{2}\lambda$, since its retardation involves not only that due to the thickness of the film, but also one more $\frac{\lambda}{2}$ retardation due to reflection into a rare medium at a dense medium boundary; likewise b_3 will lag behind b_1 by $2 \cdot \frac{3}{2}\lambda$ or 3λ; b_4 by $3 \cdot \frac{3}{2}\lambda$ or $\frac{9}{2}\lambda$, etc. The amplitude of the net reflection is then

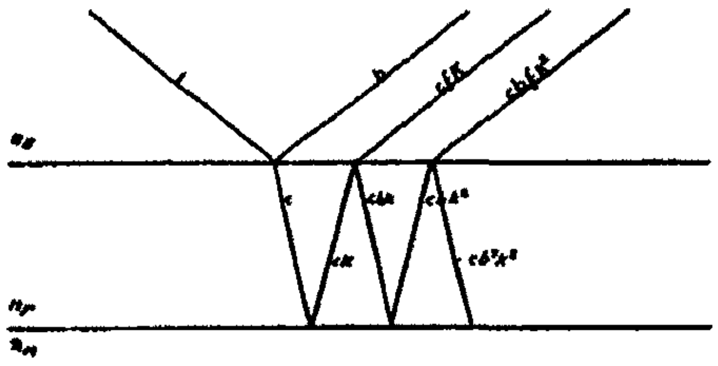

Fig. 2. Multiple reflections at a filmed surface

$$(b_0 + b_1 + b_3 + \ \ldots) - (b_2 + b_4 + b_6 + \ \ldots)$$

This, of course, represents the largest possible amplitude for a reflection, just as

$$b_0 - (b_1 + b_2 + b_3 + \ \ldots\ + b_p)$$

represents the smallest possible amplitude. Generally, then:

$$\left.\begin{aligned} b_{\text{min.}} &= b - (1 - b^2)k[1 + bk + b^2k^2 + b^3k^3 + \ \ldots\ + b^pk^p] \\ b_{\text{max.}} &= b + (1 - b^2)k[1 + b^2k^2 + b^4k^4 + \ \ldots\ + b^{2p'}k^{2p'}] - \\ &\qquad (1 - b^2)k[bk + b^3k^3 + \ \ldots\ + b^{2p'+1}k^{2p'+1}] \end{aligned}\right\} \text{(IV)}$$

AMPLITUDE OF REFLECTION OF ZERO ORDER

The quantity b, or relative amplitude of zero-order reflection, is well known and depends solely upon the indices of refraction of the transparent media, and upon the angle of refraction.

In the case of light at normal incidence b depends only upon the indices of refraction of the transparent media. The relationship, due to Fresnel, is

$$b = \frac{n_F - n_A}{n_F + n_A} \qquad \text{(V)}$$

in which n_F and n_A are the indices of refraction of the two media. The intensity of the reflected light of zero order, expressed as a fraction of the incident light is, of course, measured by b^2. Its numerical value for some values of n_F, expressed as a percentage of the incident light, is presented in table 1. In this table data are presented for the two cases corresponding to viewing of the film through air and through oil.

TABLE 1

Intensity of reflected light of zero order, expressed as a percentage of the intensity of the incident light, at air-film and oil-film surfaces, according to Fresnel's formula for normal incidence

INDEX OF REFRACTION OF FILM	AT FILM-AIR SURFACE	AT FILM-OIL SURFACE*
1.6	5.3	0.1
1.8	8.2	0.8
2.0	11.1	2.0
2.2	14.1	3.5
2.4	17.0	5.2
2.6	19.8	7.1
2.8	22.5	9.1
3.0	25.0	11.0

* Index of refraction of oil = 1.505 (45).

INDEX OF REFRACTION OF FILM SUBSTANCES

To date the method of selective iridescent filming has been applied principally, but not exclusively, to the identification of sulfides, both natural and synthetic. Accordingly, an inquiry was directed to the ascertainment of the indices of refraction of solids of the type that might be expected to make up thin films at the surface of sulfides. Such solids have rather high indices of refraction, ranging roughly from 1.8 to 2.8 (see, e.g., *International Critical Tables*). Attention is called in particular to the high indices of refraction of oxides of antimony, tin, zinc, nickel, lead, copper, iron, and mercury, all of which are higher than 2.0.

REFLECTIVITY OF POLISHED SURFACES

Besides the indices of refraction of the film and of the viewing medium, the other important quantity that plays a part in controlling the amplitudes of the reflections of various orders is the reflectivity of the polished surface in contact with the film. No direct data are available on the reflectivity of polished surfaces in contact with films having various indices of refraction. However, measurements are available of the reflectivity in air and in oil of polished minerals.

These measurements, combined with the Fresnel relationship, can be used to calculate the reflectivity $(k_{MF})^2$ against a medium of index of refraction n_F. This treatment is wholly sound if the solid is transparent, but there is some ground for doubt if it displays the property of metallic conduction. Since our knowledge of refraction in metals is far from satisfactory, the lesser evil would seem to be to assume that opaque metallic minerals can be dealt with as if transparent (39). On this assumption,

$$k_{MA} = \frac{n_M - 1}{n_M + 1} \quad \text{in air}$$

$$k_{MF} = \frac{n_M - n_F}{n_M + n_F} \quad \text{in film}$$

Solving each for n_M and equating

$$\frac{1 + k_{MA}}{1 - k_{MA}} = n_F \frac{1 + k_{MF}}{1 - k_{MF}}$$

Hence

$$\left.\begin{aligned} k_{MF} &= \frac{(1 + k_{MA}) - (1 - k_{MA})n_F}{(1 + k_{MA}) + (1 - k_{MA})n_F} \quad &\text{(a)} \\ k_{MA} &= \frac{(1 + k_{MF})n_F - (1 - k_{MF})}{(1 + k_{MF})n_F + (1 - k_{MF})} \quad &\text{(b)} \end{aligned}\right\} \qquad \text{(VI)}$$

Strictly speaking, these equations apply for normal incidence only.

The reflectivity in air of most metals varies from 30 to over 90 per cent. This is shown by table 2, which is abstracted from Wood (59). The average reflectivity in air of sulfide minerals is much lower: it ranges from 15 to 60 per cent, as may be seen from table 3. This table presents not only the reflectivity of some sulfides in air, but also their reflectivity in oil, as averaged from the data of Schneiderhoehn and Ramdohr (45), and as calculated from the average reflectivities in air with the help of formula VIa. Comparison of the calculated with the experimentally observed reflectivities constitutes a test of the validity of equation VIa. The agreement is fair, although a systematic deviation should be noted, the calculated reflectivities being lower than the corresponding observed reflectivities. This may, of course, be ascribable to the inexactitude of the formulas VI. An obvious source of error in the experimental values is the inability to polish any brittle solid so as to obtain a geometrically plane surface. Even a polish apparently perfect is merely a polish in which the defects are small enough in relation to the wave length of the visible light to be imperceptible. But from the standpoint of loss of light by reflection in a direction oblique to the plane of the section these defects may be significant. This is confirmed by Cissarz's recent observation that polished cleavage surfaces have a lower reflectivity than unpolished cleavage surfaces (3, 4, 5).

If then the hypothesis is made that all measurements of reflectivity of sulfides made to date fall short, the calculated and observed values of their reflectivity in oil (table 3) can be brought in close accord. If, for example, the true reflectivity of millerite is one-third greater than it is measured to be, the actual observations should have been 54 × 4/3 = 72 per cent and 46 × 4/3 = 61 per cent. Should such an error in observation have been made, the reflectivity in oil calculated from the 72 per cent reflectivity in air would have been exactly 61 per cent.

TABLE 2

Reflectivity of some metals in air, $(k_{MA})^2$, *in per cent (44)*

WAVE LENGTH IN A.U.	4200	4500	5000	5500	6000	7000
COLOR (TO THE EYE)	Violet	Blue	Green	Yellow	Orange	Red
Silver	86.6	90.5	91.3	92.7	92.6	94.6
Platinum	51.8	54.7	58.4	61.1	64.2	69
Steel	52	54	55	55	55	58
Gold	29	33	47	74	84	92
Copper	33	37	44	48	72	83
Nickel	56	59	55	63	65	69

The most recent measurements of the reflectivity of sulfides yield values considerably higher than those abstracted in table 3 from Schneiderhoehn and Ramdohr's standard text. The latest values are such as to substantiate the hypothesis put forth in this section of this paper. Thus, in the case of galena, viewed in orange light, Schneiderhoehn and Ramdohr give k_{MA} = 37.5 per cent, k_{MO} = 25 per cent; formula VIa yields k_{MO} (calcd.) = 18.6 per cent,—a discrepancy of 26 per cent between the observed and calculated reflectivities in oil. Corresponding figures from Cissarz (5) for cleaved galena are k_{MA} = 43.2 per cent, k_{MO} (obsd.) = 27.9 per cent, k_{MO} (calcd.) = 25.1 per cent indicating a discrepancy of only 10 per cent instead of 26 per cent. The comparison is even more startling in the case of stibnite. The corresponding discrepancies between observed and calculated values for orange light, and the mineral viewed in the *c*-orientation are 40

TABLE 3

*Reflectivity of some sulfide minerals in air and in oil**

MINERAL	AVERAGE REFLECTIVITY IN AIR (OBSERVED)	AVERAGE REFLECTIVITY IN OIL	
		Observed	Calculated
Millerite	54	46	39
Pyrite	53	46	38
Pentlandite	51	44	36
Arsenopyrite	51	39	36
Bismuthinite	44	33	28
Chalcopyrite	40	32	25
Cubanite	40	31	25
Pyrrhotite	37	29	21
Chalcostibite	37	24	21
Emplectite	36	23	20
Galena	35	26	20
Zinkenite	34	26	19
Jamesonite	33	20	18
Argentite	33	18	18
Stibnite	33	24	18
Wittichenite	31	19	16
Bournonite	31	18	16
Miargyrite	30	18	15
Pyrargyrite	28	17	14
Stephanite	27	13	13
Polybasite	27	15	13
Chalcocite	26	12	12
Stromeyerite	26	13	12
Famatinite	25	13	12
Tetrahedrite	24	15	11
Molybdenite	24	16	11
Realgar	24	8	11
Proustite	23	12	10
Enargite	22	12	10
Stannite	21	10	9
Bornite	19	9	7
Sphalerite	17	6	6
Covellite	15	8	4

* Arranged in order of decreasing reflectivity in air.

per cent (Schneiderhoehn and Ramdohr, 1931) and 9 per cent (Cissarz, 1932). Clearly, then, as better measurements are made the observed and calculated reflectivities in oil approach each other.

Such an error due to imperfect polishing as is here postulated would result in a systematic deviation between the observed and calculated values for the reflectivity in oil in the direction in which a systematic deviation is actually obtained. Such an error should be practically lacking in minerals soft enough to flow, as in chalcocite or argentite, but quite marked in the brittle or cleavable minerals, as pyrite, chalcopyrite, and galena. This is precisely what is observed in table 3.

In view of these considerations it may fairly be said that in what concerns substances that are not better electronic conductors than the substances listed in table 3, equations VI are substantially valid. It is also to the point to observe that equation V is approximately correct in the case of the good conductor, metallic potassium (61). If equation V is valid in that case, then the foundation for equations VI is valid, indeed.

AMPLITUDE OF REFLECTIONS OF VARIOUS ORDERS

From the Fresnel formula, and from the formulas describing the amplitude of the reflections of various orders *for normal incidence* there have been calculated the values of $b_0, b_1, b_2, b_3 \ldots\ldots b_p$ for $(k_{MF})^2 = 0.2, 0.5, 1.0, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, 60.0, 80.0$ per cent and for $n_F = 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0$. The amplitudes of successive reflections were calculated until one was found numerically less than 0.05 per cent (corresponding to an intensity amounting to less than 0.000025 per cent of that of the incident light). This was done for both air immersion and oil immersion ($n_O = 1.505$). For the sake of brevity these data are omitted from this paper as they are not of significance by themselves, although their calculation is necessary if $b_{\text{min.}}$ and $b_{\text{max.}}$ are to be determined.

It is of interest to note that if the reflectivity is low the convergence to zero of the b values of successive orders is rapid, but that slow convergence is the rule if the reflectivity is high. Again a low index of refraction of the film connotes rapid convergence and a high index slow convergence. For example:

with $n_F = 1.6$, $(k_{MF})^2 = 0.2$ per cent, air immersion, $b_0 = 23.0$; $b_1 = 4.2$; $b_2 = 0.0$

with $n_F = 3.0$, $(k_{MF})^2 = 0.2$ per cent, air immersion, $b_0 = 50.0$; $b_1 = 3.4$; $b_2 = 0.1$; $b_3 = 0.0$

with $n_F = 1.6$, $(k_{MF})^2 = 80.0$ per cent, air immersion, $b_0 \doteq 23.0$; $b_1 = 84.8$; $b_2 = 17.5$; $b_3 = 3.6$; $b_4 = 0.7$; $b_5 = 0.2$; $b_6 = 0.0$

with $n_F = 3.0$, $(k_{MF})^2 = 80.0$ per cent, air immersion, $b_0 = 50.0$; $b_1 = 67.2$; $b_2 = 30.1$; $b_3 = 13.5$; $b_4 = 6.1$; $b_5 = 2.7$; $b_6 = 1.2$; $b_7 = 0.5$; $b_8 = 0.2$; $b_9 = 0.1$; $b_{10} = 0.0$

As appears in table 3, the reflectivity of all sulfides in air is less than 60 per cent and in oil it is less than 50 per cent. Sulfides filmed with sub-

TABLE 4

Minimum amplitude of total light reflected normally by filmed solids immersed in air (per cent of incident amplitude) for definite values of the index of refraction of the film (1.6 to 3.0) and of the reflectivity $(k_{MF})^2$ at the film–substratum interface (0.2 to 80 per cent).

$$b_{\text{min.}} = b_0 - (b_1 + b_2 + b_3 + \dots\dots\dots + b_p)$$

REFLECTIVITY	$n_F = 1.6$	$n_F = 1.8$	$n_F = 2.0$	$n_F = 2.2$	$n_F = 2.4$	$n_F = 2.6$	$n_F = 2.8$	$n_F = 3.0$
per cent								
0.2	18.8	24.5	29.2	33.7	37.5	40.8	43.9	46.5
0.5	16.2	22.1	26.9	31.3	35.2	38.6	41.8	44.5
1	13.3	19.2	24.1	28.7	32.7	36.1	39.4	42.1
2	9.2	15.2	20.1	24.7	28.9	32.5	35.8	38.5
3	5.9	12.0	16.9	21.6	25.8	29.4	32.9	35.8
5	0.6	6.8	12.1	16.7	20.8	24.5	28.2	31.1
10	9.4	3.1	1.8	6.8	11.3	15.0	18.7	21.9
15	17.3	11.3	6.4	1.3	3.0	6.9	10.8	14.0
20	24.0	18.5	13.6	8.6	4.2	0.3	3.4	6.7
30	36.4	31.0	26.4	21.7	17.4	13.4	9.9	6.5
40	46.9	42.3	38.1	33.7	29.6	26.0	22.4	19.4
60	66.3	62.9	59.6	56.4	53.3	50.5	47.6	44.8
80	83.8	81.9	80.1	78.2	76.6	74.8	73.4	71.6

TABLE 5

Minimum amplitude of total light reflected normally by filmed solids immersed in oil, $n_O = 1.505$ (per cent of incident amplitude), for definite values of the index of refraction of the film (1.6 to 3.0) and of the reflectivity $(k_{MF})^2$ at the film–substratum interface (0.2 to 80 per cent).

$$b_{\text{min.}} = b_0 - (b_1 + b_2 + b_3 + \dots\dots\dots + b_p)$$

REFLECTIVITY	$n_F = 1.6$	$n_F = 1.8$	$n_F = 2.0$	$n_F = 2.2$	$n_F = 2.4$	$n_F = 2.6$	$n_F = 2.8$	$n_F = 3.0$
per cent								
0.2	1.4	4.5	9.7	14.5	18.7	22.4	25.9	29.1
0.5	4.0	1.9	7.1	11.9	16.1	20.0	23.6	26.8
1	6.9	1.1	4.2	10.0	13.2	17.2	20.7	24.0
2	11.1	5.3	0.1	4.7	9.1	13.1	16.7	20.0
3	14.3	8.6	3.3	1.6	5.8	9.9	13.6	16.8
5	19.4	13.7	8.5	3.7	0.5	4.5	8.3	11.8
10	28.8	23.4	18.3	13.6	9.5	5.4	1.6	1.7
15	36.1	30.8	26.0	21.5	17.4	13.4	9.7	6.3
20	42.2	37.3	32.8	28.3	24.2	20.6	16.9	13.5
30	52.5	48.1	44.1	40.2	36.5	32.9	29.5	26.4
40	61.3	57.4	54.0	50.5	47.3	44.0	41.1	38.1
60	76.2	73.6	71.1	68.7	66.5	64.0	61.6	59.7
80	89.0	87.6	86.3	85.0	83.8	82.6	81.3	80.3

TABLE 6

Maximum amplitude of total light reflected normally by filmed solids immersed in air (per cent of incident amplitude) for definite values of the index of refraction of the film (1.6 to 3.0) and of the reflectivity $(k_{MF})^2$ *at the film-substratum interface (0.2 to 80 per cent).*

$$b_{\max.} = b_0 + (b_1 + b_3 + b_5 \ldots . b_{2p'+1}) - (b_2 + b_4 + b_6 \ldots . b_{2p'})$$

REFLECTIVITY	$n_F = 1.6$	$n_F = 1.8$	$n_F = 2.0$	$n_F = 2.2$	$n_F = 2.4$	$n_F = 2.6$	$n_F = 2.8$	$n_F = 3.0$
per cent								
0.2	27.2	32.7	37.2	41.3	44.9	48.0	50.9	53.3
0.5	29.6	35.1	39.5	43.5	47.0	50.0	52.8	55.1
1	32.3	37.6	41.9	45.9	49.3	52.1	54.8	57.1
2	36.0	41.2	45.3	49.1	52.3	55.1	57.8	59.9
3	38.7	43.8	47.9	51.6	54.8	57.4	59.9	62.0
5	43.2	48.0	51.7	55.3	58.4	60.9	63.2	65.1
10	51.0	55.3	58.6	62.0	64.5	66.7	68.8	70.4
15	56.7	60.7	63.6	66.5	69.0	70.9	72.8	74.4
20	61.4	65.1	67.8	70.4	72.6	74.5	76.2	77.5
30	69.0	72.2	74.4	76.7	78.4	79.8	81.3	82.3
40	75.3	77.9	79.7	81.7	83.0	84.0	85.2	86.2
60	85.3	86.9	88.0	89.2	90.1	90.7	91.4	91.8
80	93.4	94.1	94.5	95.2	95.6	95.8	96.2	96.4

TABLE 7

Maximum amplitude of total light reflected normally by filmed solids immersed in oil, $n_O = 1.505$ *(per cent of incident amplitude), for definite values of the index of refraction of the film (1.6 to 3.0) and of the reflectivity* $(k_{MF})^2$ *at the film-substratum interface (0.2 to 80 per cent)*

$$b_{\max.} = b_0 + (b_1 + b_3 + b_5 + \ldots . + b_{2p'+1}) - (b_2 + b_4 + b_6 + \ldots . + b_{2p'})$$

REFLECTIVITY	$n_F = 1.6$	$n_F = 1.8$	$n_F = 2.0$	$n_F = 2.2$	$n_F = 2.4$	$n_F = 2.6$	$n_F = 2.8$	$n_F = 3.0$
per cent								
0.2	7.6	13.3	18.5	23.1	27.1	30.8	34.1	37.1
0.5	10.2	15.9	20.9	25.5	29.5	33.2	36.4	39.4
1	13.1	17.7	23.8	28.2	32.2	35.8	38.9	41.8
2	17.1	22.7	27.7	32.1	35.9	39.3	42.5	45.2
3	20.3	25.8	30.7	35.0	38.6	42.1	45.0	47.8
5	25.2	30.7	35.3	39.5	43.1	46.5	49.1	51.8
10	34.4	39.4	43.7	47.6	50.9	53.8	56.4	58.7
15	41.3	46.0	50.1	53.7	56.6	59.4	61.7	63.8
20	47.2	51.7	55.4	58.7	61.4	63.8	65.9	67.9
30	56.9	60.7	63.9	66.7	69.1	71.1	72.9	74.4
40	65.1	68.2	71.2	73.3	75.3	77.0	78.5	79.9
60	78.6	80.8	82.5	84.1	85.3	86.4	87.2	87.9
80	90.2	91.2	91.9	92.8	93.2	93.8	94.1	94.7

stances whose index of refraction lies, say, between 1.8 and 2.8 will have a reflectivity against the film in all cases under 40 per cent. Under these circumstances the amplitudes of reflections of the fifth and higher orders are all less than 0.5 per cent and could be neglected. In the calculations for $b_{\text{min.}}$ and $b_{\text{max.}}$ (tables 4 to 7) this approximation was not made, amplitudes being neglected only if under 0.05 per cent. Had this further approximation been allowed, slightly different values for $b_{\text{min.}}$ and $b_{\text{max.}}$ would have been obtained. The effect of neglecting high-order reflections is mentioned in this connection, as the approximation it connotes is used in some of the calculations presented in this paper.

Values of the minimum reflected amplitude of filmed solids are presented in tables 4 and 5 for the cases of air immersion and oil immersion, for various values of the reflectivity of the solid against the film substance ranging from 0.2 to 80 per cent, and for various indices of refraction of film substances ranging from 1.6 to 3.0.

Tables 6 and 7 present corresponding values for the maximum reflected amplitude.

OPTICAL ANALYSIS TO ASCERTAIN THE QUALITY OF THIN FILMS

The expression $1 - \left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ can be regarded as measuring the maximum quantity of interference of light observable in a thin film of suitable thickness. Tables 8 and 9 give the values of the ratio $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ for the various values of n_F and $(k_{MF})^2$ used in tables 4 to 7. It is obvious that high values of this ratio connote the possibility of but poor interference, and that, conversely, low values of this ratio connote the possibility of good interference.

Consider the case in which the net intensity of the reflected light (from all reflections taken together) is minimum for wave length λ_1, and assume furthermore that this represents interference of the first order. It follows that for $\lambda_2 = \frac{1}{2}\lambda_1$ the net intensity of the reflected light is maximum (17). If λ_1 is at 8000 A. U., the extreme red end of the visible spectrum, then $\lambda_2 = 4000$ A. U. is at the extreme violet end of the visible spectrum. Suppose that $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ is 25 per cent; it follows that in relation to the abundance of red and violet in the incident light, the filmed surface reflects four times as much violet light as red light, perhaps three times as much blue light, twice as much green, etc. The impression on the eye will be of a colored film, the color perceived in all probability being some shade of blue.

While it is certain that a low ratio for $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ will yield an intensely colored film—if a film of the proper thickness is prepared—it is debatable

TABLE 8

Ratio (per cent) of intensity of reflected rays whose wave lengths are in the ratio of 1 to 2 (as for 4000 A. U. and 8000 A. U.) if the ray of longer wave length is of minimum amplitude; for various values of the index of refraction of the film and of the reflectivity* $(k_{MF})^2$ *at the film–air substratum interface; air immersion*

REFLECTIVITY	$n_F = 1.6$	$n_F = 1.8$	$n_F = 2.0$	$n_F = 2.2$	$n_F = 2.4$	$n_F = 2.6$	$n_F = 2.8$	$n_F = 3.0$
per cent								
0.2	47.8	56.4	61.6	66.7	69.9	72.3	74.5	76.4
0.5	30.0	39.7	46.4	51.8	56.2	59.7	62.6	65.2
1	17.0	26.1	33.1	39.1	44.0	48.0	51.8	54.4
2	6.5	13.6	19.7	25.4	30.6	34.8	38.4	41.4
3	2.3	7.5	12.5	17.5	22.2	26.2	30.3	33.4
5	0.0	2.0	5.5	9.1	12.7	16.2	19.9	22.8
10	3.4	0.3	0.1	1.2	3.1	5.1	7.4	9.7
15	9.2	2.9	1.0	0.0	0.2	0.9	2.2	3.5
20	15.3	8.1	4.0	1.5	0.3	0.0	0.2	0.7
30	27.9	18.4	12.6	8.0	4.9	2.8	1.5	0.6
40	38.7	29.6	22.8	17.0	12.7	9.6	6.9	5.1
60	60.5	52.5	45.9	40.0	35.1	31.0	27.1	23.8
80	80.5	75.8	72.0	67.4	64.1	61.0	58.2	55.2

* It is, of course, assumed that these rays have equal intensity in the incident light.

TABLE 9

Ratio (per cent) of intensity of reflected rays whose wave lengths are in the ratio of 1 to 2 (as for 4000 A. U. and 8000 A. U.) if the ray of longer wave length is at minimum amplitude; for various values of the index of refraction of the film and of the reflectivity,* $(k_{MF})^2$, *at the film-substratum interface; oil immersion,* $n_O = 1.505$.

REFLECTIVITY	$n_F = 1.6$	$n_F = 1.8$	$n_F = 2.0$	$n_F = 2.2$	$n_F = 2.4$	$n_F = 2.6$	$n_F = 2.8$	$n_F = 3.0$
per cent								
0.2	3.4	11.4	27.5	39.5	47.6	53.0	57.8	61.6
0.5	15.4	1.4	11.5	21.8	29.8	36.4	42.1	46.4
1	27.8	0.4	3.1	12.6	16.8	23.1	28.4	33.0
2	42.2	5.4	0.0	2.1	6.4	11.1	15.5	19.6
3	49.7	11.1	1.2	0.2	2.3	5.6	9.1	12.4
5	59.5	20.0	5.8	0.9	0.0	0.9	2.9	5.2
10	70.2	35.3	17.6	8.2	3.5	1.0	0.1	0.1
15	76.5	44.9	27.0	16.0	9.5	5.1	2.5	0.9
20	80.0	52.1	35.1	23.3	15.6	10.4	6.6	4.0
30	85.1	62.8	47.6	36.4	28.0	21.4	16.4	12.6
40	88.8	70.9	57.6	47.5	39.5	32.7	27.4	22.8
60	94.0	83.0	74.3	66.7	60.9	55.0	49.8	46.0
80	97.5	92.3	88.5	84.0	81.0	77.6	74.6	72.1

* It is, of course, assumed that these rays have equal intensity in the incident light.

where the line should be drawn between conditions indicating the possibility of good interference colors and those indicating the lack of such a possibility. In this connection it is useful to recall the variation with wave length in the reflectivity of the two colored metals, gold and copper (see table 2). In the case of these metals the ratio in reflectivity for $\lambda = 4000$ A. U. and 8000 A. U. is as 28:95 and 30:89, respectively, that is, the relative intensity of the reflected violet to the reflected red light is 29 and 33 per cent, respectively. Accordingly, one might well choose 25 per cent in relative value of $(b_{\min.})^2$ to $(b_{\max.})^2$ as the limit delineating the possibility of good from that of fair interference colors. Colors about as intense as those of gold or copper would be described as fair.

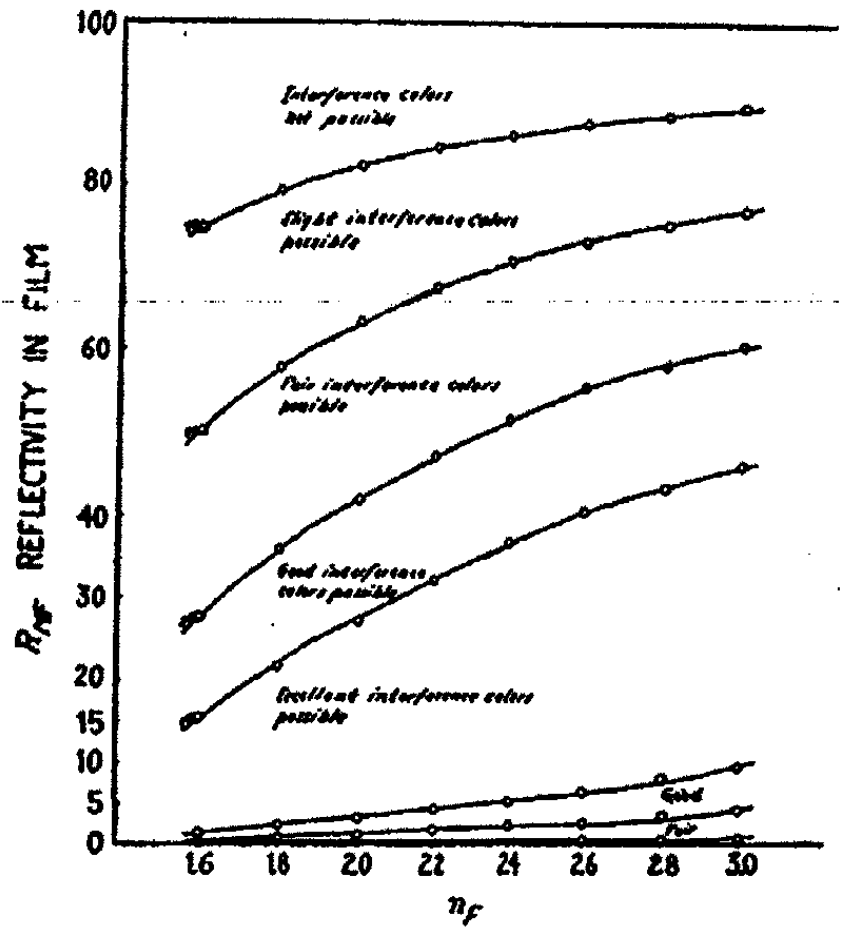

FIG. 3. Relation between index of refraction of film, n_F, reflectivity of mineral in contact with film, R_{MF}, and ratio of intensity of reflected rays whose wave lengths are in ratio of 1 to 2 (as for 0.400 and 0.800μ) if the ray of longer wave length is at minimum intensity, $\left(\frac{b_{\min.}}{b_{\max.}}\right)^2$. Air immersion.

With less justification 10 per cent has been chosen as the delineation between the possibility for excellent interference colors and that for good colors.

Many minerals usually rated as white or gray present variations in intensity of reflected light for various wave lengths such that the faintest reflectivity is but 80 to 90 per cent of the brightest. To err on the side of conservatism, therefore, 75 per cent for $\left(\frac{b_{\min.}}{b_{\max.}}\right)^2$ can be regarded as marking the impossibility of producing even a faint color.

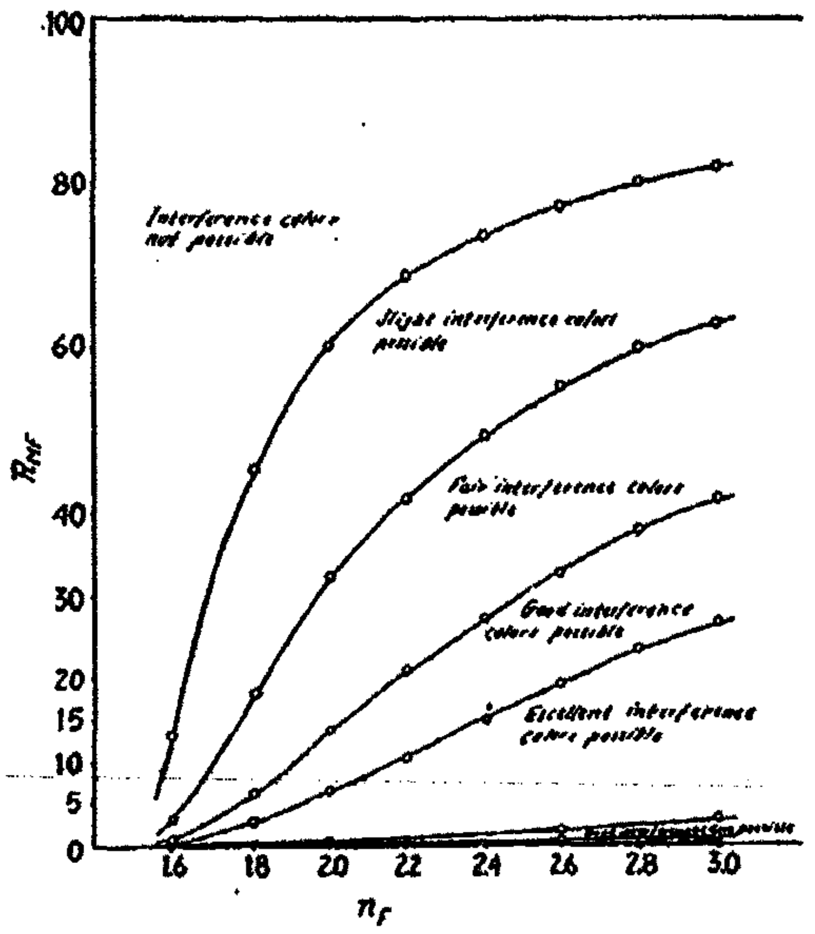

FIG. 4. Relation between index of refraction of film, n_F, reflectivity of mineral in contact with film, R_{MF}, and ratio of intensity of reflected rays whose wave lengths are in ratio of 1 to 2 (as for 0.400 and 0.800μ) if the ray of longer wave length is at minimum intensity, $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$. Oil immersion.

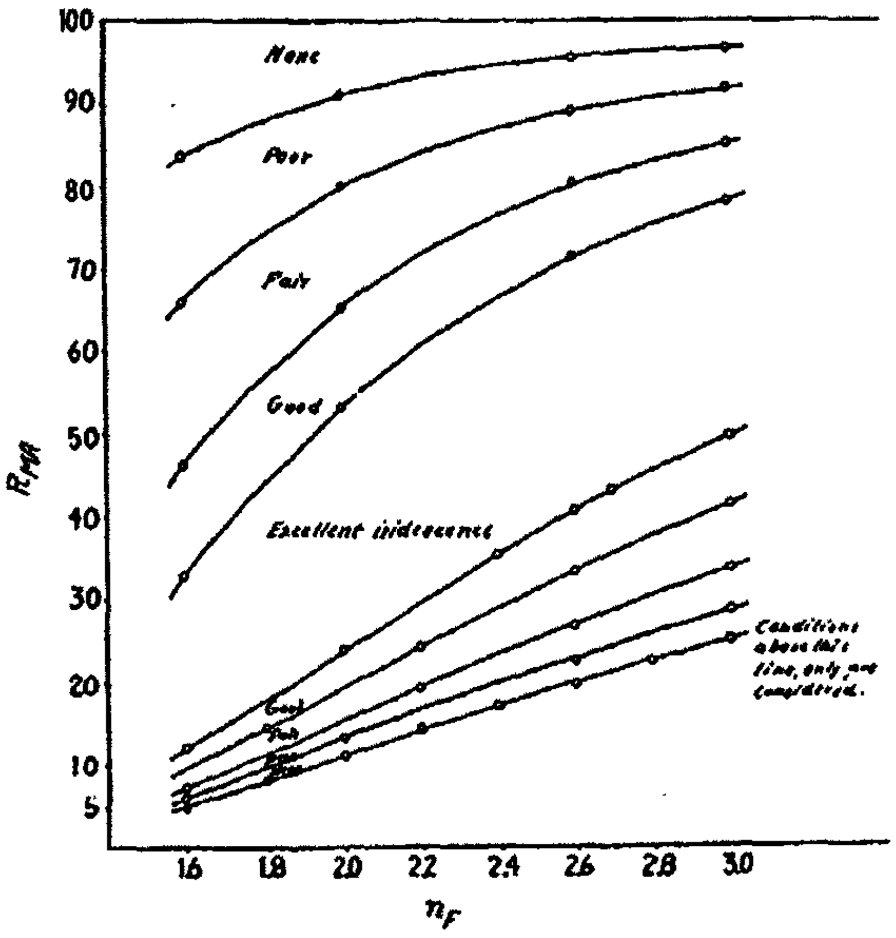

FIG. 5. Relation between index of refraction of film, n_F, reflectivity in air at mineral surface (treating mineral as if its reflectivity were due solely to its index of refraction), R_{MA}, and possibility of iridescent filming. Air immersion.

Judging from some colored minerals, as, for example, covellite, and from the color of the sky, it appears reasonable to take 50 per cent as the delineation between the possibility of producing fair iridescence and that of producing faint (or poor) iridescence.

Bearing in mind the conventions just outlined, namely, the set-up of divisional points at 10, 25, 50, and 75 per cent for $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$, the data of tables 8 and 9 have been diagrammed as figures 3 and 4. In these figures the coördinates are the index of refraction of the film and the reflectivity of the solid against the film. Lines of equal possibility of producing interference colors are drawn. Turning to figure 3, for example, it appears that if $R_{MF} = 100$ per cent, no interference colors can be obtained; likewise, if $R_{MF} = 0$ per cent. The first of these results agrees with the finding of Lord Rayleigh (60). The second implies that there is no reflection at the mineral–film boundary, hence no interference colors.

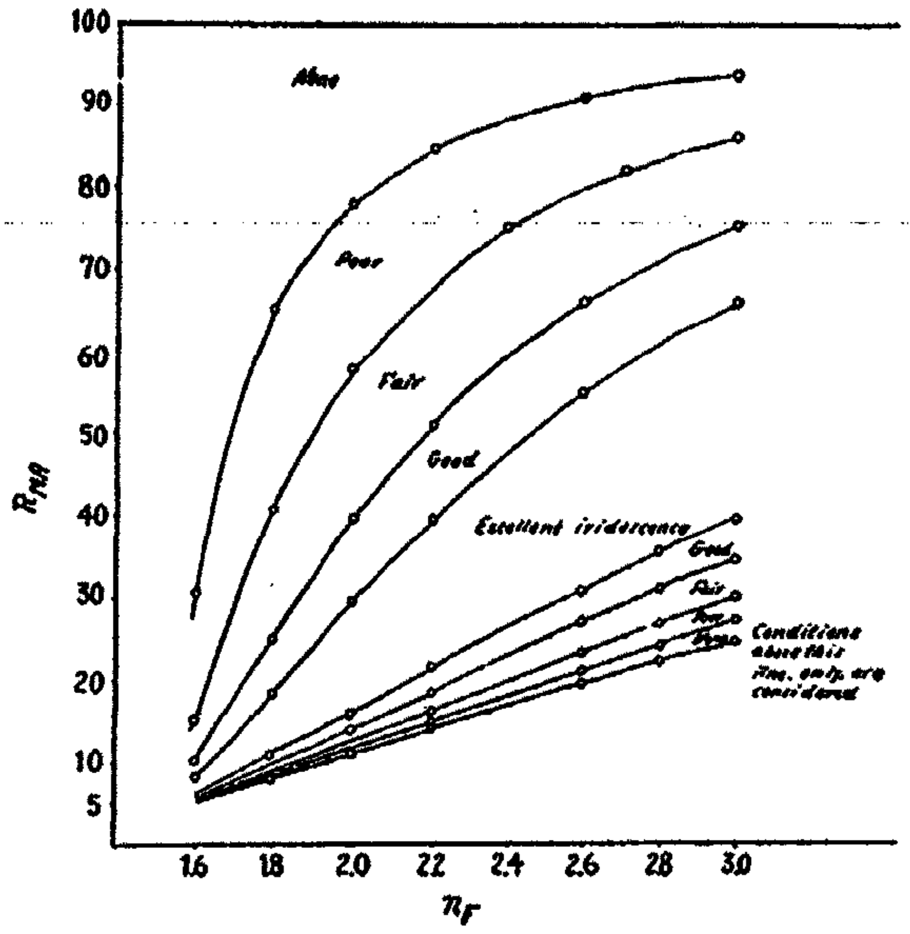

FIG. 6. Relation between index of refraction of film, n_F, reflectivity in air at mineral surface (treating mineral as if its reflectivity were due solely to its index of refraction), R_{MA}, and possibility of iridescent filming. Oil immersion.

Comparison of figure 4 with figure 3 makes it plain that a considerable difference exists between conditions as they involve air immersion and oil immersion.

In figures 3 and 4 the ordinate is the reflectivity of the solid in contact with the film. Since this quantity is generally unknown, and since the reflectivity in contact with air is generally known or readily determinable for most minerals, use has been made of the relations between k_{MA}, k_{MP}, and n_P to chart figures 5 and 6 from figures 3 and 4. In these charts the ordinate is the reflectivity of the substratum in contact with air.

Again, in this connection, emphasis must be placed on the assumption involved in the preparation of figures 5 and 6, namely, that the refractive index of an opaque (hence absorbing) medium can be obtained from its reflectivity just as if the substance in question were transparent. This in turn implies that the opaque substance is a perfect dielectric, a condition obviously not fulfilled in the case of the metals, and but imperfectly fulfilled in the case of sulfide minerals (but see Wood (61) and Phillips (39)).

AGREEMENT OF OPTICAL ANALYSIS WITH EXPERIMENT IN RESPECT TO POSSIBLE QUALITY OF THIN FILMS

It is interesting to note that considerable evidence is available to corroborate figures 5 and 6 and to give weight to the predictive value of these figures.

(*a*) Galena, when treated for a very short time with a solution of chromic trioxide, sulfuric acid, and water analogous to the solution of chromic trioxide, hydrochloric acid, and water described elsewhere (20), gives films brilliant by air immersion, but not so brilliant by oil immersion. One might expect the formation of films of lead chromate or lead sulfate (lead chloride, while possibly insoluble in the staining bath, is soluble in the wash water). The indices of refraction of these substances average 2.44 and 1.88, respectively, and the average of these average indices is 2.16. Figures 5 and 6 show that excellent iridescent films are possible if viewed in air and good if viewed under oil, since the reflectivity of galena in air is about 43 per cent (5).

(*b*) Iridescent films were not obtained on bornite, although the mineral was discolored when using either the chromic trioxide–hydrochloric acid–water solution or analogous solutions with sulfuric or hydrofluoric acids replacing hydrochloric acid, or solutions of iodine in methyl alcohol containing sulfuric or hydrochloric acids.

This experimental fact is confirmed by figures 5 and 6, from which it appears that the film should have an index of refraction lower than 2.0 to display "good" iridescence in air and 2.2 in oil. The index of refraction of copper iodide is over 2.2; cuprous and ferrous chlorides can hardly be expected to form in oxidizing baths; cupric and ferric chlorides and the cupric and ferric sulfates are soluble in the bath. The only other likely film substances are copper and iron chromates; no data are available concerning copper chromate, and chromite, $FeCrO_4$, has an index of refraction of 2.16. Pending direct contradiction the experimental case of bornite can be considered as verifying figures 5 and 6.

It might be argued that good iridescent colors form on bornite exposed to the action of oxygen, this being indeed the most characteristic feature of bornite in hand specimens. In this case the films are largely copper oxide, the index of refraction of which is very high and changes much with wave length. Constable (7) gives n as ranging from 3.1 at λ = 4500 A. U. to 2.9 at λ = 6000 A. U. and 2.55 at λ = 7500 A. U. At the same time the reflectivity of bornite in air (45) is 18.5 per cent for green light (λ = 5200 A. U. ±), 19 per cent for orange light (λ = 6500 A. U. ±), and 21 per cent for "rose" light (λ = 7000 A. U. ±). From figure 5 it is seen that interference is impossible for red and orange light, but possible (conditions below critical line) for blue and violet light. This suggests that with thickening film the flesh color of bornite should first darken to a red-brown, then become violet, then blue, these shorter wave-length colors appearing not because of destructive interference at the longer wave-length end of the spectrum, but because of constructive interference at the shorter wave-length end of the spectrum.

(*c*) After immersion in the chromic trioxide–hydrochloric acid–water bath, pentlandite takes on colors that are brilliant if viewed by air immersion but faint if viewed by oil immersion. Among possible oxidation products are the oxide of nickel and the chromates of iron and nickel.

No data are available for nickel chromate, but the indices for NiO and $FeCrO_4$ are given as 2.18 and 2.16, respectively, in the *International Critical Tables*. Constable (8) gives n (for NiO) as ranging from 2.38 to 2.00 with λ ranging from 4500 A. U. to 6800 A. U.; these values average at about 2.18. The film on pentlandite can then be regarded as having an index in the range of 2.15 to 2.2. On the other hand, the reflectivity of the mineral is reported by Schneiderhoehn as 51 per cent. At the same time, the reflectivity in oil is given as ranging from 41 per cent in green light to 47 per cent in orange light. Correcting the reflectivities to allow for surface roughness, pits, etc. by means of equations VI, treating the reflectivity in air as unknown, and making use of the ratio of the reflectivities in air and in oil, the corrected reflectivity in air becomes 66 per cent. Figures 5 and 6 show that good interference colors should be obtained in air and fair to poor colors in oil, thus confirming the experimental observations.

(*d*) Polybasite, if stained by a solution of iodine in methyl alcohol and sulfuric acid, takes on good colors in air; the colors become more brilliant still if viewed under oil. The reflectivity is about 27 per cent; the index of refraction of silver iodide is 2.22 and that of antimony oxide 2.0. Assuming an average index of refraction of the order of 2.15, it appears from figures 5 and 6 that good colors should be obtainable if the mineral is viewed in air and excellent colors if it is viewed in oil.

(*e*) Steel can be made iridescent by suitable tempering in air at a temperature below red heat.

From the reflectivity of steel (about 55 per cent) it is clear that excellent (or at least good) interference colors should be possible whether the oxide formed is ferric oxide (n in the vicinity of 3.0) or a mixture of FeO and Fe_2O_3 (8) whose index of refraction varies from 2.26 at $\lambda = 4500$ A. U. to 2.00 at $\lambda = 5500$ A. U. and 1.76 at $\lambda = 7000$ A. U. The problem is somewhat complicated here by the strong absorption of iron oxide, which makes the interference colors indistinct except for colors of the first order (8).

(*f*) Adherent films of mica on selenium display excellent iridescent colors, as may be seen by referring to the color photographs reproduced by Marcelin (34, 35). This agrees with the prediction of figure 5 in the case of a film having an index of refraction in the neighborhood of 1.6 (muscovite, $n = 1.58$) on a substratum having a reflectivity of the order of 25 per cent (selenium, $n_M = 20, 25, 35$ per cent for $\lambda = 7600, 5890, 4900$ A. U.).

(*g*) In all fairness attention should be called to the fact that figure 5 predicts failure in regards to the filming of silver with silver iodide, while the experimental fact is to the contrary (e.g., 18, 51). This can be explained away by invoking the high conductivity of silver, hence the failure of formula VIa expressing the unknown reflectivity of the metal in the film in terms of the reflectivity of the metal in air. The high reflectivity of silver is tantamount to the assumption of a very high index of refraction for that metal (of the order of 30 to 50), while modern theory of reflection at metallic surfaces places this index at from 0.16 to 0.18 (36). It can also be explained as has already been done by Evans (17) on the basis of absorption in film. In the present state of our knowledge neither "explanation" is wholly satisfying.

COLORS OF FILMS IN THE CASE THAT SUBSTANTIALLY PERFECT INTERFERENCE CAN BE PRODUCED

It is of interest to ascertain how the color of filmed minerals varies with increasing thickness of film. This can be done readily as follows:

If ϕ denotes the retardation of the reflection of first order as compared with the reflection of zero order for a given wave length of light λ, the amplitudes of the various reflections being $b_0, b_1, b_2, b_3 \ldots. b_n$, it follows that the amplitude of the x and y components of the total reflection are (remembering the $\lambda/2$ or π retardation caused by reflection from the surface of a denser medium into a rarer medium):

$$b_x = b_0 \cos 0 + b_1 \cos \phi + b_2 \cos (2\phi + \pi) + b_3 \cos (3\phi + 2\pi) + b_4 \cos (4\phi + 3\pi) + \ldots. + b_n \cos [n\phi + (n-1)\pi]$$

$$b_y = b_0 \sin 0 + b_1 \sin \phi + b_2 \sin (2\phi + \pi) + b_3 \sin (3\phi + 2\pi) + b_4 \sin (4\phi + 3\pi) + \ldots. + b_n \sin [n\phi + (n-1)\pi]$$

In the particular example $\phi = 0$, $b_y = 0$, and $b = b_x = b_{\text{max.}}$

$$\begin{aligned} b_{\text{max.}} &= b_0 + b_1 - b_2 + b_3 - b_4 \;\ldots. \\ &= b_0 + (b_1 + b_3 + b_5 + \ldots.) - (b_2 + b_4 + b_6 + \ldots.) \end{aligned}$$

In the particular example $\phi = \pi$, $b_y = 0$, and $b = b_x = b_{\text{min.}}$

$$b_{\text{min.}} = b_0 - b_1 - b_2 - b_3 \;\ldots. \; = b_0 - (b_1 + b_2 + b_3 \;\ldots.)$$

These special formulas are those already established for $b_{\text{max.}}$ and $b_{\text{min.}}$ by a less general method.

The general formulas for b_x and b_y can be simplified to:

$$\left.\begin{aligned} b_x &= b_0 + b_1 \cos \phi - b_2 \cos (2\phi) + b_3 \cos (3\phi) - b_4 \cos (4\phi) \;\ldots. \\ b_y &= b_1 \sin \phi - b_2 \sin (2\phi) + b_3 \sin (3\phi) - b_4 \sin (4\phi) \;\ldots. \end{aligned}\right\} \text{(VII)}$$

$\cos (n\phi)$ and $\sin (n\phi)$ can be expressed as functions in $\cos \phi$ and $\sin \phi$ of the n^{th} degree. Since it is rarely necessary to be concerned with reflections beyond that of the fourth order, b_x and b_y become fourth-degree functions in $\cos \phi$ and $\sin \phi$, the parameters being various summations in b_0, b_1, b_2, b_3, and b_4:

By suitable substitution b takes the form:

$$\left.\begin{aligned} b_x &= (b_0 + b_2 - b_4) + (b_1 - 3b_3) \cos \phi + (8b_4 - 2b_2) \cos^2 \phi + \\ &\qquad 4b_3 \cos^3 \phi - 8b_4 \cdot \cos^4 \phi \\ b_y &= (b_1 + 3b_3) \sin \phi - (2b_2 - 4b_4) \sin \phi \cos \phi - 4b_3 \sin^3 \phi - 8b_4 \\ &\qquad \cos^3 \phi \sin \phi \end{aligned}\right\} \text{(VIII)}$$

It is clear also that the retardation, ϕ, varies directly as the frequency of the light, that is, inversely as the wave length in air (provided the speed of light of all wave lengths through the film is the same, that is, providing the film has the same index of refraction for all wave lengths).

In order to place this analysis on the concrete basis of a typical example, consider the case in which the reflectivity of the mineral against the film is 10 per cent and the index of refraction of the film is 2.2 (reflectivity against air, 38.3 per cent). In this case

$$\begin{aligned} b_0 &= 37.6 \\ b_1 &= 27.2 \\ b_2 &= 3.2 \\ b_3 &= 0.4 \\ b_4 &= 0.0 \end{aligned}$$

TABLE 10

Relationship between wave length of light and intensity of illumination for a film of thickness 910 A. U. ($n_F = 2.2$; $(k_{MF})^2 = 10.0$ per cent, air immersion) in relation to intensity of illumination of the same surface, unfilmed

λ	ϕ	$\left(\frac{b}{b_{\text{max.}}}\right)^2$	λ	ϕ	$\left(\frac{b}{b_{\text{max.}}}\right)^2$
A.U.	*degrees*	*per cent*	*A.U.*	*degrees*	*per cent*
∞	0	100.0	1,714	840	28.7
96,000	15	98.7	1,655	870	8.4
48,000	30	94.1	1,600	900	1.2
32,000	45	87.9	1,548	930	8.4
24,000	60	78.6	1,500	960	28.7
19,200	75	67.4	1,454	990	54.8
16,000	90	54.8	1,411	1020	78.6
13,720	105	42.0	1,371	1050	94.1
12,000	120	28.7	1,333	1080	100.0
10,670	135	17.8	1,264	1140	78.6
9,600	150	8.4	1,200	1200	28.7
8,730	165	3.2	1,143	1260	1.2
8,000	180	1.2	1,091	1320	28.7
7,380	195	3.2	1,044	1380	78.6
6,860	210	8.4	1,000	1440	100.0
6,400	225	17.8	889	1620	1.2
6,000	240	28.7	800	1800	100.0
5,650	255	42.0	727	1980	1.2
5,340	270	54.8	667	2160	100.0
5,050	285	67.4	616	2340	1.2
4,800	300	78.6	572	2520	100.0
4,570	315	87.9	533	2700	1.2
4,360	330	94.1	500	2880	100.0
4,170	345	98.7	471	3060	1.2
4,000	360	100.0	445	3240	100.0
3,690	390	94.1	421	3420	1.2
3,460	420	78.6	400	3600	100.0
3,200	450	54.8	381	3780	1.2
3,000	480	28.7	363	3960	100.0
2,830	510	8.4	348	4140	1.2
2,670	540	1.2	333	4320	100.0
2,530	570	8.4	320	4500	1.2
2,400	600	28.7	308	4680	100.0
2,290	630	54.8	296	4860	1.2
2,180	660	78.6	286	5040	100.0
2,090	690	94.1	276	5220	1.2
2,000	720	100.0	267	5400	100.0
1,920	750	94.1	258	5580	1.2
1,850	780	78.6	250	5760	100.0
1,776	810	54.8			

and the equations describing the amplitude of the reflection for all wave lengths become:

$$b_x = 40.8 + 26.0 \cos\phi - 6.4 \cos^2\phi + 1.6 \cos^3\phi$$
$$b_y = 28.4 \sin\phi - 6.4 \sin\phi \cos\phi - 1.6 \sin^3\phi$$

with $b_{\text{max.}} = 62.0$; $b_{\text{min.}} = 6.8$; $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2 = 1.2$ per cent.

If $\phi = \pi = 180°$ for $\lambda = 8000$ A. U., then $\phi\lambda = 144 \times 10^4$ and for

$$\phi = 180°,\ \lambda = 8000 \text{ A. U.},\ b = b_{\text{min.}} = 6.8;$$
$$\phi = 360°,\ \lambda = 4000 \text{ A. U.},\ b = b_{\text{max.}} = 62.0;$$
$$\phi = 540°,\ \lambda = 2667 \text{ A. U.},\ b = b_{\text{min.}} = 6.8, \text{ etc.}$$

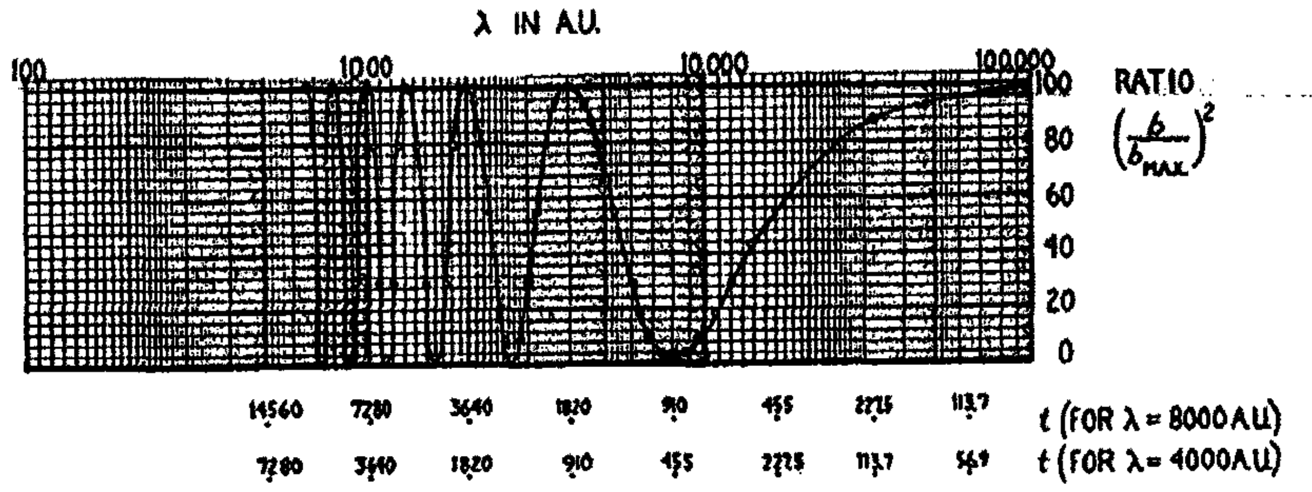

FIG. 7. Relative intensity of reflected light of various wave lengths if film is of such thickness that interference of first order occurs for $\lambda = 0.800\mu$ [$n_F = 2.2$; $(k_{MF})^2 = 10$ per cent].

Values of

$$\left(\frac{b}{b_{\text{max.}}}\right)^2 = \frac{b_x^2 + b_y^2}{(b_{\text{max.}})^2}$$

for various values of λ are presented in table 10 and are plotted in figure 7. In this figure a logarithmic scale was chosen for λ; even with that arrangement the squeezing together of successive crests and troughs of intensity of light with decreasing wave length of light is very marked. This would have been even more obvious had an arithmetic scale been chosen to plot λ.

The data of table 10 and figure 7 can be applied to thicknesses of film other than that which yields $\phi\lambda = 144 \times 10^4$. This is done by mere multiplication of the scale of abscissae by a suitable factor. Thus the case $\phi\lambda_1 = 144 \times 10^4$ requires (equation II) a film having a thickness $t_1 =$

$\frac{\lambda}{4 \times 2.2} = 910$ A. U. for maximum interference of the first order (first minimum amplitude).

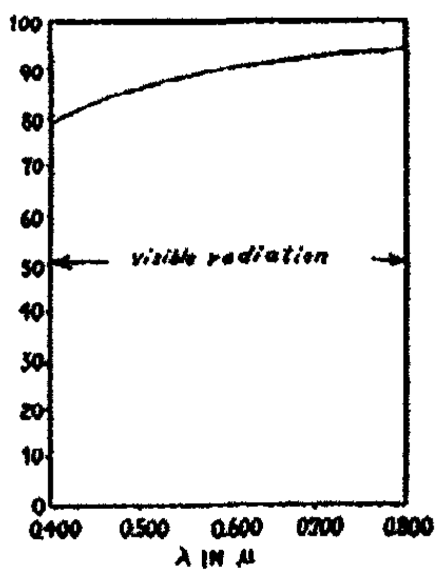

FIG. 8a. Film thickness, 152 A. U. Film color, gray-white.

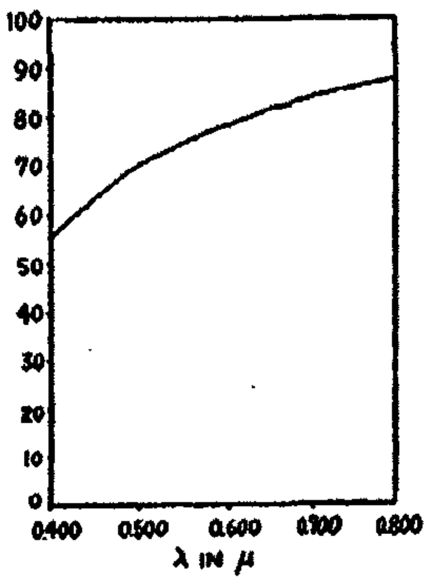

FIG. 8b. Film thickness, 227 A. U. Film color, yellowish-tan.

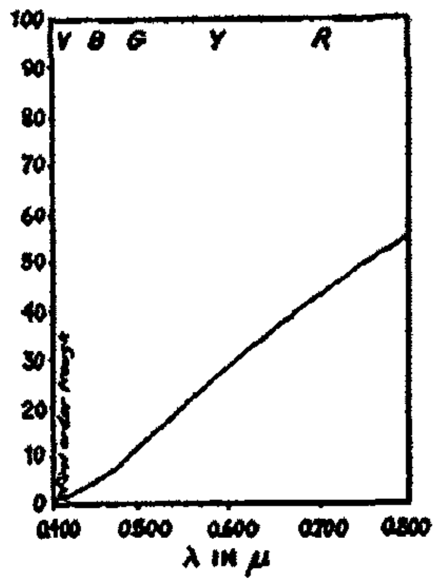

FIG. 8c. Film thickness 455 A. U. Film color, dark orange-red (orange-brown).

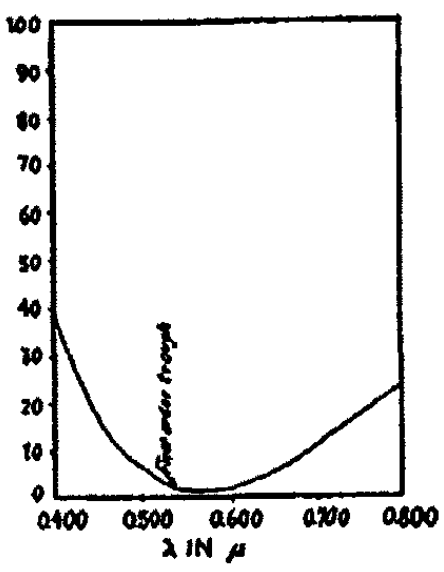

FIG. 8d. Film thickness, 637 A. U. Film color, dark purple.

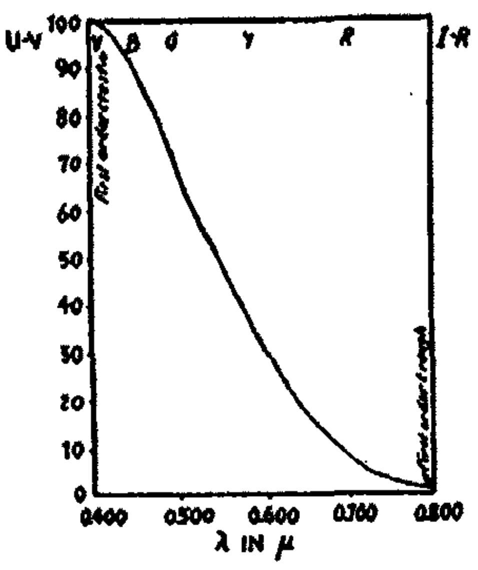

FIG. 8e. Film thickness, 910 A. U. Film color, brilliant blue.

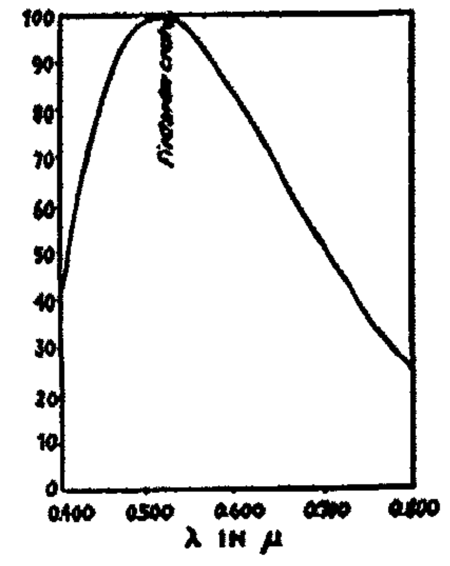

FIG. 8f. Film thickness, 1183 A. U. Film color, greenish-straw.

Likewise, for

$$t_2 = \tfrac{1}{2}t_1 = 455 \text{ A. U.},$$
$$\lambda_2 = \tfrac{1}{2}\lambda_1 = 4000 \text{ A. U.}$$

and

$$\phi\lambda_2 = 180 \times 4000 = 72 \times 10^4 = \tfrac{1}{2}\phi\lambda_1$$

It is merely sufficient, in order to plot $\left(\frac{b}{b_{\text{max.}}}\right)^2$ versus λ in the case of t_2, to read from table 10 values of λ equal to those appearing in the table multiplied by the ratio $\frac{\lambda_2}{\lambda_1}$ (which in this particular instance is ½), and to plot them against $\left(\frac{b}{b_{max.}}\right)^2$.

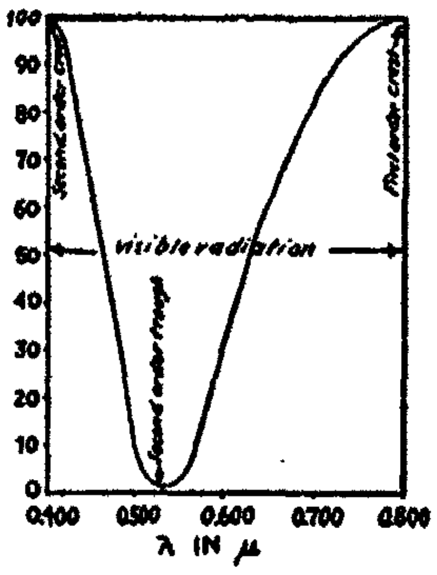

Fig. 8g. Film thickness, 1820 A. U. Film color, brilliant crimson-purple.

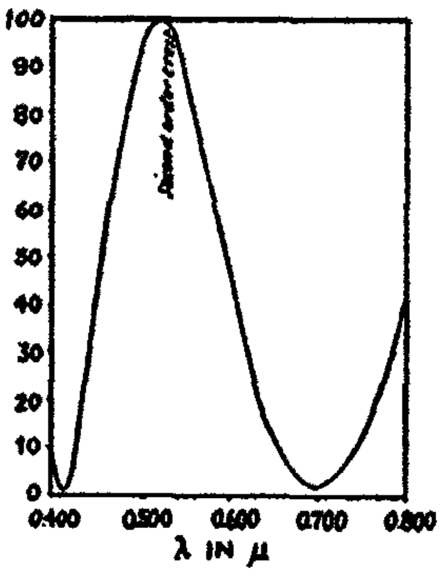

Fig. 8h. Film thickness, 2366 A. U. Film color, brilliant green.

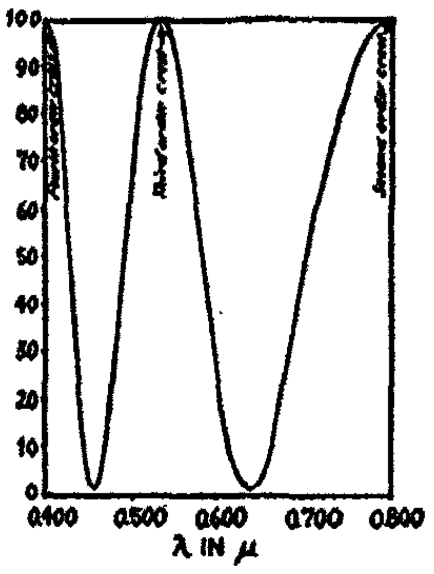

Fig. 8k. Film thickness, 3640 A. U. Film color, green.

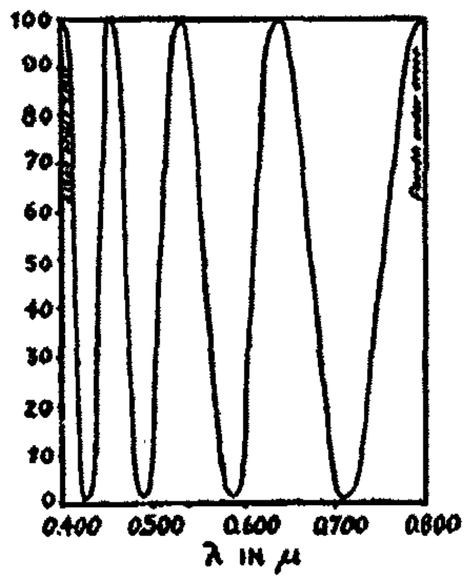

Fig. 8l. Film thickness, 7280 A. U. Film color, greenish-white.

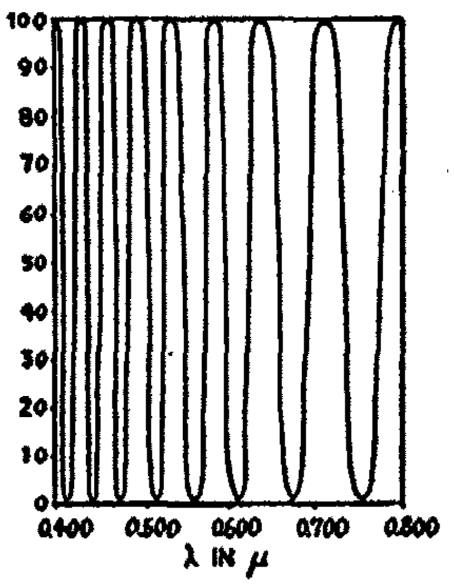

Fig. 8m. Film thickness, 14,560 A. U. Film color, gray-white.

Fig. 8 (a to m). Intensity of reflected light in relation to intensity of light of same wave length in unfilmed surface. Conditions are for possibility of substantially perfect interference (n_F = 2.2; $(k_{MF})^2$ = 0.10; air immersion). U-V = ultra-violet; V = violet; B = blue; G = green; Y = yellow; R = red; I-R = infra-red.

Figures 8a to 8m were drawn for thicknesses of film increasing from 152 A. U. to 14,560 A. U. These figures show many interesting features and are in agreement with observations from films produced experimentally: (*a*) Extremely thinly filmed surfaces behave as if unfilmed and have comparatively high reflectivities. (*b*) The thinnest films that are perceptible color the mineral faintly with a color toward the red end of the spectrum;

because of the considerable amount of yellow in the reflection, their color is some shade of tan. (*c*) Thicker films are gradually not only darker in color (lower reflectivity) but more intensely colored until a dark purple color is obtained (figure 8d). (*d*) The first blue film is one of the most characteristic (figure 8e). (*e*) No film showing a brilliant first-order green color can be produced (figure 8f). On the contrary good greens of second and third order can be prepared (figures 8h, 8k). (*f*) Films of higher order than third become increasingly near white in color (8l, 8m).

TABLE 11

Characteristics of films of various thickness ($n_F = 2.2$) formed at the surface of a solid having a reflectivity of 10 per cent against the film (38.3 per cent in air), viewed by air immersion, at normal incidence

THICKNESS OF FILM	INTENSITY OF LIGHT IN RELATION TO THAT WHICH WOULD BE REFLECTED IF UNFILMED, IN RANGE OF 4200 TO 7000 A.U.		RATIO $\frac{R_{max.}}{R_{min.}}$	ORDER OF INTERFERENCE	NUMBER OF MAXIMA AND MINIMA IN RANGE OF 4000 TO 8000 A.U.		INTENSITY OF COLORATION	INTENSITY OF ILLUMINATION	COLOR
	Minimum $R_{min.}$	Maximum $R_{max.}$			Maxima	Minima			
A.U.									
152	80	93	1.16	1	0	0	None	Very bright	White
227	58	84	1.45	1	0	0	Very pale	Bright	Tan
455	1.8	43	24	1	0	½	Strong	Dark	Orange
637	1.2	28	23	1	0	1	Strong	Very dark	Violet
910	6.5	98	15	1	½	½	Strong	Medium	Blue
1183	53	100	1.88	1-2	1	0	Very pale	Bright	Greenish-straw
1820	1.2	95	76	1-2	2@½	1	Very strong	Bright	Crimson-purple
2366	1.2	100	83	2	1	2	Very strong	Bright	Green
3640	1.2	100	83	2-4	1 + 2@½	2	Strong	Medium	Green
7280	1.2	100	83	4-8	3 + 2@½	4	Pale	Medium	Greenish
14560	1.2	100	83	8-16	7 + 2@½	8	None	Medium	Gray-white

In view of the fact that the eye is very much less sensitive to light whose wave length is near the ends of the visible spectrum than to that near the center (25), it is desirable in estimating the color perception of films from the intensity versus wave length charts (figures 8a to 8m) to neglect wave lengths shorter than 4200 A. U. and longer than 7000 A. U. The relative visibility of light of 4200 A. U. and 7000 A. U. is but 0.4 and 0.3 per cent, respectively, of light of the most visible wave length, 5560 A. U., and the relative visibility of wave lengths decreases very rapidly as the wave length decreases below 4200 A. U. or increases above 7000 A. U.

Table 11 summarizes some of the features brought out by figures 8a to 8m.

The thickness of film corresponding to incipient coloration can be obtained from figure 7. That figure has been drawn to represent the ratio $\left(\frac{b}{b_{\text{max.}}}\right)^2$ as a function of λ for a constant value of the thickness of film, t.

TABLE 12

Variations in relative intensity of extreme red and extreme violet in light reflected from a filmed solid for $n_F = 2.2$, $(k_{MF})^2 = 0.10$, with thickness of film in the range of first-order interference

t	$\left(\frac{b_{\lambda_2}}{b_{\text{max.}}}\right)^2$	$\left(\frac{b_{\lambda_1}}{b_{\text{max.}}}\right)^2$	$\left(\frac{b_{\lambda_2}}{b_{\lambda_1}}\right)^2$	COLORATION
A.U.	*per cent*	*per cent*	*per cent*	
72.8	94.2	98.8	95.4	None
145.6	80.1	94.2	85.1	None
182	69.0	92.0	75.0	None
202	62.5	90.5	69.1	Slight
228	54.8	87.9	62.4	Slight
243	50.7	86.0	59.0	Slight
280	36.5	81.5	44.8	Fair
331	21.5	74.5	28.8	Fair
347	16.5	72.0	22.9	Good
364	12.0	69.0	17.4	Good
379	8.4	67.5	12.4	Good
405	5.2	62.5	8.3	Excellent
417	3.2	60	5.3	Excellent
455	1.2	54.8	2.2	Excellent
486	1.2	48	2.5	Excellent
520	1.2	43.5	2.75	Excellent
560	1.2	36.0	3.3	Excellent
606	1.2	28.7	4.2	Excellent
662	1.2	47	2.6	Excellent
728	1.2	70	1.7	Excellent

But since λt = constant, a mere change of scale is sufficient to express the changes in $\left(\frac{b}{b_{\text{max.}}}\right)^2$ with changes in t for λ = constant: thus, the first t scale expresses variations of the ratio $\left(\frac{b}{b_{\text{max.}}}\right)^2$ for $\lambda = \lambda_1 = 8000$ A. U. and the second for $\lambda = \lambda_2 = 4000$ A. U. To get $\left(\frac{b_{\lambda_1}}{b_{\text{max.}}}\right)^2$ and $\left(\frac{b_{\lambda_2}}{b_{\text{max.}}}\right)^2$ it is merely necessary to read the ordinates for t corresponding to the two scales of t-abscissae. Results are presented in table 12.

It appears that the thinnest visible film is of the order of thickness of 190 A. U., or some fifty atomic layers.

This conclusion agrees with that of Tammann (48 to 54), who in one case regards the thinnest visible film of silver iodide as consisting of forty-five atomic layers. However, in that case Tammann's estimate of the film thickness is 500 A. U.; this would mean that an atomic layer of silver or iodine is some 11 A. U. thick; this value exceeds considerably the diameter of either the silver or iodine atoms or the silver or iodide ions, as determined by x-ray investigations of crystal structures. The concordance must therefore be regarded as rather of the nature of a coincidence.

Table 12 also shows that at first considerable thickening of the film is necessary to produce some change in brilliancy of coloration, while for thicker films, even small changes in thickness result in considerable changes in brilliancy.

This is in general agreement with the statement of Marcelin (34) that the first-order purple is most sensitive to changes in thickness. It is also in partial agreement with his statement (35) that the eye can perceive changes of shade corresponding to changes of film thickness (for $n_P = 1.6$) of the order of 7 A. U. It would seem that this statement holds only for films of such thickness as to yield the most sensitive colors, namely, in the first order purple to blue; in second- and third-order colors it is probably not approximated, and for first order below the violet as for higher orders than three, it is certainly not valid. In the judgment of the writer it is estimated that changes of color are perceivable without direct comparison (for $n_P = 2$ to 2.5) in the first-order tans if $\Delta t > 30$ to 50 A. U.; in the first order purple to blue if $\Delta t > 10$ to 15 A. U.; in the first order greenish-white to straw (the "hiatus" of Evans (12 to 19)) if $\Delta t > 50$ to 75 A. U.; in the second order yellow, red, and green if $\Delta t > 20$ to 30 A. U.

COLORS OF FILMS IN THE CASE THAT IMPERFECT INTERFERENCE ONLY CAN BE PRODUCED

The case so far considered was one corresponding to the possibility of securing practically perfect interference colors. It is of interest to consider also a case in which merely fair interference colors can be obtained at optimum thickness. The case $(k_{MP})^2 = 0.30$, $n_P = 2.2$, oil immersion, has been chosen as representative of this class of films. In this case:

$$b_0 = 18.8, \qquad b_1 = 52.9, \qquad b_2 = 5.4, \qquad b_3 = 0.6, \qquad b_4 = 0.1,$$

$$\left(\frac{b_{\text{min}}}{b_{\text{max.}}}\right)^2 = 36.4 \text{ per cent}$$

From equations VIII

$$b_x = (b_0 + b_2 - b_4) + (b_1 - 3b_3)\cos\phi + (8b_4 - 2b_2)\cos^2\phi + 4b_3\cos^3\phi - 8b_4\cos^4\phi$$

$$= 24.1 + 51.1\cos\phi - 10.0\cos^2\phi + 2.4\cos^3\phi - 0.8\cos^4\phi$$

$$b_y = (b_1 + 3b_3)\sin\phi - (2b_2 - 4b_4)\sin\phi\cos\phi - 4b_3\sin^3\phi - 8b_4\sin\phi\cos^3\phi$$

$$= 54.7\sin\phi - 10.4\sin\phi\cos\phi - 2.4\sin^3\phi - 0.8\sin\phi\cos^3\phi$$

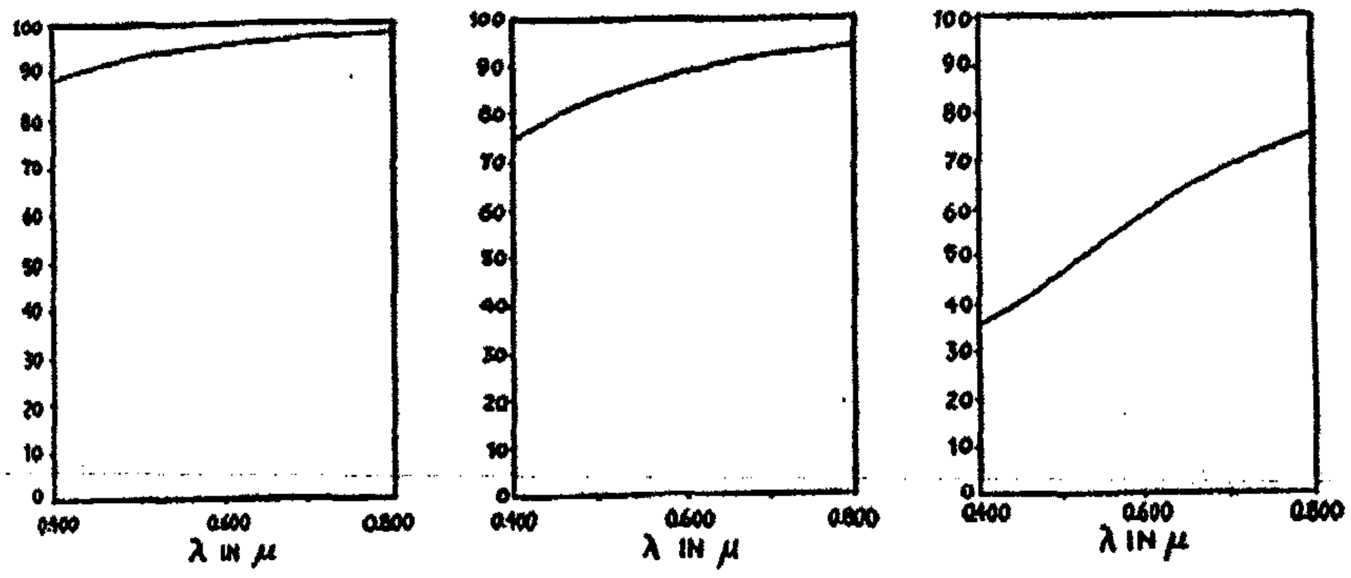

Fig. 9a. Film thickness, 152 A. U. Color, white

Fig. 9b. Film thickness, 227 A. U. Color, white

Fig. 9c. Film thickness, 455 A. U. Color, tan

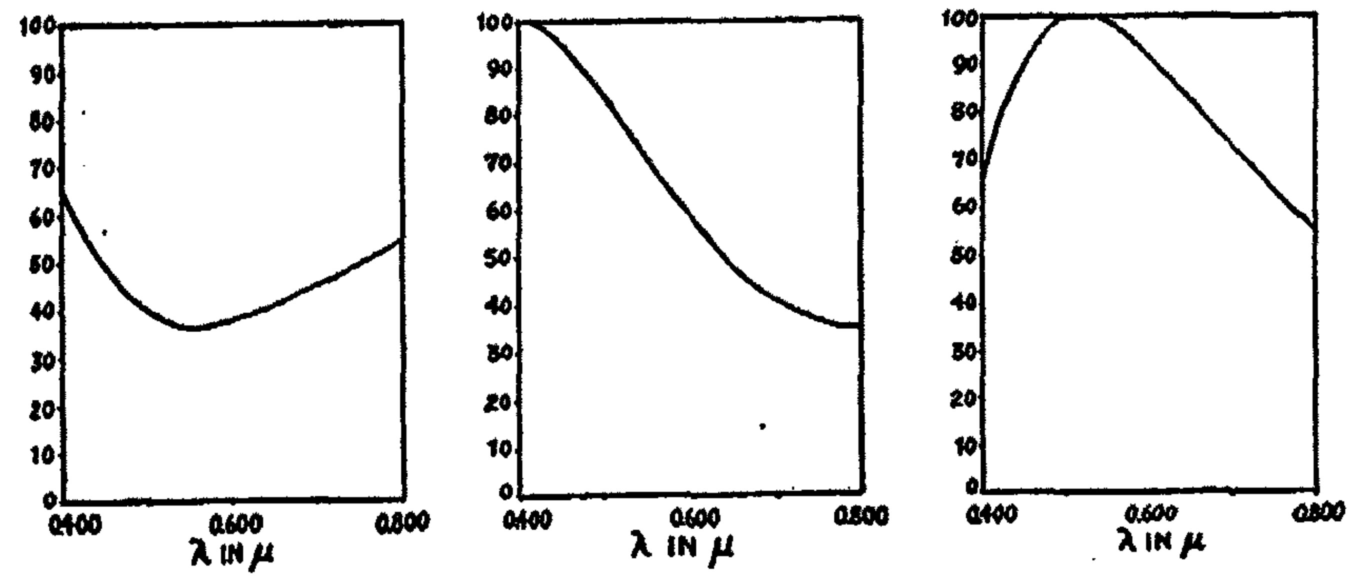

Fig. 9d. Film thickness, 637 A. U. Color, lavender

Fig. 9e. Film thickness, 910 A. U. Color, blue

Fig. 9f. Film thickness, 1183 A. U. Color, greenish-white

Fig. 9 (a to f). Intensity of reflected light in relation to intensity of light of same wave length in unfilmed surface. Conditions are for possibility of but imperfect interference ($n_F = 2.2$; $(k_{MF})^2 = 0.30$; oil immersion). Intensity of reflected light is expressed in per cent of that reflected by an unfilmed surface.

From these equations there were calculated values of b_x and b_y, hence of b^2 and of $\left(\frac{b}{b_{\max.}}\right)^2$ for ϕ increasing from 0° by 15° increments. Figures 9a to 9f have been drawn from these values in the same way as figures 8a to

8m were drawn from the values in table 10. Table 13 likewise parallels table 11.

These data show that if partial interference only can be made to occur, the colors of the films are paler than those of films obtained in those cases where complete interference is possible, and that these films are visible, but over a shorter range of film thicknesses. A detailed comparison of tables 11 and 13 is instructive.

TABLE 13

Characteristics of films of various thickness ($n_F = 2.8$) formed at the surface of a solid having a reflectivity of 30 per cent against the film (44.4 per cent in air), viewed by oil immersion

THICKNESS OF FILM	INTENSITY OF REFLECTED LIGHT IN RELATION TO THAT WHICH WOULD BE REFLECTED IF UNFILMED (IN RANGE OF 4200 TO 7000 A.U.)		RATIO $\frac{R_{max.}}{R_{min.}}$	ORDER OF INTERFERENCE	NO. OF MAXIMA AND MINIMA IN RANGE OF 4000 TO 8000 A.U.		COLORATION	LIGHT INTENSITY	APPEARANCE
	$R_{min.}$	$R_{max.}$			Maxima	Minima			
A.U.									
152	90	96.5	1.07	1	0	0	None	Very bright	White
227	77	92	1.20	1	0	0	None	Very bright	White
455	37	68	1.84	1	0	½	Very pale	Bright	Tan
637	36	57	1.62	1	0	1	Very pale	Bright	Lavender
910	36	100	2.78	1	½	½	Pale	Bright	Blue
1183	73	100	1.37	1-2	1	0	Very pale	Very bright	Greenish white
1820	36	96	2.67	1-2	2@½	1	Pale	Bright	Old rose
2366	36	100	2.78	2	1	2	Pale	Bright	Green
3640	36	100	2.78	2-4	1 and 2@½	2	Very pale	Bright	Greenish-white
7280	36	100	2.78	4-8	3 and 2@½	4	None	Bright	White
14560	36	100	2.78	8-16	7 and 2@½	8	None	Bright	White

EFFECT OF OBLIQUE ILLUMINATION, AS IN A METALLOGRAPHIC MICROSCOPE

In the foregoing analysis it was assumed that the incidence of the light falling on the filmed surface was normal. If it is not normal but oblique, everything is changed: the reflectivity, b^2, at the film surface, the reflectivity, k^2, at the substratum-film interface, and the retardation between the reflections of various orders ϕ_1, ϕ_2, ϕ_3, etc., due to the time required to traverse the film, are altered. There are also changes in the retardation due to reflection at rare medium to dense medium boundaries.

This for example, is recalled by Jung (27), who sketches the changes in the relative retardations of the component of the light vector polarized parallel and perpendicular to the plane of incidence with changes in the angle of incidence, using plane polarized incident light at 45° azimuth. According to Jung, at normal incidence there is no change of phase between the reflected components, while at grazing incidence these components differ by half a wave or $\lambda/2$. This does not mean, of course, that at normal incidence there is no retardation on reflection; Wood (62), for instance, makes a statement to the contrary. However, Wood and Jung do not agree as to the amount of the phase retardation on reflection at normal incidence, their values being $\Delta = \frac{\lambda}{2}$ and

$$\Delta = \text{arc tan}\left[\frac{-2n\kappa}{n^2(1+\kappa^2)-1}\right]$$

in which n is the index of refraction, κ the absorption coefficient, and λ the wave length. Both of these are presented on theoretical grounds.

TABLE 14

Characteristics of some microscope objectives (Bausch and Lomb)

FOCAL LENGTH	APPROXIMATE MAGNIFYING POWER	NUMERICAL APERTURE	MAXIMUM ANGLE OF INCIDENCE
mm.			
32	5	0.10	5°45′
16	10	0.25	14°30′
8	20	0.50	30°
4	25	0.85	58°20′
2 (oil)	90	1.30	59°40′

Fortunately, the phase difference between the parallel and perpendicular light vectors as determined experimentally is inconsiderable, unless the angle of incidence to the metal exceeds 30°. This appears, for example, in figure 5b of the article by Dayton (10), in which data for iron are presented after Jamin (26). At an angle of incidence to the metal of 25°, Δ is about $\frac{1}{60}\frac{\lambda}{2}$, that is, but 3 degrees of arc. As will appear presently, even with the widest-angle lens in use as a dry objective, the incidence to the mineral surface through the film rarely exceeds 25° (table 15).

In the case of oil-immersion objectives an incidence possibly as great as 40–45° may be encountered, particularly if the index of refraction of the film is low. In that case the relative retardation on reflection of the two components of polarized incident light, respectively parallel and perpendicular to the plane of incidence, may rise to $\frac{1}{12}\frac{\lambda}{2}$ or 15 degrees of arc.

It happens that in the examination of polished surfaces under a reflecting microscope the light impinging upon the object under examination ranges all the way from normally incident light to oblique light forming an angle i, whose sine is the numerical aperture of the objective divided by the index of refraction of the immersing medium. (Maximum i is about 60°.) For various objectives made by Bausch and Lomb, the focal length, approximate magnifying power, numerical aperture, and maximum angle of incidence are as given in table 14. This is in part according to W. L. Patterson (38).

VARIATION IN AMPLITUDE OF REFLECTIONS WITH INCIDENCE OF LIGHT; AIR IMMERSION

It is, therefore, of interest to examine first what happens to the amplitude of the reflections of various orders for angles of incidence up to 60° for both oil and air immersion. This can be done by means of the general Fresnel formula describing the reflectivity of a transparent substance at oblique incidence,

$$R = b^2 = \frac{1}{2}\left\{\left[\frac{\sin (i - r)}{\sin (i + r)}\right]^2 + \left[\frac{\tan (i - r)}{\tan (i + r)}\right]^2\right\} \qquad \text{(IX)}$$

in which i and r are the angles of incidence and refraction related by

$$n_A \sin i = n_F \sin r$$

For air immersion $n_A = 1$ so that $\sin i = n_F \sin r$.

To proceed with a similar estimation of the change in reflectivity at polished opaque mineral surfaces with changes in incidence, the assumption is again made that the reflectivity of the polished mineral can be regarded as related to the index of refraction as if the mineral were transparent. In the case of normal incidence,

$$(k_{MF})^2 = \frac{n_M - n_F}{n_M + n_F}$$

From this relationship n_M can be calculated if n_F and $(k_{MF})^2$ are known. For example, if $n_F = 2.2$ and $(k_{MF})^2 = 0.10$, $n_M = 4.235$. Extending the general formula describing the reflectivity at oblique incidence to polished opaque substances:

$$R = k^2 = \frac{1}{2}\left\{\left[\frac{\sin (r - r')}{\sin (r + r')}\right]^2 + \left[\frac{\tan (r - r')}{\tan (r + r')}\right]^2\right\} \qquad \text{(X)}$$

From the values of b and k, values of $b_0, b_1, b_2, \ldots\ b_p$, of $b_{\text{min.}}$, $b_{\text{max.}}$ and $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ can be calculated as functions of the incidence. Table 15 presents a typical analysis of this sort for $n_F = 2.2$, $(k_{MF})^2 = 10.0$ per cent at normal incidence.

It is interesting to observe that within the whole range of air-immersion lenses, even for incidences as high as 60°, there is no appreciable change in k_{MF}. Also one should note that there is no appreciable change in b provided an incidence lower than about 30 to 35° is used, while the change in b is marked at high obliquity (at 60° incidence an increase in b of over 15 per cent is noted).

TABLE 15

Variation with angle of incidence, i, using air immersion, in the case $n_F = 2.2$ if R_{MF} is 10 per cent at normal incidence, of the amplitude of the zero-order reflection, b; of the amplitude of the first-order reflection in the film layer, k_{MF}; of the amplitudes of reflection in air of various orders, $b_0, b_1, b_2 \ldots . b_p$; and of the ratio of the intensity of minimum illumination to maximum illumination, $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$

Angle of incidence, i, in degrees	0	20	30	40	45	50	55	60
Angle of refraction (in film), r, in degrees	0	8°56½′	13° 8′	17° 0′	18°45′	20°23′	21°52′	23°11′
Angle of refraction (in substratum), r', in degrees	0	4°38′	6°48′	8°44′	9°37′	10°26′	11°10′	11°48′
b in per cent	37.6	37.6	37.8	38.3	38.9	39.8	41.2	43.5
k_{MF} in per cent	31.6	31.6	31.6	31.6	31.6	31.6	31.6	31.7
b_0	37.6	37.6	37.8	38.3	38.9	39.8	41.2	43.5
b_1	27.2	27.2	27.1	27.0	26.8	26.6	26.2	25.7
b_2	3.2	3.2	3.2	3.3	3.3	3.4	3.4	3.5
b_3	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.5
b_4	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1
$b_{\text{min.}}$	6.9	6.9	7.1	7.6	8.4	9.4	11.1	13.7
$b_{\text{max.}}$	62.0	62.0	62.1	62.4	62.8	63.4	64.3	66.1
$\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$	1.2	1.2	1.3	1.5	1.8	2.2	3.0	4.3

Thus the analysis presented in this paper, up to the calculation of the ratio $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$, for normal incidence, applies to a very high approximation for the partly oblique illumination obtaining in the case of all objectives weaker than the 8 mm. objective, and including that objective, but it does not apply to the same high degree of approximation in the case of higher-power objectives.

It is seen from table 15 that, even if using a 4 mm. lens (maximum incidence near 60°), there is little change in the possible perfection of the interference with change in incidence. In all cases $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ is less than 10 per cent, thus indicating that the interference for individual rays of every possible obliquity (considered singly) remains in the zone of possible excellence. This does not mean that this is true of the total effect; indeed, it will later be shown that, strictly speaking, this is not always the case.

Two additional cases will be considered briefly with $n_P = 2.2$, one in which k_{MP} is large, the other small, compared to the value chosen for table 15. Specifically 1 per cent and 40 per cent were chosen as type values for $(k_{MP})^2$. In the first case n_M is 2.689; in the second, 9.73. In the case $n_P = 2.2$, k_{MP} small, increasing the angle of incidence makes the iridescence worse and worse. On the other hand, in the case $n_P = 2.2$, k_{MP} large, increasing the angle of incidence makes the iridescence better, at least up to an angle of incidence of 60°. It would seem that perfect iridescence, $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right) = 0$, should be obtained in the latter case for an incidence somewhere between 70 and 80°, and that for a still higher incidence the iridescence would become poorer and poorer until grazing incidence, at which position it would be nil since there is no refracted ray in the film at grazing incidence.

TABLE 16

Variation with angle of incidence of the reflectivity in the film and of the maximum and minimum amplitudes of reflection of surfaces having reflectivities of 1 per cent (case A) and 40 per cent (case B), respectively, against the film; $n_P = 8.2$

Angle of incidence to film, i, in degrees		0	30	35	40	45	50	55	60
Amplitude of reflection from film surface, b, in per cent		37.6	37.8	38.0	38.3	38.9	39.8	41.2	43.5
Amplitude of reflection from substratum, k_{MF}, in per cent	"A"	10.00	10.01	10.02	10.02	10.03	10.04	10.06	10.12
	"B"	63.25	63.25	63.25	63.25	63.25	63.25	63.25	63.25
Maximum amplitude of net reflection, $b_{\text{max.}}$, in per cent	"A"	45.9	46.1	46.3	46.5	47.1	47.9	49.2	51.2
	"B"	81.7	81.7	81.8	81.9	82.1	82.4	82.9	83.7
Minimum amplitude of net reflection, $b_{\text{min.}}$, in per cent	"A"	28.7	28.9	29.1	29.5	30.1	31.1	32.6	35.0
	"B"	33.7	33.5	33.2	33.0	32.2	31.3	29.8	27.3
$\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$, in per cent	"A"	39.1	39.3	39.5	40.3	41.8	42.2	43.9	46.8
	"B"	17.0	16.8	16.5	16.2	15.4	14.5	12.9	10.7

This explains, for example, why films of barium stearate on polished chromium formed by the successive transfer of unimolecular layers of barium stearate at the surface of water by the method of Langmuir and of Blodgett (2, 31, 6) are most brilliantly colored when viewed at some particular, highly oblique incidence.

Table 16 shows that there is very little change in k with change in incidence, whether k^2 is 1 per cent or 40 per cent at normal incidence, just as there is very little change in it if k^2 is 10 per cent (table 15). Table 16 shows also the variations in the amplitude of reflections of various orders, and in $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$, with variations in incidence of the light for the two cases in which the reflectivity in the film, at normal incidence, is 1 per cent and 40 per cent, respectively. The change in the trend of $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ with change in incidence is of interest.

For practical purposes the important thing to remember is that even for an incidence of 60° corresponding to a numerical aperture of 0.866 for air-immersion lenses, the change in the quality of the iridescence with changes in incidence of the light is not considerable, so that the analysis of interference effects when using a 4 mm. objective limits itself to a study of the effect of the various retardations caused by the various incidences.

VARIATION IN RETARDATION OF REFLECTIONS OF VARIOUS ORDERS WITH VARIATION IN INCIDENCE

It is now of interest to find out what change is effected by changing incidence in the retardation of the first-order reflection over the zero-order reflection. Since the effective thickness of the film must be $t \cos r$ it is sufficient in figure 7 to change the axis of abscissae by a translation equivalent to $\cos r$.

Figures 10a, 10b, and 10c show the relative intensities of illumination at various wave lengths in the two cases of normally incident light and light incident at 60°. It will readily appear that when dealing with color shadings due to very thin films (first-order tan) the use of a high-power lens giving rise to very oblique rays is not very objectionable. All it does is to require somewhat greater film thickness for visibility. On the other hand, in dealing with colors of the second to fourth orders the use of a high-power lens is bound to have a marked damping effect, as shown by figure 10c, since where a maximum occurs due to normal incidence a low intensity is had due to highly oblique incidence, and where a minimum occurs due to normal incidence a substantial intensity due to highly oblique incidence is obtained. Comparison of figures 10a, 10b, and 10c strongly suggests that with increasing thickness of film the height of the successive maxima of total illumination will gradually decrease, reaching some minimum value, while the height of the minima will gradually increase, reaching some maximum value. The net effect of simultaneous incidence at various angles will be to bleach the film, as compared with the effect that would be obtained if all the incident light struck the film at the same angle.

VARIATION IN AMPLITUDE OF REFLECTIONS WITH INCIDENCE OF LIGHT; OIL IMMERSION

In the case of an oil-immersion lens having a numerical aperture of 1.30, the oil having an index of refraction of 1.505, the inclination α of the most

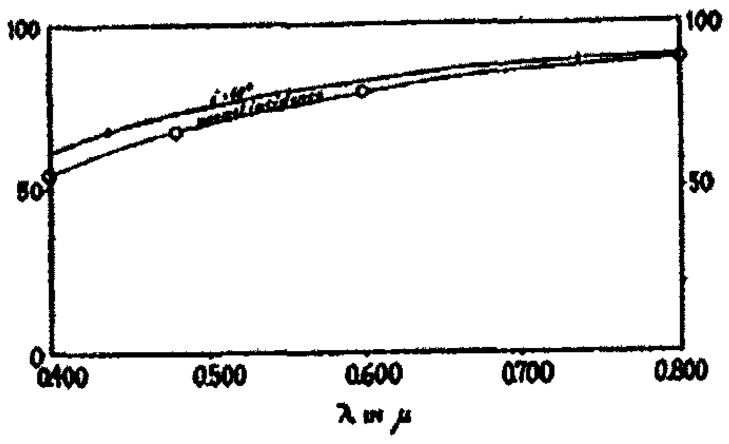

FIG. 10a. Film thickness, 227 A. U.

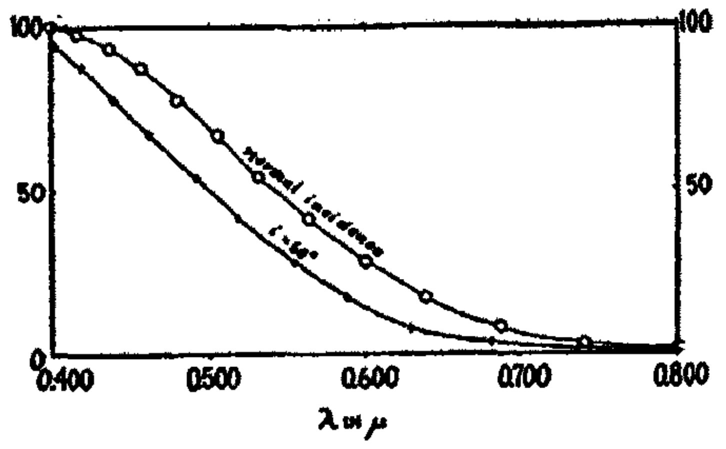

FIG. 10b. Film thickness, 910 A. U.

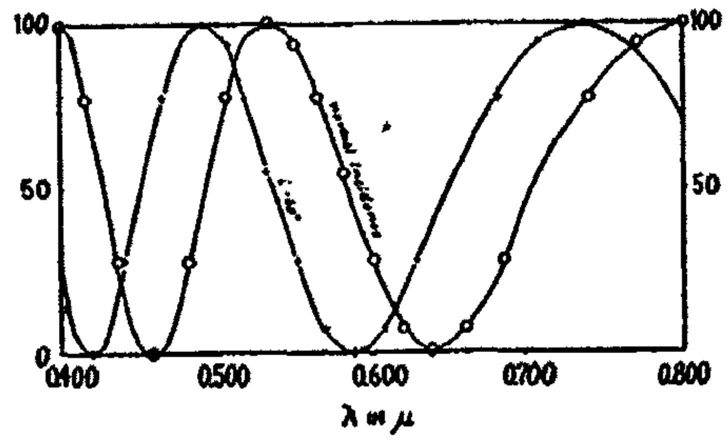

FIG. 10c. Film thickness, 3640 A. U.

FIG. 10 (a to c). Relative intensities of illumination at various wave lengths for normally incident light and light incident at $i = 60°$ if $n_F = 2.2$, $(k_{MF})^2 = 10$ per cent.

oblique ray admitted by the lens is such that $\sin \alpha = \frac{1.30}{1.505} = 0.864$, $\alpha = 59°50'$, or practically 60°.

Table 17 parallels table 15, for the case of oil immersion. It is seen that, while b varies considerably with change in incidence, there is practically no change in k_{MF}. It is clear that the effect of miscellaneous obliquities of incident rays is much more marked in the case of oil immersion than in the case of air immersion.

In figure 11 are plotted the relationship between distance along the face of the objective from center to edge, and the corresponding values of $b_{\text{min.}}$, $b_{\text{max.}}$, and $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$.

TABLE 17

Variation with angle of incidence, i, using oil immersion ($n_O = 1.505$), in the case $n_F = 2.2$, if R_{MF} is 30 per cent at normal incidence, of the amplitude of the zero-order reflection in the oil layer, b; of the amplitude of the first-order reflection in the film layer, k_{MF}; of the amplitudes of reflection in oil of various orders, $b_0, b_1, b_2 \ldots b_p$; and of the ratio of the intensity of minimum illumination to maximum illumination, $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$

Angle of incidence, i, in degrees	0	20	30	40	45	50	55	60
Angle of refraction (in film), r, in degrees	0	13°32′	20° 0′	26° 6′	28°56′	31°37′	34° 5′	36°20′
Angle of refraction (in substratum), r', in degrees	0	3°55½′	5°44½′	7°23′	8° 8′	8°49′	9°26′	9°58½′
b, in per cent	18.8	18.9	19.1	20.1	21.1	22.8	25.2	28.8
k_{MF}, in per cent	54.8	54.8	54.8	54.8	54.8	54.8	54.8	54.9
b_0	18.8	18.9	19.1	20.1	21.1	22.8	25.2	28.8
b_1	52.9	52.8	52.8	52.6	52.3	52.0	51.4	50.3
b_2	5.4	5.5	5.5	5.8	6.0	6.5	7.1	7.9
b_3	0.6	0.6	0.6	0.6	0.7	0.8	1.0	1.3
b_4	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
$b_{\text{min.}}$	40.2	40.1	39.9	39.0	38.0	36.6	34.4	30.9
$b_{\text{max.}}$	66.8	66.8	66.9	67.4	68.0	69.0	70.4	72.3
$\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$	36.2	36.1	35.6	33.5	31.2	28.1	23.9	18.3

RELATIONSHIP OF WAVE LENGTH TO AMPLITUDE OF REFLECTED LIGHT; OIL IMMERSION

It is proposed to determine the λ-b curve for the total reflected light from all parts of the lens and for a given thickness of film, t.

For any one value of λ, b is the sum of all the individual values Δb of the elementary rays. It can fairly be assumed that the illumination on the object is uniform, and that each unit area on the lens face contributes equally to this illumination. Hence, the light coming from all the points A on the face of the objective situated at distance x from the center can be regarded as coming from x such points. As a first approximation the objective can be regarded as made up of ten concentric annular bodies of average radii equal to 1/20, 3/20, 5/20, 7/20, 9/20, 11/20, 13/20, 15/20, 17/20, 19/20 of the outer radius of the front lens of the objective. The abundance of the light from these bodies is as 1, 3, 5, 7, 9, 11, 13, 15, 17, 19. Values of $b_{\text{min.}}$ and $b_{\text{max.}}$ as a function of x are presented in figure 11.

Table 18 presents the *weighted average value of b* for the case t = 910 A. U., for various values of λ ranging down from ∞ to 500 A. U. These values were obtained from curves (not presented in this paper) in which individual values of b against λ were plotted for various values of x, namely, 1, 3, 5, 7, 9, 11, 13, 15, 17, and 19.

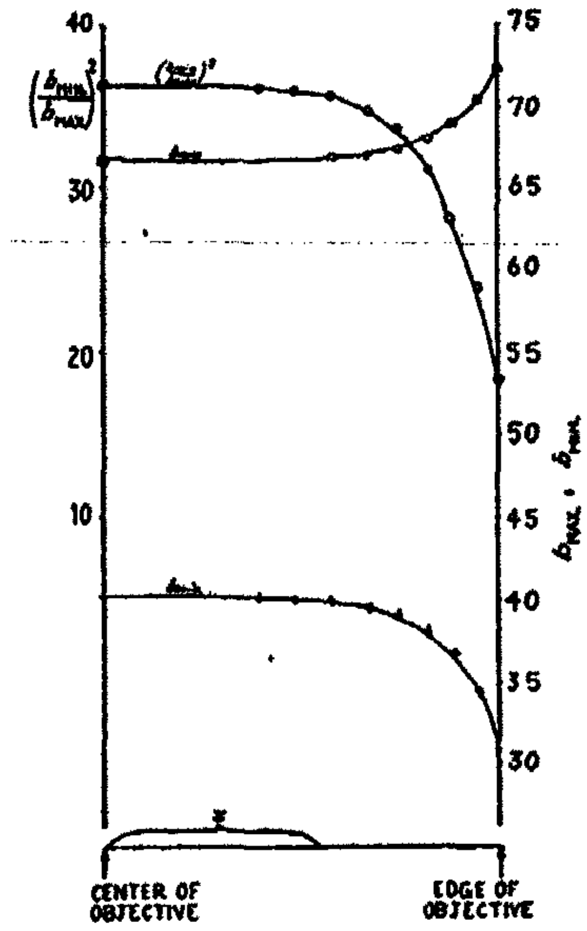

FIG. 11. Values of $b_{\text{min.}}$, $b_{\text{max.}}$, and $\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$ for an oil-immersion lens (n_D = 1.505, numerical aperture = 1.30) if n_P = 2.2 and k_{MP} = 30 per cent.

The intensity of the reflection for the various maxima and minima is obtained by squaring the various maxima and minima in 'b' which can be read from a charted presentation of the data of table 18. These particular intensities, together with the ratio of successive pairs, are presented in table 19. Figure 12, which corresponds to figure 7, and which must be compared with it, sums up in graphical form the damping action of a wide-angle lens on the brilliancy of iridescent films.

In this theoretical estimation of the damping action of wide-angle lenses on iridescence, the tacit assumption has been made that the phase retardation on reflection at the surface of the opaque solid is not a function of the

TABLE 18

Variations with wave length, λ, in weighted average amplitude of reflection from filmed mineral surface viewed with an oil-immersion objective N.A. = 1.30, if $n_F = 2.2$, $(k_{MF})^2 = 0.30$, $t = 910$ *A.U.*

λ	b	λ	b	λ	b
A.U.	*per cent*	*A.U.*	*per cent*	*A.U.*	*per cent*
∞	68.0	2,500	46.9	930	50.0
50,000	67.5	2,300	41.6	880	59.4
30,000	65.9	2,250	41.6	840	61.5
20,000	63.3	2,200	42.4	800	57.8
16,000	60.4	2,000	53.9	760	51.1
13,000	56.7	1,850	63.4	740	49.3
10,000	49.0	1,750	66.1	720	51.1
8,625	43.6	1,700	66.1	690	57.9
7,750	40.4	1,600	61.9	670	60.6
7,250	39.1	1,500	54.2	650	59.3
6,750	38.7	1,400	46.0	620	53.5
6,500	39.3	1,350	44.8	600	49.8
6,000	41.7	1,300	47.9	580	54.8
5,000	52.0	1,250	54.9	560	60.1
4,000	64.6	1,200	61.4	550	60.3
3,700	66.8	1,150	63.8	520	52.3
3,500	67.4	1,100	61.6	510	50.0
3,300	67.1	1,000	50.3	500	52.0
3,000	63.8	960	47.9		

TABLE 19

Intensities of maxima and minima in light reflected from a filmed mineral viewed with an oil-immersion objective, N.A. = 1.30, if $n_F = 2.2$, $(k_{MF})^2 = 0.30$, $t = 910$ *A.U.; also ratio of each minimum to the corresponding maximum*

	INTENSITY		RATIO
	per cent		*per cent*
Maximum zero order	46.3		
Minimum first order		14.9	32
Maximum first order	45.6		
Minimum second order		17.2	38
Maximum second order	44.1		
Minimum third order		20.0	45
Maximum third order	40.7		
Minimum fourth order		22.8	56
Maximum fourth order	37.9		
Minimum fifth order		24.2	64
Maximum fifth order	36.8		
Minimum sixth order		24.8	67
Maximum sixth order	36.3		
Minimum seventh order		25.0	69

incidence. This, however, is possibly not strictly true (11, 23, 27). Obviously, variations in the phase retardation with incidence will make the various amplitude–wave length curves (e.g., such as shown in figure 11) still more out of step. Unfortunately so little is known concerning the changes in phase retardation with incidence that it is impossible to evaluate the effect of this variable on the amplitude of the net reflected light in function of wave length.

Table 19 and the consideration just outlined give theoretical justification for the observation otherwise frequently made in the laboratory that iridescent films of a high order are bleached when viewed by high-power oil-immersion objectives, while still fairly well colored when viewed with low-power, dry objectives.

Comparing films giving interference colors of high order with first-order films it is clear that their quality is impaired if viewed with low-power objectives because of the crowding together of maxima and minima within the visible spectrum; if the viewing is through high-power objectives, a further impairment in the quality of the film arises from the increasing damping in the maxima and minima of the amplitude of the net reflection with increasing thickness of film. This defect is particularly acute in the case of oil-immersion objectives and adds itself in this case to a third defect arising from the usually inadequate reflection at the film–oil boundary.

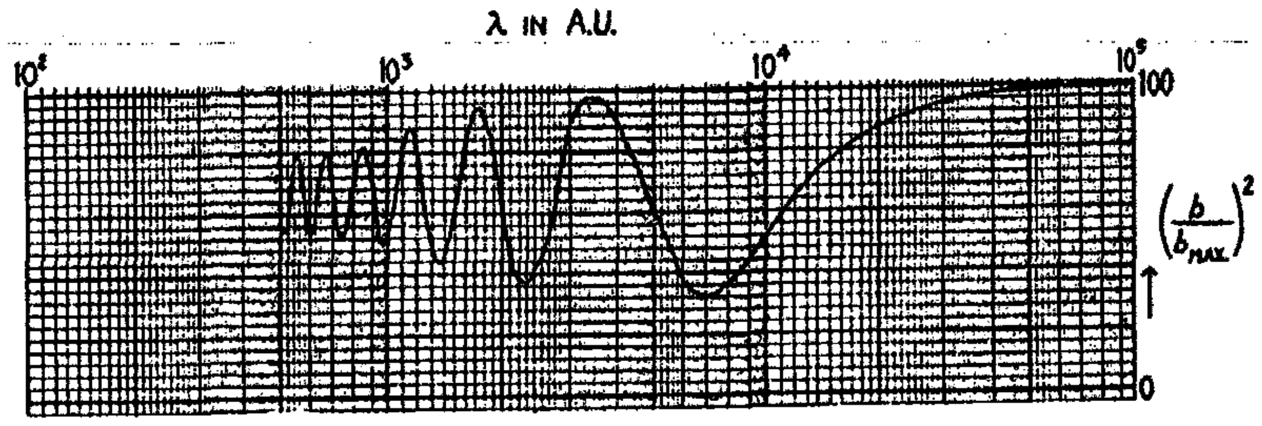

FIG. 12. Relative intensity of reflected light of various wave lengths if film is of such thickness that interference of first order occurs for λ = 8000 A. U. ($n_F = 2.2$; $(k_{MF})^2 = 30$ per cent), using an oil-immersion lens having a numerical aperture of 1.30.

INTERFERENCE EFFECTS CAUSED BY ABSORBING FILMS WHICH ABSORB IN NON-SELECTIVE FASHION

It is of importance to consider the effect of films displaying absorption, first of a non-selective character, then of a selective character.

In the case of non-selective absorption, let T be the distance that must be traveled by light in the absorbing film in order that the amplitude be

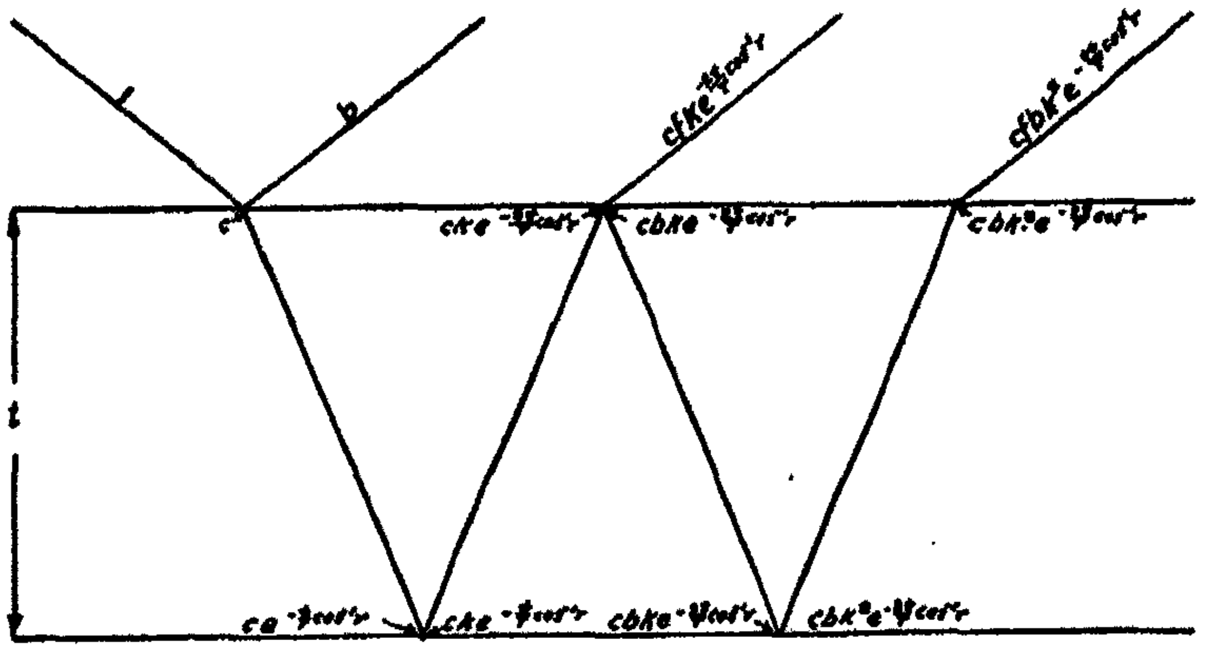

Fig. 13. Multiple reflection at a filmed surface, filmed by an absorbing substance

TABLE 20

Damping factor due to absorption in film for single (α) *and multiple reflections* (α^2, α^3, α^4, *etc.*):

$$\alpha = e^{-2\frac{t}{T}}$$

$\frac{t}{T}$	α	α^2	α^3	α^4
0.010	0.9802	0.961	0.942	0.923
0.020	0.9608	0.923	0.887	0.852
0.050	0.9049	0.819	0.741	0.670
0.100	0.8187	0.669	0.550	0.488
0.150	0.7408	0.549	0.407	0.301
0.200	0.6704	0.444	0.296	0.197
0.300	0.5488	0.301	0.166	0.090
0.400	0.4494	0.202	0.091	0.041
0.500	0.3679	0.135	0.050	0.018
0.600	0.3012	0.092	0.027	0.008
0.700	0.2466	0.060	0.015	0.004
0.800	0.2019	0.041	0.008	0.002
0.900	0.1653	0.027	0.005	0.001
1.000	0.1353	0.018	0.002	
1.200	0.0908	0.008	0.001	
1.500	0.0498	0.002		
1.800	0.0274	0.001		
2.000	0.0183			
2.500	0.0069			
3.000	0.0025			
4.000	0.0003			

reduced *e*-fold (*e* being the base of naperian logarithms). The amplitude of successive reflections from the film surface is as follows:

$$b_0 = b$$
$$b_1 = (1 - b^2)\, k\, e^{-2\frac{t}{T}\cos r^{-1}}$$
$$b_2 = (1 - b^2)\, bk^2\, e^{-4\frac{t}{T}\cos r^{-1}}$$
$$b_p = (1 - b^2)\, b^{p-1}\, k^p\, e^{-2p\frac{t}{T}\cos r^{-1}}$$

in which p, t, r, b, k have the same significance as previously. This is made obvious by mere inspection of figure 13.

TABLE 21

Amplitude of reflection by filmed solid in air (per cent of incident amplitude) due to multiple reflection at normal incidence for $n_F = 2.2$, $(k_{MF})^2 = 10$ *per cent, for various values of* t/T (T = *thickness at which amplitude is reduced from 1 to* e^{-1}, *and* t = *thickness of film*)

$\frac{t}{T}$	b_0	b_1	b_2	b_3	$b_{\text{min.}}$	$b_{\text{max.}}$	$\left(\frac{b_{\text{min.}}}{b_{\text{max.}}}\right)^2$
0	37.6	27.2	3.2	0.4	6.8	62.0	1.2
0.050	37.6	24.6	2.6	0.3	10.1	59.9	2.8
0.100	37.6	22.3	2.1	0.2	13.0	58.0	5.0
0.200	37.6	18.2	1.4	0.1	17.9	54.5	10.8
0.300	37.6	14.9	1.0	0.1	21.6	51.6	17.5
0.400	37.6	12.2	0.6	0.0	24.8	49.2	25.4
0.500	37.6	10.0	0.4	0.0	27.2	47.2	33.2
0.600	37.6	8.2	0.3	0.0	29.1	45.5	40.9
0.700	37.6	6.7	0.2	0.0	30.7	44.1	48.4
0.800	37.6	5.5	0.1	0.0	32.0	43.0	55.4
0.900	37.6	4.5	0.1	0.0	33.0	42.0	61.8
1.000	37.6	3.7	0.1	0.0	33.8	41.2	67.3
1.200	37.6	2.5	0.0	0.0	35.1	40.1	76.7
1.500	37.6	1.4	0.0	0.0	36.2	39.0	86.2
1.800	37.6	0.7	0.0	0.0	36.9	38.3	92.9
2.000	37.6	0.5	0.0	0.0	37.1	38.1	95.0
2.500	37.6	0.1	0.0	0.0	37.5	37.7	99.0
3.000	37.6	0.0	0.0	0.0	37.6	37.6	100.0

At normal incidence $\cos r = 1$, and if $\alpha = e^{-2\frac{t}{T}}$, b_p takes the form:

$$b_p = (1-b^2)\, b^{p-1}\, k^p\, \alpha^{+p} \tag{XI}$$

Values of α, α^2, α^3, α^4, in terms of $\frac{t}{T}$ are given in table 20.

Consider again the particular case $n_F = 2.2$, $(k_{MF})^2 = 10$ per cent. Values of b_0, b_1, b_2, b_3, for various thicknesses expressed in terms of t/T, at normal incidence are given in table 21.

From this tabulation it is abundantly clear that as $\frac{t}{T}$ exceeds 0.2, 0.4, 0.7, and 1.2, respectively, the optimum quality of the interference colors is reduced from excellent to good, fair, poor, and none.

This is portrayed in a most graphic manner by figures 14a to 14j in which are plotted simultaneously the b^2–λ curves for various thicknesses of film ranging from 200 A. U. to 2400 A. U., first in the case that the absorption is nil ($T = \infty$; dash lines), secondly in the case of rather strong but non-selective absorption ($T = 2000$ A. U.; solid lines), and lastly in the case of selective absorption (dash and dot lines). Attention is now drawn to the first and second sets only. Figures 14a to 14c show that for thin films (in the special case under consideration) there is little difference as between the absorbing and the non-absorbing films. A considerable and constantly increasing difference is manifest as films are made thicker. This is shown by figures 14g to 14j which contrast the brilliant interference colors resulting from non-absorbing films with the dully tinted gray-whites of absorbing films.

It is of interest to note that if the reflectivity of the solid is too high, for a given index of refraction of the film, to permit more than the poorest interference (see, e.g., figure 5, upper part of chart), this defect can be eliminated to some extent if the film is absorbing. In such a case, as the film thickens the amplitude of the reflections which have traveled through the film are gradually reduced and become of an order of magnitude small enough to interfere, constructively and destructively according to the wave length, with the zero-order reflection. Thin films in such a case fail to display interference colors, but thicker films may begin to display them, so that theoretically at least, good second- and third-order colors should be possible for a surface which fails to give first-order colors, or gives but poor colors of that type.

INTERFERENCE EFFECTS CAUSED BY ABSORBING FILMS WHICH ABSORB SELECTIVELY

This problem is somewhat more complicated, but it can be treated just as the foregoing problem, making use of tables 20 and 21 together with the fundamental general equations VIII.

Figures 14a to 14j present the relationship between the reflectivities and wave length in such a way that direct comparison is possible between the characteristics of a selectively absorbing film [$n_F = 2.2$; $(k_{MF})^2 = 10$ per cent; air immersion; normal incidence, dash and dot lines], a non-selectively absorbing film [$T = 2000$ A. U.], and a perfectly transparent film. The selectively absorbing film was chosen arbitrarily to have the λ–T relationship summarized in table 22. This relationship is such that by transmitted light the substance will have a strong orange or red color (relative paucity of violet, blue, and green).

Figure 14a shows that a solid filmed in such a manner as is here postu-

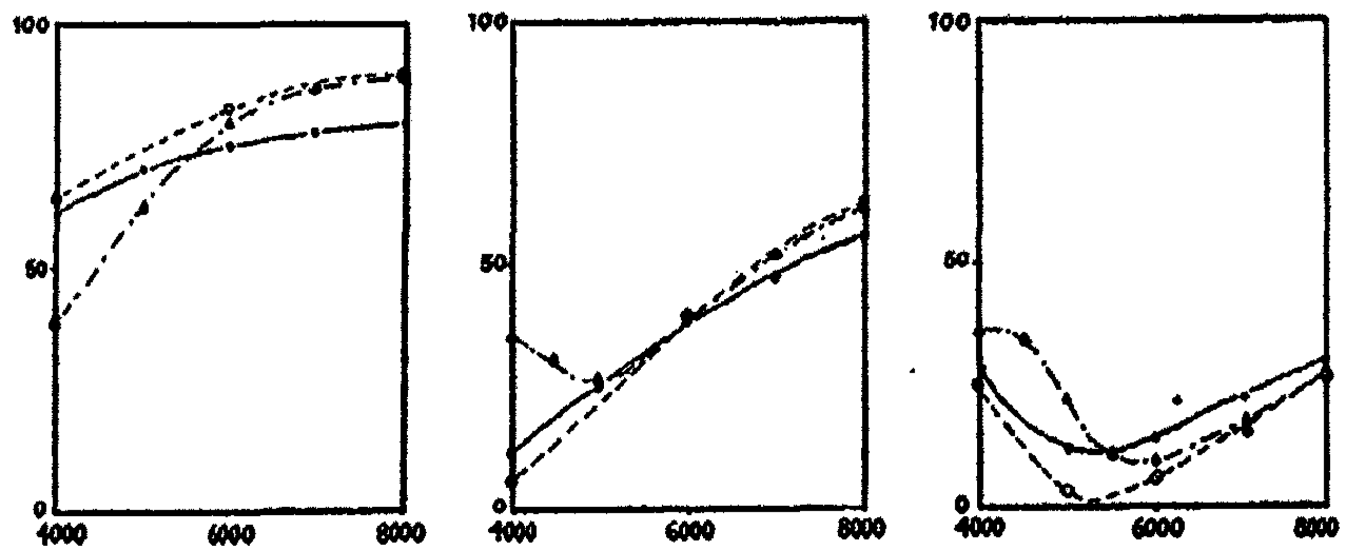

Fig. 14a. Film thickness, 200 A. U. — — —, tan; ———, pale tan; —·—·—, brown.

Fig. 14b. Film thickness, 400 A. U. — — —, orange; ———, orange; —·—·—, red-brown.

Fig. 14c. Film thickness, 600 A. U. — — —, dark purple; ———, purple; —·—·—, dark blue.

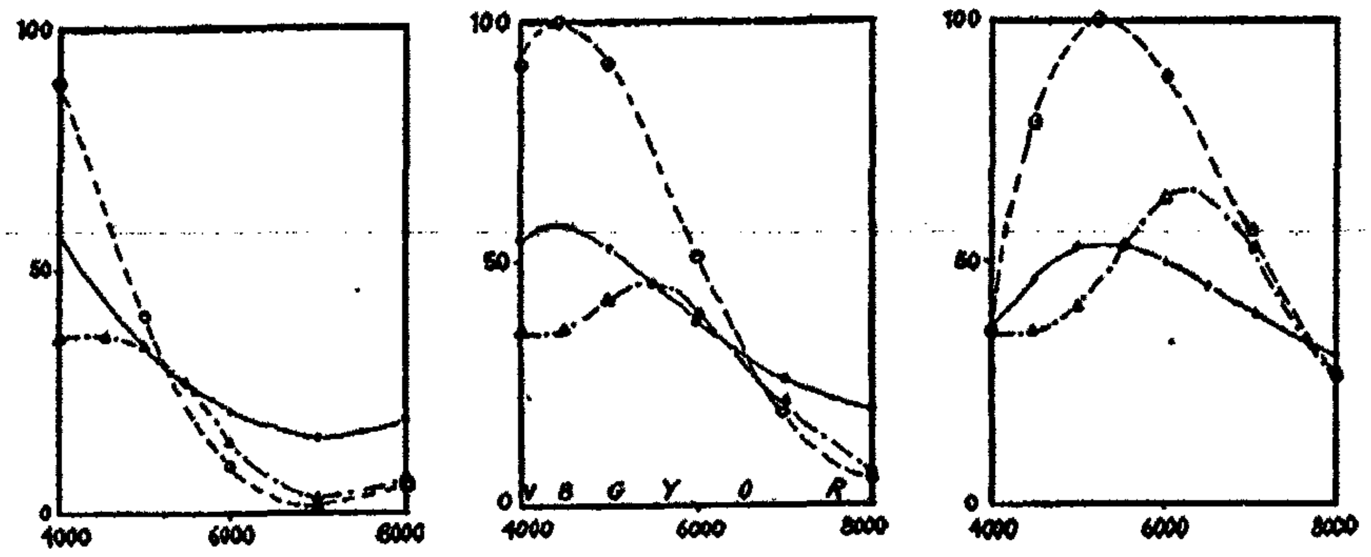

Fig. 14d. Film thickness, 800 A. U. — — —, brilliant blue; ———, blue; —·—·—, dark blue-green.

Fig. 14e. Film thickness, 1000 A. U. — — —, clear light blue; ———, slate blue; —·—·—, gray-green.

Fig. 14f. Film thickness, 1200 A. U. — — —, pale green; ———, steely gray; —·—·—, grayish-yellow.

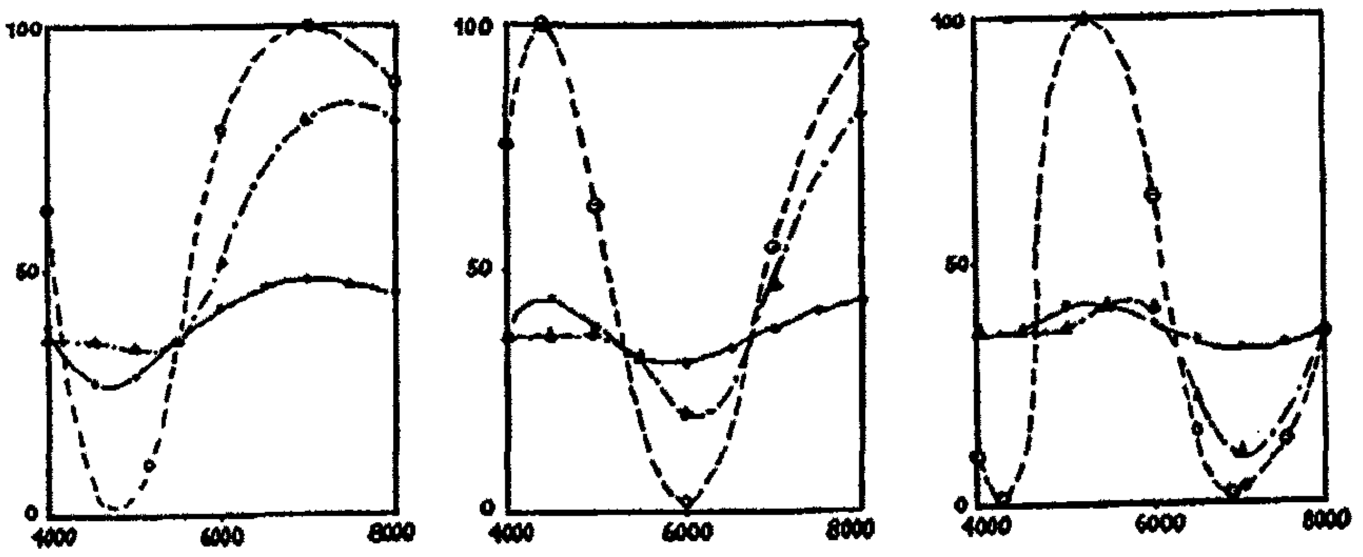

Fig. 14g. Film thickness, 1600 A. U. — — —, orange; ———, reddish-gray; —·—·—, grayish-red.

Fig. 14h. Film thickness, 2000 A. U. — — —, brilliant violet; ———, lavender-gray; —·—·—, grayish-purple.

Fig. 14j. Film thickness, 2400 A. U. — — —, brilliant green; ———, gray; —·—·—, gray-green.

Fig. 14. Relative intensities of light reflected by a filmed surface, in relation to the light that would be reflected by the same surface, if unfilmed, in the case $n_F = 2.2$, $(k_{MF})^2 = 10$ per cent, if (a) the film is not absorbing (— — —), (b) the film is absorbing uniformly at all wave lengths according to table 26 for $T = 2000$ A. U. (———), (c) the film is absorbing more in the short wave-length than in the long wave-length end of the spectrum, according to table 26 (—·—·—).

lated acquires a substantially equivalent color at a lesser thickness than a solid filmed by a non-selectively absorbing substance or by a transparent substance. This advance in sequence of colors with thickness is confirmed by figures 14b to 14f, but it apparently has disappeared in thicknesses giving second-order colors.

By analogy it would seem that a film substance absorbing the red and orange more than the blue, violet, and green would display interference colors only when its thickness is greater than is indicated by the theory for transparent films.

In the case of a film substance absorbing the central part of the visible spectrum more than the edges, the first color might well be some shade of violet or violet gray followed by red (or brown), gray [first intermediary "hiatus," to follow the terminology of Evans], blue, gray [the "hiatus" of Evans], grayish-orange, gray-violet, green, etc. The various colors just listed would correspond to the various thicknesses shown in figures 14a to 14j.

TABLE 22

Arbitrarily chosen relationship between absorption and wave length of a selectively absorbing substance (T is the thickness of film substance resulting in an e-fold reduction in amplitude)

λ	T
A.U.	*A.U.*
4000	200
4500	400
5000	1000
5500	2000
6000	4000
6500	8000
7000	10,000
7500	16,000
8000	20,000

Thus, selective absorption could cause not only deviations in the color scale–film thickness relationship, but also the appearance (at least in extraordinary cases) of exceptional color sequences.

It is of interest to compare these theoretical curves with some experimental curves, figures 15a to 15j. These charts, redrawn from data by Constable (7), deal with the interference colors on iron and nickel. It is clear that the quality of the interference decreases materially with thickness, and that this deterioration is of the type pictured by figure 14. The only difference between these figures is that with increasing film thickness the curves (figure 15) show lesser and lesser amplitudes. This may be caused by an irregularity and roughness of the films that increases with

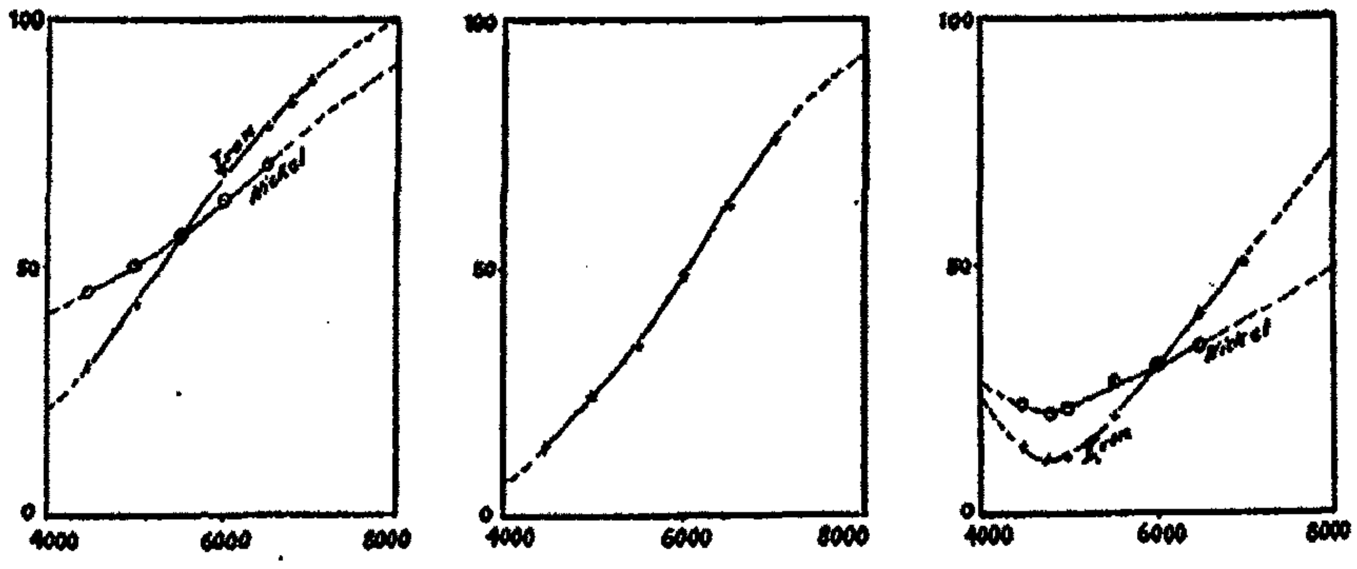

FIG. 15a. I
Iron, straw
Nickel, faint brown

FIG. 15b. I Iron, brownish-yellow

FIG. 15c. I
Iron, red-brown
Nickel, light brown

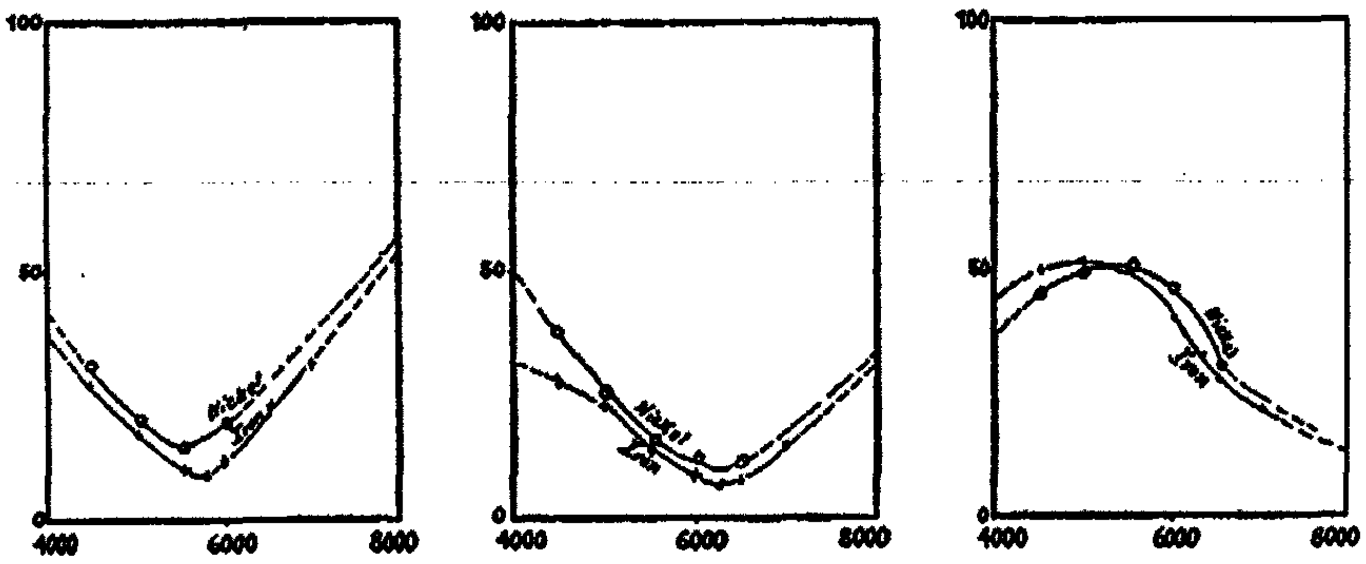

FIG. 15d. I
Iron, violet
Nickel, violet

FIG. 15e. I
Iron, very intense blue
Nickel, very dark blue

FIG. 15f. I
Iron, steely blue-green
Nickel, greenish-gray

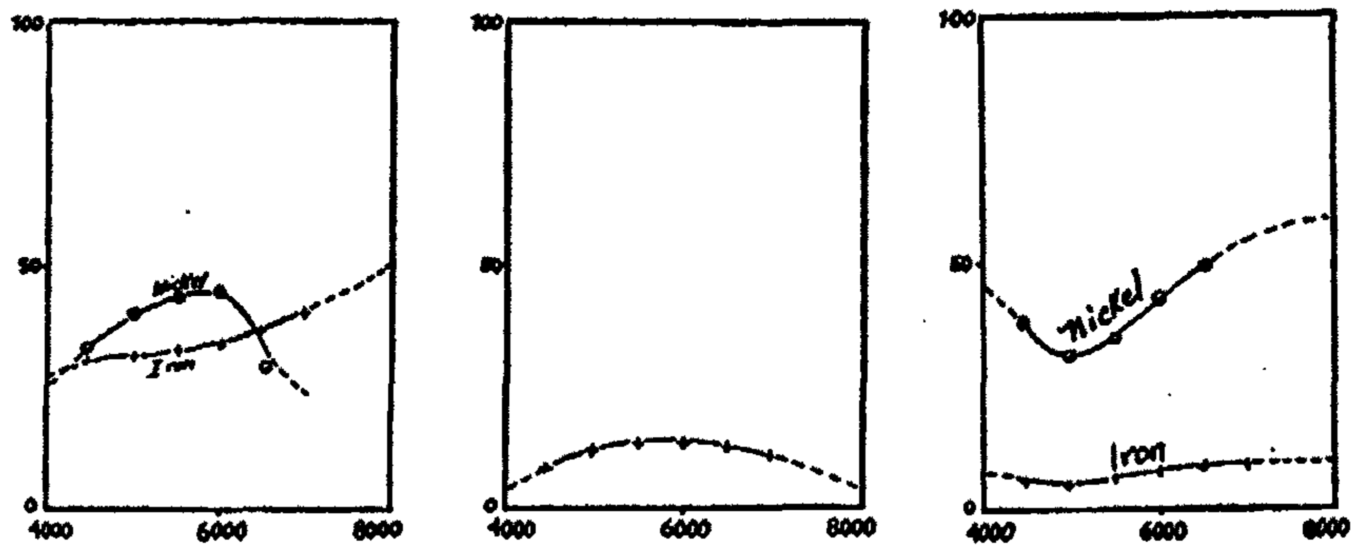

FIG. 15g. II
Iron, yellow
Nickel, yellow

FIG. 15h. II Iron, orange

FIG. 15j. II
Iron, red-brown
Nickel, full brown

FIG. 15. Wave length-intensity relationship for the reflection of filmed nickel and iron according to Constable (7a). The metals were filmed by oxidation and the intensity of the light reflected from the filmed surfaces was determined spectrophotometrically.

the thickness, resulting in a smaller amplitude of specular reflection and a greater amplitude of diffuse reflection.

LIMITATIONS AND ASSUMPTIONS IN THIS ANALYSIS

The analysis that is presented in this paper pertains to the condition

$$n_M > n_F > n_A$$

Five other conditions can be regarded to exist; they are described by permutations of *M*, *F*, and *A*. A study of all these permutations would cover entirely the field of thin films.

This analysis has involved but one assumption which can be questioned, namely, that the reflectivity of an opaque medium can be expressed in terms of its refractive index and of the refractive index of the adjoining medium as if the opaque were a transparent medium. This assumption is probably invalid in those cases in which the opaque medium is a good conductor of electricity, but it is acceptable in the case of sulfide minerals, since these minerals cannot be regarded as possessing metallic conductance (39).

Other assumptions have tacitly been made in the numerical examples. These are that the reflectivity of the polished surface and the index of refraction of the film do not vary with the wave length of the light. These assumptions are convenient as a first approximation, but it must be kept in mind that as a rule indices of refraction vary in regular manner with the wave length (as a first approximation according to the Cauchy formula (63)

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

in which n is the index of refraction, λ the wave length, and A, B, C experimental constants) and that there are many exceptions related to the existence of absorption bands.

Treatment of the general problem of color of film versus thickness is possible by equations developed in this paper (by carrying out individual calculations for each wave length and each thickness of film).

In the analysis dealing with oblique incidence, such as is obtained with high-power microscope objectives, it is further implicitly assumed that the film is isotropic. This assumption is necessarily a limitation.

Finally, it has been assumed that the light used is truly white light, that is, that the abundance of rays of various wave lengths is such as to include all wave lengths in the proper amounts. Clearly this is merely an approximation more or less approached experimentally with incandescent lights fitted with suitable absorbing filters.

In spite of these various limitations and assumptions the analysis presented in this paper agrees remarkably with experiment, at least in so far as experimentation has been carried at present. It gives, furthermore, a sound basis for further experimentation, pointing out the optical conditions which must be secured in order for success to be possible.

In another article some of the chemical phases of the production of thin films will be discussed; this will lead to another set of limitations which must be observed in order to be successful in the production of characteristic iridescent films on minerals (or more generally on solids) which it is desired to identify. In later articles detailed accounts will be presented of the results obtained with various filming solutions and various minerals and synthetic preparations.

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THE ELECTRICAL CONDUCTIVITIES AND VISCOSITIES AT 25°C. OF SOLUTIONS OF POTASSIUM, SODIUM, AND LITHIUM CHLORIDES, IN WATER AND IN ONE-TENTH MOLAR HYDROCHLORIC ACID[1]

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When this work was commenced, very few data on the conductivities of mixtures of electrolytes were available. During the time the experiments were being performed, or since their completion, contributions by Stearn (8) and by Ruby and Kawai (7) appeared.

Our experiments involved the determination of the electrical conductivities at 25°C. of solutions of potassium chloride, sodium chloride, and lithium chloride up to weight concentrations of 4 to 5 *M*, in the absence and in the presence of 0.1 *M* hydrochloric acid. Parallel density and viscosity measurements were carried out. The potassium chloride and sodium chloride used were of A. R. quality. The former was recrystallized once from hot water, and both materials were used only after heating until decrepitation had ceased. Since A. R. lithium chloride was not obtainable at the time, a good specimen with certificate of analysis and obtained from a reputable firm was used instead. It was heated to 200°C. in a stream of dry hydrogen chloride and, after cooling in dry nitrogen, proved to be at least 99.95 per cent pure, in accordance with the analysis supplied, the residue being chiefly ferric chloride. Hydrochloric acid was prepared as required by diluting the constant-boiling mixture obtained by repeated distillation of the analytically pure acid under the conditions laid down by Hulett and Bonner (4). In making up the solutions, the required weight of salt was dissolved either in conductivity water or in

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[1] The work described in this and the two following papers was carried out during the academic years 1921–1925. The experiments were done with considerable care and, although the lack of close temperature control has obviously lessened the value of the transference and diffusion data, the writer thinks publication well justified, in view of the large concentration range covered and the continued absence of similar measurements in the literature. The original idea was to discover a possible correlation between the effects of added alkali metal chloride on the mobility and the activity of the hydrogen ion, the link being furnished by the molecules of the solvent. No such correlation was found, and it is easier now to see why this is the case than it was fifteen years ago.—A. J. A.

0.1 *M* hydrochloric acid, respectively. Subsequent analyses were made for hydrochloric acid by titration with 0.02 or 0.04 *N* sodium hydroxide, using methyl red as indicator, and for total chloride ion by back titration, using chromate as indicator, after adding an excess of silver nitrate, previously standardized against a weighed quantity of potassium chloride or sodium chloride. All the usual precautions were adopted, both in the preparation of the solutions and in the analyses, and it is believed that a high degree of accuracy was obtained. In view of the convenience of possible correlation with transference data, and for other reasons depending on the use of concentrated solutions, concentrations, in this as in the following papers, are usually expressed in weight units, i.e., as moles per thousand grams of water.

TABLE 1

Potassium chloride + 0.1006 M hydrochloric acid at 25°C.

Pyknometer A: weight empty = 30.3696 g.; weight filled with water = 42.1786 g.
Pyknometer B: weight empty = 31.3171 g.; weight filled with water = 43.6321 g.
Time of outflow for pure water = 393.3 seconds

MOLARITY OF KCl	WEIGHTS OF PYKNOMETERS		SPECIFIC GRAVITY	TIMES OF OUTFLOW	MEAN TIME OF OUTFLOW	RELATIVE VISCOSITY
	A	B				
	grams	*grams*		*seconds*	*seconds*	
1.558	42.9902	44.4756	1.0655	371.0	371.8	1.0061
				371.7		
				371.9		
				371.7		
2.746	43.5178	45.0306	1.1102	363.4	363.4	1.0254
				363.3		
				363.3		
3.922	44.008	45.5285	1.1507	361.4	361.4	1.0574
				361.2		
				361.5		
				361.5		
4.304	44.139	45.6798	1.1627	362.3	362.4	1.0710
				362.5		
				362.2		
				362.4		

DENSITY AND VISCOSITY MEASUREMENTS

The density measurements were made in the usual manner in duplicate, using Sprengel pyknometers of about 12-cc. capacity. For the latter a quartz viscosimeter of the pattern used by Washburn and Williams (9) was employed. The instrument was immersed in a thermostat, and its exact position controlled by means of the clamp recommended by Applebey (2). It was filled from a pipet of about 65-cc. capacity, and all precautions taken to ensure cleanliness and absence of traces of dust. The measurements were carried out using a one-fifth second stop watch, and runs on any particular solution were repeated until three approximately consecutive readings agreed to within 0.2 second. The time of outflow for distilled water was 393.3 seconds at 25°C. Before use, the viscosimeter was tested to see how closely it obeyed Poiseuille's law, by measuring the time of outflow for pure water at 20°, 25°, and 35°C. The results were only moderately good, the product $\eta/\Delta \cdot t$, where η, Δ, and t are, respectively, viscosity (taken from the table of Thorpe and Rodger), density, and time of outflow, being 2.274×10^{-5}, 2.282×10^{-5}, and 2.286×10^{-5}, respectively.[2] The typical data given in table 1 will give an idea of the degree of accuracy attained.

TABLE 2

Viscosity data for acid solutions

POTASSIUM CHLORIDE IN 0.1006 MOLAR HYDROCHLORIC ACID			SODIUM CHLORIDE IN 0.1042 MOLAR HYDROCHLORIC ACID			LITHIUM CHLORIDE IN 0.1018 MOLAR HYDROCHLORIC ACID		
Weight molarity	$\Delta_{25°}^{25°}$	Relative viscosity	Weight molarity	$\Delta_{25°}^{25°}$	Relative viscosity	Weight molarity	$\Delta_{25°}^{25°}$	Relative viscosity
	1.0018	1.0070		1.0019	1.0072		1.0018	1.0070
0.09663	1.0064	1.0070	0.09705	1.00585	1.01495	0.09618	1.00425	1.02065
0.1981	1.0109	1.0054	0.19745	1.0099	1.0261	0.1958	1.0068	1.03555
0.2503	1.0133	1.0053	0.2496	1.0120	1.0297	0.2526	1.00795	1.0415
0.5053	1.0245	1.0032	0.5032	1.0222	1.0526	0.5001	1.01405	1.0788
0.7649	1.0359	1.0031	1.0075	1.0412	1.1014	1.0015	1.0254	1.1556
1.011	1.0465	1.0031	1.3723	1.0542	1.1385	2.002	1.0469	1.3168
1.558	1.0686	1.0061	2.080	1.0796	1.2247	2.104	1.0493	1.3345
2.079	1.0893	1.0124	2.4645	1.0922	1.2747	2.734	1.0621	1.4450
2.746	1.1134	1.0254	2.9095	1.1071	1.3401	3.834	1.0833	1.6628
3.811	1.1507	1.0531	3.189	1.1161	1.3826	4.135	1.0885	1.7282
3.922	1.1541	1.0574	3.740	1.1338	1.4757			
4.304	1.1661	1.0710	4.290	1.1501	1.5774			
			5.521	1.1859	1.8531			
			5.531	1.1866	1.8553			

The results set out in tables 5 and 2 (neutral and acid solutions, respectively) were plotted on a large scale and compared with recent published data. Our densities for lithium chloride solutions agree sufficiently well with those in the *International Critical Tables* and with the measurements of Jones and Bradshaw (5). In the case of sodium chloride the agreement

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[2] The instrument was constructed by the Thermal Syndicate, which made the original viscosimeter of Washburn and Williams, and followed the design of the latter as closely as possible.

is close with the I. C. T. throughout the whole range, whilst diverging at higher concentrations from those of Ruby and Kawai (7). The potassium chloride results are in good concordance throughout with the I. C. T., with the data of Ruby and Kawai and, up to 0.2 *M*, with those of Jones and Talley (6). At higher concentrations the figures of the last authors deviate very suddenly in the direction of higher densities.

Above 0.5 *M*, our viscosity figures for lithium chloride are appreciably higher than those given in the I. C. T. In the case of sodium chloride, they agree well throughout with those of Ruby and Kawai and with the figures in the I. C. T., within the possible error attributed to the latter. Our results for potassium chloride over the greater part of the concentration range lie below those of Ruby and Kawai and above those of the I. C. T. From 1 *M* downwards the deviation from the latter set of figures is greater than the probable error attributed to them. Agreement with the values of Jones and Talley is good for the most dilute solutions, but less satisfactory from 1 *M* upwards. We find the minimum viscosity value at about 0.75 *M*, as do Ruby and Kawai, whereas, according to the *International Critical Tables* and to Jones and Talley, it is near 1 *M*. In view of the developments of the last few years, it is of interest to note the "positive" values for the viscosity of 0.1 *M* potassium chloride, obtained by us in 1923 and published by Ruby and Kawai in 1926, but in neither case followed up.

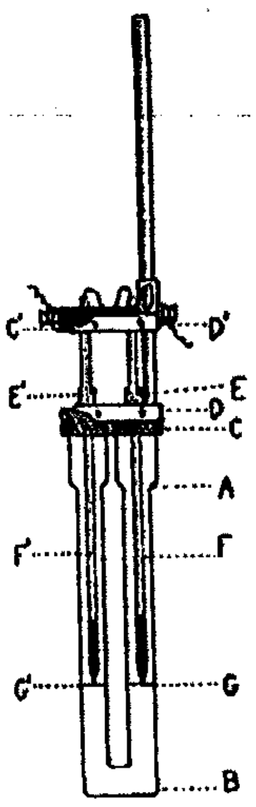

FIG. 1

In the case of the solutions containing hydrochloric acid, we can only compare one example of our data with previous work. Our interpolated values for the density and viscosity of 0.4 *M* KCl + 0.1 *M* HCl agree exceedingly well with the figures of Ruby and Kawai.

CONDUCTIVITY MEASUREMENTS

Owing to the considerable concentration range to be covered and the high conductivities to be anticipated, cells of special design were used, with movable electrodes which permitted a suitable variation of cell constant. The smaller of the two is illustrated in figure 1 (the larger one, used for solutions above 2 *M*, was similar, but with limbs about twice as long). The U-tube AB was 15 cm. in length and of 1.2 cm. internal bore, with 1 cm. between the limbs. The ends, of 2 cm. diameter and ground off flat, fitted snugly into circular grooves cut into the square ebonite head C. This carried the fixed jaw D of a pair of vernier callipers reading to 0.05 mm., and also two short bushed metal rods EE′. Through the latter and corresponding holes in C passed two closely sliding glass tubes FF′, into which were sealed the electrodes GG′. The last were stout platinized platinum discs, 1 cm. in diameter and 0.5 mm. thick. The upper ends of FF′ ran up through holes in a second piece of ebonite C′ and were there cemented in position. C′ was attached to D′, the movable jaw of the callipers, and carried the usual mercury cups and terminals. Care was taken during the construction to make the limbs of AB and the tubes FF′ truly parallel. When this was done and the moving parts were working freely, the cell gave reproducible and concordant results, as is shown by the results in table 3, where three separate specimens of the same solution (0.1162 *M* KCl + 0.0998 *M* HCl) were used, necessitating the dismantling and reassembly of the cell between each set of readings.

TABLE 3

Results on three separate specimens of the same solution (0.1162 M KCl + *0.0998 M* HCl)

SOLUTION	VERNIER READING	CELL CONSTANT	RESISTANCE ARM	RESISTANCE OF CELL	SPECIFIC CONDUCTIVITY
	cm.		*ohms*	*ohms*	*reciprocal ohms*
I	12.00	22.35	500	434.45	
			300	434.40	5.1440×10^{-2}
			200	434.60	
II	14.00	27.24	400	529.72	
			600	529.50	5.1446×10^{-2}
			300	529.56	
III	10.00	17.47	300	339.24	
			200	339.48	5.1462×10^{-2}
			400	339.52	

The remainder of the apparatus used comprised the usual calibrated meter bridge and P. O. resistance box, an ordinary buzzer, and head phones. Tests for reproducibility and for values of cell constant were made at frequent intervals throughout the work and, just as in the above case, all recorded figures are the results of experiments made on at least three separate portions of the same solution, at least three measurements with different resistances in the bridge arm being made with each filling. In general, the cell was found to give less reproducible readings as the electrodes approached the junction of the two limbs. This was only to be anticipated, in view of the greater relative effect of any small maladjustment. Apart from that however, the values for the cell constant determined with 0.1 N potassium chloride and 1.0 N potassium chloride (taking $K_{25°}$ as 0.01288 and 0.1116, respectively) differed somewhat from one another, probably owing to polarization. Table 4 illustrates this point. The values of K are calculated in each case from the mean of three separate measurements of cell resistance, using different resistances in the balancing arm. The actual cell resistances were of the order of 2000–3000 and 200–300 ohms with 0.1 and 1.0 N solutions, respectively.

TABLE 4

Values for the cell constant

VERNIER READING V	MEASUREMENTS WITH 0.1 N KCl		MEASUREMENTS WITH 1.0 N KCl	
	Cell constant K	$\frac{\Delta K}{\Delta V}$	Cell constant K	$\frac{\Delta K}{\Delta V}$
cm.				
18.00	36.889	2.419	36.932	2.352
17.00	34.47	2.42	34.58	2.490
16.00	32.05	2.419	32.09	2.40
15.00	29.631	2.421	29.69	2.43
14.00	27.21	2.415	27.26	2.435
13.00	24.795	2.419 (mean)	24.825	2.421 (mean)

For all vernier readings, the values of K using 1 N potassium chloride are higher than those obtained using 0.1 N potassium chloride, and by an average of 0.18 per cent. Moreover, whereas the latter change regularly and linearly with change in vernier reading, this is not the case with the former, the values of $\Delta K/\Delta V$ showing appreciable variation, although their mean value is practically the same as with the 0.1 N solution.

In practice, no attempt was made to use the linear relation between cell constant and vernier reading. Instead, the cell constants were carefully determined at a series of vernier settings, and all determinations carried out at one or another of these particular settings, the latter being chosen so that the cell resistances as far as possible were always of the same magnitude. For the majority of the highly conducting solutions, the values

TABLE 5

Viscosity and conductivity data for neutral solutions

POTASSIUM CHLORIDE				SODIUM CHLORIDE				LITHIUM CHLORIDE			
Weight molarity	$\Delta^{25°}_{25°}$	Relative viscosity	Specific conductivity × 10³	Weight molarity	$\Delta^{25°}_{25°}$	Relative viscosity	Specific conductivity × 10³	Weight molarity	$\Delta^{25°}_{25°}$	Relative viscosity	Specific conductivity × 10³
0.1004	1.0048	1.00045	12.88	0.0925	1.00414	1.0105		0.0899	1.0022	1.0147	
0.2004			24.78	0.1077			11.455	0.0977			9.394
0.2500	1.0114	0.9992	30.553	0.1824	1.0073	1.0182		0.1784	1.0048	1.0274	
0.5031	1.0232	0.9979	58.554	0.1997			20.25	0.1968			17.77
0.7485	1.0336	0.9974	83.90	0.2235	1.00905	1.0222		0.2211			19.79
1.016	1.0454	0.9978		0.2497			24.761	0.2235	1.0057	1.0342	
1.027			111.59	0.4504	1.0182	1.0423		0.4440	1.0111	1.0661	
1.469	1.0637	1.0010	152.90	0.5046			46.847	0.4461			36.998
2.026			202.11	0.9158	1.0365	1.0868		0.7300	1.0175	1.1075	55.69
2.091	1.0883	1.0068		1.007			84.75	0.9031	1.0215	1.1332	
2.106	1.0891	1.0069		1.326	1.0513	1.1266	105.60	0.904			66.78
2.604	1.1075	1.0153	250.45	1.880	1.0708	1.19105		1.433	1.0337	1.2194	94.91
3.401			(304.86)	1.984			143.95	1.798	1.0410	1.2761	
3.918	1.1527	1.0507		2.674	1.0981	1.2963	176.05	1.840			113.55
3.956	1.1544	1.0518	341.80	2.904	1.1054	1.3299		2.669	1.0594	1.4274	142.9
4.153	1.1614	1.0610		3.019			190.03	3.292	1.0715	1.5461	159.1
4.272	1.1653	1.0633	358.25	3.654	1.1293	1.4504	210.8	3.688	1.0793	1.624	
				4.260	1.14815	1.5642	226.6	3.859			170.63
				4.802			237.5	4.222	1.0888	1.7391	176.05
				4.812	1.1647	1.6795					
				5.190	1.1756	1.7617					
				5.809	1.1925	1.9096	249.15				

of K obtained with 1.0 N potassium chloride were used, and for the more dilute solutions, averages of the K values obtained with the two calibrating solutions.

Table 5 contains the data for the neutral halide solutions. The bracketed figure for 3.401 M potassium chloride, when plotted, appears to be low.

TABLE 6

Values of Λ for a series of volume concentrations

c	POTASSIUM CHLORIDE			SODIUM CHLORIDE			LITHIUM CHLORIDE		
	Λ		$\Lambda\eta$	Λ		$\Lambda\eta$	Λ		$\Lambda\eta$
0.1	128.9	128.62* 128.34† 129.0†	128.9	107.0	106.66* 106.82† 106.8†	108.0	96.5	95.5*	97.6
0.2	124.5	123.9* 124.2†	124.4	102.0	101.55* 101.7†	103.8	90.3	89.9*	93.0
0.5	117.9	117.2* 116.7† 117.06† 118.8†	117.7	93.35	93.31* 92.2† 93.45† 93.92†	97.9	81.5	81.0* 80.8†	87.5
1.0	112.0	111.86* 111.60†	111.9	85.4	86.36†	93.7	73.0	73.1*	84.5
1.5	108.1		108.4	79.8		91.4	67.0		82.6
2.0	105.6	105.70†	106.3	74.9	75.91†	90.7	61.7	61.7*	81.5
2.5	103.6		105.1	70.3		90.5	56.9		80.5
3.0	100.7		104.0	65.8		90.4	52.5	52.9*	79.6
3.5	97.2		102.5	61.6		90.5	48.4		78.9
4.0	(93.4)	96.25†	(100.7)	57.5	60.11†	90.7	(44.5)	44.7*	(78.5)
5.0				49.5	44.7*	91.9			

The bracketed figures were obtained by a slight extrapolation.

* From International Critical Tables.

† From Landolt-Börnstein Tabellen.

From these data the equivalent conductivity, Λ, is readily obtained by means of the expression

$$\Lambda = \frac{\kappa(1000 + w)}{M\Delta_{4^\circ}^{25^\circ}}.$$

where κ, w, and M are specific conductivity, weight of salt, and moles of salt per thousand grams of water, respectively. Values of Λ and of $\Lambda\eta$ have been calculated in this way and plotted. $\Delta_{4^\circ}^{25^\circ}$ for water has been taken as 0.99707. Table 6 contains the results for a series of round volume concentrations (c), as also the figures for Λ quoted in standard works of reference. For the lower concentrations, our values of Λ are definitely higher than those given in the *International Critical Tables*. Except in the case of lithium chloride, where the agreement is good, very few reliable data appear to exist for more concentrated solutions, and our figures to some extent fill this gap, more particularly for sodium chloride. The Λ/c curve for potassium chloride shows a point of inflection at about 2.2 N, and it is possible that our Λ values above 3 N are too low. As will be seen from table 5, the specific conductivities concerned are very high and polarization may conceivably have caused trouble.

The $\Lambda\eta$ products are of interest. In the case of potassium chloride, their values above 3 N may be affected by the circumstance just mentioned. But at 4 N, the figure for lithium chloride is practically independent of concentration, although Λ itself is still very rapidly falling, whilst in the case of sodium chloride, the product passes through a flat minimum at about 3 N, and only varies very slightly over the concentration range 1.5 to 5 N. The factors which govern the viscosity of ionic solutions have been considered by Bernal and Fowler (3). In concentrated solutions at 25°C., they will essentially consist of (a) the resistance to shear presented by the ionic lattice, which may be expected to increase with some high power of the concentration, and (b) the transfer of momentum by the Brownian movement of the ions, regarded as independent massive particles. This term, less important than the first, will depend on the masses of the ions and will be proportional to concentration. It was suggested by one of us some years ago (1) that, omitting factors making for "negative" viscosity (also considered by Bernal and Fowler, but regarded as of minor importance in concentrated solution), ionic mobility is determined solely by considerations arising out of the Debye-Hückel-Onsager theory, and that the increase in viscosity due to increase in ionic concentration, as usually measured, is governed by the same factors which enter into that theory, some mechanism involving preferential adsorption of ions of one sign on the walls of the viscosimeter being involved. The application of a viscosity correction would therefore allow for, or eliminate, the retarding effects of the Debye-Hückel-Onsager forces on the mobility of an ion. This view amounts to saying that, in the Bernal-Fowler analysis, factor a is all-important. We think that the above results for sodium chloride and lithium chloride support the essential correctness of the assumption. When the viscosity correction is applied in sufficiently concentrated solution, the effect of changes in concentration, and hence in interionic forces, is very nearly eliminated. The existence of factor b will mean of course a certain over-correction, and this will be more important with sodium ions than with lithium ions, as is found.

Table 7 contains the conductivity data for the acid solutions.

In order to elucidate the effect of increasing concentration of alkali halide on its conductivity and to compare with one another solutions of the different alkali halides, we have adopted the following procedure. We multiply κ, the conductance of a 1-cm. cube of solution, by the factor

$$\frac{1000 + w_1 + w_2}{1000\Delta^{25°}_{4°}}$$

where w_1 and w_2 are the weights of hydrogen chloride and alkali metal chloride dissolved in 1000 g. of water. The product gives us κ' or the

TABLE 7

Conductivity data for acid solutions

KCl in 0.0998 *M* HCl				NaCl in 0.09633 *M* HCl				LiCl in 0.1010 *M* HCl			
Weight molarity	$\Delta^{25°}_{4°}$	Specific conductivity $\times 10^3$	$\Lambda'\eta$	Weight molarity	$\Delta^{25°}_{4°}$	Specific conductivity $\times 10^3$	$\Lambda'\eta$	Weight molarity	$\Delta^{25°}_{4°}$	Specific conductivity $\times 10^3$	$\Lambda'\eta$
0.0	0.9989	38.89		0.0	0.9988	37.69		0.0	0.9989	39.355	
0.1162	1.0042	51.45	110.8	0.1136	1.0035	47.23	89.66	0.09955	1.0011	46.24	77.31
0.2066	1.0084	61.15	110.4	0.2085	1.0070	55.02	90.05	0.2008	1.0038	53.185	78.25
0.2596	1.0106	66.84	110.5	0.3026	1.0110	62.57	89.93	0.4055	1.0086	66.30	78.36
0.4806	1.0204	89.44	108.4	0.5071	1.0186	78.39	89.85	0.817	1.0184	90.10	77.96
0.7649	1.0330	118.02	107.4	0.9885	1.0370	111.5	88.28	1.661	1.0374	128.36	76.76
1.0015	1.0428	139.94	105.5	1.372	1.0509	134.3	87.32	2.104	1.0463	143.65	76.28
1.558	1.0655	189.9	103.5	2.011	1.0740	168.5	87.16	2.734	1.0587	161.87	75.95
2.058	1.0846	231.04	102.1	2.465	1.0892	187.5	86.66	3.435	1.0731	176.83	75.56
2.746	1.1102	282.2	100.3	2.910	1.1034	204.9	87.22	3.834	1.0798	183.76	75.73
3.062	1.1213	305.21	100.2	3.018	1.1072	208.5	87.16				
3.922	1.1508	357.2	98.5	3.740	1.1299	229.5	87.64				
4.304	1.1626	377.4	97.9	4.290	1.1460	241.0	88.06				
				5.521	1.1823	257.5	90.07				

specific weight conductivity,—the conductance between electrodes 1 cm. apart, of 1 *gram* of water containing added electrolyte of weight concentrations corresponding to w_1 and w_2. This is then multiplied by the viscosity, η, of the solution, and from the product $\kappa'\eta$ is subtracted the value of $\kappa'\eta$ when w_2 is zero, i.e., $\kappa'\eta$ for the appropriate solution of hydrochloric acid at the head of table 7. The result is the increment in $\kappa'\eta$ caused by the addition to the hydrochloric acid solution of alkali metal chloride of weight concentration M. If this be divided by $M/1000$, we get $\Lambda'\eta$, the *effective* equivalent conductivity, corrected for viscosity, of the alkali metal halide in the hydrochloric acid solution as solvent. The actual expression is

$$\Lambda'\eta = \frac{\kappa(1000 + w_1 + w_2)\eta}{M\Delta} - \frac{\kappa_0(1000 + w_1)\eta_0}{M\Delta_0}$$

where κ_0, η_0, and Δ_0 refer to the "solvent." It will be noted that, if w_1 is zero, then the expression reduces, as it must, to that deduced after table 5 for $\Lambda\eta$.

No attempt has been made to smooth out the data, and the errors of experiment are obvious. In spite of this, there is no doubt that the tendency towards constancy of the $\Lambda'\eta$ values is a very marked one, even more so than in table 6, as would be expected from the method of calculation adopted. In the case of sodium chloride and lithium chloride, the extreme variation does not exceed 4 per cent, in spite of the very great concentration range covered. As before, the figures for sodium chloride pass through a minimum, whilst those for lithium chloride tend to become smaller as concentration rises. And, as before, the figures for potassium chloride fall off continuously, and to a much greater extent than with lithium chloride. The results, as a whole, are in accordance with the previous discussion. In addition, they suggest that the data for the more concentrated acid-free potassium chloride solutions may not be subject to experimental error, as was hinted above, but rather that the third viscosity factor considered by Bernal and Fowler, in the present case a raising of the "structural temperature" of water, is of importance in concentrated potassium chloride solutions, although masked by the existence of the other factors tending to increase viscosity. From our present point of view, it would mean that the use of the viscosity correction is necessarily inadequate to compensate for the retarding effect of the ionic lattice on the mobilities of the ions in a potassium chloride solution.

SUMMARY

1. The electrical conductivities, densities, and viscosities have been determined at 25°C. for solutions of potassium, sodium, and lithium chlorides in water and in one-tenth molar hydrochloric acid. The weight concentrations of the alkali metal chlorides were varied between about 0.1 *M* and upper limits of 3.8 to 5.8 *M*.

2. The dependence of the equivalent conductivity–viscosity product on the concentration of the alkali metal chloride, dissolved either in water or in 0.1 *M* hydrochloric acid, is discussed in the light of the views of Bernal and Fowler on the nature of the viscosity of electrolytic solutions.

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HITTORF TRANSFERENCE NUMBERS OF SOLUTIONS OF POTASSIUM, SODIUM, AND LITHIUM CHLORIDES IN WATER AND IN ONE-TENTH MOLAR HYDROCHLORIC ACID

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Apart from quite early experiments and the few data obtained by Mackay (12) on mixtures of potassium sulfate and potassium chloride, and by Braley and Hall (3) on solutions containing sodium chloride and potassium chloride, no work on transference in mixtures of simple electrolytes had appeared when we commenced our experiments. With the exception of further papers arising out of the work of Braley and Hall (15, 7, 16, 4), the only experiments published since by the Hittorf method have been those of Van Rysselberghe (17) and of Bennewitz, Wagner, and Küchler (1). Longsworth (10) has applied the moving boundary method to mixtures of hydrochloric acid and potassium chloride. In our own work, the concentration of hydrochloric acid was kept constant at 0.1 *M* or nearly so, and that of the alkali metal chloride varied over a considerable range. Parallel experiments with solutions free from hydrochloric acid, and with 0.1 *M* hydrochloric acid alone, were also carried out. The omission of experiments with more concentrated solutions of hydrochloric acid has made it impossible for us to test the MacInnes (11) formula for transference numbers in a mixed electrolyte. According, however, to Van Rysselberghe and Nutting (18), the presence of hydrochloric acid as one of the constituents in any case makes the measurements "less suitable" for the purpose of testing such formulas.

EXPERIMENTAL

The transport tube (figure 1a) was 2.25 cm. in internal diameter and about 1 meter in total length. Cuts at the points a and b were joined together by wide rubber tubing. The inlet tubes c, d, e, and f were closed by rubber stoppers during an experiment. The ends A and F were also closed by rubber stoppers through which passed the electrodes, the cathode being a silver disc, 2 cm. in diameter, covered with a layer of precipitated silver chloride during an experiment, and the anode a rod of the purest cadmium obtainable. The whole tube was firmly mounted in a wooden stand on the laboratory bench, and all measurements were made at the prevailing room temperature. Two such transference tubes in series were generally used. The coulometer was placed between them and, under these conditions, agreement between the values given by the two tubes showed the absence of possible current leakage.

When working with 0.1 *M* hydrochloric acid, and to a much greater extent when using mixtures of hydrochloric acid and the alkali metal chlorides, it was found that the acid content of the middle anolyte (DE in the figure) decreased appreciably long before, say, the concentration in the middle catholyte (BC) increased; the change soon extended to the middle layer itself (CD), thus rendering the experiment useless. To counteract this difficulty, the tube Fb was replaced in such cases by F'b' (figure 1b), which was provided with a horizontal side-arm of capacity between E' and G of the same order as E'F'. In this way the volume of the anolyte was approximately doubled. In spite however of this change, the existence of the "middle layer effect" resulted in a very considerable curtailment of the series of experiments on hydrochloric acid–lithium chloride mixtures.

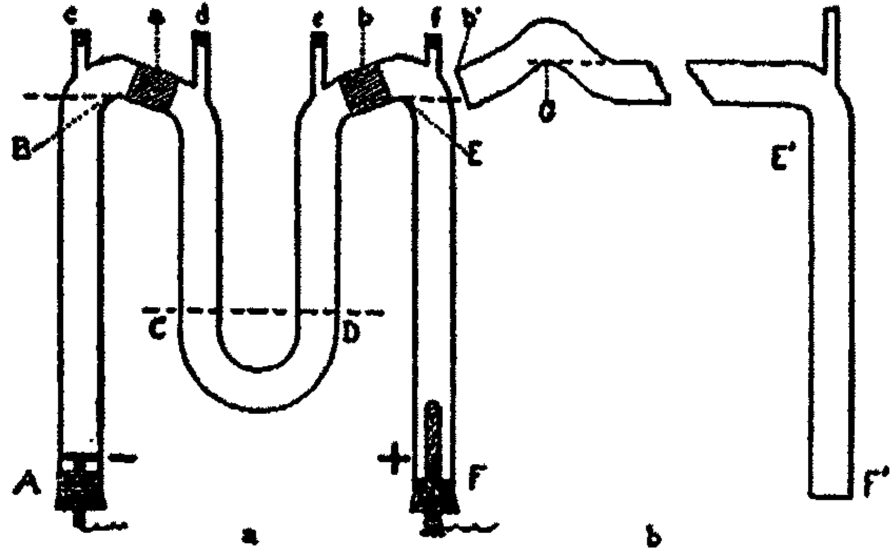

Fig. 1. The transport tube

The silver coulometer was set up and employed in accordance with the directions of the Bureau of Standards (1916). The platinum crucible was of about 100-cc. capacity. The anode, of assay silver, was surrounded by a porous alundum thimble. In some experiments, where large weights (up to 4 or 5 g.) of silver were deposited, the capacity of the coulometer was increased to about 250 cc. by placing the anode thimble in a separate glass vessel provided with a wide-bore siphon which made connection with the platinum crucible. A number of experiments were carried out with the iodine coulometer of Washburn and Bates (21). In accuracy, reproducibility, and convenience, this instrument left nothing to be desired, provided that the quantities of electricity measured were relatively small, not exceeeding 0.005 faraday. But in long-continued experiments, or when using relatively heavy currents, migration of I_3^- ions caused trouble, and for this reason and because of the heavy cost of the large quantities of potassium iodide necessary, we reverted to the silver coulometer.

The source of the chemicals used and the preparation and the analysis of the solutions have been dealt with in the preceding paper, but it is necessary to mention a difficulty met with when using the cadmium anodes. These were naturally of the purest metal available at the time. The first consignment gave no trouble; the very small loose residue observed when they were corroded anodically was of the same color as the metal, and was attributed to irregular solution of the same. Subsequent specimens however, from another source, gave a deposit distinctly lighter in color than the metal and, simultaneously, when working with acid solutions, the discrepancy between the hydrogen ion transference numbers calculated from the changes in concentration of anolyte and catholyte became more pronounced. These effects were traced to the presence of small quantities of basic material in the cadmium, which would of course neutralize some of the acid in the anolyte during an experiment. Further investigation showed this substance, probably zinc oxide, to be present throughout the whole mass of the metal, not merely superficially. Unfortunately, its distribution proved not to be uniform, and this fact made it impossible to work out a correction factor. However, as will be seen from the tables, the errors introduced appear to be small.

The experimental procedure presented no novel feature. The currents and durations of run used in practice varied between 0.02–0.1 ampere and six to twenty-four hours, respectively, the actual values being determined by the concentration relations. At the end of a run, stoppers d and e (figure 1a) were removed. Two identical glass tubes, doubly bent, were lowered to the same depth (C, D) in the limbs of the center U, and the portions BC and DE, middle catholyte and middle anolyte, respectively, simultaneously removed by suction into two tared stoppered flasks. CD, the middle layer, was pipetted out. Cathode and anode tubes were then detached, closed by waxed corks, thoroughly shaken, their contents run out into tared flasks, and the tubes washed out with several small portions of test solution, the washings being run into the same flasks. In the case of AB, the partially reduced silver chloride was broken up by a glass rod, and a more thorough washing was naturally necessary to remove the last traces of solid precipitate. After determining the total weights of the different portions, weighed fractions were titrated for acid and for total chloride, the amount of cadmium in the anode layers being known from the coulometer result, and the amount of alkali metal cation being obtained by difference. If either middle anolyte or middle catholyte had changed in composition, its data were of course included with those of the anolyte or catholyte, respectively. If the middle layer had altered, the experi-

TABLE 1

Results for solutions of a single electrolyte

WEIGHT MOLARITY	TEMPERATURE IN °C.	FARADAYS PASSED	EQUIVALENTS TRANSFERRED		η_c
			From anode	To cathode	
			Hydrogen chloride		
0.0970		0.005508	0.004599	0.004584	0.8344
			0.004606	0.004587	
0.0970		0.005735	0.004784	0.004780	
			0.004798	0.004786	
			Potassium chloride		
0.0978	18	0.004093	0.002016	0.002015	0.493
			(0.001992)	0.002006	
0.0987	18	0.004922	0.002442	0.002436	
0.1192	15	0.004215	0.002076	(0.002057)	
			0.002079	0.002080	
0.3878		0.01689	(0 008079)	(0.008415)	0.4884
			0 008248	0 008252	
1.167	18	0.03059	0.01473	0.01472	0.4846
2.032	17	0.04239	0.02044	0.02057	0.4835
2.09	20	0.03165	0.01529	0.01534	
				0.01528	
3.185		0.05346	0.02563	0.02582	0.481
			Sodium chloride		
0.0964	19	0.005327	0.002079	(0.002002)	0.3897
			0.002074	0.002082	
0.0989	16	0.005805	0.002261	0.002256	
			0.002259	0.002263	
0.1010	17	0.005373	0.002093	0.002095	
			0.002097	0.002094	
0.1997	23	0.010025	0.003787	0.003798	0.3777
			0.003784	0.003774	
0.306	17	0.009575	0.003629	0.003440	0.373
			0.003563	0.003644	
0.417	20	0.010012	0.003729	0.003721	0.3717
			0.003727	0.003712	
0.993		0.014765	0.005369	(0.00532)	0.3635
			0.005357	0.00537	
2.34	17	0.02752	0.00986	0.00969	0.355
			0.00990	0.00967	
2.92		0.02796	0.00987	(0.0097)	0.353
			0.00982	0.00991	

TABLE 1—*Concluded*

WEIGHT MOLARITY	TEMPERATURE IN °C.	FARADAYS PASSED	EQUIVALENTS TRANSFERRED		n_c
			From anode	To cathode	
Lithium chloride					
0.1008	17	0.006478	0.002037		0.315
			0.002036	0.002049	
0.2529	19	0.01138	0.003419	0.003444	0.301
			0.003411	0.003447	
0.5182	15	0.01916	0.005556	0.005458	0.288
			0.005558	0.005482	
1.102	20	0.02694	0.007226	0.007223	0.268
			0.007223	(0.007255)	
2.257	22	0.04570	0.01170	0.01175	0.255
			0.01155	0.01162	
4.832	25	0.05264	0.01296	0.01277	0.244

ment was discarded. From the results obtained, the quantities of the different electrolytes transferred can readily be computed, and there seems no need to give a specimen of such a calculation.

RESULTS

Table 1 contains the results for solutions of a single electrolyte. The amounts of electrolyte transferred are given in every case, as affording the best indication of the degree of accuracy obtained. The cationic transference numbers in the last column are average values, and those experimental figures which have been omitted in calculating them are bracketed.

The value for 0.1 *M* hydrochloric acid is in good agreement with the accepted figure. The results for the alkali metal chlorides are plotted in figure 2 in the form of n_c against the logarithm of the volume normality. Values taken from standard reference works are also shown. Our figures for potassium chloride and sodium chloride tend to fall slightly below the latter. Apart from the uncertainty introduced by the temperature variation, we think they are to be relied on experimentally. There is, however, one point to which attention does not seem to have been drawn hitherto. Apparent or Hittorf transference numbers are affected by differential ionic hydration. The relation between the true and the Hittorf cationic transport numbers for a simple salt as deduced by Washburn (20) is

$$T_H = T_T - N_W^F \cdot N_s/N_w$$

where N_W^F is the net transfer of water to the catholyte per faraday of electricity passed, and N_s/N_w the ratio of moles of salt to moles of water in the solution. Strictly speaking N_s/N_w in this expression should be replaced by the corresponding ratio for the electrode layer at the conclusion of the experiment, the relation quoted being rigorous only if the quantity of water transferred to the catholyte or anolyte during a run can be neglected in comparison with the water present at the start. The correct expressions for the left-hand side of the equation, depending on whether catholyte or anolyte is analyzed, are respectively

$$T_H(1 + n/N_w^c \cdot N_W^F) \quad \text{and} \quad T_H(1 - n/N_w^a \cdot N_W^F)$$

where n is the number of faradays passed during the experiment, and N_w^c, N_w^a the moles of water in catholyte and anolyte at the start.

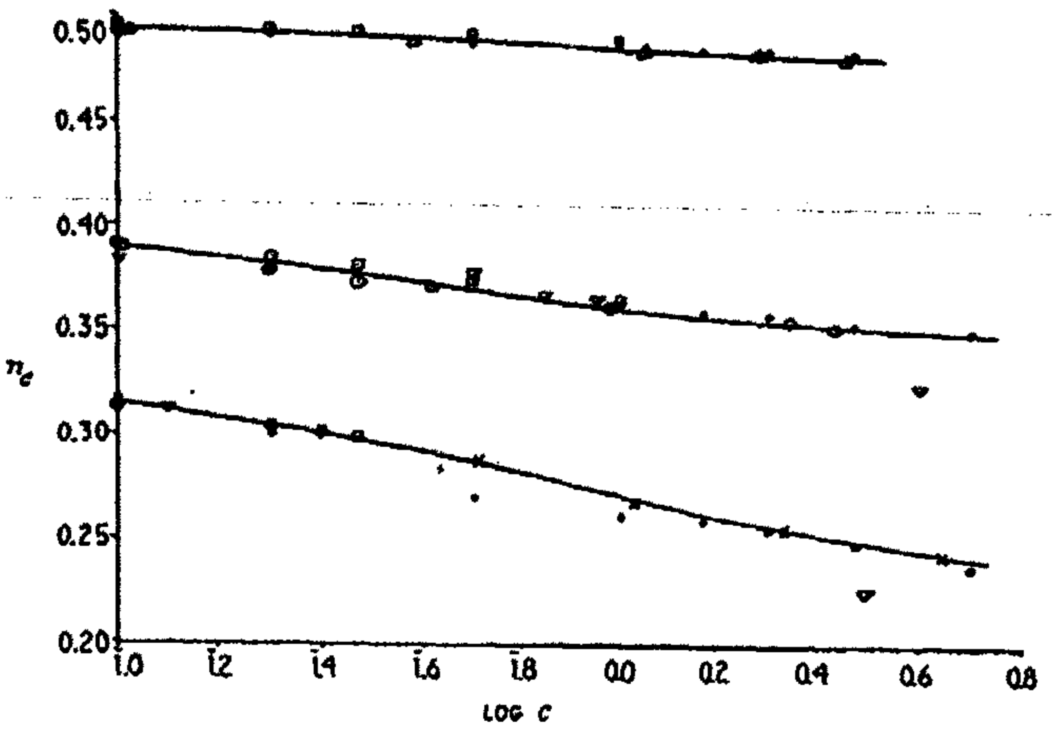

FIG. 2. n_e, plotted against the logarithm of the volume normality

Authors' data	*Other data*
△, potassium chloride	⊡ potassium chloride, from International Critical Tables
⊙, sodium chloride	▽, sodium chloride, from Landolt-Bornstein
×, lithium chloride	● lithium chloride, from Kohlrausch-Holborn

Analyses of anolyte and catholyte will therefore, in principle, give different values for T_H, and values which will depend on the duration of the run. The values derived from the analysis of the anolyte should be the greater, but the data in table 1 show no sign of such a trend. In our experiments, n varied between 0.004 and 0.053. N_w^c and N_w^a were about 5, except in the very few experiments in which the middle anolyte had changed in composition, when N_w^a was 8 to 9. According to the work of Remy (14) and of Velisek (19), N_W^F decreases as concentration increases, though rather less rapidly than the latter. If we take as a basis the figures quoted by these authors (at 1 N in fair agreement with the earlier data of Washburn), the calculated correction terms are of the following order:

	$0.1\ N$	$3\ N$
Potassium chloride	0.004	0.002
Sodium chloride	0.009	0.002
Lithium chloride	0.013	0.007

These relations in turn imply that, whilst in concentrated solutions the experimental values of T_H will only be affected by perhaps 0.001, in 0.1 N solutions the anodic and cathodic values for potassium chloride, sodium chloride, and lithium chloride obtained in our experiments should have differed by about 0.004, 0.007, and 0.008, respectively. The obvious

TABLE 2

Data obtained for the mixtures

NO. OF EXPERIMENT	WEIGHT MOLARITY		TEMPERATURE IN °C.	FARADAYS PASSED	EQUIVALENTS OF HCl TRANSFERRED		EQUIVALENTS OF RCl TRANSFERRED	
	HCl	RCl			From anode	To cathode	From anode	To cathode
Potassium chloride								
1	(0.0995	0.0984	23	0.01461	0.008971	0.009001	0.00151	0.00153)
2	0.1007	0.1008	18	0.00978	0.00625	0.00621	0.001212	0.001204
3	0.1068	0.2538	18	0.02005	0.00954	0.00954	0.004384	0.00440
4	0.1050	0.4930	18	0.02985	0.01006	0.01003	0.00913	0.009175
5	0.1028	1.024	18	0.03460	0.006598	0.006635	0.01317	0.01312
6	0.1131	2.076	17	0.04159	0.004821	0.004784	0.01653	0.01679
7	0.1112	2.909	18	0.04814	0.003598	0.003576	0.02226	0.02240
8	0.1137	3.420	20	0.04280	0.003195	0.003106	(0.02132)	0.01958
Sodium chloride								
9	0.1013	0.1001	20	0.01123	0.00743	0.007425	0.00097	0.00099
					0.00740	(0.00723)	0.00097	0.00094
10	0.0985	0.1976	19	0.009637	0.005226	0.005200	0.001268	0.001331
					0.005212	0.005228	0.001294	0.001295
11	0.1072	0.4558	21	0.01591	0.006305	0.006157	0.003346	0.003244
					0.006261		0.003326	
12	0.1063	1.035	14	0.02474		0.005736		0.006615
						0.005737		0.006542
13	0.0952	1.978	21	0.02481	0.002942	0.003023	0.007645	0.00760
					0.002913	0.002915	0.007790	0.00773
14	0.1089	2.365	20	0.03951	0.00437		0.01371	
15	0.1049	4.775	21	0.05554	0.002715		0.01832	
Lithium chloride								
16	0.1173	0.08945	20	0.009874	(0.007241)	0.006971	(0.0005205)	0.000566
					(0.007305)	0.006945	(0.0005190)	0.000531
17	0.1006	0.3099	17	0.01181		0.005621		0.001730
						0.005624		0.001767

absence of any such effect indicates that the high hydration values quoted for 0.1 *N* solutions in the papers of Remy and Velisek referred to are spurious, and due to electroösmotic effects. The experimental errors in our own work must be responsible for masking at higher concentrations the presence of smaller effects in the predicted direction.

Table 2 contains the data for the mixtures. Those not used in subsequent calculations are bracketed. Where appreciable disagreement exists between the anodic and cathodic figures for amounts transferred, the latter have been preferred, partly because of the possibility of disturbance arising out of the basic material in the anode, but chiefly on account of the "middle layer" effect. This effect was responsible for two experiments only having been carried out with hydrochloric acid–lithium chloride mixtures. In the second of these, the middle layer underwent a very slight change in composition during the run, and it was realized that experiments with higher concentrations of lithium chloride were impracticable with the transference tubes in use. The first experiment with hydrochloric acid–potassium chloride mixtures, carried out at a somewhat higher temperature than the others, has not been utilized. When worked up, it gives results in no way concordant with the remainder, and presumably some unsuspected error was present. In experiments 14 and 15, the values quoted for the quantities transferred are means of the anode and cathode figures; these differed appreciably from one another.

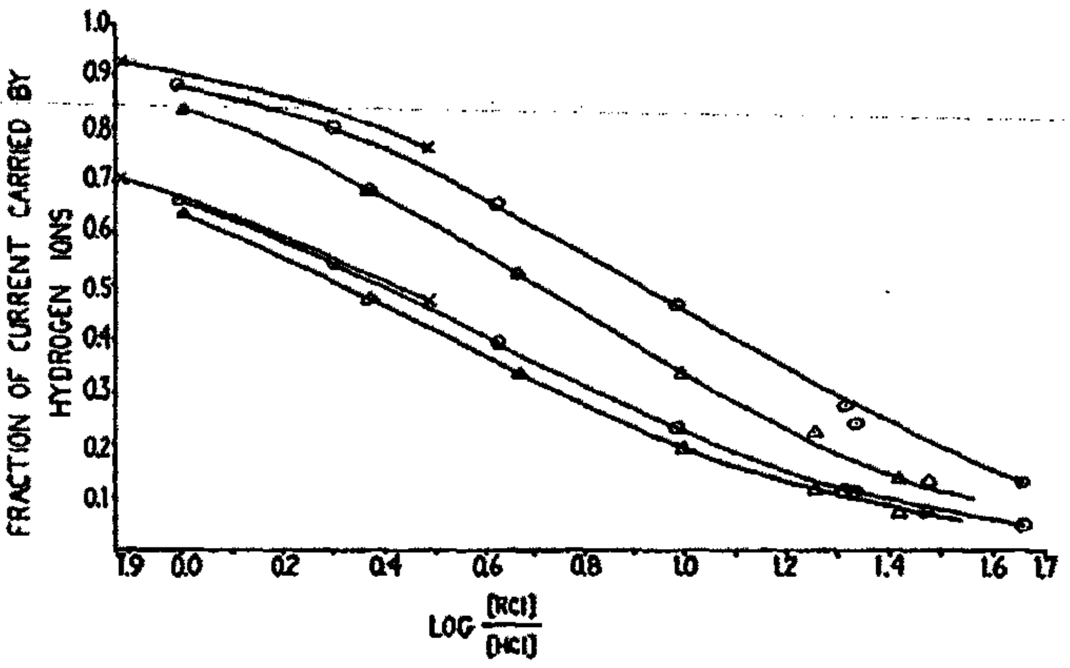

FIG. 3. Fraction of the current carried by the hydrogen ions plotted against the logarithm of the ratio [RCl]/[HCl]. △, potassium chloride; ⊙, sodium chloride; ×, lithium chloride.

From the total quantity of electricity passed and the amounts of HCl and RCl transferred, the shares of the H^+, R^+, and Cl^- ions in carrying the current can be directly calculated, any transference of water being neglected, as in the discussion which follows. Figure 3 contains, plotted against the logarithm of the ratio [RCl]/[HCl], the fraction of the *total* current and of the *cationic* current carried by the hydrogen ions (lower and upper set of graphs respectively). At high concentration ratios the experimental points are seen to deviate appreciably from the curves. This is of course due to the considerable effect caused by slight errors of analysis when using concentrated RCl solutions with relatively small concentration changes.

DISCUSSION

The existence of the errors just mentioned, apart from temperature and concentration differences, makes impossible any correlation with the conductivity results reported in the preceding paper, and the following discussion is based solely on the transference data recorded above.

Each experiment gives us the number of faradays (F), and hence the fraction of the total current (T), carried by each species of ion. Expressing the molarities (M_i) of the same ions as fractions (x) of the total ionic molarity (ΣM_i), division of the T values by the corresponding x values gives us figures proportional to the relative mobilities of the ions (λ) in that particular solution. The ratios $\lambda_H/\lambda_H + \lambda_{Cl}$ and $\lambda_R/\lambda_R + \lambda_{Cl}$ in their turn give n_H and n_R, the cationic transport numbers of HCl and RCl in the mixture, which can be compared with the values given by the single electrolytes at the same total molarity. The following tabulated example will make this clear. The data are those of experiment 11 (table 2).

	H^+	Na^+	Cl^-	
M_i	0.1072	0.4558	0.5630	$\Sigma M_i = 1.1260$
x	0.0952	0.4049	0.5000	
F	0.00624	0.00331	0.00636	$\Sigma F = 0.01591$
T	0.3922	0.2080	0.3997	
λ	4.119	0.5139	0.7994	

For the two cations, we have that $l_H : l_{Na} = 8.013:1$; and, as $\lambda_H + \lambda_{Cl}$ and $\lambda_{Na} + \lambda_{Cl}$ are, respectively, 4.918 and 1.313, n_H becomes 0.8373 and n_{Na} 0.3913.

Table 3 contains the values of l_H/l_R, n_H, and n_R for the experiments (omitting the first) recorded in table 2. The bracketed figures in the second column are based on the mobilities at 18°C. of H^+ ions and R^+ ions in 0.1 N solutions of HCl and RCl, respectively, *viz.*, H^+, 294; K^+, 55.1; Na^+, 36.4; Li^+, 27.5 (8). Column 5 contains the cationic transference numbers for the neutral alkali metal halide solutions at concentrations equal to the total concentrations of the acid solutions.

Whilst the effects of the small inaccuracies in analysis referred to above are magnified by the method of calculation used, there are nevertheless certain general conclusions to which the results point. The values of n_H in column 3 are less affected by experimental error than are the other ratios. We found (table 1) n_H to be 0.8344 for 0.1 N hydrochloric acid. It is known to rise with increase of concentration up to, at all events, 1 N (thus Kraus (9) gives 0.835 for 0.1 N at 18°C., rising to 0.840 at 0.5 N and to 0.844 at 1 N), whilst according to Buchböck (6), it falls to 0.824 at 2.5 N. At the lowest concentrations of added RCl, our figures show no difference exceeding the probable experimental error, either amongst themselves or from the values for pure hydrochloric acid solutions. At concentrations of added potassium chloride or sodium chloride greater than 1 M, n_H clearly diminishes, in general agreement with the result of Buchböck just quoted. On the other hand, whilst the n_R values, which bear the full brunt of any analytical error, are clearly far from being accurate, in every case except in experiment 6, which is obviously erroneous, they are greater than the n_R values for the corresponding solutions of the pure salts. In particular, n_K in HCl + KCl solutions tends to be above, not less than, 0.5. The values for l_H/l_R conform to the other results; in the most dilute mixtures, they are very near or rather less than the bracketed figures in the same column, and they definitely decrease at higher concentrations of RCl.

TABLE 3

Values of l_H/l_R, n_H, and n_R for experiments recorded in table 2

NO. OF EXPERIMENT	l_H/l_R	n_H	n_R	n_R (NEUTRAL SOLUTIONS)	
2	5.15	0.842	0.508	0.491	KCl
3	5.16	0.841	0.505	0.489	
4	5.16	0.843	0.510	0.486	
5	5.02	0.830	0.494	0.484	
6	5.29	0.823	0.466	0.482	
7	4.21	0.814	0.5105	0.481	
8	4.84	0.830	0.502	0.481	
	(5.334)				
9	7.56	0.8385	0.407	0.382	NaCl
10	8.06	0.834	0.384	0.377	
11	8.01	0.837	0.391	0.369	
12	8.49	0.832	0.369	0.360	
13	7.96	0.820	0.363	0.355	
14	6.92	0.822	0.401	0.354	
15	6.76	0.786	0.352	0.35	
	(8.076)				
16	10.16	0.8385	0.349	0.304	LiCl
17	9.88	0.838	0.343	0.292	
	(10.69)				

Qualitatively, these effects are of the same nature as those predicted by Bennewitz, Wagner, and Küchler (1; see also 13), in their extension to mixtures of electrolytes of Onsager's theory of conductance in highly dilute solutions. As the retarding interionic forces will be greater, the smaller the average mobility of the ions comprising the ionic atmosphere, the mobility of H^+ ions in a solution of HCl + RCl will be less than in a solution of hydrochloric acid. The reaction accompanying the retardation of the H^+ ions will result in an acceleration of the R^+ ions, whilst the motion of the Cl^- ions will be very slightly decreased. The measurements of the same authors (Hittorf transference numbers in HCl + KCl) are in qualitative agreement with the extended theory, as also are those of Longsworth (10) (transference measurements by moving boundary method in HCl + KCl), of Bray and Hunt (5) (conductance measurements in HCl + NaCl), and of Miss Taylor (16) (Hittorf transference numbers in HCl + NaCl). In all these cases, the share of current carried by the alkali metal ion compared with that carried by the H^+ ion is relatively high, but, in general, the observed effects are less than those predicted. This is ascribed to the fact that the total concentration of electrolyte in the experimental work (0.1 to 0.2 *N*) was too high for the strict application of the theory.

If, however, the views of Bernal and Fowler (2) are correct, the theory will need considerable quantitative modification. According to these authors, the velocity of actual bodily transport of the hydrogen or H_3O^+ ion in aqueous solutions will be of the same order as that of other ions, and four-fifths of its observed velocity will be due to Grotthuss conduction, acting by a mechanism of proton jumps from one water molecule to another. They give good reason for assuming that, whilst the chloride ion is actually 4-coördinated with water molecules, no transport of water takes place when it moves, but merely an exchange of coördinated water. The potassium, sodium, and lithium ions, on the other hand, will carry with them on migration increasing proportions of their coördinated water,—in 1 *M* solution about one, two, and five molecules, respectively, per ion, judging from the results of Washburn (20), Remy (14), and Velisek (19) already referred to.[1] Applied to solutions of hydrochloric acid, these conceptions agree well with the results of Buchböck (6), who found, in 1 *N* solution, N_w^F to be 0.24. This gives an average hydration value of 0.27 for the hydrogen ion if the chloride ion transports no water with it, and this in turn corresponds to 27 per cent of the cationic current being due to actual movement of H_3O^+ ions, and 73 per cent to Grotthuss conduction. The theory also accounts for the fact that, whereas the Hittorf cationic transference numbers for solutions of the alkali metal chlorides decrease

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[1] As mentioned, Bernal and Fowler assume all these univalent ions to be 4-coördinated, and reject a coördination number of six for the lithium ion, suggested by a consideration of energy of hydration.

with increasing concentration, the reverse is true for solutions of hydrochloric acid up to, at all events, 1 *N*. In the latter case, increasing concentration will retard the mobility of the chloride ion, owing to interionic effects, but up to a point will have relatively little influence on the frequency of proton jumps. On the other hand, the decrease in the transference number reported by Buchböck in 2.5 *N* solutions can reasonably be ascribed to a steric effect, due to the presence of increasing quantities of the large 4-coördinated chloride ions, which decreases the frequency of proton jumps.

If now, in accordance with these ideas, the conductivity of the H_3O^+ ion in dilute solution is chiefly due to Grotthuss migration of protons, clearly the predictions of the extended Onsager theory must be modified in the sense that smaller effects are to be expected, which is in accordance with what was found by previous workers. On the other hand, our data suggest that the effects in more concentrated solutions of RCl may be considerable, and, in particular, that the relative mobilities of the R^+ ions are apparently increased when hydrochloric acid is present, even in solutions where the ratio [HCl]:[RCl] is low. Whilst it is not difficult to imagine that proton migration may become less easy as the structure of the solution becomes "tighter" in the sense of Bernal and Fowler, owing to the increasing numbers of water-coördinating cations, it is less easy to see why the mobilities of the latter should simultaneously increase, as appears to be the case, and it is hardly profitable at the moment to discuss the point. It may, however, be mentioned that we have considered the possibility of the presence of added hydrochloric acid so modifying the conditions in a solution of an alkali metal chloride as to decrease the average size of the hydration shell permanently attached to the cations, thus increasing the relative mobility of the latter. In such a case, one would expect the apparent volume of the salt to be greater dissolved in a solution of hydrochloric acid than in pure water. The density measurements in the preceding paper are sufficiently accurate to test this possibility at 25°C. We have calculated from these data the apparent volumes occupied by 0.25, 1, and 3 moles of potassium chloride, sodium chloride, and lithium chloride dissolved respectively in (a) 1000 g. H_2O + 0.1 *M* HCl and (b) 1000 g. H_2O + 0.1 *M* RCl. The results are as follows:

MOLES OF RCl ADDED	APPARENT VOLUMES IN CC.					
	KCl		NaCl		LiCl	
	In HCl	In KCl	In HCl	In NaCl	In HCl	In LiCl
0.25	7.12	7.19	4.45	4.54	4.55	4.35
1.0	29.34	28.83	18.63	18.50	18.49	18.48
3.0	91.83	91.89	60.25	61.01	57.19	57.76

There is no evidence whatever of any effect of the kind looked for, and this has been confirmed by plots of the whole series of apparent molar volume against molarity; within the experimental error, the points fall on the same curve, whether the RCl be dissolved in water or in 0.1 *M* hydrochloric acid.

In conclusion, brief reference may be made to the "middle layer effect", which, it may be remembered, was the cause of the curtailment of the projected series of runs with hydrochloric acid–lithium chloride mixtures. Experimentally, this manifested itself by a decrease in concentration of acid in the "middle anode" layer at an early stage in the transference experiment. It was noticed with 0.1 *M* hydrochloric acid, was accentuated when potassium chloride or sodium chloride was present in addition, and became very pronounced with hydrochloric acid–lithium chloride mixtures. Primarily, of course, the effect is due to the fact that the anode layer is losing hydrogen ions by transference and these are being replaced by cadmium and chloride ions. After a time, the fraction of the ionic transference between the anode and middle anode layers which is due to hydrogen ions is bound therefore to fall below the corresponding fraction at the boundary between the middle anode and the middle layers, and the phenomenon is not noticed in the time necessary for an experiment with acid-free RCl solutions because the mobilities of the R^+ ions are so much less than that of the hydrogen ion. Calculation readily shows that the effect will be heightened by the addition of an alkali metal chloride to the hydrochloric acid solution, and to a degree corresponding qualitatively to what was found, but also, on the classical theory of conduction, to the *same degree* in every case. If, however, the extended Onsager theory be applied, then, again qualitatively, it can be shown that the magnitude of the effect should increase in the order KCl < NaCl < LiCl, as was found. The very considerable difference between the behavior of hydrochloric acid–lithium chloride and hydrochloric acid–sodium chloride solutions can not be explained, but it may be pointed out that it appears analogous to the large increase in n_{Li} in acid, as compared with neutral solutions of lithium chloride, exhibited in table 3.

SUMMARY

1. The transference numbers of solutions of potassium, sodium, and lithium chlorides, both in water and in one-tenth molar hydrochloric acid, have been investigated at room temperature by the Hittorf method over considerable ranges of concentration. Both anode and cathode layers were analyzed, and the majority of the experiments were done in duplicate.

2. The agreement with neutral solutions between the values obtained by analysis of the anode and cathode layers suggests that the high hydration values which have been ascribed to the alkali metal cations in dilute

solution, as the result of transference measurements with and without a reference substance, are spurious.

3. In the acid solutions, the hydrogen ion and the alkali metal cations appear to carry, respectively, less and more of the current than would be expected from their mobilities in solutions of the corresponding single electrolyte. Connected with this is the existence of a so-called "middle layer effect," which causes certain experimental difficulties.

4. These last phenomena are discussed in the light of (i) the extended Onsager theory due to Bennewitz, Wagner, and Küchler and (ii) the views of Bernal and Fowler on the nature of the conductance of the hydrogen ion.

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THE DIFFUSION OF ONE-TENTH MOLAR HYDROCHLORIC ACID THROUGH AQUEOUS SOLUTIONS OF POTASSIUM, SODIUM, AND LITHIUM CHLORIDES

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The measurements described in this paper were carried out twelve years ago, subsequent to work on the diffusion of sodium chloride already communicated to this Journal (5). Although the remarkable effects of the presence of other electrolytes on rates of ionic diffusion were already known, particularly from the experiments of Arrhenius (2), no systematic work on the subject had been carried out, and it was thought that such work might be of interest when considered in conjunction with analogous determinations of conductance and transference data (described in the preceding papers), and with the measurements on the effects of strong electrolytes on the activity coefficient of the hydrogen ion, then becoming available in considerable number. Since the experiments were completed, Onsager and Fuoss (10) have published, for dilute solutions, a very detailed consideration of the whole complex of subjects involved, whilst McBain has recently treated the subject of diffusion in mixtures of electrolytes both theoretically and practically in an important paper (8). His experimental technique is obviously superior to the one we were using in 1924, but our results, covering, as they do, three different electrolyte mixtures over a wide concentration range, appear to us worth publication.

EXPERIMENTAL

The apparatus and method of work were essentially as already described (5), and little need be added. Our original intention was to study the rate of diffusion of hydrochloric acid *from* 0.1 M HCl + n M RCl *through* n M RCl, all concentrations being referred to 1000 g. of water. The diffusion apparatus therefore at the start of an experiment would have contained two superposed solutions, with the same weight molarity of RCl referred to the solvent. In actual fact this was found to be impracticable. The differences in density (e.g., 0.0013 to 0.0015 at n = 4) were too small to allow of certain manipulation without possibility of mixing. Consequently, in all experiments recorded below, the concentration on a volume basis of the pure RCl solution constituting the upper layer was never allowed to exceed that of the RCl in the corresponding lower layer containing hydrochloric acid. This ensured its density being sufficiently less than that of the latter, and minimized the possibility of error by mixing. The actual density differences (at 25°C.), as calculated from the data of Nickels and Allmand, varied between 0.0018 and 0.0055 with potassium chloride, between 0.0015 and 0.0038 with sodium chloride, and between 0.0018 and 0.0074 with lithium chloride. In the case of the measurements with 6 *M* sodium chloride, the density difference (no figures available) was certainly smaller than the lower of the two figures quoted for the experiments with this salt, a fact which may well be responsible for the high value of the diffusion coefficient found in this case. The weight concentrations of RCl given in the tables refer to the upper, acid-free solutions used.

The source of the chemicals, as also the methods of preparing the solutions and carrying out the analyses, was as described in the papers of Nickels and Allmand.

RESULTS

As in the case of the work on the diffusion of sodium chloride solutions already described, the temperature varied somewhat from experiment to experiment. In order to render the results comparable, and to utilize in conjunction with them the viscosity data of Nickels and Allmand, we have recalculated the values of the diffusion coefficients to a common temperature of 25°C., using for this purpose the formula $K_{25^\circ}/K_t = 1 + 0.03 (25 - t)$. The few values of temperature coefficient which can be deduced from our results show considerable divergencies from one another, and we can claim no more than very approximate accuracy for the value of 0.03. Our general conclusions are not affected thereby.

In table 1 the columns contain, respectively, the weight molarity of the upper, neutral layer, the initial temperature, the temperature change during the experiment, the number of diffusiometers used, the mean value of K_t found, the mean value of K_{25° calculated as above indicated, the viscosity of the neutral chloride solution, and the diffusion coefficient–viscosity product.

Figure 1 contains the values of $(K\eta)_{25^\circ}$ plotted against *M*. Inspection reveals the existence of irregularities which can only be attributed to experimental error, for it is easy to show that the assumption of values other than 0.03 for the temperature coefficient of diffusion would not alter matters in this respect. The actual curves have been smoothly drawn and, in particular, no attempt has been made to include the points obtained with 0.114 *M* potassium chloride, 2.55, 2.97, and 5.99 *M* sodium chloride, and 2.05 *M* lithium chloride.

Examination of the detailed results (not reproduced) given by different

TABLE 1

M	t IN °C.	$\Delta t°$	NUMBER OF DETERMINATIONS	K_t (mean)	$K_{20°}$	$\eta_{20°}$	$(K\eta)_{20°}$
Potassium chloride							
0.058	15.6	−0.2	4	4.10	5.26	1.0005	5.26
0.114	15.6	+0.1	4	4.22	5.41	1.0003	5.41
0.232	15.7	+0.2	4	4.68	5.99	0.9992	5.98
0.470	13.8	0.0	1	4.73	6.42		
	17.1	+0.1	2	5.61	6.94		
	15.7	−0.1	3	5.13	6.56		
	15.7	+0.2	2	4.67	5.97		
	15.4	+0.1	2	4.79	6.17		
	15.6	+0.2	2	4.63	5.94		
					6.33	0.9980	6.32
0.982	16.3	+0.1	2	5.31	6.70		
	15.6	+0.2	1	5.40	6.92		
	13.8	0.0	1	4.92	6.57		
					6.73	0.9977	6.72
1.96	16.2	−0.2	2	5.37	6.79		
	16.3	+0.1	1	5.34	6.73		
	15.6	+0.2	1	5.23	6.71		
					6.74	1.0048	6.77
3.03	14.4	0.0	4	4.79	6.31	1.0316	6.51
4.13	15.7	+0.1	4	4.48	5.73	1.0646	6.10
Sodium chloride							
0.050	16.1	+0.3	4	3.76	4.87	1.0045	4.89
0.100	15.5	−0.3	4	4.17	5.36	1.009	5.41
0.195	13.1	−0.3	4	4.38	5.94	1.018	6.05
0.487	16.5	−0.1	2	5.09	6.39		
	15.2	−0.1	4	4.93	6.38		
					6.38	1.044	6.66
1.014	15.6	+0.05	4	4.80	6.15	1.093	6.72
1.905	15.95	−0.05	4	4.46	5.67	1.193	6.76
2.55	15.7	−0.1	2	3.96	5.05	1.278	6.45
2.97	16.3	−0.2	4	3.57	4.52	1.342	6.06
4.42	15.7	+0.2	4	3.04	3.88		
	14.5	−0.1	2	2.90	3.81		
	17.1	+0.2	4	2.98	3.69		
					3.79	1.595	6.05

TABLE 1—*Concluded*

M	t in °C.	$\Delta t°$	NUMBER OF DETERMINATIONS	K_t (mean)	$K_{25°}$	$\eta_{25°}$	$(K\eta)_{25°}$
Sodium chloride—*Concluded*							
5.47	17.0	0.0	4	2.69	3.34	1.829	6.11
5.99	16.8	+0.3	4	2.67	3.33		
	15.7	−0.1	1	2.58	3.29		
					3.31	1.953	6.47
Lithium chloride							
0.055	14.3	−0.3	4	3.54	4.68	1.010	4.73
0.108	14.6	−0.3	4	4.09	5.37	1.016	5.46
0.219	14.4	−0.1	4	4.55	6.00	1.032	6.19
0.492	14.4	+0.1	4	4.68	6.17	1.073	6.62
1.00	14.5	−0.2	4	4.54	5.97	1.149	6.86
2.05	14.4	+0.2	4	3.76	4.96	1.318	6.54
3.06	13.9	−0.4	4	3.19	4.25	1.501	6.38
4.31	14.6	−0.2	4	2.38	3.12	1.760	5.49

diffusiometers with the same solution shows concordance to have been least satisfactory when working with potassium chloride. The table shows similar lack of agreement between different experiments on the same solution (see particularly the results at 0.470 M). Nevertheless, when plotted, the potassium chloride results give a relatively smooth curve at the higher concentrations. The values of K_t given by the different diffusiometers for the 0.114 M solution (4.44, 4.39, 3.92, 4.11) showed worse concordance than was found in any other case. If, instead of using the arithmetical mean of all four results, as has been done in the table, the average of the first two figures be taken, then $(K\eta)_{25°}$ becomes 5.67, and the point will fall on the curve as drawn. The other discrepant points mentioned above could similarly be brought on or near to their corresponding curves by weighting values of K_t in close agreement with one another. In view, however, of the arbitrary element in such a procedure, we have preferred to leave matters as they are.

DISCUSSION

Whilst the different K/M curves (not reproduced) are very different in nature, it is obvious from the figure that the application of the viscosity correction has brought the three K values into rather close concordance over the concentration range 1 to 3 M. In particular, they all pass through a maximum of about 6.8 to 6.9, in the region of 1.3 to 1.5 M RCl. Nevertheless they are still quite distinct from one another over their whole course. And, in particular, the K_η values in sodium chloride pass through a minimum at about 4.7 *M*.

Neither the nature of our experiments, which obviously can only furnish average diffusion coefficients, nor the present state of the theory of concentrated solutions of mixtures of strong electrolytes justifies any discussion of the details of our results, and we will merely draw attention to certain outstanding points.

The "classical" theory for this type of diffusion was worked out by Arrhenius (2) and by Abegg and Bose (1). Assuming, as was then usual, that mobilities were independent of concentration, assuming also that ionization was complete, and neglecting any effect of viscosity, the conclusions were come to that the diffusion coefficient of the hydrogen ion is increased by the addition of an alkali metal chloride, the relative order of effectiveness in this respect being KCl > NaCl > LiCl, and that a final maximum value is reached, independent of which chloride be added or of any further increase in its concentration, of value RTl_{H^+}/F. Giving l_{H^+} the "infinite dilution" figure of 349.7, we obtain 8.98 as this limiting value of $K_{25°}$. These authors also draw attention to the fact that this increased mobility of the hydrogen ion must necessarily be accompanied by diffusion in the opposite direction, against a concentration gradient, of the alkali metal cation, i.e., by counter diffusion.

Our own experiments all exhibited this last phenomenon in that, at the conclusion of a run, a concentration gradient of the salt RCl was found to exist in the diffusiometer, the concentration increasing from the lowest layer upwards, invariably involving the three lower layers, and usually the uppermost as well. Further, we found the diffusion rates of 0.1 *M* hydrochloric acid through 0.05 *M* RCl, the lowest concentration used by us, to increase in the order LiCl < NaCl < KCl (figure 1b), in accordance with the simple theory. The actual effect of the addition of RCl of this concentration was, however, much greater than that calculated from the equation of Abegg and Bose, whilst the maximum observed values of $K_{25°}$ depended on the nature of the alkali metal chloride, fell off when the concentration of the latter was increased beyond a certain point, and were all far below the calculated limiting value of 8.98 (see table 1).

When considered in the light of the modern theory of strong electrolytes, it appears that the primary effect of interionic forces in cases of diffusion is thermodynamic in nature (10); the value of the driving force on the ions which causes their movement down a concentration gradient will be different from its value in an ideal solution. In the present case, the relevant data have been obtained by Harned and his collaborators (7). The activity coefficient of 0.1 *N* hydrochloric acid is first lowered by the addition of an alkali metal chloride, passes through a minimum, and then, at higher concentrations, where short-range repulsive forces become important, rises rapidly. The order of effectiveness as regards the initial lowering is KCl > NaCl > LiCl, whilst the order in respect of the increase in γ found at higher concentrations is LiCl > NaCl > KCl. Consequently the thermodynamic effect of interionic attraction, considered alone, would be to increase still further the discrepancy between the predictions of the classical theory and our actual results.

In addition, however, whilst interionic forces will have relatively little effect on ionic mobilities when the diffusion of single salts is considered (6), in our case, where two electrolytes are diffusing through one another, the mobility of an ion will be affected by its ionic environment in the twofold manner postulated by Debye and Hückel when considering the problem of electrolytic conductance (10), i.e., both electrostatic and hydrodynamic (electrophoretic) ionic interaction will come into play, and the ionic mobilities valid at infinite dilution can not be employed. Nickels and Allmand, in their paper on conductance–viscosity relations in these systems, have given reasons for concluding that, if the viscosity correction be applied to the conductance data, the effects of these interionic reactions are, to a first approximation, eliminated or compensated for. And this is the justification for applying the viscosity correction to the present diffusion data, as has been done in figure 1. If however, this were a complete solution of the problem as far as concerns ionic mobilities, the values of $K\eta$ would be expected to rise in concentrated RCl solutions, in accordance with the increase in γ_{HCl}, more particularly in lithium chloride solutions and least so in potassium chloride solutions. And the ideal limiting value of 8.98 should be exceeded. Apart from the course of the $K\eta/M$ curve in sodium chloride solution above 5 M, no such rise is observed. $K\eta$ falls off beyond 1.4 M, whilst the values in potassium chloride exceed those in lithium chloride, not *vice versa*. And the maximum observed value of $K\eta$ is far below 8.98.

We think that these facts should be considered in the light of the results of the transference measurements described in the preceding paper. Nickels and Allmand found that, in mixtures of 0.1 M HCl + n M RCl, the results could only be explained on the assumption that the mobility of the R^+ ion was enhanced and that of the H^+ ion lowered, when compared with their values in solutions of the single electrolytes RCl and HCl. Whilst the experimental data did not permit of these phenomena being analyzed with any accuracy, they certainly suggested that the effect was more important in concentrated than in dilute solutions of RCl, and that it was more pronounced in lithium chloride than in sodium chloride solutions, and in sodium chloride than in potassium chloride solutions.

The same phenomenon, whatever its mechanism, would appear to be playing an important part in our diffusion experiments. For, a depression of the hydrogen-ion mobility (*i*) over and above that demanded by the original Debye-Hückel theory, and compensated for in our case by bringing in the viscosity term, (*ii*) most marked in lithium chloride and least marked in potassium chloride solutions, and (*iii*) increasing in importance as the concentration of RCl rises would be capable of accounting for the relative positions of the $K\eta/M$ curves beyond the maximum, as shown in figure 1.

Qualitatively these results, like those of the transference experiments, are in agreement with the extension of the Onsager theory of conduction in highly dilute solutions put forward by Bennewitz, Wagner, and Küchler (3). But the effects are much more considerable than those predicted by this theory. At one time, Nickels and Allmand were inclined to explain their migration data in terms of a transfer of momentum from rapidly moving H_3O^+ ions to more slowly moving alkali metal cations, the result of the former overtaking the latter during migration. Even assuming the correctness of the views of Bernal and Fowler (4) on the composite nature of the mobility of the hydrogen ion (see the discussion in the preceding paper), it was possible to account for many, though not all, of the observed results on these lines, assuming of course conservation of kinetic energy and of momentum. We did not, however, pursue our ideas any further after reading the paper of Bennewitz *et al.* referred to above, and

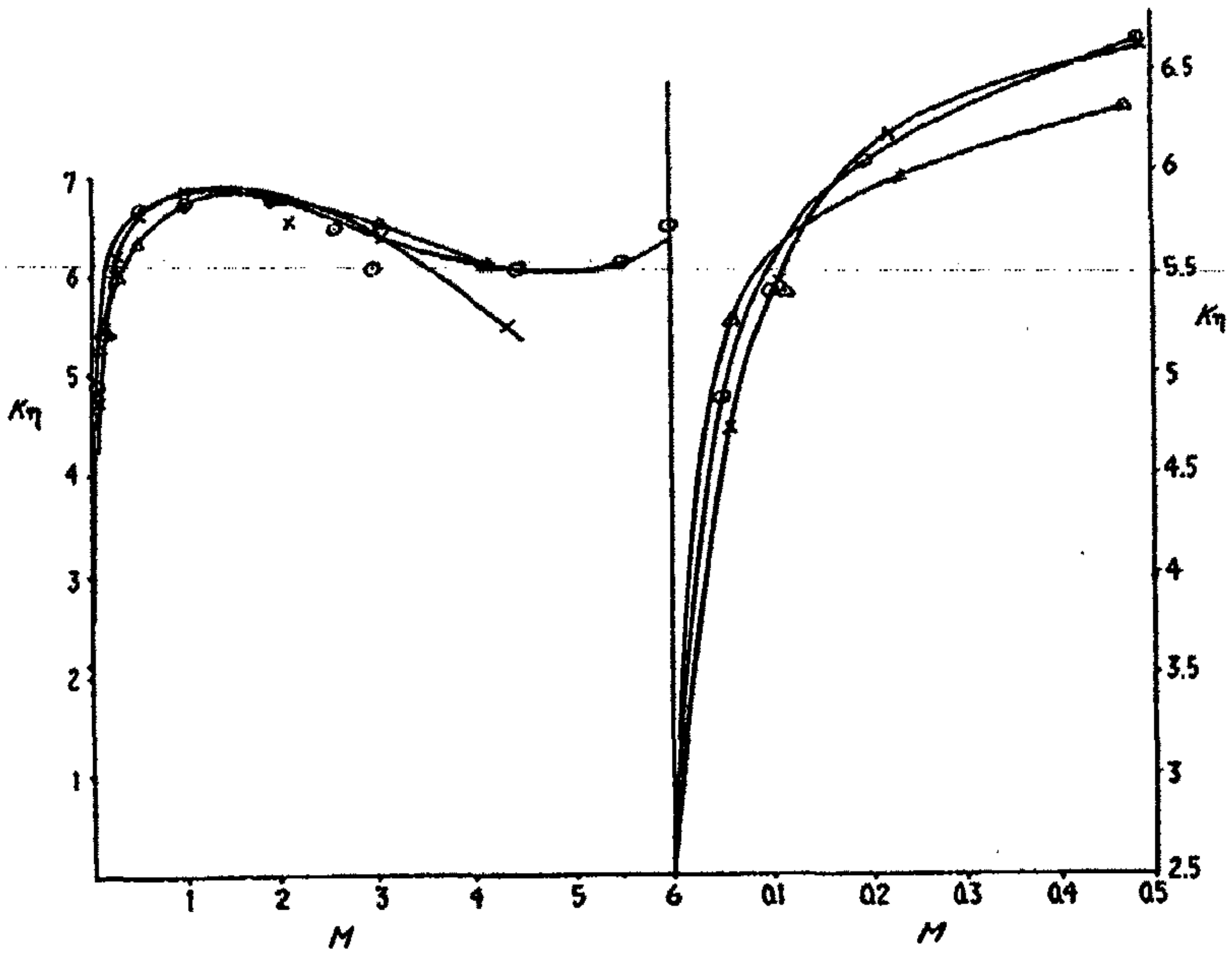

Fig. 1. Values of $(K\eta)_{25^\circ}$ plotted against M. △, potassium chloride; ⊙, sodium chloride; ×, lithium chloride.

only mention the matter because somewhat related views have been suggested by McBain and Liu (9) in connection with diffusion experiments where more than one kind of diffusing particle is involved.

With regard to the form of the $K\eta/M$ curve in sodium chloride at high concentrations of this salt, we make no specific suggestion. It is natural to imagine that it is due to the increase in γ_{HCl} finally overcoming the effect of the retarded mobility of the hydrogen ions. On the other hand, the curves are reminiscent of the less pronounced, but similar, minima found in the corresponding conductance experiments of Nickels and Allmand, when $\Lambda\eta$ for sodium chloride, dissolved either in water or in 0.1 M hydrochloric acid, was plotted against M. It was then suggested that these minima might be due to overcompensation of the interionic retarding effects when the full viscosity correction is applied. In any case, the minima in that instance can not be connected either with hydrochloric acid or with any thermodynamic effect.

SUMMARY

1. The diffusion of one-tenth molar hydrochloric acid at room temperature through aqueous solutions of potassium, sodium, and lithium chlorides has been studied, using alkali metal chloride solutions of concentrations varying from 0.05 M up to 4.1 to 6 M. The values of the diffusion coefficients have been recalculated to a common temperature of 25°C.

2. When plotted against the molarity of the alkali metal chloride, both the diffusion coefficient (K) and the product of the diffusion coefficient and the viscosity of the solution ($K\eta$) yield curves which are different for the three alkali metal chlorides. Nevertheless the $K\eta$ curves are nearly coincident over the concentration range 1 to 3 M.

3. The results are discussed from the points of view of (*i*) the Arrhenius theory of electrolyte dissociation, (*ii*) the Debye–Hückel theory, and (*iii*) the extended Onsager theory due to Bennewitz, Wagner, and Küchler.

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NEW BOOKS

Properties of Matter. By C. F. CHAMPION and N. DAVY. 296 pp.; 161 fig. New York: Prentice-Hall, Inc., 1937.

This book is written for advanced students of physics and chemistry who have already a good background of physics. The subject matter is treated entirely from the point of view of physics and contains the following chapters: I. Unit and dimensions. II. Acceleration due to gravity. III. Newtonian constant of gravitation. IV. Elasticity. V. Compressibility of solids and liquids. VI. Seismic waves. VII. Capillarity. VIII. Surface film. IX. Kinetic theory of matter. X. Osmotic pressure. XI. Diffusion. XII. Viscosity. XIII. Errors of measurement; method of determining Planck's constant.

The first seven chapters remind one of the usual textbook of physics. To be sure the treatment is concise and the material is up to date. In chapter VIII one finds the new ideas of surface films expounded. The treatment on kinetic theory (chapter IX) covers mean free path phenomena (viscosity, diffusion, heat conduction), properties of gases at low and intermediate pressures and at high pressures, determination of Avogadro's number, Brownian movement, production of high vacua, and the measurement of low pressures. All of this material is contained in thirty-six pages! Obviously the treatment has to be very condensed indeed. The chapter on osmotic pressure (chapter X) contains a short statement of the Debye-Hückel theory (ten pages); it is evident that the authors waste no words for the essentials are stated clearly. The last two chapters on diffusion and viscosity are written in the same way. The concluding chapter on errors of measurement is excellent. But one is surprised to find as an example the determination of Planck's constant by eight methods, considering that the book does not deal with atomic physics or quantum mechanics. The names of Bohr and Planck only occur in the error treatment and in no other place in the book. Examples and problems are appended for each chapter, as well as answers and hints. It has been the intention to bring out in this review those features of the book which might interest the physical chemist. The volume contains a wealth of material which is discussed ably and clearly. The only fault one would possibly find with the text is the attempt to cover so much in so little space.

GEO. GLOCKLER.

Annual Tables of Constants and Numerical Data. (Inst. de Chimie, Paris). *Numerical Data on the Raman Effect* (1931-34). By M. MAGAT. 112 pp. Paris: Gauthier-Villars, 1934.

The author has analyzed and collected the research carried on in the field of Raman spectroscopy for the years 1931-34. He has coördinated the work of the several authors by giving the average wave length in case a given Raman line has been obtained by several observers. Intensities of lines are also given wherever possible. The whole volume is divided into three parts: I. Inorganic compounds (elements, compounds, electrolytes and complex structures). II. Organic substances (aliphatic saturates and unsaturates, benzene and derivatives, terpenes, heterocyclic compounds, oximes, sugars, carotenoids, mixtures). III. Theory (vibration pattern and literature references). Literature references are given for the various sections. An index, which is really a table of contents, completes the arrangement. The volume is of course a most helpful tool to the research worker and is a welcome addition to the *Annual Tables*.

GEO. GLOCKLER.

The Avitaminoses. By WALTER H. EDDY and GILBERT DALLDORF. Foreword by James Ewing. ix + 338 pp.; xxix plates. Baltimore, Maryland: The Williams & Wilkins Co., 1937. Price: $4.50.

As pointed out in the foreword by Dr. Ewing, this is the first comprehensive review in English on the pathological effects of vitamin deficiencies. The book will appeal especially to pathologists, clinicians, and physicians, but is a valuable work to biochemists and teachers of nutrition who also should keep abreast of the important theories, facts, and practices in this rapidly growing field of knowledge. The book is a sequel to the *Vitamin Manual* published by the senior author in 1921. One can hardly find a more striking demonstration of the enormous advances which have been made in this subject than by contrasting the earlier volume with the present one.

The book is divided into two parts. Part I, consisting of chapters I to XXVII, considers the nature of vitamins A, B, C, D, and E and also that of the other vitamins now regarded as components of the original vitamin B complex. The functions of each of these vitamins are discussed in separate chapters, as are also the clinical and subclinical manifestations and forms of each vitamin deficiency. The anatomical manifestations of vitamin A and C deficiencies are discussed in separate chapters, as are also the morbid anatomy of vitamin B deficiency and the morbid effects related to the supply of vitamin D. There are also separate chapters on beriberi, scurvy, pellagra, and rickets. Part I concludes with chapters entitled, respectively, "The Vitamins and Resistance to Infection," "Morbid Effects of Certain Complicated Dietary Experiments," and "Vitamins and Blood Regeneration."

Part II, consisting of three chapters, is especially valuable in that these chapters cover the standard methods for vitamin bio-assay, various clinical tests of vitamin deficiencies, and tables giving vitamin A, B, and C values of many common foods in terms of international units per ounce and vitamin G values in Sherman-Bourquin units.

Each chapter in part I is followed by a valuable bibliography. Part II also contains important references to the literature. The book is profusely illustrated by excellent plates, tables, and figures, all of which add greatly to its value. Both an author and a subject index are included.

Considerable courage is required to write a book in a field of knowledge which is advancing so rapidly that some of the statements made will be obsolete by the time the book is printed. *The Avitaminoses* has had this misfortune, but such errors of this nature as do occur do not detract from the main value of the work. On the whole the subject matter has been chosen wisely and treated thoroughly, efficiently, and critically. Only in a few places would serious difference of opinion arise regarding the material selected, or its treatment. Even this does not, in the opinion of the reviewer, detract from the worth of the book.

L. S. PALMER.

Soil Conditions and Plant Growth. By Sir E. JOHN RUSSELL. 7th edition. viii + 655 pp. New York: Longmans, Green and Co., 1937. Price: $7.00.

The seventh edition of this famous book dealing with soil conditions and plant growth is characteristic of preceding revisions. It brings up to date the essential features of present-day knowledge in this field. While each chapter has been modified and much of the text rewritten, the size of the volume has not been materially altered. Some additional textual matter has, however, supplanted the former appendix on methods of soil analysis. The size remains at around 650 pages, and it is a very handy volume for general reading.

The purpose of the book, as the author states in the preface, is "to present the student with a broad outline of the subject, including sufficient detail to give reality to the treatment, but avoiding always the tediousness of the card index record." In this it most admirably fits its purpose. It is a volume for the general student in soils and plant growth rather than for the specialist in some particular aspect of this field. However, the revised and up-to-date bibliography is of great value to technicians and general students alike.

One of the most important revisions has to do with the discussion of the influence of the various elements on plant growth, including both major and minor elements. The latter are classed in this revision under the general heading of stimulative or prophylactic elements,—among the metals copper, boron, manganese, zinc, and iron, while among the non-metals the class includes sulfur, titanium, and silicon, as well as chlorides, iodides, and fluorides. Each is discussed individually. Chapter III, on the composition of the soil, has been entirely rewritten, and particular attention has been given to the clay fraction, including the modern concept of the structure of the clay minerals. One of the most extensive additions is that under chapter IV, dealing with soil development and classification. In this the subject matter has been practically doubled, bringing together the latest views of pedologists. At the end of the book chapters VIII and IX have been combined under the chapter heading "Soil Fertility in Nature and in Farm Practice."

The author is at his best in this latest volume. Assisted by a number of Rothamsted colleagues he has made this revision the last word in summation of present-day knowledge in this important field.

M. F. MILLER.

A Catalogue of the Epstean Collection. New York: Columbia University Press, 1937. Price: $1.50.

Students of the history of photography and of some phases of photochemistry will welcome this catalogue of the Epstean collection. In addition to making the collection more useful, it will serve as a bibliography of the earlier works on photography. The collection, which is housed in the Rare Book Departments of the Columbia University Library, includes 1418 titles. The subject matter covers practically the entire field of photography, as well as some aspects of related arts and sciences. The book is attractively bound and printed.

ROBERT LIVINGSTON.

Radioactivité. By MME. PIERRE CURIE. 563 pp. Paris: Hermann et Compagnie, 1935. Price: 150 frs.

In 1910 Mme. Curie published her well known *Traité de Radioactivité* (two volumes), which presented with some additions the material then contained in her regular lectures at the Sorbonne on the subject of radioactivity.

Although the present book also represents her lecture course—as recently given—it would be a mistake to assume that it is a revision of the earlier treatise. In fact no more striking evidence of the advances of nuclear chemistry and physics in twenty-five years could be had than by noting the differences between these two works.

It is true that the framework of the radioactive transformations in the three families had already been traced in 1910, but the law of atomic displacement in the periodic system, the significance of isotopes and radioactive indicators, the nature of gamma radiation, the origin of the actinium family, the explanation of beta- and gamma-ray spectra, the Gamow theory of the nucleus and its energy barrier, all remained to be discovered. All of this has been adequately treated by Mme. Curie in the 1935 work, as well as the then very new discovery of artificial radioactivity.

It is truly a fitting close to a brilliant career that Mme. Curie should have lived from the epoch-making discovery of radium jointly with her husband and its isolation and study through a period of unabated activity and usefulness, including the establishment of a new radium institute, on down to the brilliant discovery of artificial radioactivity in her own laboratory by her daughter Mme. Irene Curie-Joliot and her husband, Frederic Joliot.

The present volume will be most useful to all radioactivists and others working in the field of nuclear physics. It is replete with illustrations and tables, as well as a long list of transformation constants. While literature references and an index would have added to its value, it is nevertheless indispensable in any library or to any worker in atomic transmutation.

S. C. LIND.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 22: Kalium. Lieferung 2. 26 × 18 cm.; pp. xi + K 247–514. Berlin: Verlag Chemie, 1937. Price: 31.50 RM.

This section of the volume on potassium deals with the compounds with nitrogen (nitride, azide, amide, nitrohydroxylamite, dipotassium nitrite, hyponitrite, nitrite, and nitrate), the normal and acid fluorides, chloride, hypochlorite, chlorite, chlorate, and perchlorate. As usual, the physical and physicochemical properties are very completely dealt with. Since in some cases the methods of preparation and manufacture are closely similar to those for the corresponding sodium compounds, these descriptions are abbreviated and reference is made to the volume on sodium. The electrolytic technical method for the preparation of potassium chlorate is given in full; that for the perchlorate is abbreviated. Potassium nitride, K_3N, appears to be formed by thermal decomposition of the azide. The colored solution of potassium in liquid ammonia is not colloidal. The nitrite (m.p. 441°C.) is best prepared by the interaction of sodium nitrite and potassium carbonate in solution. The industrial preparation of potassium nitrate (used for gunpowder) from Chile nitre (sodium nitrate) began about 1850; the direct technical production from potassium chloride and nitric acid is now possible. The manufacture of potassium chloride is not described in this volume, although the properties of the salt and its solutions are very fully dealt with (122 pages). The thermal decomposition of potassium chlorate, both with and without catalysts, is well discussed; the catalytic activity of manganese dioxide is said to be probably due to local heating. It is interesting to note that the formation of the perchlorate by electrolysis of solutions of chlorate, the modern industrial method, was observed by Stadion in 1816.

The volume is one which maintains the high standard of the whole work and contains a large amount of useful and interesting information very accurately and critically set out.

J. R. PARTINGTON.

Lehrbuch der physikalischen Chemie. By K. JELLINEK. Band V, Lieferung 3. 24 × 16 cm.; pp. xx + 577–989. Stuttgart: F. Enke, 1937. Price: 41 RM.

This concluding part of the fifth volume brings Prof. Jellinek's well-known and very useful work to a conclusion. The author deserves congratulations on the successful completion of his work, and it may be predicted that this book will for a long time fulfil a very useful function. It provides a comprehensive course of physical chemistry set out in a form which will appeal to those who are not familiar with more than the elements of the calculus, since all of the more difficult parts of the mathematics are clearly explained in the book, a procedure which is much more satisfactory than merely stating the results. The experimental methods and the numerical results are also given due prominence, so that the work will make an appeal to the research worker. In the present volume the main sections are on dielectrics and dipole moments, magnetism and magnetic moments, molecular spectra, the theories of Kossel and Lewis, forces between molecules, crystallography and crystal structure, lattice energies, the structure of metals, contact potentials, radiation and absorption, and photochemistry. In all these subjects a good foundation for study is laid, and those who possess the earlier volumes will do well to complete the work by adding this last volume to their libraries.

J. R. PARTINGTON.

SOME RECENT WORK ON GELS[1]

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Received July 8, 1937

In this paper the term "gel" is used in such a way that it includes the jelly-like structures as they are found with aluminum oxide, ferric oxide, silicon dioxide, agar, gelatin, soaps, etc. They are coherent, more or less elastic, and contain a certain excess of a liquid phase, and their particles are of strictly colloidal size. Sometimes attention will be given to closely related systems, concentrated suspensions or pastes, containing a much larger amount of solid particles visible under the microscope (diameter about 1 to 10μ).

1. Most colloid chemists are in agreement that in gels we are dealing with structures of fairly different natures. Several years ago Miss Laing and McBain (30) emphasized that transparent gels of sodium oleate are very distinct from many other gels in that they are identical as to vapor pressure, electrical conductivity, etc., with the sols from which they have set. But so far it has not been possible to distinguish gels by a particular property. Heymann (23) found that the volume change in sol-gel transformation is very characteristic and allows an arrangement of gels into certain groups. This does not imply that volume change is to be taken as the only criterion.

Heymann used a very sensitive dilatometer immersed in a thermostat which was kept constant to 0.003°C. The capillary in which the change of volume was determined was very fine; a change of meniscus of 1 cm. corresponded to a volume change of 0.0016 cc. The volume of the sol which was turning to a gel amounted to about 80 cc. A volume change of 0.0002 per cent of the total volume could thus be measured.

Thixotropic gels, i.e., gels capable of an isothermal, reversible sol-gel transformation, being liquefied on shaking and setting spontaneously, show no change of volume. This was the case, for instance, with a concentrated sol of iron oxide (Graham) containing 9.44 per cent solid phase and a small amount of sodium chloride; the meniscus did not change its position more than a few tenths of a millimeter in an irregular way. This behavior fully agrees with the exceedingly small difference between sol

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

and gel in this type of gel. The transformation is probably due to a first and very mild stage of coagulation (15, 41), as it is caused by electrolytes in electrocratic (hydrophobic) sols, where no marked change in the distribution of water molecules between liquid and solid phase or in the chemical nature of the compounds occurs. The sodium oleate sols, mentioned above, also show no change in volume when being transformed to a gel (24).

A second type of gel, those of gelatin and agar, showed a small decrease in volume when the sol which had been formed on heating was cooled to room temperature and allowed to set to a gel at this temperature. With gelatin it was 0.05 to 0.06 cc. per 100 g. of gelatin, a value fairly independent of the pH between 3.8 and 8.8.

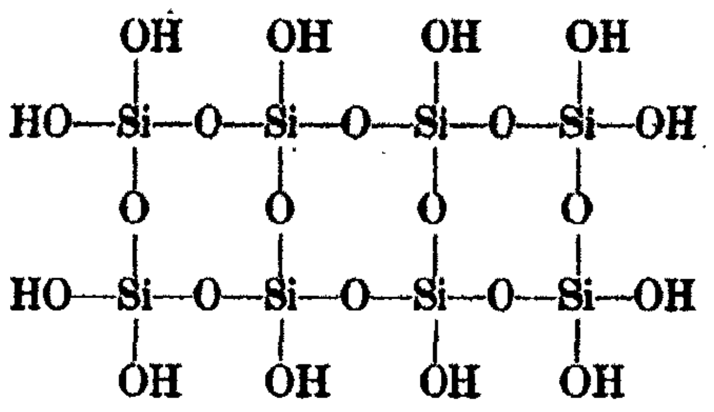
Colloidal aqueous solutions of methylcellulose, on the other hand, show a small increase in volume,—from 0.08 to 0.13 cc. per 100 g. of methylcellulose. This sol undergoes an inverse sol–gel transformation (22), i.e., the gel is formed with rising temperature, and is liquefied to a sol when the temperature decreases. The volume change was determined by letting the sol set to a gel at 35.7°C., or by comparing the volume of the sol at 34°C. with that of a gel which had been formed at 55°C. and had been cooled down to the former temperature before it had had time to liquefy.

In these cases a change of hydration is probably the cause of the volume change, the particles of the gel being more strongly hydrated in gelatin and agar and dehydrated in methylcellulose. Several other facts confirm this assumption. When gelatin is dissolved in water, the volume contraction is larger at low temperatures, where a gel is formed, than at higher ones, where a sol is formed. With methylcellulose dehydration with rising temperature is made probable by the parallel marked decrease of relative viscosity, i.e., of the ratio η_s/η_w, η_s being the viscosity of the sol, η_w that of water. It may be concluded that the viscosity of the sol decreases more strongly with the rise of temperature than that of the solvent, and that this is due to the relative volume of the dispersed particles becoming smaller.

If a gel of silicic acid is formed on mixing a sodium silicate solution with aqueous hydrochloric acid, the volume change is also positive, but much larger, about ten times, than in the cases mentioned so far; it amounts to about 0.8 cc. per 100 g. of silicon dioxide in the first hours until gel formation has occurred. Obviously gel formation is correlated here with a further polymerization of the mono- and di-silicic acids which Willstätter (45) has shown to be formed originally, e.g.,

$$2H_2Si_2O_5 = H_2Si_4O_9+H_2O$$

The large increase in volume is due to the water split off by this chemical reaction. The particles formed are polysilicic acids (38) such as



The volume change goes on for a very long time; even after five months there was no sign of a limit being reached. The volume increase after the gel has formed is about 1 cc. per 100 g. of silicon dioxide. Hence it is quite possible that the whole network structure of this gel is united by primary valences. In any case, silicic acid gel formation is irreversible, and the colloidal units in different temporary stages of the process may have a fairly different chemical constitution.

The rather extraordinary properties of silicon dioxide gel as to elasticity, irreversibility, etc., may be correlated with this structure, which is very different from that of gels of aluminum oxide, ferric oxide, etc. The gel formation going on in maturing viscose solution is also accompanied by a similarly large increase in volume.

2. Though we have become more thoroughly acquainted with thixotropic gels only in the course of recent years, thixotropic transformation, taken in a very general sense, is perhaps the most frequent phenomenon of this kind known. It is not confined to true gels like those of aluminum oxide, ferric oxide, vanadium pentoxide, etc., where the particles are of colloidal size (4, 41). Many concentrated suspensions of sufficiently finely powdered substances (minerals, etc.), containing a certain percentage of particles with a diameter of about 1μ, are liquefied on shaking and set again to a stiff, solid paste when left to themselves (6, 7). On the other hand, setting need not go so far that a gel is formed. The "anomalous viscosity" of many concentrated sols may be reduced reversibly by shaking, a change of behavior which may be found to turn gradually into the normal sol–gel transformation, if the concentration of the sol is increased (21). In all cases a structure is destroyed by mechanical treatment and forms again spontaneously. It is perhaps doubtful whether we are really dealing always with the same mechanism. In the case of dilute sols it is most surprising that they are still able to set to a gel, as is, for instance, the case with vanadium pentoxide sol down to a concentration of about 0.1 per cent. In concentrated suspensions, containing 70 per cent and more of solid powder, it is more surprising that they are readily liquefied.

Thixotropy is always bound to a loose packing of particles, i.e., to a certain excess in the amount of liquid (6). This is evident in gels and needs no special discussion. It is not equally obvious in pastes of concentrated suspensions containing coarse particles (clays, Solnhofen slate, etc.). Here the degree of packing may be tested by measuring the sedimentation volume of a somewhat less concentrated suspension. On the whole, the rule holds well that suspensions whose particles fill a large volume of sedimentation, and hence have a tendency to be loosely packed, are markedly thixotropic. It is surprising, however, that a comparatively small deviation from the state of closest packing is sufficient to produce a certain degree of thixotropy.

We have a counterpart to thixotropy, i.e., a phenomenon bound to a very close packing, in Osborne Reynolds' dilatancy (34, 35, 44). A behavior due to dilatancy is readily found in wet sand, and is thus frequently observed on a moist beach. When trodden upon or pressed the sand turns dry and hard, but it becomes moist again as soon as the pressure is released. Osborne Reynolds explained this behavior in the following way: The particles of the sand are closely packed, the amount of liquid being just sufficient to fill the free space between the particles. (With spherical particles of equal size this free space amounts to 26 per cent of the total volume. Spring (40) proved this to be true for a fine sand with spherical particles.) When the particles are displaced by some force from outside, the volume occupied by the interstices increases and the amount of liquid is no longer sufficient to fill the free space; the mass turns hard and dry. On releasing the pressure the particles return to their original state of close packing, the liquid is able to fill the free space, and the whole mass is moist again. It was shown experimentally (6) that concentrated aqueous suspensions having a small volume of sedimentation, hence being closely packed (quartz, fluorspar, Monax glass, porcelain, etc.), are dilatant. A certain independence of the particles of each other—a lack of any tendency to adhere to each other and to form clusters—seems to be essential for close packing.

Dilatancy may not be confused with another phenomenon which is similar, but only when being compared superficially. Some thixotropic sols and suspensions of coarser particles set more rapidly to a solid system when moved gently, whereas they are liquefied by intense shaking (8, 20a, 26). A suspension of finely powdered gypsum in water is solidified in a few seconds when rolled between the palms of the hand, whereas it needs about ten minutes to set spontaneously. A thixotropic, old sol of vanadium pentoxide, containing a suitable amount of acid or a lithium salt, turns to a gel in one minute if the test tube is tapped on the table; it takes many hours to solidify spontaneously. This phenomenon has been called rheopexy. Both in rheopexy and in dilatancy movement favors solidification. But in rheopexy the final state is that of a gel or solid paste, though the structure of a gel or paste formed by rheopectic setting is probably different from that of those which have formed spontaneously.

In dilatancy the solid state produced by the movement is unstable; the system, left to itself, returns to a more liquid or even distinctly liquid state. The following experiment makes this evident: If the dilatant mass of finely powdered quartz or starch in water is picked up with a spatula, the hard cake sticking to the latter runs down as a treacly liquid as soon as the movement has stopped.

Rheopexy is probably due to a certain coagulation of the particles as soon as they have been made to approach each other by the movement of the liquid. That colloidal solutions may be coagulated by being stirred or shaken is a well-known fact (9, 11, 13). A non-spherical shape of the particles seems to be an important factor for producing rheopexy. Furthermore, with vanadium pentoxide sol a certain special structure of secondary particles, according to recent experiments, appears to be essential. This is why only a few electrolytes, acids and lithium salts, are able to produce the phenomenon.

The importance of coagulation in rheopexy becomes clear, when the simple mechanical treatment is replaced by ultrasonics. Ultrasonic waves of high energy are known to liquefy thixotropic gels (3, 14, 16). This was shown to be due to the strong destructive effect caused by the collapse of cavities which are produced when the liquid is unduly stretched in the expansion phase of the sound waves. Thixotropic pastes with coarser particles (gypsum, etc.) are also liquefied by ultrasonics of high energy. Several pastes of this kind, being both thixotropic and rheopectic (for instance, pastes of gypsum and of Solnhofen slate), may, however, also be solidified rapidly if exposed to ultrasonics of smaller energy (1, 26). This effect is so pronounced that it may easily mask the liquefying effect mentioned above. When the test tube containing the liquefied suspension is removed from the interior of the oil fountain from which the sound waves pass into the test tube, the system unavoidably traverses a region of weaker action of the ultrasonics, and there solidification occurs quickly. This solidification effect has nothing to do with the action of cavitation, because it also occurs under conditions—under hydrostatic pressure and *in vacuo*—where no cavitation takes place. It is correlated with the coagulating action of ultrasonics on emulsions, suspensions, smokes, etc., which is caused by the phenomenon of Kundt's dust figures, i.e., by the accumulation of particles of suitable size in the nodes or antinodes of stationary sound waves (39).

Not much can be said yet on the theory of thixotropy and related phenomena. Obviously we are dealing with an interaction of forces of attraction and repulsion. Hence the particles which are moving in Brownian movement in a certain excess of liquid, thus forming a fluid system, may be made to settle in certain distances, thus producing a structure and a more or less solid system. In many thixotropic gels and pastes repulsion may be mainly due to electrical forces, as they are instrumental in causing the stability of aqueous colloidal solutions. But we know of thixotropic systems of organic substances in insulating liquids (37), for example, of mercaptobenzothiazole in benzene, toluene, etc. Hence solvation (and hydration) may also be essential in keeping the particles apart. The nature of the forces of attraction is even more enigmatical. It is obvious that in most thixotropic systems strong chemical forces can not be responsible. Weak forces, like those of van der Waals, appear from the first to be much more likely. But the following fact causes some trouble: There are quite a number of cases known where it has to be assumed that the particles in a thixotropic gel are fairly wide apart (20), the average distance between them being up to 0.1μ. Perhaps the modern conception of van der Waals forces, as developed by London, will allow this difficulty to be overcome (17, 27).

3. Hydration comes into play in sol-gel transformation, which has mainly interested us so far. But it is only one feature among others, and not so decisive as in some other phenomena shown by gels. Here swelling must be particularly mentioned. Quantitative values are obtained by determining the swelling pressure. It has been determined with an apparatus of the following type (12): A disc of the gel, exposed to a measured pressure, is separated from the liquid by a porous membrane; it lies on the bottom of a cylindrical vessel of dried white china clay. The liquid is imbibed by the gel and the ensuing change in volume is measured under different pressures. Swelling pressures have so far not been determined successfully on a large scale, except for the swelling of rubber in organic liquids. Gelatin could be investigated only in pure water. In salt solutions it was strongly peptized; it passed through the pores of the membrane in too large an amount in the rather long time which is needed to reach equilibrium.

Isinglass was found to be much tougher and more resistant to peptization than gelatin (5). A number of electrolytes could be investigated, and a not too narrow range of pH.

In agreement with previous, more qualitative, work the experiments proved swelling to be a reversible, but not a simple, phenomenon (25, 29). The influence of the pH may be attributed to a Donnan equilibrium (31, 36, 46). The amphoteric protein combining with acid or alkali forms dissociated salts, whose ions are strongly bound to the structure of the protein gel; hence water is taken up by the gel until an equilibrium between the ions in the gel and in the liquid outside is established. A minimum in the absorption of water and in swelling may be expected at the isoelectric point of the protein; this has indeed been found in several cases, also with isinglass (5). Its isoelectric point is 5.9. In figure 1 the ordinate is log γ, where γ is the concentration of the gel, i.e., the amount of isinglass in 1000 cc. of isinglass and liquid, the abscissa is the pH, the swelling pressure always being 3060 g. per square centimeter. At a pH of about 6.5, close to the isoelectric point, there is a maximum in γ, hence a minimum in swelling.

Salts in aqueous solutions deviating only slightly from neutrality influence swelling to about the same degree as the changes in pH in figure 1; but this effect can not be correlated with a change in pH. One example may be sufficient to prove this assertion. During swelling in a 0.2 *N* solution of sodium sulfate the pH of the external solution (and of the gel) was found to be 8.5. If swelling depended only on a change in pH, according to figure 1, we would have expected increased swelling; the concentration of the gel could have changed from 612 (in the distilled water used the pH was found to be 6.0) to 520 at pH = 8.5,—swelling pressure 3060 g. per square centimeter. Instead of that, the concentration in the sulfate solution was found to be 865, i.e., swelling had decreased. Hence we have a transport of liquid in and out of the gel, not depending on the pH. The simple conception of a Donnan equilibrium mentioned does not cover all facts concerned with the influence of foreign substances on swelling (25, 29).

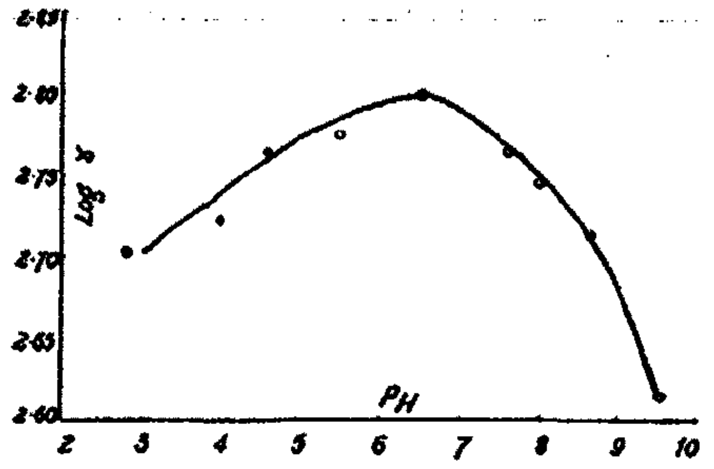


FIG. 1. Variation of swelling with pH

When comparing the action of different neutral salts, the ions are found to be arranged according to the lyotropic or Hofmeister series: $Li^+ < Na^+ < K^+$ and $SO_4^{--} < F^- < Cl^- < NO_3^- < I^- < CNS^-$. These are considered to agree with the order of their hydration (25, 29, 33).

Generally the term "bound" water has been favored for the water whose amount in the gel is changed by foreign substances independently of changes in pH. The importance of a "binding" of water in colloidal and biological phenomena has been strongly emphasized (16a; cf. also 19), and the difficulties which are encountered concerning "bound" or "immobilized" water have also been frequently discussed (cf. 2a, 28). Perhaps the following conception may prove valuable in explaining the influence of neutral electrolytes and non-electrolytes in swelling. It has been shown (18, 42, 43) that at constant temperature a gradient of concentration of one substance may cause an unequal distribution of another substance, not only of ions, which was originally uniformly distributed. A uniformly distributed electrolyte (sodium chloride) or a non-electrolyte (sugar) could be made to diffuse, and thus to become unequally concentrated in a column of a solution by a concentration gradient of a non-electrolyte (alcohol). (This phenomenon is in some way similar to Soret's phenomenon, where, owing to a temperature gradient, a substance in an originally uniform solution is distributed unequally.) In these cases of anomalous diffusion, a movement of both solute and solvent has to be taken into account. The force to which the effect is due is the affinity between solute and solvent active in causing solubility, etc. A gel whose structure maintains a gradient of concentration between the micelles and the medium of dispersion at any time would particularly favor an exchange of substance, owing to this kind of anomalous diffusion, i.e., to this very general Donnan effect.

This assumption has the advantage that it does not make such a strict distinction between the swelling of a protein like isinglass in pure water and in solutions of neutral salts and non-electrolytes on the one hand, and in solutions of acids and alkalis on the other. It was not very satisfactory that a fundamental difference had to be assumed as to swelling in these two groups, whereas actually the laws governing swelling pressure are always practically the same. This does not imply that the behavior of gels, when swelling in acids and alkalis or in neutral solutions, is identical in all points. There are distinct differences as to appearance and to extension or contraction, when comparing, for instance, the swelling of collagen fibers in acids or alkalis or in neutral salt solutions (25). But, I believe, they may be explained by the fact that we are dealing with the swelling of different substances, namely, of protein salts on the one hand, and of more or less neutral proteins on the other.

It is readily understood why swelling is such a complex phenomenon, because of the additional way in which it depends on the concentration of the foreign substance. The distribution of water between gel and medium depends actually on all substances present, and their number will generally be more than three, if there is one foreign substance besides protein and water, because the protein will probably react and form a compound.

It was mentioned above that the hydration correlated to the sol–gel transformation of gelatin does not change appreciably with a change in pH. This need not be in contradiction to the marked influence of the pH upon the swelling of proteins such as gelatin or isinglass. In sol-gel transformation we are dealing with dilute gels; in swelling with concentrated gels. In swelling the uptake of water, the properties of the micelles, etc., may distinctly depend on the transition of neutral protein into protein salt. In the dilute gel, capable of turning to a sol and vice versa, these differences may have become quite irrelevant as to the distribution of water, whereas some other factor causing hydration may still be sufficiently active to produce the observed change in volume.

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STUDIES IN THIXOTROPY. II

THE THIXOTROPIC BEHAVIOR AND STRUCTURE OF BENTONITE[1]

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INTRODUCTION

As the result of extensive work by previous investigators we now possess knowledge of the general influence of such important variables as concentration of disperse phase and electrolyte, temperature, pH, various addition agents, etc., upon the thixotropic activity of several systems. There has as yet, however, been no systematic investigation of the effect of particle size of disperse phase upon thixotropy in any system, despite the fact that the importance of this variable has been recognized (1, 3, 15).

Previous neglect of such an important variable may be attributed perhaps to the difficulty of obtaining suitable quantities of suspensions of particles of varying average size, particularly when the particles exist in the low range of colloidal dimensions.

The present authors have described a centrifugal method (6) involving the use of the so-called supercentrifuge, by means of which it has become possible to make particle size fractionations in colloidal systems and measure the particle size distribution in the resulting fractions. Using this technique the authors have been able to prepare a series of particle size fractions of the colloidal clay mineral bentonite and to study the thixotropic properties of the resulting suspensions of particles of varying average particle size.

In addition to the notable thixotropy of its aqueous suspensions, bentonite exists naturally over a suitable range of particle sizes to enable the production of a series of particle size fractions.

The present work is divided into three parts: I. Production of the particle size fractions; II. Study of the structure of the bentonite particle; and III. Study of the thixotropic behavior as a function of particle size.

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

I. PRODUCTION OF THE PARTICLE SIZE FRACTIONS[2]

Although the chief constituent of bentonite is montmorillonite (14), it is mineralogically a heterogeneous substance, and when the properties of different fractions are to be compared and complication in the interpretation of results is to be avoided, great care must be taken that the composition of every fraction finally obtained is the same.

The raw natural bentonite was obtained in powdered form and dispersed in distilled water (about 1 per cent concentration) with an electrically driven agitator. From this time on the bentonite remained in suspension and was never allowed to dry. Most of the impurities were in the coarser particle size range and were removed by gravity sedimentation after several months' storage. A few impurities came out in the particle size range just above the largest fraction actually used in experiments.

The remaining suspension of colloidal particles was fed into the supercentrifuge, which consists essentially of a balanced vertical bowl rotated at a high rate of speed by an electric motor (6). The suspension flows continuously into the bowl at the bottom, and as it flows through the bowl the suspended particles are settled out onto the walls. The coarsest particles settle out near the bottom, the finer particles traveling farther up the bowl before they are finally deposited on the walls.

The walls of the bowl were fitted closely with a flexible celluloid liner which could be removed when it carried a suitable quantity of sedimented material. When this liner was removed from the bowl the bentonite it held was in the form of a stiff jelly, which could be scraped off and stored in glass jars. This jelly ranged in appearance from the opaque muddy yellow color characteristic of the larger particles settled out at the bottom of the liner to the transparent golden yellow color revealed by the very fine particles at the top of the liner. In the early stages of the fractionation, it was therefore possible in scraping the jelly-like sediment from the celluloid liner to grade the particle size roughly by color alone. Each fraction scraped off the liner was redispersed in distilled water and rerun through the centrifuge under conditions giving a greater spread of sedimentation. For example, the fine fraction obtained from the first run was re-run with the centrifuge bowl rotating at a higher rate of speed than previously, so that the relatively large particles of this fine fraction tended to settle out at the bottom of the bowl while the finest particles of all would settle out at the top of the bowl.

By a long series of such successive runs and redispersions, the originally

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[2] The bentonite used was of the Wyoming variety and was mined by the American Colloid Company. The mine is near Colloid Spur, Wyoming, along the CB&Q Railroad, two miles northeast of Upton, in Weston County, Wyoming. The actual deposit covers part of Section 27, Township 48, north of range 65, west of the 6th P. M.

polydisperse bentonite suspension was separated into six fractions of varying average particle size, five of which were used in the experiments. The resulting suspensions were subjected to electrodialysis to effect the removal of exchangeable metallic ions, after which their particle size distribution curves were measured by the method described previously (6). These hydrogen bentonite suspensions served as stock suspensions of the material used in all later experiments.

TABLE 1

Average equivalent spherical diameters of bentonite fractions

FRACTION NO.	RANGE DIAMETERS IN mμ		
	$D_{\text{min.}}$	$D_{\text{max.}}$	$D_{\text{av.}}$
1	11.0	18.2	14.3
2	13.5	23.5	20.3
3	23.0	32.6	28.1
4	28.8	43.1	33.8
6	48.0	165.0	87.0

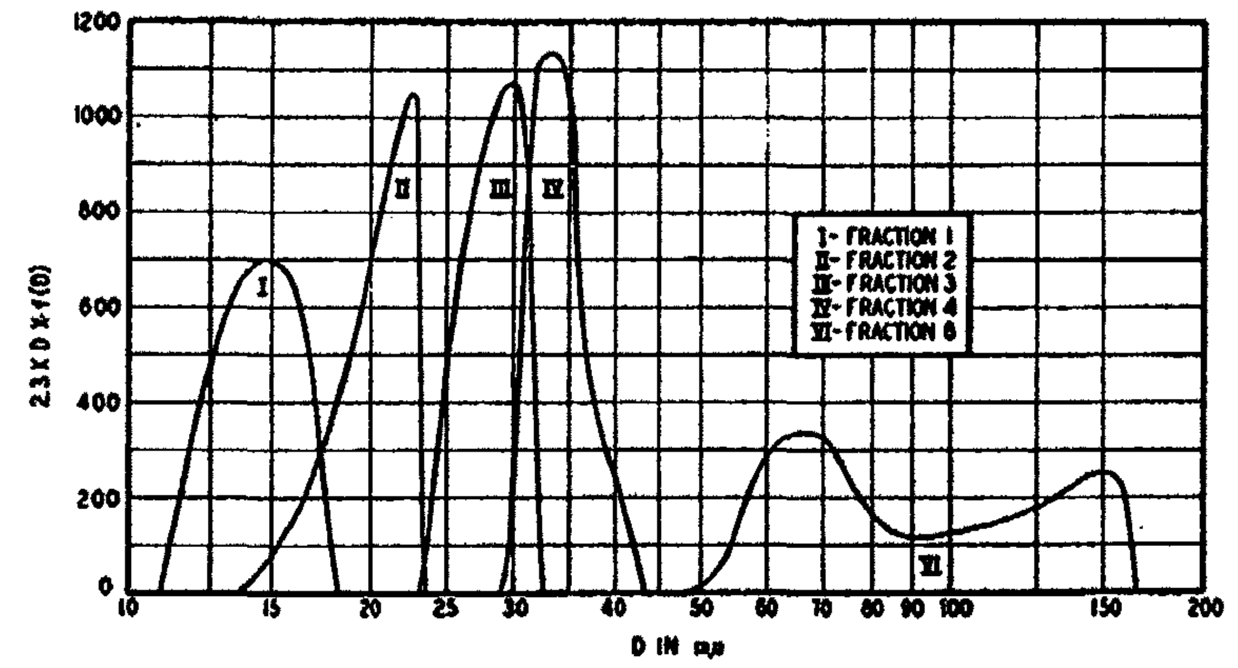

FIG. 1. Bentonite fractions obtained by centrifugal fractionation

The distribution curves, as usual, are reported in terms of equivalent spherical diameters and are plotted in figure 1. The log of equivalent spherical diameter is plotted as abscissa, and the ordinate is so adjusted that the area under the curves between any two values of D is proportional to the weight per cent of the material existing between these two diameters. For purposes of future plots, the average equivalent spherical diameter of each fraction tabulated in table 1 has been defined as that diameter, $D_{\text{av.}}$, which divides the fraction into two equal weights of particles, one group having diameters larger and the other group having diameters smaller than $D_{\text{av.}}$.

The chemical analyses of the largest and of the smallest particles are compared in table 2, with regard to the important constituents.

As will be noticed from table 2, the chemical analyses of both fractions check quite closely. The presence of alkaline and alkaline earth elements calls for some explanation. A sample of fraction 1 was subjected to drastic acid washing with 2 *N* hydrochloric acid. By this treatment it was found possible to remove practically all the (Na_2O+K_2O) and CaO. On the other hand, no MgO was removed by this treatment, an indication that the MgO is embedded much more firmly in the lattice than the Na, K, and Ca. Electrodialysis for an indefinitely long period would probably remove the (Na_2O+K_2O) and CaO removed by acid washing. The amount of these constituents, however, is negligible compared to the quantities of potassium hydroxide eventually added to induce gelation; indeed the amount is small compared to the equivalent weight of the bentonite, and it will be seen that the equivalent weights of the limiting fractions 1 and 6 are identical within the limit of experimental error.

TABLE 2

Chemical analyses of dialyzed bentonite

Based on weights of clay which had been dried to constant weight at 105°C.

	FRACTION 6: LARGEST PARTICLES	FRACTION 1: SMALLEST PARTICLES
	per cent	*per cent*
Loss at 105°C	0.00	0.00
SiO_2	61.68	61.56
Fe_2O_3	4.28	4.36
R_2O_3*	24.68	24.56
CaO	0.24	0.20
MgO	2.60	2.57
$Na_2O + K_2O$ (as Na_2O)	0.21	0.25
SO_3	0.08	0.085

* Includes Al_2O_3, TiO_2, Mn_3O_4, and P_2O_5.

X-ray examination gave identical powder patterns for fraction 1 and fraction 6.

The base-exchange capacity was determined by electrometric titration with sodium hydroxide. The titration curves for the largest and the smallest particles are compared in figure 2. The curves are practically coincident and indicate an exchange capacity of 92 milliequivalents per 100 grams of clay, or an equivalent weight in the usual sense of 1090.

All of the suspensions showed strong dityndallism upon stirring, evidence of the anisometric shape of the particles.

The difference in physical appearance of the five fractions shows up in the comparative spectrophotometric analyses shown in figure 3, where per cent transmission is plotted against wave length of transmitted light.

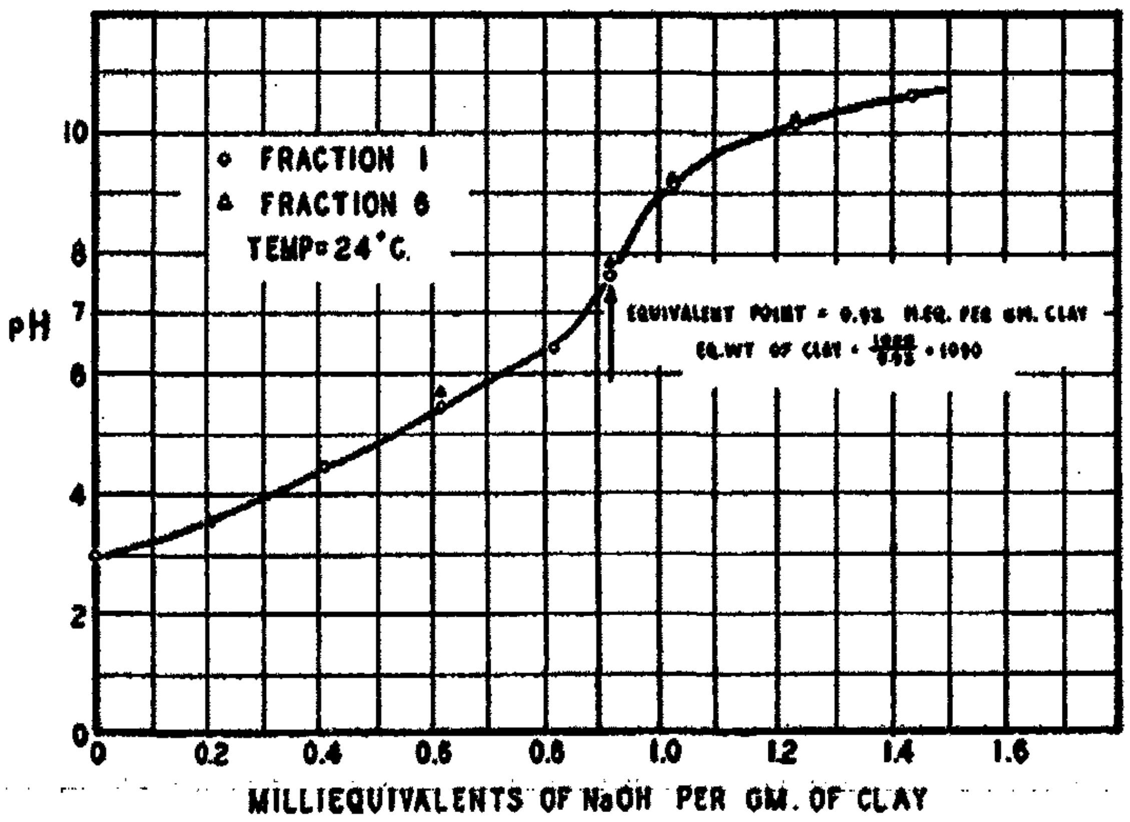

FIG. 2. Potentiometric titration of fractions 1 and 6 with sodium hydroxide

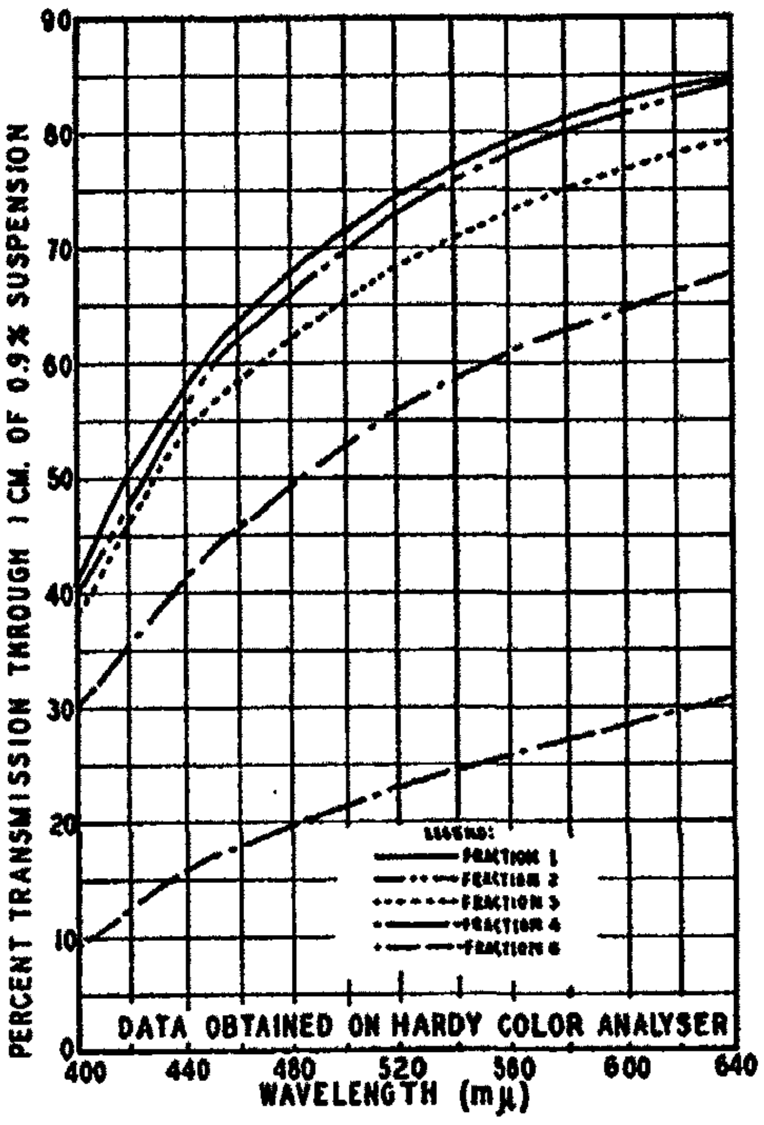

FIG. 3. Light transmission curves. 0.9 per cent hydrogen bentonite suspensions. Thickness of transmitting layer = 1 cm.

Fraction 1 is easily seen to be the most transparent. It is evident that the greatest absorption will take place in the ultra-violet.

The fractions appear to be similar except for particle size, and it thus becomes possible to interpret the differences in colloidal behavior upon the basis of this variable without complication.

II. STUDY OF THE STRUCTURE OF THE BENTONITE PARTICLE

In recent years our knowledge of the structure of clays has undergone rapid advancement. Marshall (12) has given a most enlightening summary of the latest developments in this field. The theory is now held that the cations concerned in base exchange go directly into the crystal lattice of the clay in a manner analogous to zeolites. Among the clays, bentonite is notable for its unusually large exchange capacity as well as for its ability to swell strongly in water. Hofmann, Endell, and Wilm (7) have proposed a layer lattice structure for montmorillonite, the chief constituent of bentonite. The structure proposed consists of superimposed layers of silica and alumina, as shown in figure 4, reproduced from a recent article by Hofmann and Bilke (8). Water molecules can enter between the groups of Si-Al-Si planes and force them apart, thus causing the swelling. The structure shown is an idealized one, and Marshall (12) has postulated that it is possible for several isomorphous replacements to occur. Thus aluminum is supposed capable of replacing silicon, in which case an exchangeable cation would go along with the aluminum to neutralize what would otherwise be a net negative charge on the lattice. In addition, it is possible that the broken oxygen bonds at the edges of the particles can hold metals and hydrogen, and it is possible that some of the oxygen atoms linked to silicon can react with water to form hydroxyl groups, in which hydrogen is replaceable. While the structure proposed by Hofmann et al. may undergo modification in the light of future research, its importance lies in its emphasis of the very open porous structure possessed by what we shall continue to call the bentonite particle.

The following measurements made on the particle size fractions of bentonite should throw additional light on the structure of bentonite in suspension.

Figure 5 shows a plot of pH versus the log weight per cent concentration of hydrogen bentonite. Measurements were made on fractions 1, 3, and 6 by means of a Beckmann glass electrode. No difficulty was experienced in reproducing the results, which were checked on a Leeds and Northrup glass electrode. It is seen that the pH–concentration relation is practically the same for all three fractions. The data are well represented by the equation

$$a_{\mathrm{H}^{\cdot}} = 0.00118W^{0.87}$$

where a_{H^+} is the activity of hydrogen ion and W the weight per cent concentration of hydrogen bentonite based on evaporation to dryness at 105°C. The analogous relation for a weak acid such as acetic acid would show a W exponent of around 0.5, whereas a strong acid like hydrochloric acid would have a W exponent approaching 1. Marshall and Gupta (13) have also noted what a strong acid hydrogen bentonite appeared to be as a result of hydrogen-ion activity measurements. In view of the fact that the deter-

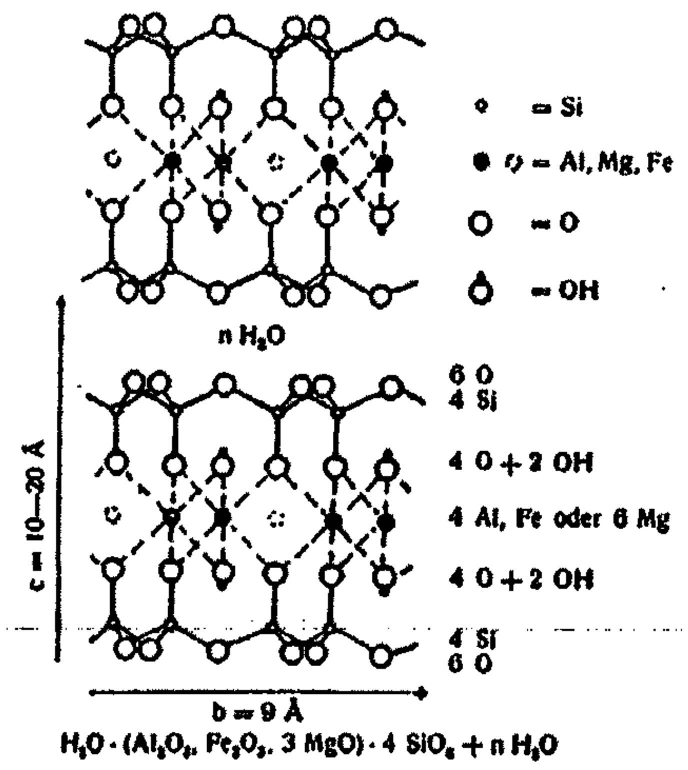

FIG. 4. Montmorillonite

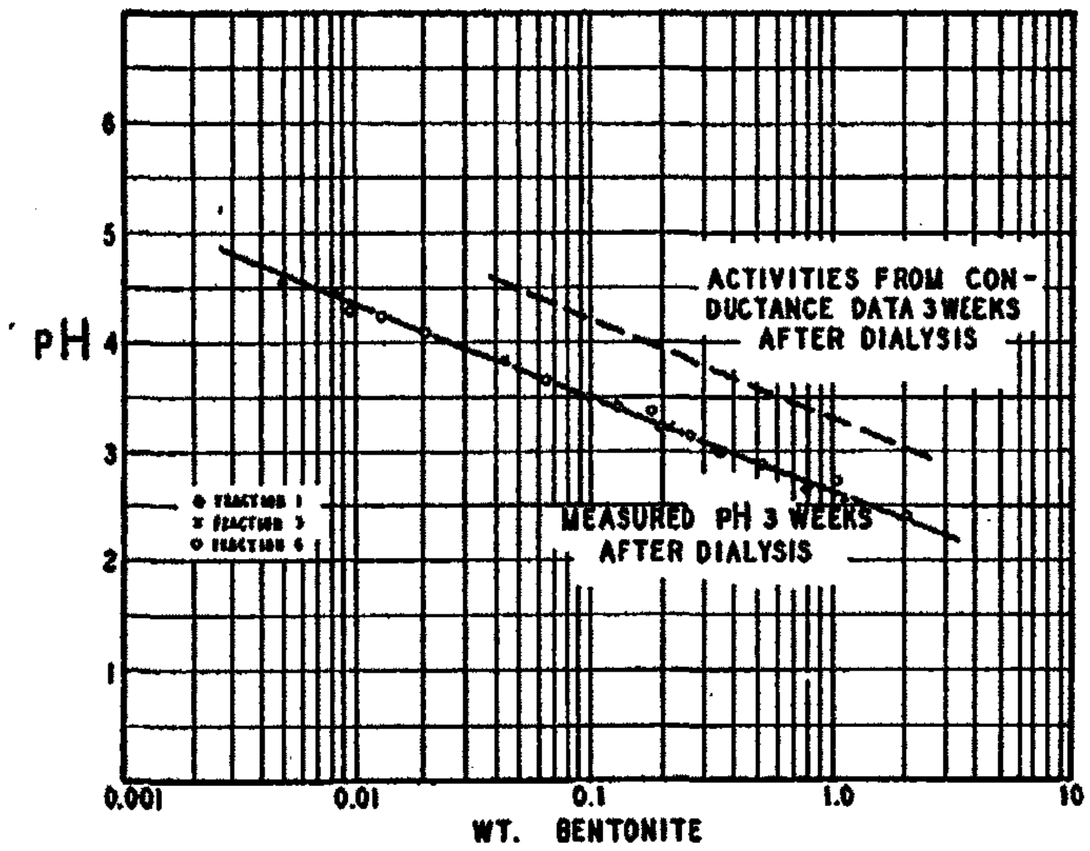

FIG. 5. Hydrogen-ion activity in hydrogen bentonite suspensions at 23-24°C.

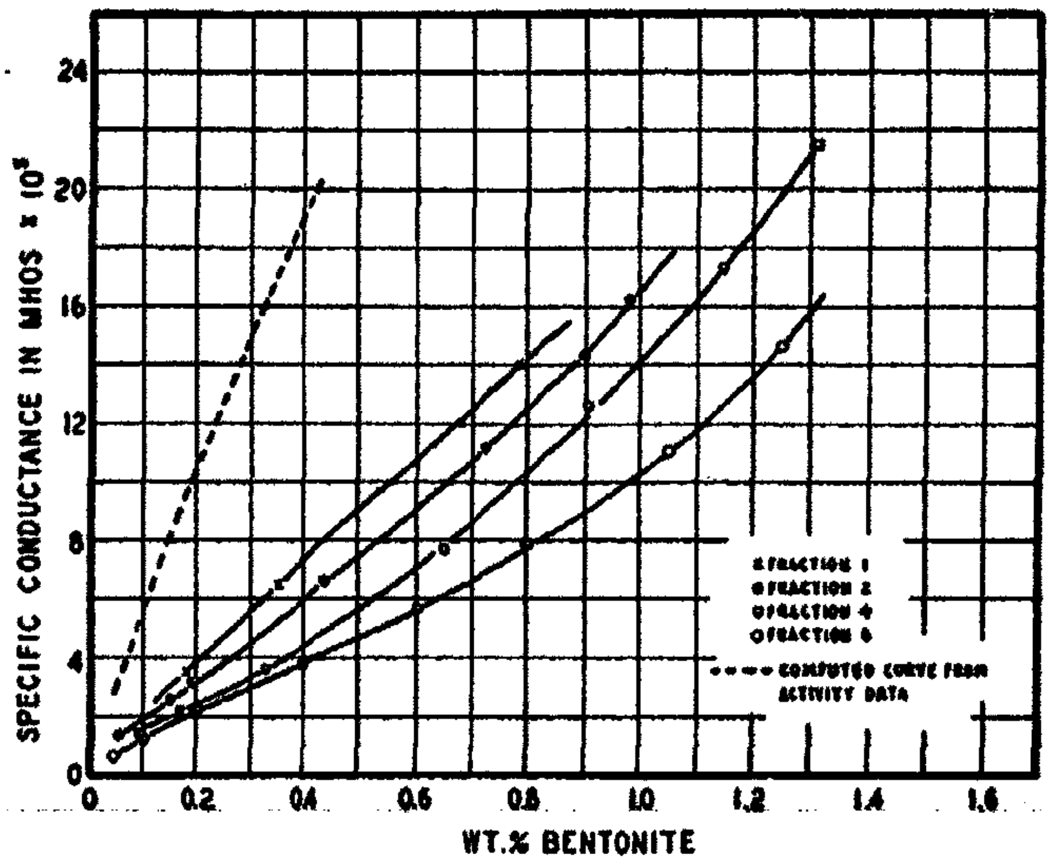

Fig. 6. Conductance data for hydrogen bentonite. Aqueous suspensions at 25°C.

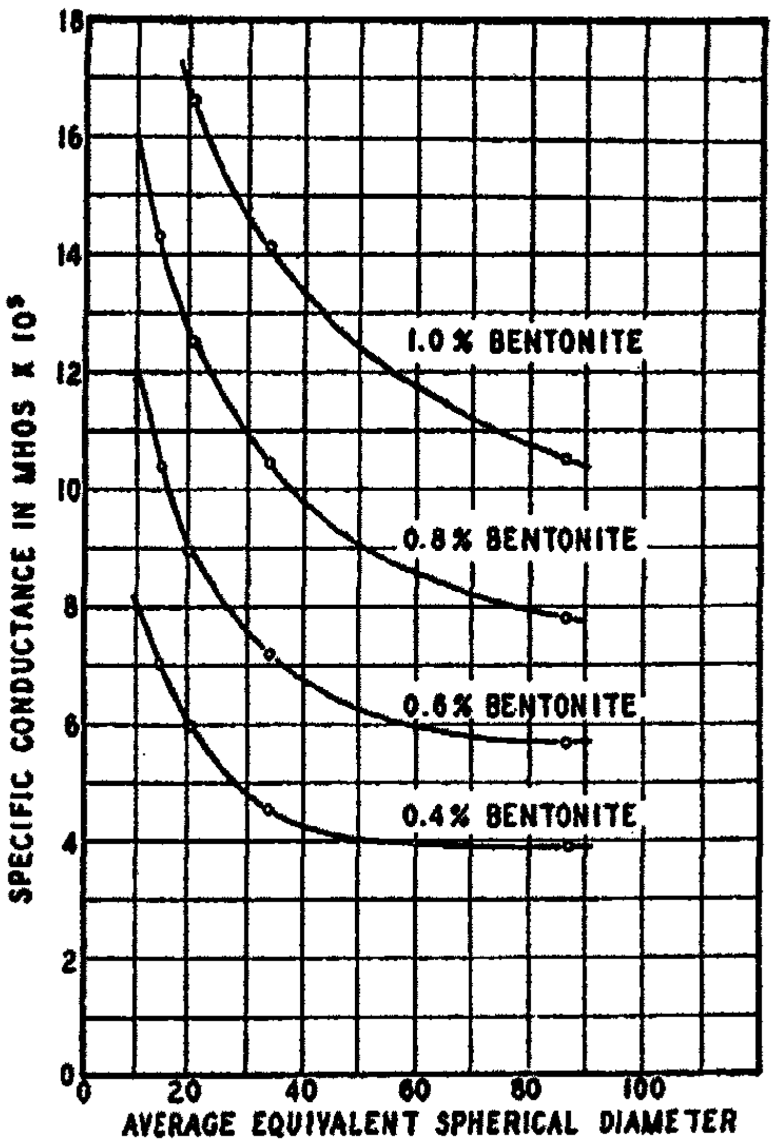

Fig. 7. Effect of particle size on conductance of bentonite solutions. Temperature, 25°C.

mination of hydrogen-ion activity is essentially an equilibrium measurement, it was decided to see how the hydrogen-ion in hydrogen bentonite behaved in conductance, which is a non-equilibrium measurement.

Conductances were measured by the Kohlrausch method at a frequency of 1000 cycles. A check upon the operation of both the glass electrode and the conductance equipment was obtained by measuring hydrogen-ion activities and conductances of a series of standard hydrochloric acid solutions. The experimental results checked well with those in the *International Critical Tables.*

The results of the conductance measurements are seen in figure 6, where the specific conductance in reciprocal ohms is plotted against the weight per cent of hydrogen bentonite for several different particle size fractions. The specific conductance increases as the concentration of bentonite increases and as the particle size decreases. This increase in specific conductance with a decrease in particle size is emphasized in figure 7. Here specific conductance is plotted against average equivalent spherical diameter at constant concentration.

The most interesting and important feature of the conductance results emerges when they are compared with the hydrogen-ion activity measurements. In the relatively dilute suspensions involved, one is inclined to feel that the hydrogen ion, if acting normally, should display an equivalent conductance not widely different from its limiting conductance. Since the hydrogen ion ordinarily carries the greater part of the current in systems wherein it is present, it should be possible to calculate the conductance of a hydrogen bentonite suspension with a reasonable degree of accuracy from the value of its hydrogen-ion activity. Assuming that the activity a_{H^+} is equal to the concentration C_{H^+}, we have, by the usual definition:

$$\Lambda_{H^+} = \frac{1000\,L}{C_{H^+}}$$

where L = specific conductivity in mhos and Λ = equivalent conductivity in mhos. Substituting for C_{H^+} its value in terms of the weight concentration of bentonite and solving for L we obtain:

$$L = \frac{\Lambda_{H^+}C_{H^+}}{1000} = \frac{0.00118W^{0.87}\Lambda_{H^+}}{1000}$$

Assuming that in these dilute suspensions

$$\Lambda_{H^+} = \Lambda_{\infty H^+}$$

$$L = \frac{0.00118\,\Lambda_{\infty H^+}W^{0.87}}{1000}$$

At 25°C. $\Lambda_{\infty H^+} = 349.7$ (*International Critical Tables*, Vol. VI., p. 230). The final expression for L at 25°C. then becomes:

$$L \times 10^5 = 41.2W^{0.87}$$

This relation is plotted in figure 6 for comparison with the experimentally determined conductance data. The resulting curve shows that values of the specific conductance calculated from activity measurements are in excess of 200 per cent of the highest experimental values realized. Allowance for the conductance of the negative clay particles would make the calculated conductances even higher.[3]

A further comparison of the pH and conductance is seen in figure 5, where the heavy broken line represents pH values computed from the highest experimental specific conductances (fraction 1) plotted against the corresponding concentrations of hydrogen bentonite.

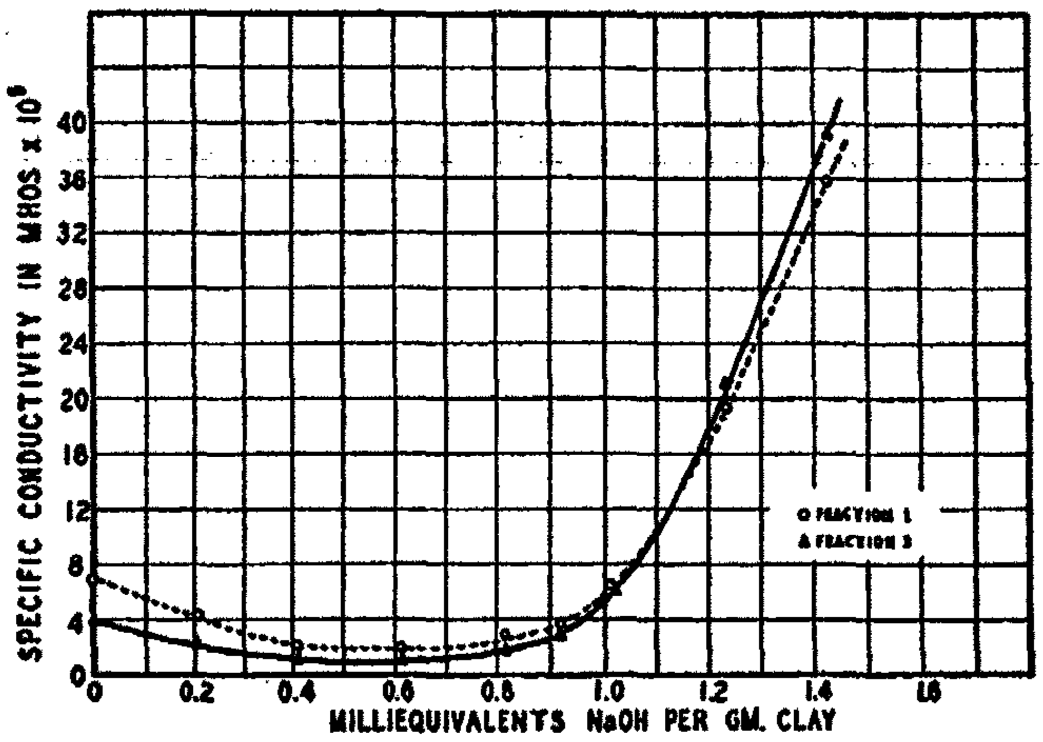

FIG. 8. Conductometric titration curves of bentonite fractions at 25°C.

Figure 8 shows conductometric titrations for fraction 1 and fraction 3. At the equivalent point it is seen that the specific conductance of sodium bentonite is only about 25 per cent lower than that of hydrogen bentonite. Inasmuch as the equivalent conductance of the sodium ion is only 50, whereas that of hydrogen ion is 350 at 25°C., the reduction in conductance is not as great as might be expected and indications are that the sodium

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[3] Since writing the manuscript the authors have been informed that similar discrepancies between conductometric and potentiometric pH have been recorded with AgI sols by Verwey and Kruyt (Z. physik. Chem. **A167**, 159 (1933)) and with gum arabic sols by Pauli and Ripper (Kolloid-Z. **62**, 162 (1933)).

ion is more strongly dissociated from the lattice of the particles than hydrogen ion.

Finally, a determination was made of the relative quantity of electrolyte (potassium hydroxide) required to flocculate the various fractions.

Experimental determination of flocculation values

It is very difficult to reproduce flocculation values for clay suspensions accurately, because of the great influence of such factors as method of shaking, method of dilution, etc. Fortunately, in the present experiments we are primarily interested in relative values. By adhering to a standard procedure in every case, it was possible to obtain reasonably reproducible values which are certainly relatively correct.

The experiments were conducted in test tubes at a constant concentration of 0.05 per cent bentonite. The stock suspension was diluted to such an extent that upon addition of the desired quantity of standard potassium hydroxide the final concentration of bentonite would amount to just 0.05 per cent. The potassium hydroxide was added from a pipet, the test tube being shaken during the addition. After addition of potassium hydroxide, the test tube was shaken for half a minute and then allowed to stand for twenty-four hours, at the end of which time the presence or absence of sedimented flocs was noticed. The determination of a flocculation value is a trial and error procedure during which a series of suspensions must be made up, treated with different amounts of potassium hydroxide, and observed.

The results are reported in table 3, in terms of the milliequivalents of potassium hydroxide per gram of bentonite required to produce flocculation under the standard experimental conditions. A plot of flocculation number against average equivalent spherical diameter (figure 9) shows that over twenty times as much potassium hydroxide is required to flocculate fraction 1 as is required to flocculate fraction 6.

The preceding experimental results might be explained on the basis of two theories. According to the structure proposed by Hofmann et al., dispersion of bentonite in water involves the forcing apart of the ultimate plates of Si-Al-Si, which comprise layers of the lattice. There is no theoretical reason why such a process could not result in ultimate particles 10 A.U. thick and of indefinite length and breadth. The fractionation procedure would then be separating particles of substantially the same thickness, but of different lengths and breadths. Since the particles would be very thin in comparison to their other two dimensions, fraction 1 composed of the so-called smallest particles would have practically the same surface as fraction 6, composed of the largest particles. It is easy to understand on this basis why the electrometric titration curves and pH-concentration relation are similar for both large and small fractions. It is not so easy to account on this basis for the large difference in quantity of potassium hydroxide required to flocculate the various fractions. Furthermore, all fractions, unresolvable in the ordinary microscope, produce about the same amount of twinkling in the ultramicroscope. If the particles in all fractions were the same thickness, one would expect to find evidence in the ultramicroscope of the greatly increased length and width necessarily possessed by the larger fractions.

TABLE 3

Flocculation numbers of bentonite fractions

FRACTION NO.	AVERAGE EQUIVALENT SPHERICAL DIAMETER	FLOCCULATION NO.
	mμ	
1	14.3	22–26
2	20.3	16–20
3	28.1	9–10
4	33.8	3–4
6	87.0	1–2

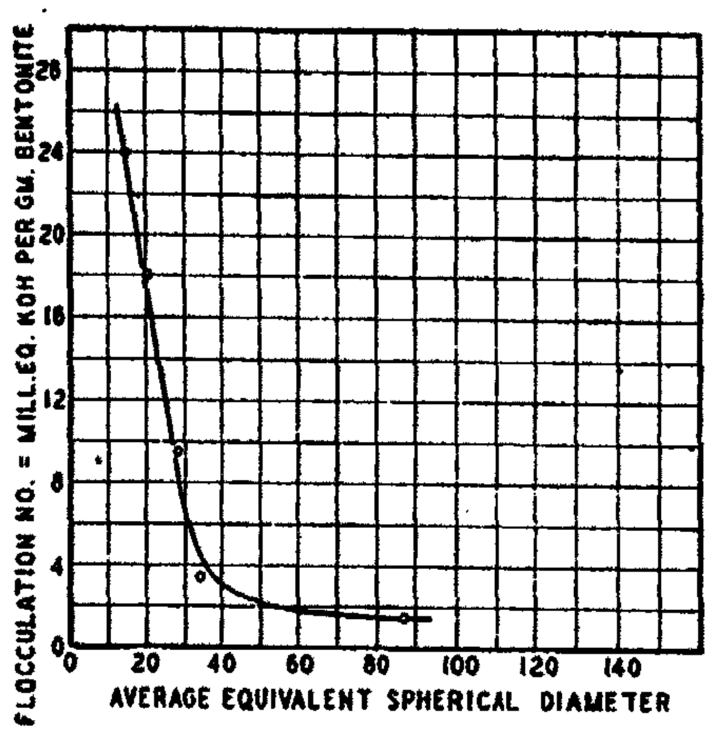

FIG. 9. Flocculation of hydrogen bentonite with sodium hydroxide

The alternative explanation, which we feel fits all of the facts better, is the assumption of the very open porous layer structure. From this point of view the particles in fraction 6 may be thicker as well as longer and broader than the particles in fraction 1. The layers of groups of Si–Al–Si planes are, however, far enough apart to enable the passage in and out of water molecules, metallic ions, and hydrogen ions. Thus each portion of the whole mass of the bentonite particle contributes its share of exchangeable cations, and each portion of the mass of the whole structure can furnish hydrogen ions which contribute to the overall hydrogen-ion activity of the suspension. On the other hand, the true external surface per unit weight must obviously be greater in fraction 1 than in fraction 6, if the particles in fraction 6 are to be thicker than the particles in fraction 1. A smaller external specific surface accounts for the smaller amount of potassium hydroxide required to flocculate fraction 6 in comparison to fraction 1.

The large discrepancy between the conductance and activity measurements indicates that the hydrogen ions are bound quite closely to the large negatively charged particles. We prefer to view bentonite as a colloidal electrolyte possessing a large porous multivalent anion which has many hydrogen ions very closely associated with it. The structure of the particle is so open that these ions can register an effect upon activity measurements where they undergo no net displacement from the particle. On the other hand, it is well recognized that it takes work to separate two bodies of opposite charge, and the larger the charge the greater the work. Hence the hydrogen ions might be expected to be more closely associated with the larger particles of greater negative charge than with the smaller particles, an expectation confirmed by the decrease in specific conductance with increase in particle size.

III. STUDY OF THE THIXOTROPIC BEHAVIOR OF BENTONITE AS A FUNCTION OF PARTICLE SIZE

Thixotropic behavior was studied by measurement of setting times by the inverted-tube method. The method has been used many times previously in investigations of thixotropy and is most convenient for obtaining relative data. Broughton and Squires (2) discussed the inverted-tube method in comparison to other methods, and concluded that it was capable of giving consistent results.

All experiments were conducted in Pyrex tubes of 10.3 to 10.5 mm. internal diameter. The tubes were 100 mm. in length and were in every case filled with exactly 4 cc. of the material to be tested. In all cases the sample to be tested was prepared directly in the tube by addition of proper amounts of the stock suspension of hydrogen bentonite, standard electrolyte, and distilled water. All ingredients were measured in calibrated pipets. After being filled, the tubes were fused shut with a blast lamp.

It was early discovered that the results depended to some extent upon the method of inverting the tube. Thus, if great care were taken in inversion, the setting time obtained would be less than if slight shaking occurred during inversion. For this reason it was deemed wisest to eliminate as far as possible any effects due to the observer's personal method of inversion, by constructing an instrument capable of performing the inversion in a reproducible manner. Figure 10 shows a scale drawing of the instrument finally evolved. Since its action is that of a physical pendulum, it has been called the physical pendulum thixotrometer. The tube to be tested is made secure upon the rotary wheel by the clamp C, located at a distance of 7⅝ in. from the axis of rotation. Upon release of the lever L, the wheel is caused to rotate through 180° by weight P. When P has traveled through 180° and reached the dotted position shown, the tube held by clamp C has been inverted. The wheel would now normally revert to its initial position, were it not for the action of the sandpaper brakes which engage the surface the instant counterclockwise rotation starts to occur. Since the wheel is traveling with zero velocity at the end of its 180° path, the sandpaper brakes simply prevent it from accelerating in the opposite direction, and the whole inversion is performed with substantially no jar being delivered to the tube under test. It is possible to adjust the apparatus to invert tubes of different weights by moving the weight P in or out on its supporting arm.

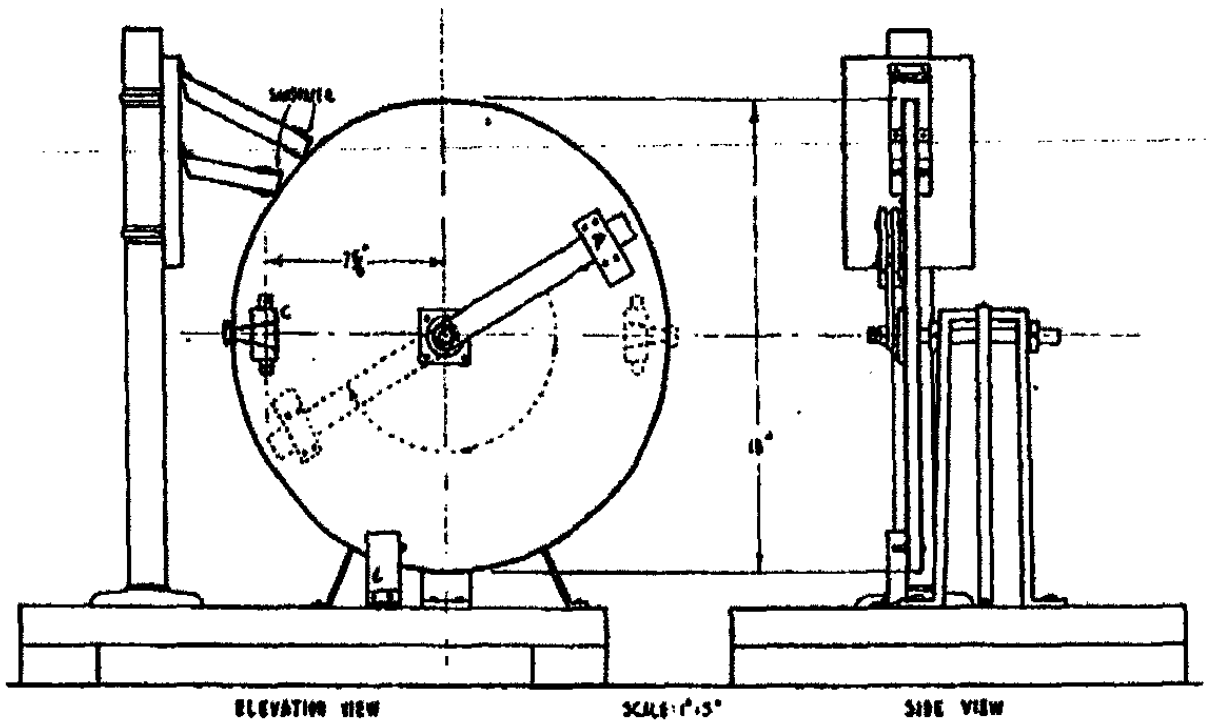

Fig. 10. Physical pendulum thixotrometer

It is essential to place the tube in the same position in clamp C for each test. The practice followed was to have the meniscus of the material in the tube just even with the lower front edge of the clamp. No difficulty was encountered in obtaining reproducible results with this apparatus.

The procedure followed in obtaining the setting time was one of successive approximation. The particular sample under test was agitated strongly by shaking the test tube violently. Tests showed that 5 seconds' violent shaking was in general sufficient to break down the gel structure completely. The tube was then immersed in a constant-temperature bath controlled to ±0.05°C., and the time noted. After a lapse of time believed to be sufficient, the tube was gently removed from the bath, placed on the inverter, and inverted. If any flow occurred down the wall of the tube, the sample was considered as not set and the above process repeated, the sample being allowed to "set" for a longer period. By trial and error it was possible to find a time interval below which flow would occur and above which there would be no flow. This time interval is called the setting time, and its reciprocal is known as the rate of gelation. By following such a test procedure, the effect of variation in many significant quantities has been established.

The electrolyte added was potassium hydroxide, because its action upon hydrogen bentonite is a simple one, resulting in the formation of potassium bentonite and water. In effect only one ion is added to the system instead of two, as in the case of a salt, and interpretation of results is facilitated. Potassium hydroxide was found to effect the formation of stronger gels in shorter times at lower concentrations than either sodium hydroxide or lithium hydroxide.

After addition of electrolyte the setting time did not assume a constant value immediately, but tended to fall in value and approach an asymptotic condition about twenty-eight days after preparation. The setting times reported are in most cases those at the end of twenty-eight days.

Figure 11 shows the effect of particle size upon the setting time. The concentration of bentonite is 0.85 per cent in every case, and at a given concentration of potassium hydroxide the time required in forming a gel of given strength increases as the size of the particles increases.

Figure 12 shows the large decrease in setting time effected by increase in concentration of bentonite and increase in temperature. The temperature effect appears to be irreversible, in that gels which have reached a well-defined setting time at 25°C. upon being heat-treated several days at 40°C. and then lowered again to 25°C. do not exhibit their old setting time at 25°C. but a setting time much nearer the final value reached at 40°C. In all cases but one to be mentioned below, increase in temperature resulted in a decrease in setting time. It was postulated that setting time might go through a minimum as temperature was increased, but careful measurements up to 140°C. under many varied conditions failed to reveal anything but a continuous decrease in setting time with increase in temperature. These tests were not carried to higher temperatures, as it was feared that fundamental changes might take place in the bentonite particles in such a manner as to make the results incomparable to those at lower temperatures.

Figures 13 and 14 emphasize the effect of particle size by plotting setting time against average equivalent spherical diameter.

The present authors have reported the discovery of rheopexy in bentonite (5). This is a phenomenon much more difficult to measure even than thixotropy. The thixotropic setting time is obtained on a system which undergoes violent agitation to break up the structure and is then allowed to set to a gel undisturbed. The rheopectic setting time obtained on the same system is always much lower, owing to the fact that during the period of set the system is subjected to gentle mechanical action such as tapping. It is not at all certain just what type of motion is most conducive to rheopectic behavior. It was found as a result of subjecting the

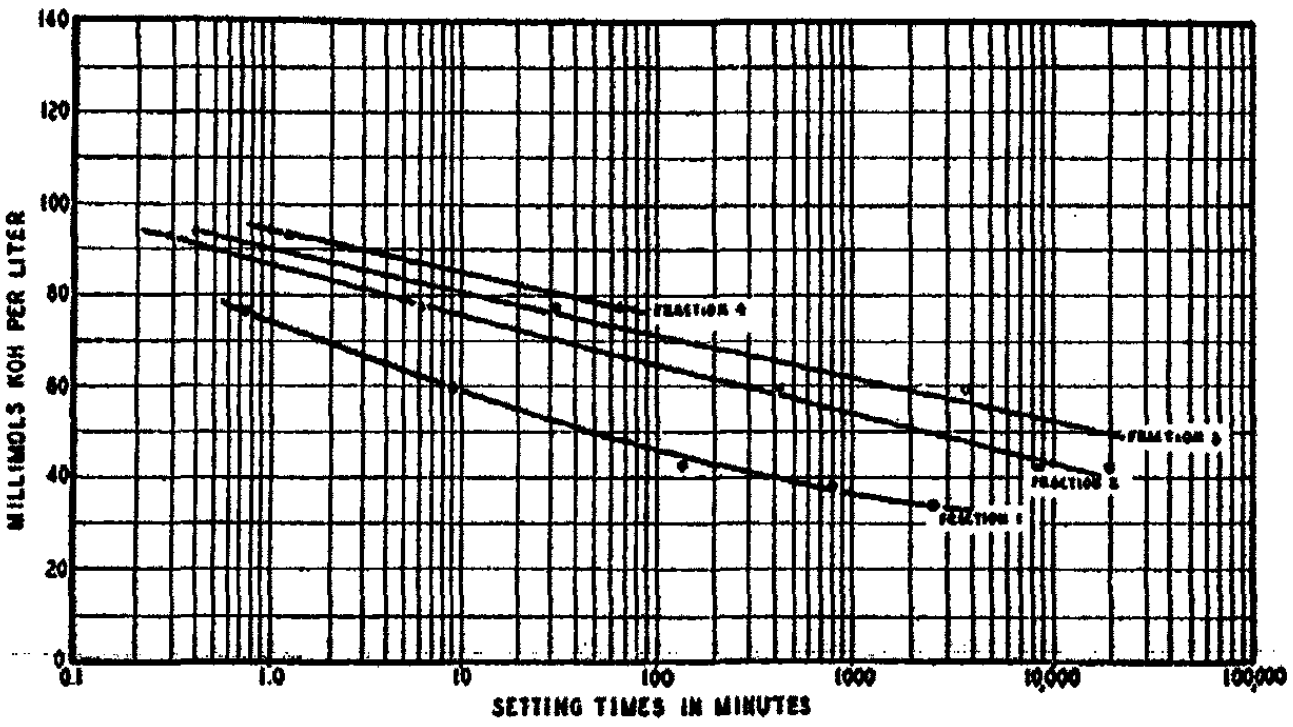

FIG. 11. Thixotropic setting times of bentonite suspensions at 25°C. Concentration of bentonite = 0.85 per cent.

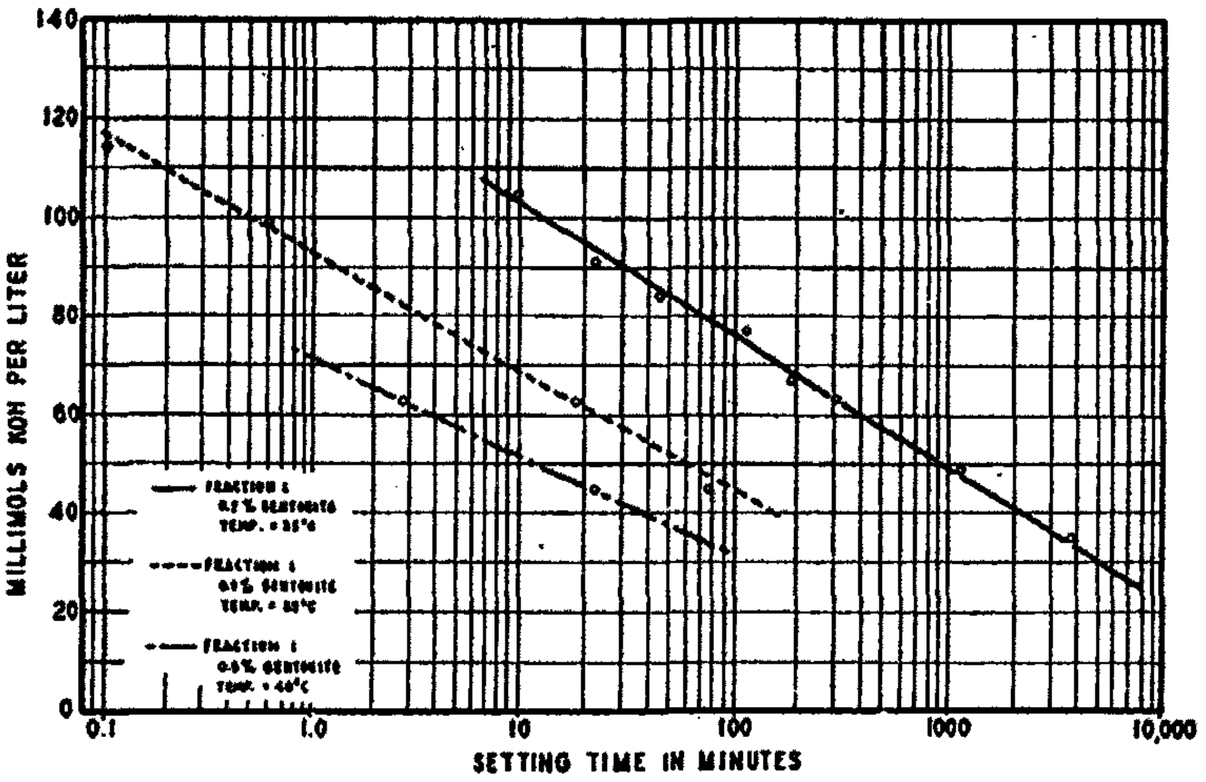

FIG. 12. Influence of concentration of dispersed phase on thixotropic setting time

tubes to various kinds of mechanical contortions that the following procedure seemed to produce the most rapid gelation: The tube, 100 mm. in length, was grasped 20 mm. from the top between the thumb and third finger, and was then made to oscillate like a pendulum about the point where it was grasped. The amplitude of the oscillations was 15° to 20° on each side of the vertical position, and the frequency employed was about two hundred and fifty complete oscillations per minute. In extreme cases the gels subjected to this treatment during their period of set reached a given strength hundreds of times faster than if they were left to set alone. The effect of such treatment in decreasing the setting time of a given gel is truly remarkable. In many instances it was possible to trap small air bubbles within the gels by proper agitation, and to use the motions of these bubbles as telltales for the motions of the various layers within the gel. It was observed that the motion described above caused the small bubbles to vibrate up and down as though they were entrapped in an elastic medium. Furthermore, the bubbles on one side of the tube would be traveling up while those on the other side would be traveling down.

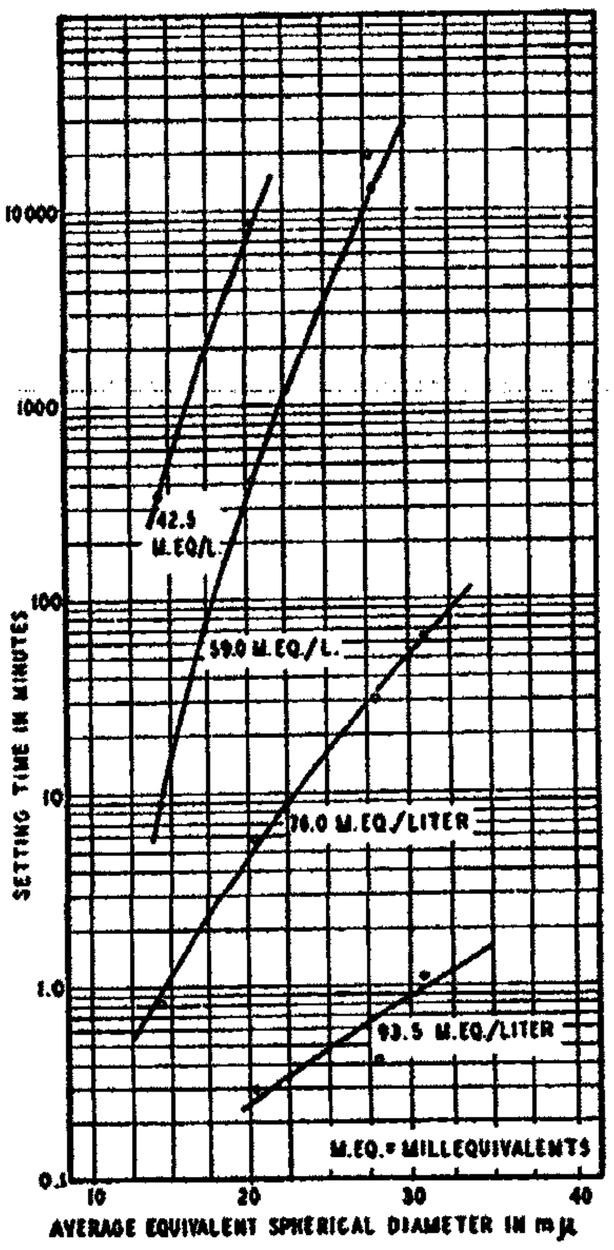

FIG. 13. Thixotropic setting time of 0.85 per cent bentonite suspensions at 25°C.

The bubbles were observed to vibrate up and down with a frequency equal to the number of complete oscillations of the tube. This bubble motion indicated the motions of the corresponding layers of gel. It was undeniable that the motion induced a velocity gradient across the tube, resulting in gentle shear between the various layers of gel. At any point in the tube the direction of the gradient, and hence the direction of the shearing stress, reversed with each oscillation of the tube.

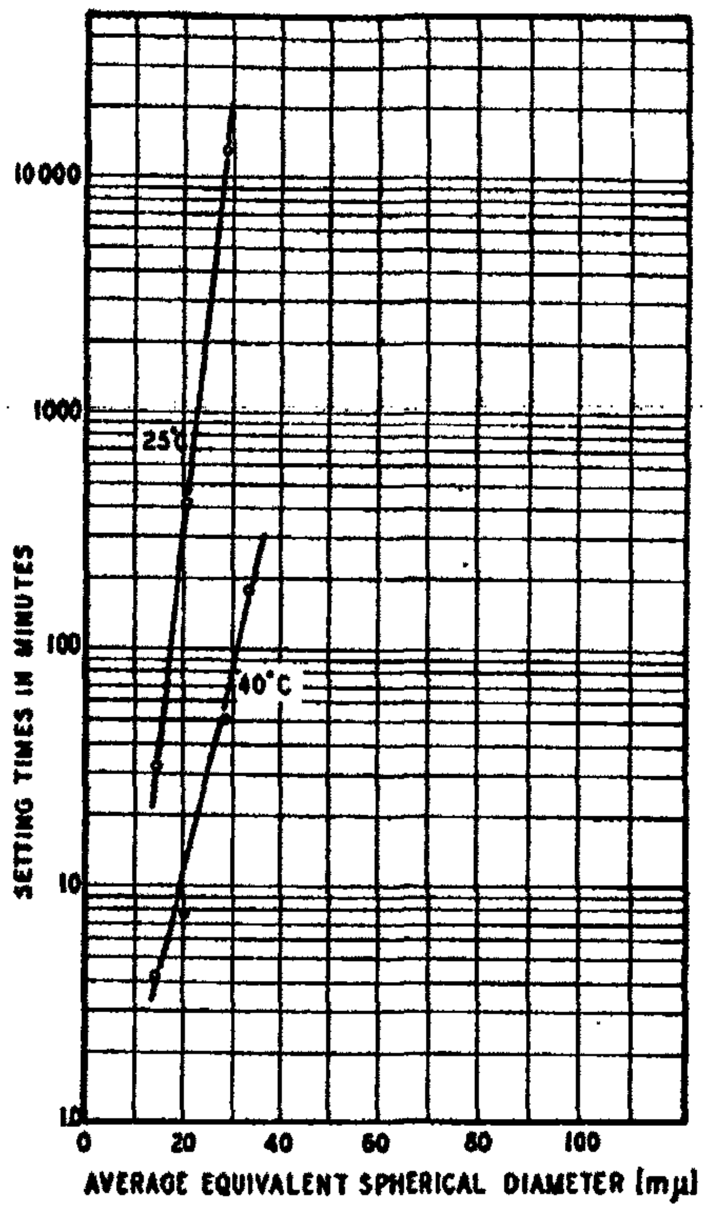

FIG. 14. Effect of particle size on setting times at different temperatures. 0.85 per cent bentonite; 59.5 millimoles of potassium hydroxide per liter.

While it should be possible to construct a machine to simulate mechanically the motion just described, it is questionable whether any additional information obtained from such a machine would assist in the task of obtaining a satisfactory qualitative explanation of rheopexy.

Figure 15 shows the rheopectic setting time (determined by the above method) compared with the thixotropic setting time.

In general, the type of electrolyte added has notable effects upon the setting time. At a concentration of 0.85 per cent bentonite, there was no evidence of gel structure until about 2.5 milliequivalents of potassium hydroxide per gram of bentonite had been added (over twice the exchange capacity!), whereas at this same concentration of bentonite, gels which exhibit strong thixotropy and rheopexy can be produced upon addition of 0.0049 milliequivalent of tetraethylammonium hydroxide per gram of bentonite.

The pH as such seems to have no particular effect upon thixotropy. Thixotropic and rheopectic gels of 0.85 per cent bentonite may be produced at any pH from 1 to 12. Addition of hydrochloric acid to hydrogen bentonite will produce a thixotropic gel at a pH of 1, which is not much different from one produced at a pH of 12 by addition of potassium hydroxide or one produced at a pH of 7 by addition of proper relative quantities of potassium hydroxide and potassium chloride.

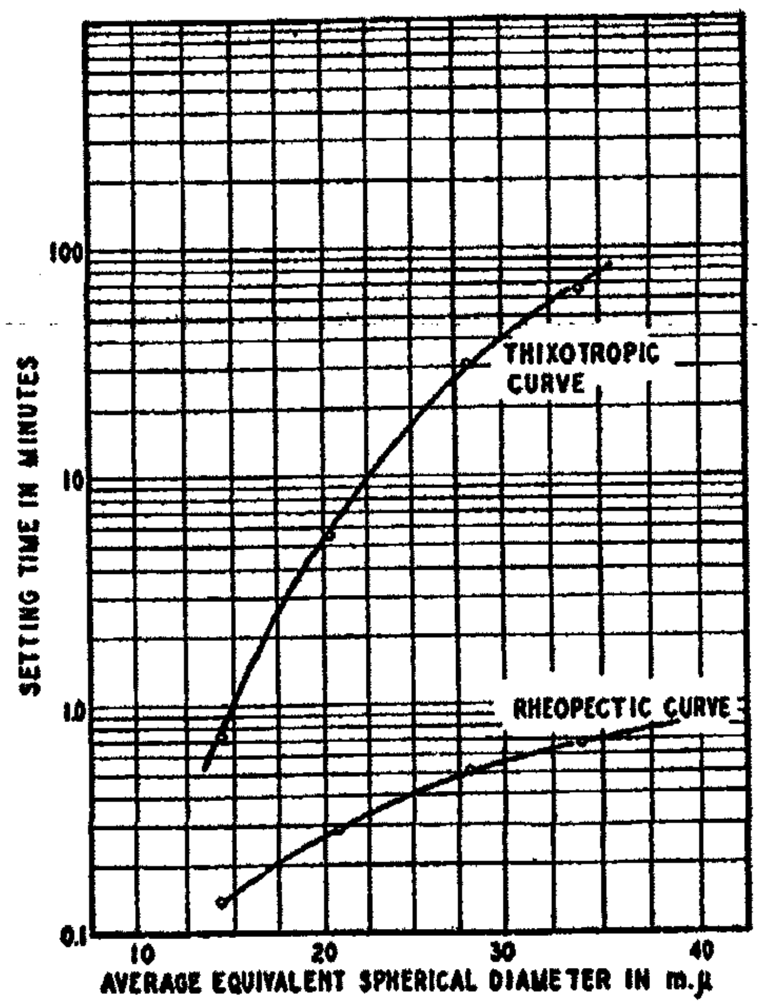

FIG. 15. Influence of particle size on setting times. 0.85 per cent bentonite; 76.5 millimoles of potassium hydroxide per liter; temperature, 25°C.

An interesting series of gels was produced by addition of dialyzed iron oxide sol (positively charged) to hydrogen bentonite (negatively charged). Addition of 0.0247 g. of ferric oxide per gram of hydrogen bentonite gave a gel which had a thixotropic setting time in excess of one hundred and thirty hours and a rheopectic setting time of two minutes. Additional ferric oxide lowered the thixotropic setting time to a few minutes. Positively charged aluminum oxide (Al_2O_3) sol (dialyzed) gave a similar effect,[4] but a quantity of negatively charged vanadium pentoxide sol just sufficient to flocculate the quantity of iron oxide sol added above had no effect. The setting time of the gels produced by addition of ferric oxide sol was greatly increased by an increase in temperature in strong contrast to the effect of temperature upon the potassium bentonite gels.

Ultramicroscopic examination of the gelation of these well-defined fractions served to corroborate previous work by Hauser (4), in which the particles were reported to lose their Brownian movement gradually and come to a complete rest. The present observations were carried out with a recently developed General Electric type H3 "capillary mercury vapor lamp" as a light source, thereby greatly increasing resolution and intensity of reflection.

If potassium hydroxide equal to 9 milliequivalents per gram of bentonite is added, it is possible to observe in the ultramicroscope the changes which are responsible for larger scale thixotropic behavior. The individual particles cluster up, forming particle clouds which in turn form a loose structure of secondary clusters intermeshed with patches and channels of freely mobile dispersing medium. The Brownian motion of the particles forming the clouds stops completely, whereas a few single particles can be seen in free motion in the patches and channels of dispersing medium.

If this structure is submitted to any influence producing relatively strong shear, the clouds break up and all the particles are again in individual Brownian motion. If the system is now allowed to remain undisturbed, the clouds will re-form and Brownian action will gradually cease.

If the freshly prepared specimen containing electrolyte is subjected to relatively gentle tapping or shear, the formation of the clouds into secondary clusters is more rapid. Under these circumstances, the structure formed by the secondary clusters of clouds is more sharply defined. Presumably we are observing rheopectic behavior upon a microscopic scale.

When larger quantities of electrolyte are added, the clouds form more rapidly and are of notably denser structure. An excess of electrolyte produces spontaneous aggregation into individual flocs of relatively high density. Such dense flocs appear brilliantly white in the field. These dense white flocs cannot be noticeably dispersed, and to all intents indicate the presence of the final stage of flocculation of the system.

Microscopic research is now being continued with the new equipment, and results will be reported in a later publication.

An important feature of the present investigation of bentonite gels is

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[4] The formation of a thixotropic gel in a kaolin suspension to which an aluminum sol had been added has been described recently by J. Pryce-Jones in a private communication to one of us. This phenomenon has a close resemblance to complex coacervation as described by Bungenberg de Jong (Kolloid-Z. 79, 228 (1937)).

the unexpectedly low concentrations at which gelation occurred. This is in contrast to Freundlich's extensive work on the thixotropy of bentonite (3), where it was difficult to obtain structure at concentrations of bentonite less than 10 per cent by weight. This difference is probably accounted for by the fact that Freundlich allowed his hydrogen bentonite to dry, and made up his gels from the dry powder. Lewis, Squires, and Thompson (10) have shown that the drying of hydrogen bentonite results in irreversible deplasticization.

Hydrogen bentonite, once dried, will not swell in water to a degree even approximating the swelling of the metallic bentonites. This may be due to the reaction of some of the hydroxyl groups on adjacent particles, with the elimination of water and the formation of oxygen bridges, which effectively cement many particles into one large particle.

For the qualitative detection of structure in very weak gels, the so-called bubble test is very valuable. This test rests upon the fact that a bubble will always rise in a Newtonian liquid, since such a liquid cannot sustain tangential shear. Thus bubbles will always rise in the thickest oil. On the other hand, as soon as a yield point is developed, a finite tangential stress or shear such as exerted by a small bubble beneath the surface of a liquid may be sustained.[5] If a gel is shaken down to a sol and then allowed to "set," entrapped bubbles may be observed rising at a slower and slower rate, until eventually they come to a complete stop. At this point the yield point has become great enough to resist the shearing stress produced by the buoyant force.

This test has shown that in many specimens agitation has reduced the system to the sol condition, or at least to such a weak gel that it will retain no visible bubbles and will not be cloudy, as it might be expected to be if it were retaining individual bubbles too small to see. In other cases, the bubble test shows that even the most violent agitation will fail to break up the gel completely, the bubbles coming to rest instantly after agitation. In many cases such gels, even though very weak after agitation, will often increase in strength upon "setting," indicating that a process of construction is proceeding within them. While thixotropy is referred to as a sol-gel transformation, it may well include those cases where the gel cannot be broken down completely.

In the case of the finest bentonite fraction (fraction 1), it was possible to use the bubble test to observe structure qualitatively at concentrations of bentonite as low as 0.01 to 0.05 per cent. Needless to say, a strong electrolyte such as potassium chloride must be added to the hydrogen bentonite to observe structure at such low concentrations.

Very little has been written concerning the actual structure of gels which

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[5] J. Pryce-Jones differentiates between true gels and false body systems.

exhibit strong thixotropy. Freundlich gives a summary of the proposed theories in his monograph on thixotropy (3). It appears that all authors are in agreement that the suspended particles become loosely locked into place to form a structure which will resist shear. Disagreement occurs when attempts are made to theorize as to the mechanism by which the particles become locked into place. The solvation or water hull theory attributes the structure to the formation of quasi-solid hulls of adsorbed water around the particles, the hulls eventually increasing to such sizes that they coalesce and impart rigidity to the system as a whole. As solvation is generally considered to decrease with an increase in temperature, it is difficult to see how on the basis of this theory one could account for the great decrease in setting time occurring with an increase in temperature.

Lewis, Squires, and Thompson (10) have advanced an essentially mechanical picture of the gelation process in clays in which the structure is conceived as being built up of the loose, completely random packing of platy particles. This picture is similar to that of Freundlich, who has pointed out the correlation between loose packing, plasticity, and thixotropy. To account for gel formation at the low concentration of 0.1 per cent, the pure mechanical picture of gelation due to packing must assume ratios of length and breadth to thickness of the individual particles of the general order of 1000-2000:1. Ultramicroscopic examination lends no support to the assumption of such ratios. The theory of gelation due to mechanical packing might account for the facts of thixotropic behavior in concentrated suspensions like those investigated by Freundlich, but to account for gelation of this type in more dilute suspensions the mechanical theory is unsatisfactory.

In his monograph on thixotropy, Freundlich describes a theory which attributes the formation of a gel of the type under discussion to the constituent particles becoming locked into place in equilibrium positions, wherein the force of attraction between particles (assumed to be of the extended van der Waals type described by Kallman and Willstätter (9)) is just balanced by the force of repulsion due to the mutual repulsion of the diffuse double layer. The presence or absence of electrolyte regulates the effective sphere of action of the repulsive force by regulating the value of the zeta potential, and hence determines whether there is a completely stable suspension, coagulation, or the intermediate stage of thixotropy.[6]

In order for a gel of a given strength to be formed, a suitable number of the particles must take up their equilibrium positions, and as this process is one which occurs at random, it will take a finite time which we measure

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[6] See also the recent publications by H. C. Hamaker (Rec. trav. chim. **55**, 1015 (1936); **56**, 3, 727 (1937)).

as the setting time. The more pronounced the Brownian movement of the particles, the greater their chance of slipping into the equilibrium position from which they have no tendency to depart. The smaller the particle and the higher the temperature, the greater is this Brownian movement and hence the greater the speed of gel formation.

On the basis of ultramicroscopic examination, it seems most probable that in the formation of a gel the particles are not necessarily distributed uniformly throughout the total volume, but are grouped together in primary clusters, which in turn coalesce to form a network throughout the whole volume interwoven with patches and channels of free dispersing medium. It is possible that rheopexy manifests itself in the presence of any gentle motion which tends to help the primary clusters to aggregate into the secondary network responsible for the rigidity of the structure. Violent mechanical action will break down not only the secondary network but also the primary clusters of particles. We feel that this theory of gel formation and structure is capable of accounting for all known facts, even in the most dilute gels, and is in full accord with the most recent ultramicroscopic observations.

SUMMARY

1. Natural bentonite has been subjected to a centrifugal fractionation procedure which has yielded five fractions of varying average equivalent spherical diameter of 14.3 to 87 mμ.

2. The exchange capacity and pH–concentration relation of all particle size fractions of hydrogen bentonite are identical within the limit of experimental error.

3. The specific conductance of hydrogen bentonite suspensions increases with a decrease in average equivalent spherical diameter of the suspended particles, but is much less than would be calculated from the hydrogen-ion activity of the same suspensions.

4. Under corresponding conditions of concentration of bentonite and electrolyte and temperature, the smaller the average equivalent spherical diameter of the suspended particles, the shorter the time required for the formation of a gel of given strength.

5. In suspensions of the finest particles of bentonite, it is possible to detect evidence of gel structure at concentrations of bentonite less than 0.05 per cent.

6. Ultramicroscopic observation indicates that gelation consists in the formation of primary clusters of individual particles, followed by secondary aggregation of these clusters into a network intermeshed with channels and patches of free dispersing medium.

7. Discussion of the results has indicated that they lend support to the

open porous structure of the bentonite particle and the "equilibrium field of force theory" of gel structure.

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ERRATA

The following corrections should be made in the first paper in this series, J. Phys. Chem. **40,** 1169 (1936):

Page 1179. The ordinate in figure 4 should be $(100)W/T$.

Page 1179. $R_2 = 2.17$ cm.

Page 1180. The ordinate in figure 5 should be $f(\dot{D})/10^7$.

THE COLLOIDAL PROPERTIES OF THE CLAYS AS RELATED TO THEIR CRYSTAL STRUCTURE[1]

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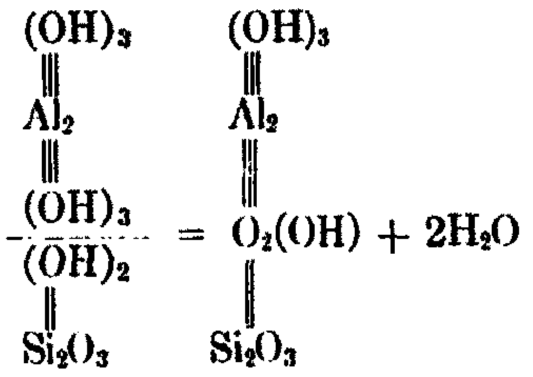
The generalizations made by L. Pauling (22) in 1930 regarding the structures of micaceous minerals have been particularly important in helping to elucidate the nature of the clays. Later work in many laboratories has confirmed and extended that of Pauling, so that we may now take the general structural characteristics of the clays as well established.

Two chief structural units are involved. The first is the alumina or aluminum hydroxide sheet, which consists of two sheets of close-packed oxygen atoms or hydroxyl groups within which are embedded aluminum atoms in such positions that they are equidistant from six oxygen atoms. Actually only two-thirds of these octahedral positions are occupied by aluminum in this gibbsite structural unit. A similar unit, in which all octahedral positions are occupied by magnesium, is known as the brucite sheet. The second unit consists of a sheet of oxygen atoms in a more open packing. Silicon atoms are present in the tetrahedral positions where they are in contact with four oxygen atoms, three in the sheet and one above. The single sheet has the composition Si_2O_3, and the fourth valency of the silicon is satisfied either by OH groups, giving a unit $Si_2O_3(OH)_2$, or by linkage with a gibbsite sheet. One can regard the linkage as having arisen by loss of water from $Al_2(OH)_6$ and $Si_2O_3(OH)_2$, thus



$$\begin{array}{c} (OH)_3 \\ \| \\ Al_2 \\ \| \\ (OH)_3 \\ \hline (OH)_2 \\ \| \\ Si_2O_3 \end{array} = \begin{array}{c} (OH)_3 \\ \| \\ Al_2 \\ \| \\ O_2(OH) \\ \| \\ Si_2O_3 \end{array} + 2H_2O$$

Using these two units it seems possible to build up a whole variety of structures having different proportions of the alumina and silica sheets.

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

Actually in the clays we know of only two general types in which the ratios are 1:1 and 1:2, respectively (19).

CLAYS OF THE 1:1 TYPE

Here the structural units may be fully hydrated as in halloysite, $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ (21), or condensed together as in metahalloysite (21), kaolinite (5), nacrite (6), and dickite (7). These last four all have the approximate formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and differ only in the relative positions of the gibbsite and silica units. The general appearance of these structures may be gathered from figure 1 (the silicon and aluminum atoms are here somewhat enlarged; the hydroxyl groups are shaded darker than the oxygen atoms).

Colloidal properties of the 1:1 clays

Halloysite and kaolinite occur in great quantities in a moderately pure condition, and their colloidal properties have been extensively studied in connection with the ceramic industries. In many cases, however, no attempt has been made to distinguish between them. Halloysite crystallizes less perfectly than kaolinite and is very difficult to recognize under the microscope. The colloidal fractions of many ceramic clays consist of kaolinite or of halloysite, with the possibility that the finest fractions may also contain more reactive clays like beidellite (4). Pure samples of kaolinite always have a low base-exchange capacity, up to 6 milliequivalents per 100 grams. Halloysites give higher values than this for the finest fractions, but it is difficult to decide whether this is characteristic or due to impurities. Edelman (2) regards it as characteristic.

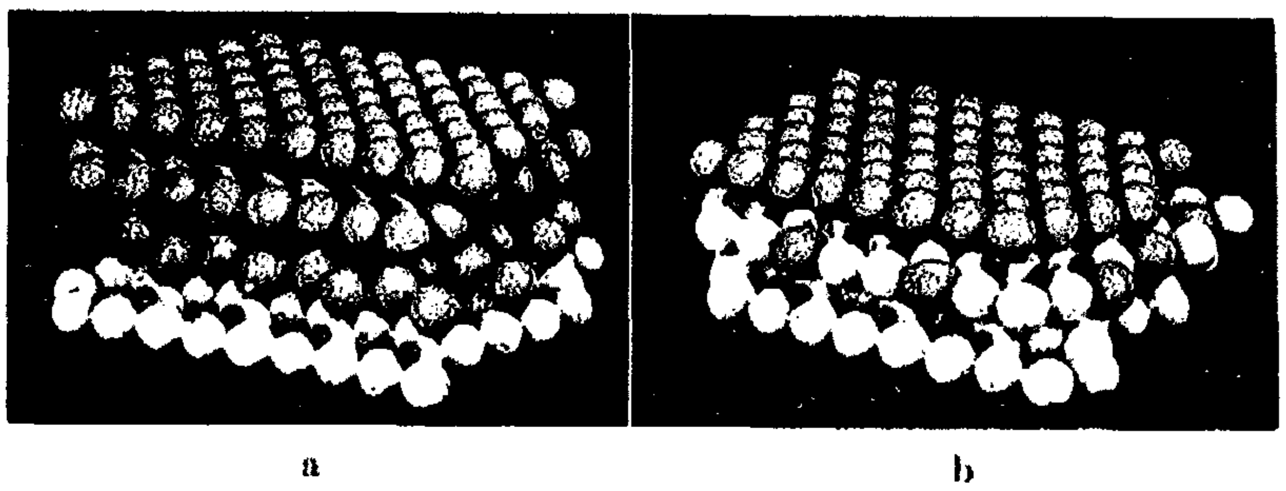

FIG. 1. Clays of the 1:1 type. (a) halloysite; (b) metahalloysite, kaolinite, nacrite, dickite.

The distribution of particle sizes within the clay fraction proper (< 2μ) has not been determined with any accuracy except in a few cases, so that generalizations are dangerous. So far as we know kaolinite generally occurs in particles larger than 100 mμ.

Considerable variations in the SiO_2/Al_2O_3 ratio occur both with kaolinite and halloysite. Kaolinite gives ratios from 2.94 to 1.85, and halloysite from 2.06 to 1.65 (24, 25). Magnesium and iron do not replace aluminum to any great extent. No studies appear to have been made on the variation of colloidal properties with chemical composition.

In general, the clays of the 1:1 group show little or no evidence of high reactivity such as we shall find in the 2:1 group associated with the expanding lattice. There seems, however, to be no theoretical reason why clays of the 1:1 type should not exist which might owe their reactivity to wide spacings and replacements like that of montmorillonite and beidellite.

CLAYS OF THE 2:1 TYPE

Here only one type of structural unit is known, in which the alumina sheet is symmetrically condensed with two silica sheets. This is the structure of the *micas* and of the *closely related vermiculites*. The simplest members of this class of minerals are pyrophyllite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$, and talc, $Mg_3O_3 \cdot 4SiO_2 \cdot H_2O$. These are comparatively well crystallized as they occur in nature, and their structures have been determined (8). Hofmann, Endell, and Wilm (13) first pointed out the close similarity in x-ray diagram between pyrophyllite (figure 2a) and montmorillonite (which is the major constituent of most bentonites), the chief difference being that the latter showed a single line close to the central beam whose angular deflection varied inversely with the moisture content of the sample. Thus they were led to the valuable concept of an expanding lattice formed of pyrophyllite sheets whose distance apart varied with the water content of the clay. Beidellite, found in a few bentonites and in many clay soils, was afterwards shown to give precisely the same x-ray lines, including the variable one (14). Gruner has extended the series to include nontronite, a clay mineral in which ferric iron has largely replaced aluminum (9).

Considering now the chemical formulas for these minerals, the nearest simple approximations derived from the chemical formulas were taken as follows: montmorillonite, $MgO \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$; beidellite, $Al_2O_3 \cdot 3SiO_2 \cdot nH_2O$; nontronite, $Fe_2O_3 \cdot 3SiO_2 \cdot nH_2O$. In order to reconcile these and the analyses on which they are based with the pyrophyllite units of structure, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$, the following replacements are found to be necessary. They may occur independently or together. Three magnesium atoms can replace two aluminum atoms in the gibbsite sheet, as pointed out by Hofmann, Endell, and Wilm (13). It is also possible for magnesium plus one equivalent of another cation to replace aluminum (19). Iron can replace aluminum, the iron being either bivalent or trivalent. The former case is similar to that of magnesium, but does not appear to be of great importance in naturally occurring clays. Replacement by ferric iron is very common and leads eventually to the nontronites (18). Aluminum plus one equivalent of another cation can replace silicon, as is known to occur in the feldspars and micas (19). (Other possibilities are phosphorus for silicon and titanium for aluminum.) Whenever an atom of lower valency replaces one of higher we may regard the lattice as acquiring a negative charge which must be balanced by positive cations. These may either be incorporated within the pyrophyllite unit sheet, if suitable positions are available, or be relegated to the spaces between the sheets, where they will be associated with water molecules. Those incorporated are the non-exchangeable cations; those between the sheets form the major portion of the exchangeable cations. Thus the reactive clays may be represented as in figure 2b. Here the water molecules, which fill up the spaces, are omitted. The smaller spheres between the sheets represent calcium and magnesium atoms, the larger ones potassium.


a b

FIG. 2. Clays of the 2:1 type. (a) pyrophyllite; (b) montmorillonite, beidellite, nontronite, magnesium bentonite.

In these reactive clays we thus have a very wide isomorphous series. Examination of the available analyses (19) showed that in beidellites the predominant replacement was that of aluminum plus cations for silicon; in montmorillonites it was magnesium plus cations for aluminum or three magnesium atoms for two aluminum atoms, often accompanied by the beidellitic replacement; and in the nontronites iron for aluminum. An end member of the series is probably Foshag and Woodford's (3) magnesium bentonite, in which practically all the aluminum has been replaced by magnesium, although no x-ray data have so far been published. Hofmann, Endell, and Bilke (12) have examined a synthetic magnesium silicate which they conclude is this same end member.

The relationship between the exchangeable and the non-exchangeable cations will thus be determined by the electrical and geometrical conditions which operate when the crystal is first built up. The replacement of one exchangeable ion by another does not affect the composition of the pyrophyllite unit. On the other hand the change from the non-exchangeable to the exchangeable form must be regarded as more deep-seated. Depending on circumstances, it may or may not involve actual breakage of the valency bonds holding the framework atoms together.

An instance of very deep-seated changes accompanying the liberation of non-exchangeable magnesium is afforded by the fine grinding experiments first performed by Kelley, Dore, and Brown (16). They showed that the base-exchange capacity of many clays could be considerably increased by grinding. It was concluded (17) that the essential part of the grinding process was to make the magnesium more readily accessible by *cleavage along or breakage across the structural planes of the clay.* X-ray studies indicated that amorphous material accumulated as grinding proceeded, suggesting actual destruction of the crystal lattice (15). Optical and chemical evidence strongly supports this conclusion. A sample of Putnam clay (<100 mμ) was ground in a rubber-lined ball mill with agate balls for 168 hours. The electrical double refractions of the ground and unground materials were then compared, both before and after electrodialysis. Before electrodialysis the ratio of the electrical double refraction of ground to unground material was 0.18; after electrodialysis it was 0.09. The base-exchange capacities as determined by the ammonium acetate method were 77 (unground) and 131 (ground) milliequivalents per 100 grams of ignited clay. Differences in chemical character were revealed by washing with $N/10$ acetic acid. The unground clay released only 0.067 per cent of sesquioxides (ignited basis) in three successive treatments and none thereafter. The ground clay released 10.38 per cent of sesquioxides in nineteen successive treatments, the last of which gave 0.26 per cent, i.e., more than the three treatments on the unground clay. Silica was also brought into solution. Thus the ground clay can no longer be regarded as a beidellite; its behavior approaches more nearly that of a permutite, mixed with a little unchanged beidellite. Fine grinding, therefore, does not simply cleave the crystals in their planes of weakness, but breaks and distorts every part of the lattice. The exchange capacity of the new material will depend on its particular molecular structure, and it need not bear any simple relationship to the value for the unground material.

Besides these clays with an expanding lattice we have indications of certain less reactive clays which more nearly approach the micas in chemical composition. Hofmann, Endell, and Wilm (14) found in certain clay soils a mineral similar to montmorillonite in its x-ray diagram but without the expanding lattice. Grim and Bray (4) have characterized a sericite-like mineral in shales and in clay soils derived from shales and have drawn attention to its importance. It is possible that these minerals may bear close relationship to the vermiculites investigated by Gruner (10).

THE REACTIVE CLAYS AS COLLOIDAL ELECTROLYTES

This picture of a montmorillonite or beidellite crystal leads us to anticipate some unusual properties. One might expect that the distance apart of the structural pyrophyllite units would be influenced in several ways. It has been shown that polar organic molecules can replace water between the sheets (14) and that non-polar liquids are unable to force the sheets apart. Experiments with different cations have shown that in equilibrium with liquid water the spacing between the sheets is nearly the same for the calcium and hydrogen clays (14 A.U.) but much greater for the sodium clay (>23 A.U.). At lower vapor pressures the three ions give almost identical spacings (11). The ease with which the spacings can vary suggests that materials may exist in which at a given instant the spacings may have different values in the same crystal. That is, instead of having a single characteristic spacing there would be a distribution of spacings caused, for instance, by differing replacements and hence differing resultant charges on different layers. One can regard the resultant charge as holding the lattice together, this tendency being opposed by the disrupting action of the water dipoles. Comparing a fully hydrated with a dehydrated clay, it will be clear that the sheets are much less firmly held together in the former. On the other hand, the orientation of the water dipoles in the intense ionic field can be regarded as a stabilizing influence in the hydrated system, since the orientated dipoles will tend to hold the sheets together more efficiently than would non-orientated molecules (26, 27).

Considering this electrical field between the layers, we can form a close estimate of the surface density of charge by recalculation of the base-exchange capacity in terms of ions per unit cell. For beidellites the values range around 0.4 to 0.5, and for montmorillonites around 0.5 to 0.7 equivalents per unit cell. In calculating the density of charge these values should be halved, since each unit cell exposes two surfaces. The smallest value given above corresponds to 4.45×10^{13} electrons per cm.^{2} and the largest to 7.8×10^{13}; conversion to practical units gives 7.1×10^{-6} and 12.4×10^{-6} coulombs per cm.^{2}, respectively. In making these calculations complete dissociation of the exchangeable ions from the surface is assumed. The distribution of the positive dissociated ions in the water between the lattice sheets is unlikely to be uniform. If it were, then one could calculate the strength of the ionic solution between the sheets to be about 2.3 *N* for the calcium montmorillonite investigated by Hofmann and Bilke (11), in which the exchange capacity is 0.69 per unit cell and the free space between the layers is 11.1 A.U. (c = 20.7 A.U.). For the sodium clay, which gives a wider spacing, the value would be considerably less than this. The hydrogen clay, with practically the same spacing as the calcium clay, would probably not be completely dissociated, and in any case hydrogen clays behave as hydrogen-aluminum clays, owing to reaction of hydrogen ions with aluminum of the lattice (23).

The electrical double layer surrounding the particle may be considered to arise in two ways: (*a*) by dissociation from the plane surface of the lattice sheet, just as occurs between lattice sheets, and (*b*) by the unsaturation arising from the breakage of bonds at the edge of the sheets. Taking a sheet which is large in comparison with its thickness, then one can use the charge per unit cell as calculated from the base exchange and the potential of the electrical double layer, in order to calculate the thickness of the double layer normal to the plane of the sheet. Thus for sodium-putnam clay (beidellite) with an exchange capacity of 0.48 ion per unit cell, Baver (1) found a potential of 0.0454 volt. Using the condenser formula

$$\zeta = \frac{4\pi\sigma e}{D}$$

and assuming the normal value for D, the effective thickness of the double layer is found to be 3.8×10^{-8} cm. This, however, is to be regarded as an artificial value, since D should probably not be 81, owing to the orientation of the water dipoles and, further, the assumption of complete dissociation may be incorrect.

If the structure proposed for the reactive clays is correct, then each clay particle may be regarded as an electrical insulator in a direction normal to the plane of the sheets and a good conductor in the plane of the sheets. It is interesting to inquire whether there is any experimental evidence which would confirm these peculiar properties. It is known that clay particles orientate themselves in the electric field (20); this orientation has been used in order to measure their double refraction. In electrodialysis such an orientation occurs along with a compaction of the clay to form a solid mass on the anode membrane. When electrodialysis experiments are carried out with increasing quantities of clay, it is found that the current passing shows an increase of many times its former value as soon as the clay has formed a solid structure between the fixed membranes. If this structure is broken by means of a glass rod, then the current suddenly falls off, although the total amount of conducting material remains the same.[2]

Experiments have been carried out in order to determine whether this effect has any connection with the thixotropy of clays. Determinations of conductivity on a thixotropic sodium-putnam system only showed a slight increase (about 5 per cent) on setting. Thus in the thixotropic system there is little or no preferred orientation. The experiments on electrodialysis would lead one to conclude that there the clay particles

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[2] Dr. R. Bradfield first told me of this last demonstration.

arrange themselves with the plane of the sheets in the electrical lines of force.

MECHANICAL PROPERTIES OF THE CLAYS

It will be clear from this description of clay structures that these may influence the bulk mechanical properties in several ways. In both groups of clays the platy character will facilitate the arrangement of adjacent particles in quasi-parallel groups. In addition, the high degree of hydration of the reactive clays may make it possible for comparatively slight mechanical forces to break the single crystals by the gliding of one plane over another. These effects have not yet received theoretical treatment, although they would appear to be of importance in studies of plasticity and cohesion.

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THE SORPTION OF CHLORINE BY SILICA GEL[1]

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Received June 22, 1937

As was observed by Reyerson and Cameron (1), comparatively few studies had been made on the sorption of the vapors of the halogens by porous sorbents. Such a complete study on a family of elements so closely related chemically might well throw new light on the problems of sorption by porous materials. A series of experiments was begun in this laboratory, and the results of the investigations on the sorption of bromine and iodine by silica gel and charcoal have been reported (1). The present work completes the study as far as silica gel is concerned. Upon completion of sorption studies on charcoal it will be possible to compare the behavior of the halogens toward these two porous sorbents.

Magnus and Müller (2) carried out a series of measurements on the adsorption of chlorine by silica gel in an all-glass system at 0, 20, and 40°C. However, no desorption measurements were made, and the method used differed considerably from that described by us; this raised the question of the reversibility of the sorption.

APPARATUS AND MATERIALS

The construction of the actual sorption system was essentially the same as that previously described (1). It consisted of an all glass–quartz system having no stopcocks. For a complete description of this system reference may be made to the previous paper. Figure 1 shows the essential portions of the apparatus. The quartz spring balance (A) was supplied by the Bell Telephone Laboratories (5). It was approximately 25 mm. in diameter and consisted of twelve turns. The Bodenstein quartz-spiral manometer (B), which was used as a null point instrument, and the travelling microscope were the same instruments used in the previous work.

With the air pressure in the outer jacket of the Bodenstein manometer adjusted so that the pointers were matched, pressure measurements on the mercury manometer were read by means of an accurate cathetometer. The manometer readings were corrected to 0°C. Zero readings were taken with the apparatus evacuated and under actual run conditions.

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

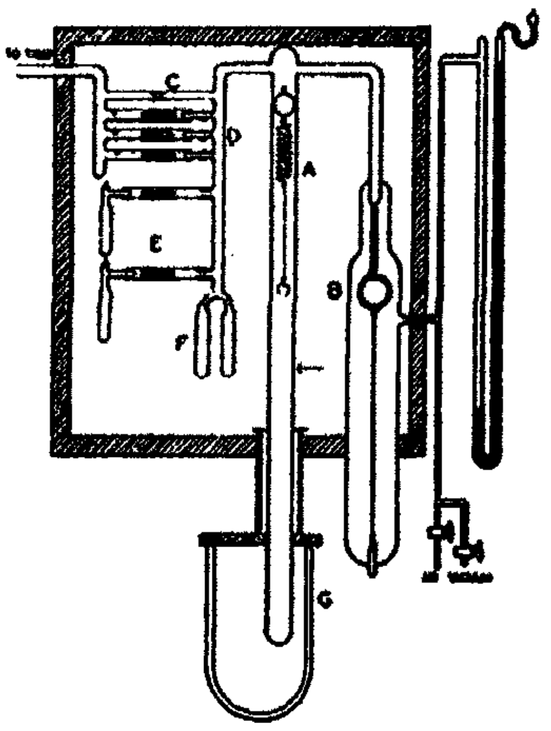

FIG. 1. Sorption apparatus. A, sorption tube; B, Bodenstein manometer; C, lead to high vacuum system; D, breakoffskys; E, sample bulb; F, storage bulbs; G, cryostat.

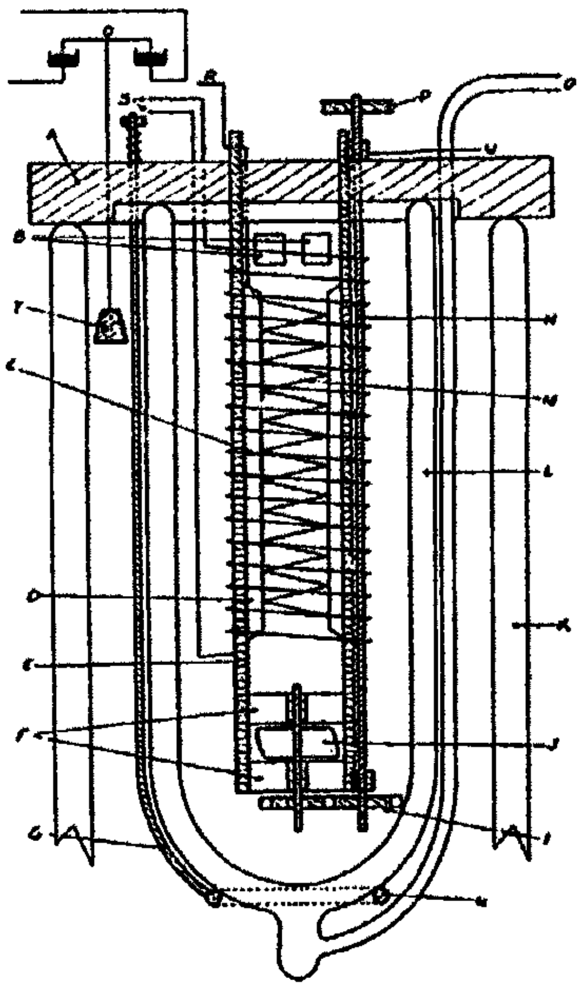

FIG. 2. Vertical section of cryostat. A, asbestos-Bakelite base; B, circulation windows; C, heating coil; D, platinum coil supports; E, Bakelite form; F, fan mount and bearings; G, brass support rods; H, brass ring; I, brass gears; J, Bakelite fan; K, outer Dewar; L, inner Dewar; M, platinum resistance coil; N, brass axle; O, outlet to vacuum; P, pulley wheel; Q, float contacts; R, leads to platinum coil; S, leads to heating coil; T, float.

The chlorine was introduced into the bottom of the adsorption tube (A) through the breakoffsky (E) and its temperature (or vapor pressure) controlled by means of a precision cryostat (4) shown in detail in figure 2. Constant low temperature was controlled in the following manner. A Dewar flask, K, containing liquid air surrounded a second Dewar flask, L, containing the constant-temperature bath liquid. The air pressure between the walls of L, which regulated the amount of cooling, was controlled by means of a vacuum system connected to O. Heat was supplied through the coil, C, mounted on the Bakelite form, E. The bath liquid was circulated by means of the Bakelite fan, J, driven by the motor-pulley system P, N, I. Windows, B, were cut into the frame to insure proper circulation of the liquid. The form, E, was mounted on the base, A, and around this was mounted the Dewar flask, L, by means of a brass ring, H, and three brass rods, G.

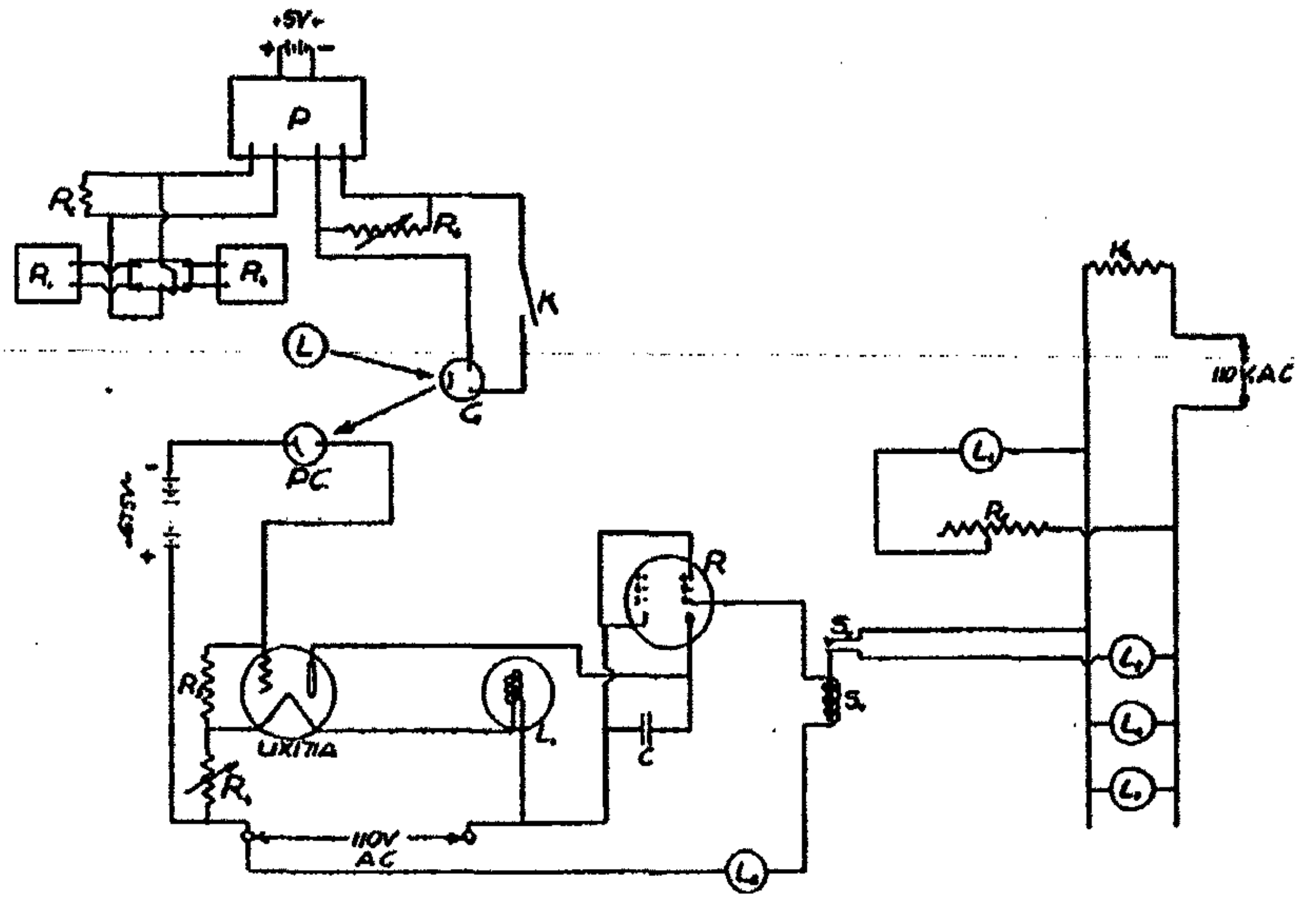

Fig. 3. Thermoregulator circuit. C, condenser (capacity, 2 microfarads); G, high sensitivity galvanometer; H_c, cryostat heating coil; K, key; L, 6-volt lamp; L_1, 25-watt lamp (110 volts): L_2, 75-watt lamp (110 volts); L_3, L_4, L_5, L_6, lamps (110 volts); P, potentiometer; P.C., photoelectric cell, type P.J. 23; R, base of telephone relay, type E-W, S6; R_1, R_2, 10,000-ohm variable resistance boxes; R_3, high resistance, graphite grid leak; R_4, 200-ohm variable resistor; R_5, 63-ohm slide-wire rheostat; R_6, 400-ohm variable shunt; S_o, solenoid; S_w, mercury switch.

The current applied to the heating coil through the leads, S, was controlled by means of a thermoregulator, the circuit of which is shown in detail in figure 3. A constant supply of heat, nearly sufficient to balance the cooling, was supplied through the lamp bank L_3, L_4, L_6, and slide-wire rheostat, R_5, from a 110-volt A.C. source. The bath was held to constant temperature in the following manner. A coil of platinum wire, R_c, was used as a thermosensitive element and its leads were connected to a potentiometer, P, set to the electromotive force of the resistance thermometer circuit corresponding to the desired temperature. A high sensitivity galvanometer, G, was connected to the potentiometer through the shunt, R_4. An image of the lamp, L, was formed by the mirror of the galvanometer upon a narrow slit in a screen which covered the photoelectric cell, P. C. Thus when the temperature of the cryostat dropped, the galvanometer mirror was deflected and the beam from the lamp fell upon the sensitive plate of the cell. The photoelectric current generated was amplified by means of a U.X.171A radio tube, to the grid of which the photoelectric tube was connected. In the plate circuit of the amplifier tube was placed a telephone relay, type E-W, S6, R, and a mercury switch, S_w, which closed a circuit to the lamp bulb, L_5, thus supplying sufficient additional current to the heating coil, H_c, to bring the temperature back to the desired value. At this point the light beam passed off the slit onto the screen shading the photoelectric cell and the circuit to the balancing heater then opened, which allowed cooling to begin. The bath liquid used in these studies was ethyl bromide, which proved to be highly satisfactory.

The liquid air supply in the outer Dewar flask was maintained at constant level by use of a device shown in detail in figure 4. The float, F, operated through the contacts, K, and the relay, R, a solenoid, S, which in turn actuated an air valve, V. This valve opened and closed a low-pressure air supply to the storage Dewar flask, D_1, thus forcing liquid air over into the Dewar flask, D, which contained the cryostat.

With this apparatus it was possible to control the temperature of the chlorine within less than 0.01°C. of the desired value. This variation produced no measurable change on the Bodenstein manometer.

The procedure followed in calibrating the spiral and in preparing the adsorption system and adsorbent for the sorption studies was nearly identical with that described by Reyerson and Cameron (1). For that reason, a very brief discussion will be given at this time.

The spring balance used had a sensitivity of approximately 0.065 mg. per 0.01 mm. The calibration was made using a mica pan suspended from the spiral, which weighed approximately 0.04 g. Spring length measurements made under the same load were duplicable, after an interval of two months, to a few thousandths of a millimeter. All measurements were made by means of the travelling microscope previously mentioned.

The sorption system was evacuated for approximately one hundred hours at a pressure of 10^{-5} mm. of mercury. During this period the temperature of the sorbent was raised at intervals to several hundred degrees Centigrade. A preliminary flushing out of the system with halogen was carried out before admitting the sample to be used in the studies.

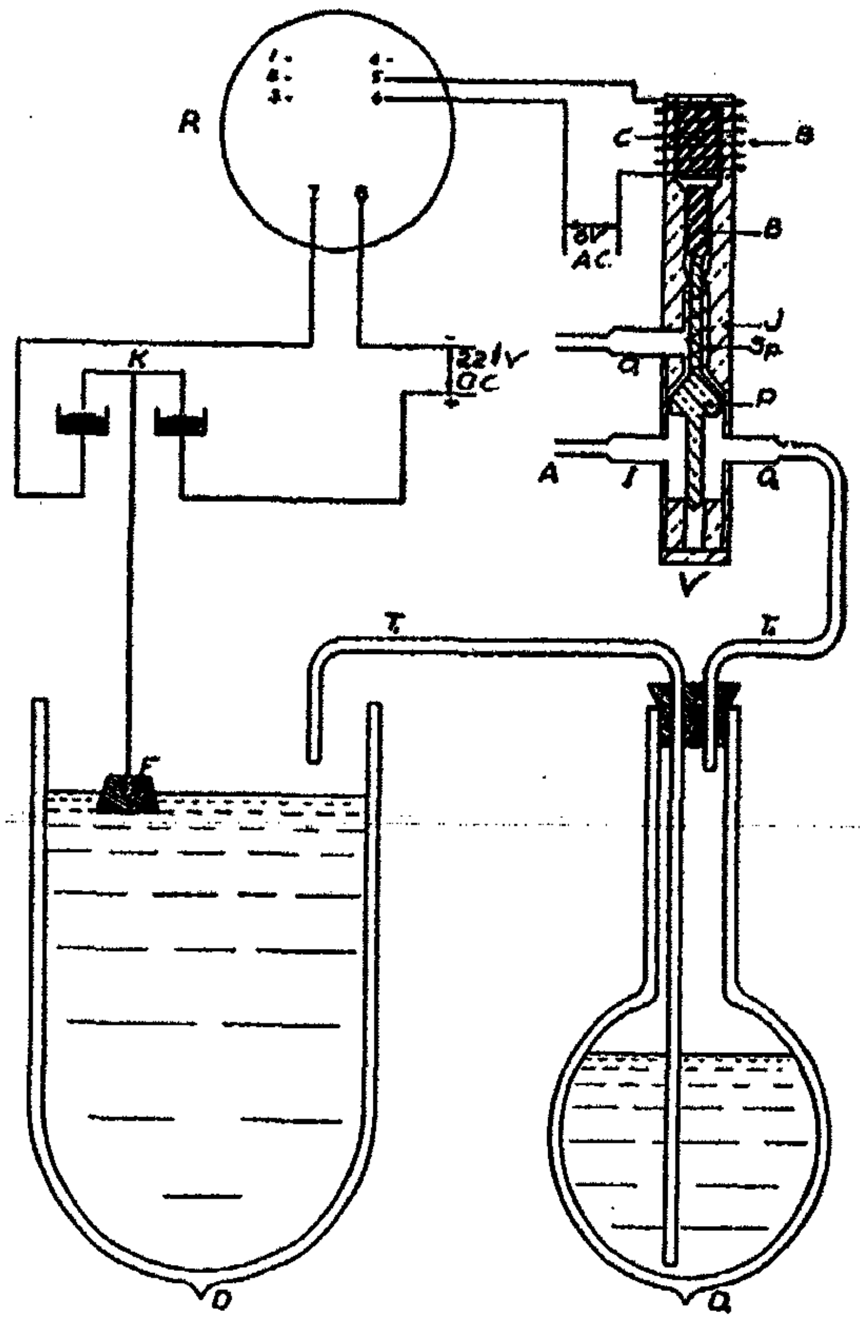

Fig. 4. Constant level liquid air device. A-I, low-pressure air supply; B, iron base; C, iron core; D, outer Dewar of cryostat (1 gallon); D_1, storage Dewar (½ gallon); F, float; J, brass jacket; K, float contacts; O_1, air outlet; O_2-T_2, tube for air conduction to storage Dewar; P, brass plunger; R, base of telephone relay, type E-W, S6; S, solenoid; Sp, spring; T_1, tube for liquid air conduction; V, air valve.

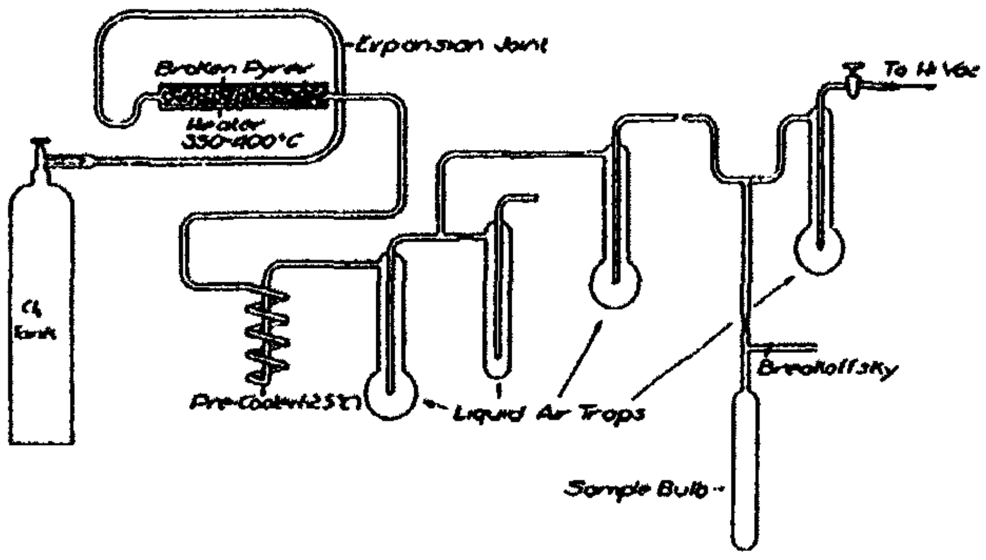

Fig. 5. Chlorine purification system

The temperature of the oven containing the sorption system was read on a thermometer suspended beside the sorption tube. This thermometer had been previously calibrated against one bearing a Bureau of Standards calibration certificate. The oven temperature was controlled by means of a long thin-walled glass regulator bulb filled with mercury and terminating in a control capillary. This operated a thermionic relay system varying an external resistance in series with the heater grid. Temperatures were constant to ±0.1°C.

The chlorine used was prepared from high grade tank chlorine. A diagram of the purification system is given in figure 5. A considerable quantity of chlorine was released from the tank in order to flush out the system before a sample was collected. It was passed through a heater, at about 400°C., to break down the oxides of chlorine, then through a precooler at -25°C., and frozen down in a liquid air trap under vacuum. The system was then sealed off between the precooler and the trap and pumped for several hours at a pressure of 10^{-5} mm. of mercury. A vacuum distillation was then carried out at this pressure and the middle portion of the chlorine collected. The first and last portions were sealed off and disposed of. This was repeated several times. The final sample was collected in the sample bulb equipped with a breakoffsky and sealed off under high vacuum. The purification system was protected from the mercury vapor pumps by a liquid air trap.

TABLE 1

Spring calibration

TEMPERATURE	LOAD	LENGTH	SENSITIVITY
°C.	*grams*	*mm.*	*mg. per 0.01 mm.*
35.9	0.0558	50.497	
	0.1558	66.092	0.064124
	0.2558	81.500	0.064909
51.0	0.0558	50.425	
	0.1558	65.984	0.064271
	0.2558	81.364	0.065019
81.5	0.0558	51.128	
	0.1558	66.473	0.065167
	0.2558	81.800	0.065244

The silica gel used was of the commercial glassy type. It was a sample of the same gel used in the bromine and iodine research, and a complete discussion of its preparation may be found by a reference to that work (1).

RESULTS

Sorption isotherms were carried out with the adsorbent maintained at temperatures of 35.9, 51.0, 66.5, and 81.5°C. Equilibrium was established

TABLE 2

Sorption of chlorine by silica gel

PRESSURE CORRECTED	X/M	TIME FOR READING
	Isothermal at 35.9°C.: adsorption	
mm. of Hg	*millimoles per gram of sorbent*	*hours*
0	0.0	2.0
4.2	0.0399	4.0
9.6	0.0576	2.5
18.3	0.1064	2.6
41.1	0.2226	2.2
114.0	0.3468	2.5
171.1	0.4726	3.2
238.1	0.5719	2.1
329.1	0.7316	3.2
456.7	0.9187	3.5
586.8	1.1218	2.8
727.3	1.2921	3.0
	Isothermal at 35.9°C.: desorption	
646.6	1.2053	2.3
511.0	1.0288	2.1
401.1	0.8514	2.0
263.0	0.6554	2.0
138.7	0.4284	1.7
68.1	0.2891	1.8
34.4	0.1880	2.0
0	0.0	2.0
	Isothermal at 66.5°C.: adsorption	
0	0.0	2.1
15.5	0.0267	4.3
45.0	0.0890	2.1
99.9	0.1540	2.4
198.8	0.2695	2.7
337.0	0.3995	3.4
484.7	0.5144	2.1
575.3	0.5954	2.0
721.2	0.7013	2.3
	Isothermal at 66.5°C.: desorption	
625.9	0.6313	2.8
411.6	0.4666	2.6
273.0	0.3446	2.3
155.7	0.2226	2.1
69.1	0.1255	2.7
45.0	0.0890	2.2
0	0.0	2.2

TABLE 2—*Concluded*

PRESSURE CORRECTED	X/M	TIME FOR READING
	Isothermal at 51.0°C.: adsorption	
mm. of Hg	*millimoles per gram of sorbent*	*hours*
0	0.0	2.1
5.5	0.0266	3.3
24.5	0.0746	2.2
55.5	0.1359	2.3
115.6	0.2318	2.1
184.3	0.3234	1.7
299.5	0.4611	2.2
444.2	0.6086	2.0
684.0	0.8360	2.7
	Isothermal at 51.0°C.: desorption	
730.1	0.8707	2.4
551.5	0.7099	1.8
348.3	0.4949	1.7
258.2	0.3980	1.7
131.7	0.2470	2.1
79.4	0.1626	1.9
36.0	0.0888	1.8
14.0	0.0338	2.0
5.5	0.0240	2.1
0	0.0	2.1
	Isothermal at 81.5°C.: adsorption	
0	0.0	2.3
4.8	0.0098	3.2
33.2	0.0570	2.2
125.8	0.1373	1.7
218.2	0.2113	2.4
353.3	0.3138	2.1
491.9	0.3940	3.1
638.9	0.4859	2.8
	Isothermal at 81.5°C.: desorption	
720.1	0.5301	2.3
560.3	0.4350	2.1
425.9	0.3593	2.2
353.3	0.3138	1.8
286.8	0.2648	1.9
165.2	0.1810	1.7
75.2	0.1034	2.2
24.5	0.0446	1.7
0	0.0	2.2

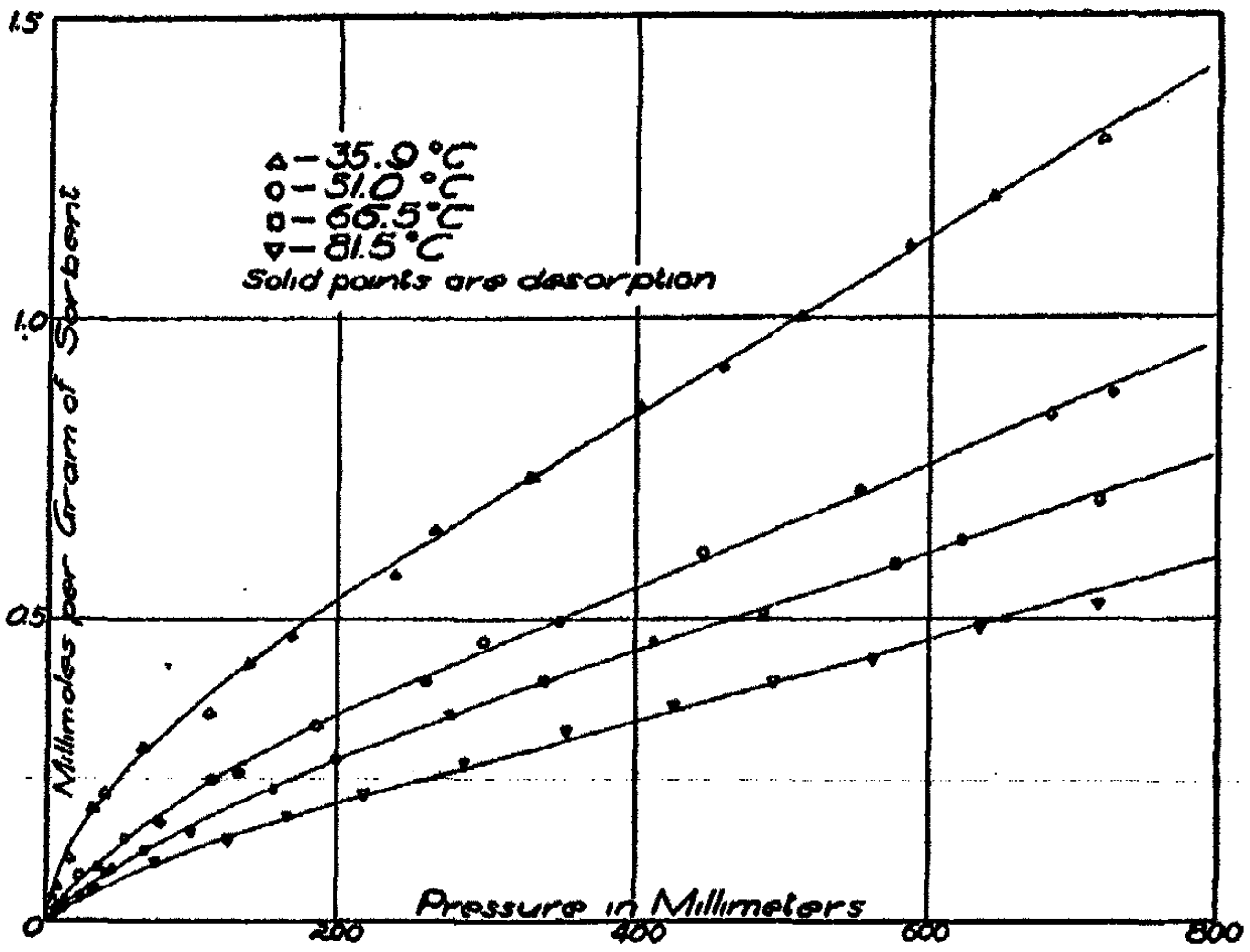

FIG. 6. Sorption of chlorine by silica gel

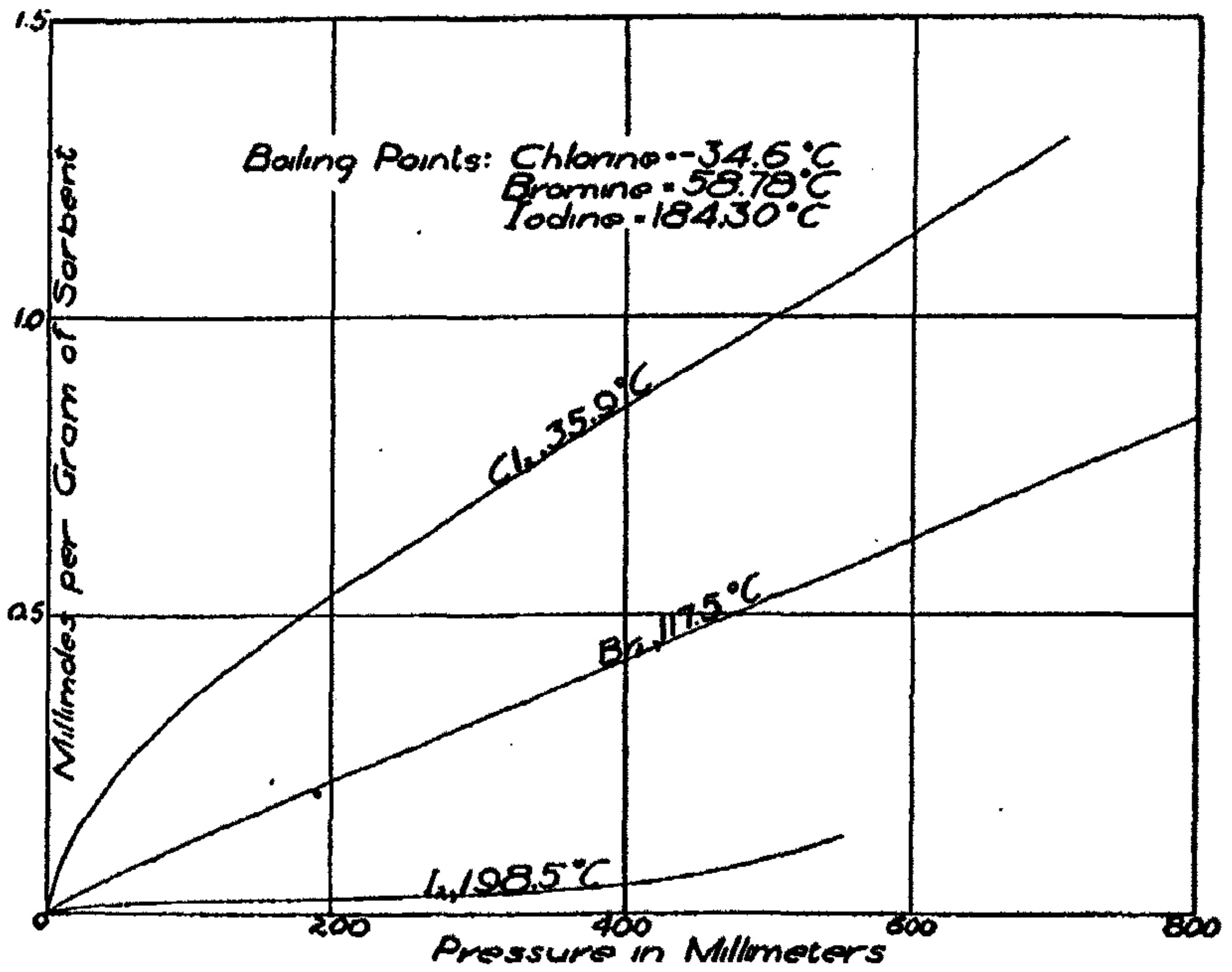

FIG. 7. Sorption of chlorine, bromine, and iodine by silica gel

rapidly in most cases; no measurable change in the amount adsorbed occurred after fifteen minutes. However, to insure equilibrium being established, approximately two hours were allowed for each determination. Adsorption measurements were followed by desorption measurements at the same temperature. Spring calibrations for the various temperatures are given in table 1. The weight of the calibration pan and fibers was 0.0558 g. The calibration was then made in steps of 100 mg. The sensitivity is expressed in milligrams per 0.01 mm. elongation of the spiral. The data for the sorption measurements are given in table 2. No buoyancy correction was made, since calculations showed it to be negligible.

DISCUSSION

Figure 6 shows graphically the four isothermals recorded in table 2. Millimoles of chlorine sorbed per gram of silica gel are plotted as ordinates against vapor pressure of chlorine as abscissae. The results indicated that adsorption and desorption were fully reversible and that there was no evidence of hysteresis.

The isotherms show a somewhat greater increase in amount sorbed per unit pressure change at the lower vapor pressures. As the pressure increases, the curves tend to flatten out somewhat. The isotherms for chlorine are concave toward the pressure axis, while those for bromine and iodine were convex. However, the amount of convexity diminished with increasing temperature in the case of bromine and iodine. Hence for comparable temperatures, considerably above the boiling points, the curves are more nearly similar.

The amount of halogen sorbed under nearly comparable conditions decreases with increasing atomic weight, as shown in figure 7. The isotherm for chlorine was approximately 70°C. above its boiling point, for bromine approximately 60°C., and for iodine approximately 15°C. No more comparable data were available in the case of iodine. The boiling points of chlorine, bromine, and iodine as given by the *International Critical Tables* are -34.6, 58.78, and 184.30°C., respectively. At 35.9°C., 0.85 millimole of chlorine is sorbed per gram of gel under a pressure of 400 mm. Under the same pressure, 0.41 millimole of bromine is sorbed at 117.5°C. and 0.05 millimole of iodine at 198.5°C., per gram of gel.

The data for chlorine fit fairly well the Freundlich empirical isotherm. A plot of log X/m against log p gives a reasonably straight line. The expression given by McGavack and Patrick (3) likewise fits the experimental results. Both of these expressions are most satisfactory at higher vapor pressures. The data do not fit the Langmuir equation for monomolecular adsorption. A plot of $\frac{P}{X/m}$ against P gives a curve which is concave toward the pressure axis.

SUMMARY

Adsorption and desorption of chlorine by silica gel were measured at 35.9, 51.0, 66.5, and 81.5°C. The adsorption occurred rapidly and was fully reversible in all cases measured.

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DETERMINATION OF ICE-WATER RELATIONSHIPS BY MEASUREMENT OF DIELECTRIC CONSTANT CHANGES[1]

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The use of freezing-point data for calculating the activity of water in various substances, both colloidal and non-colloidal, is very general. It is seldom that one wishes to know the activity at the temperature of freezing. What is desired is the activity at some higher temperature. In the case of many substances the activity at room temperature is desired, or perhaps at body temperature. With soils it is desirable to know the activity, or effective concentration, of the water at the temperature of the soil in contact with the plant root systems.

Two major assumptions are made in making the transition from one temperature to another. The first of these is that the non-aqueous components of the system lower the activity of the water component by the same amount at the two widely separated temperatures. The second assumption is that the measurement of the activity at the lower temperature has been made under equilibrium conditions. In the case of the first assumption we have very little data, at least in the literature on soils. It is with the second assumption that the work reported here is principally concerned.

There has been a revival of interest in the freezing-point method of attacking the problems of water relationships in soils, since Schofield and Botelho Da Costa (4) published their results on the estimation of wilting coefficients from freezing-point data. One of the most significant points in their paper is that by using improved technic, that is, less supercooling and less difference in temperature between the cooling jacket and the partially frozen sample, they obtained values always lower than those obtained by the regular technic. In the drier range the freezing-point lowerings were only one-half those found by the older method.

A question may well be raised then as to whether the values they have obtained by their new technic are for equilibrium conditions. Briggs (2) and, later, Kistler (3) have pointed out that the determination of bound water by the freezing method is uncertain because of the fact that equilibrium conditions are not readily established in ice-water-colloid systems.

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

It is highly improbable that there is established a condition approaching equilibrium when the freezing-point determination is made. The total time required is only a few minutes, during which changes of temperature within the sample range from many degrees above freezing to a degree or more below the *freezing point*.

The method which we wish to present here offers the possibility of making freezing-point determinations under conditions of thermal equilibrium. This method, which has been described elsewhere (1), is based upon the change in dielectric constant which takes place when water in the liquid state forms ice or when ice melts to form liquid. The material to be studied is made a part of the dielectric of an electrical condenser. Since the capacity of the condenser is a function of the dielectric constant of this material, any change in dielectric will be reflected in the capacitance of the condenser. In the liquid state water has a dielectric constant of about 80. After freezing the dielectric constant of the ice formed is about 4, provided alternating current of the proper frequency is used in making the measurement. The frequencies used in this work for making capacitance measurements were about 1800 kilocycles per second.

Measurements are made of the capacitance of the condenser at various temperatures above and below the freezing point. These values are plotted against temperature in order to obtain the freezing point, which is indicated by a break in the curve.

The circuit used in making the measurements is shown schematically in figure 1. O is an oscillator which emits radio frequency waves at a frequency of 1800 kilocycles per second. L, C_s, and C_x form a receiving circuit which may be tuned to the oscillator. C_x is the condenser containing the material to be studied, and C_s is a calibrated variable condenser. Resonance between the two circuits is obtained for a definite amount of capacitance required from the two condensers C_x and C_s. A decrease in capacitance of C_x, such as takes place when the water in the material freezes, may be compensated by an increase in the capacitance of C_s. Thus by recording the capacitance C_s necessary to tune the circuit, we have a record of the change in capacitance of C_x. The changes in the two condensers are equal but opposite in sense.

The condensers used were glass vessels with metallic electrodes on the outside, the sample of material being placed within the vessel between the two electrodes. Figure 2 shows one of these condensers. There is a glass wall between the material and the electrode. This makes a rather complicated dielectric for the condenser. The proportional part which the glass plays in determining the capacity of the condenser depends upon the dielectric constant of the rest of the material between the plates.

In order to illustrate this point figure 3 is given. The results shown were obtained on a condenser similar to the one shown in figure 2. It was filled with liquids of known dielectric constant, and then its capacity was measured. The condenser is more sensitive to changes in dielectric constant

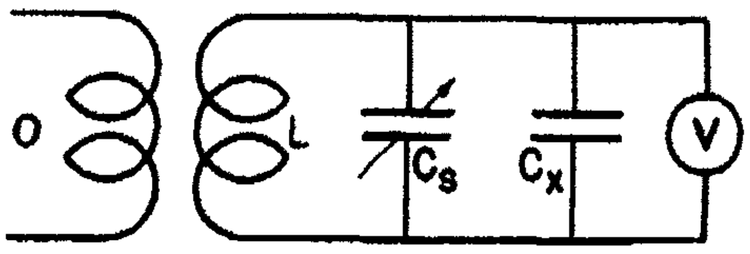

Fig. 1. Diagram of the circuit

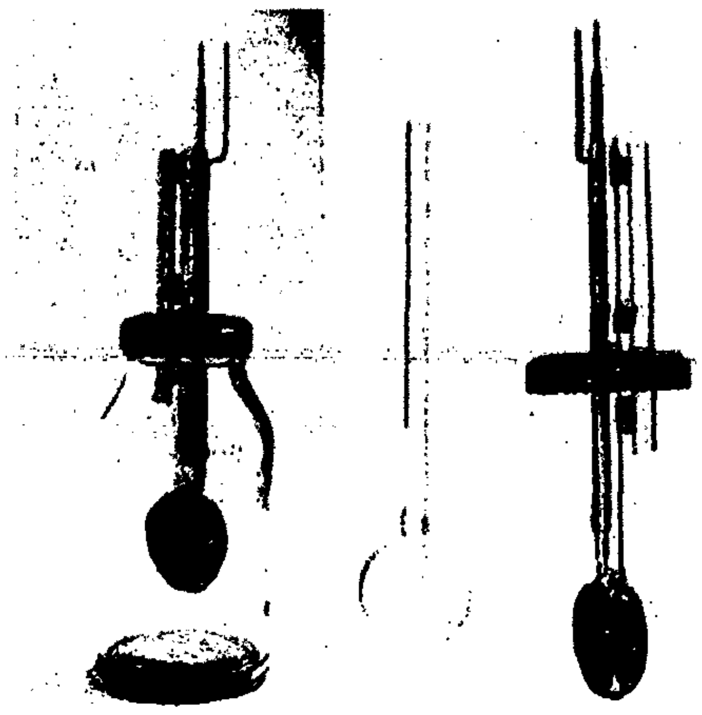

Fig. 2. One of the condensers

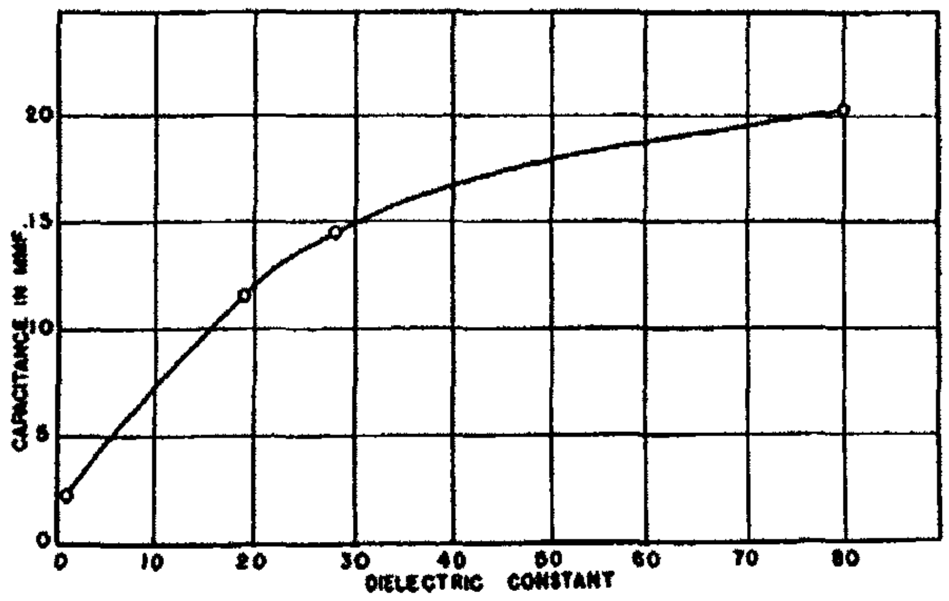

Fig. 3. Calibration of condenser

in the lower part of the range covered than in the upper part. The shape of the vessel and thickness of its walls will influence the shape of the curve.

Some of the results obtained by the method described will be given in order to show the kind of data which can be obtained.

Figure 4 shows the results obtained by melting ice in a condenser. The graph consists essentially of three straight line portions. One represents the ice phase, another the liquid phase, and the third the transition. The transition is abrupt. Also shown on the same figure is the melting curve for frozen one-half molar sucrose solution. The break in the curve, which occurs at -0.94°C., corresponds very closely to the theoretical freezing-point lowering of this solution. This sloping line indicates that ice is being melted as the temperature is raised.

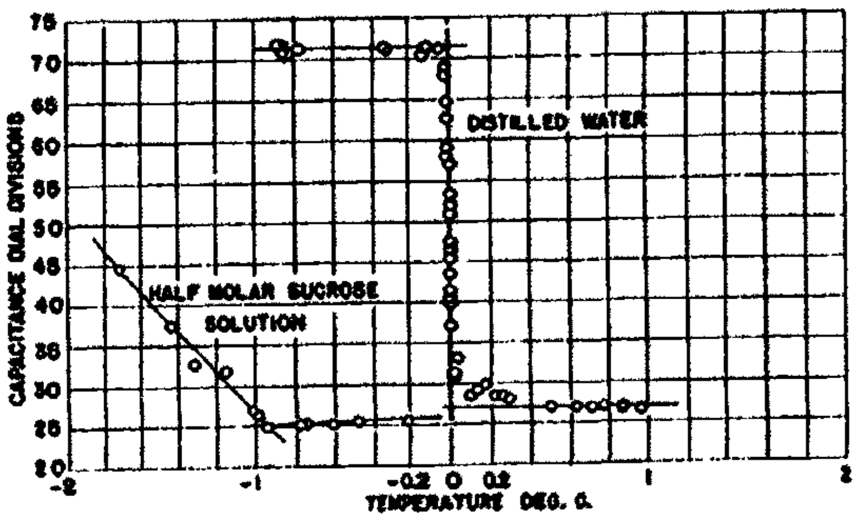

FIG. 4. Results obtained by melting ice in a condenser

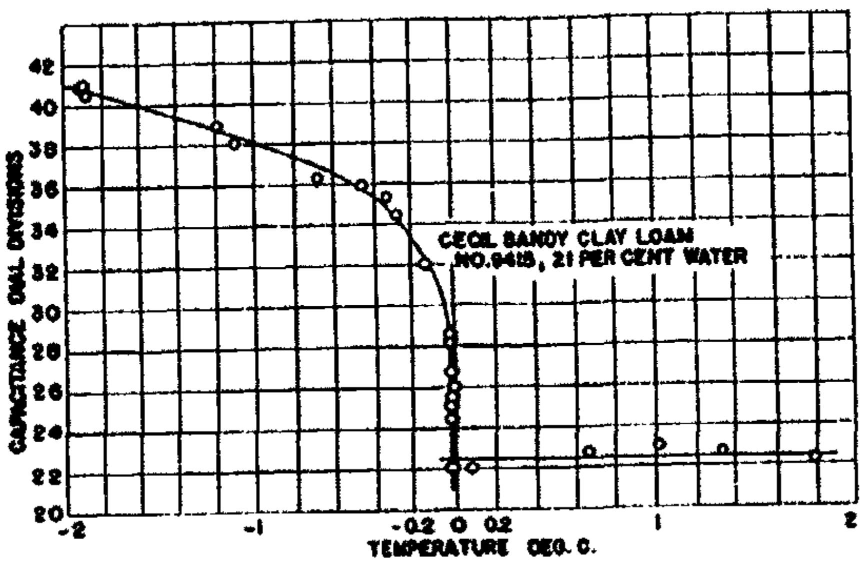

FIG. 5. The melting curve for a very wet soil

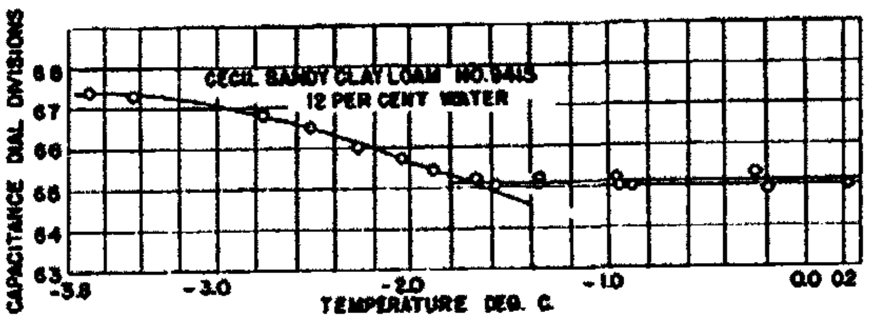

FIG. 6. The melting curve for the same soil as in figure 5 but in a much drier condition

Figure 5 shows the melting curve for a very wet soil. Much ice melts very near to the melting point of ice alone, as would be expected. Figure 6 shows the same soil in a much drier condition. Note that the freezing point, as indicated by the break in the curve, occurs much below 0°C.

Figure 7 shows the freezing curve for potato tuber. The freezing point is not as low as those found for stored potatoes by Wright and Harvey (5).

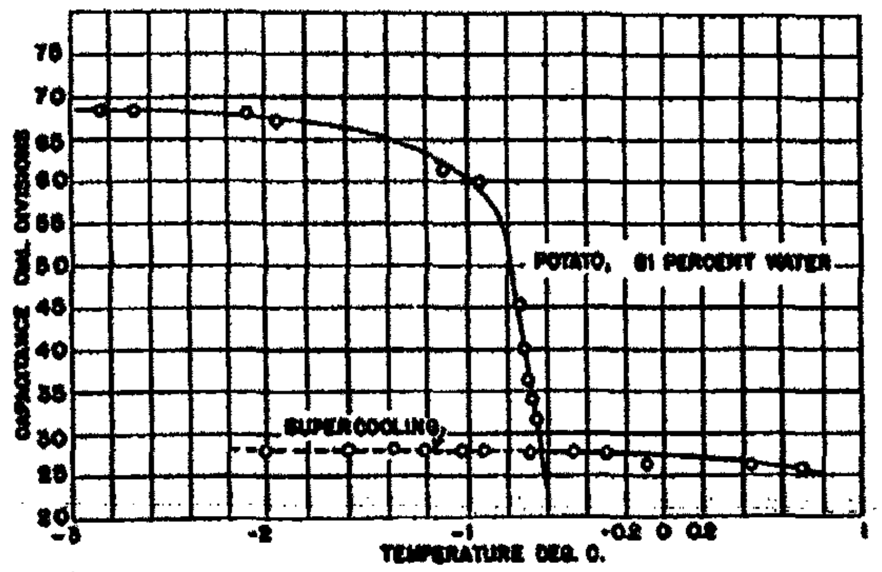

FIG. 7. The freezing curve for potato tuber

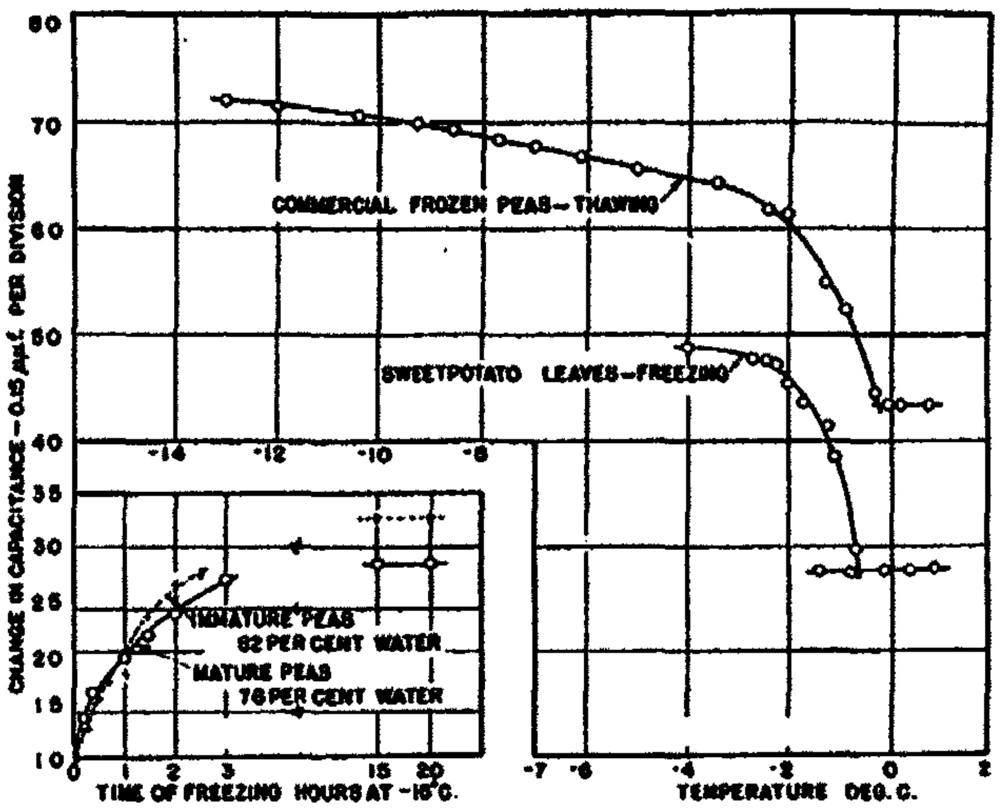

FIG. 8. The melting curve for "frozen-pack" green peas

This potato had been out of the ground only a short time. The dotted portion of the curve represents the region of supercooling.

Figure 8 shows the melting curve for some commercial "frozen-pack" green peas. One may infer that some ice begins to melt at a rather low temperature. Also, the curve indicates by its slope that the peas must be kept several degrees below 0°C. in order to keep them frozen. Shown in the lower left-hand corner of the figure are data of a different kind. Here time is a variable instead of temperature. An attempt was made to determine how much time was required to freeze completely some fresh green peas at a given temperature. The condenser containing the peas was kept at −16°C. and its capacitance measured at various periods of elapsed time. The time of complete freezing is indicated by the time elapsed before the curve becomes parallel to the X-axis. Both mature and immature peas were used. The difference in total change in capacitance in the two cases is probably due to the difference in water content which is indicated on the figure.

There are not much data available as yet on the question of whether or not the freezing points determined either by this method or by the customary thermometric method are equilibrium values. There are, however, some figures that have a bearing on the question, which can be given. Four curves were obtained for a sample of Cecil soil colloid; two were freezing curves and two were melting curves. The freezing points indicated by the freezing curves were −3.1 and −3.2°C., and those for melting were −3.2 and −3.0°C. On the same sample no freezing was indicated by the thermometric method. The colloid contained only 8 per cent moisture.

On this same colloid with 35 per cent moisture, values of −1.05, −1.00, and −1.07°C. were obtained by the dielectric method and −1.25°C. by the thermometric method using a minimum of supercooling.

SUMMARY

A method for studying some aspects of ice-water relationships in colloidal systems has been presented. Data obtained on several types of substances are shown and discussed. The method gives promise of making freezing-point measurements under equilibrium conditions.

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THE ADSORPTION NATURE OF CHROME TANNING[1]

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Friedrich Knapp, in 1858, discovered that certain compounds of chromium reacted with animal skin and converted it into leather. This finding passed through a slow process of manufacturing developments and adjustments until today the great bulk of shoe upper leather is "chrome-tanned." Coincident with the announcement of his discovery, Knapp propounded an hypothesis to explain it. He concluded that the phenomenon was a purely physical one (i.e., that the outside surfaces of the skin fibers were coated with chrome), or what would be termed adsorption, in the early conception of that term. During the eighty years which have passed since Knapp's discovery and hypothesis, leather chemists have struggled to reach a sound understanding of the ultimate conditions and forces which underlie the interaction between skin substance and chrome tanning material. Participating in that struggle are to be found the names of many workers who have contributed to the general science of colloidal phenomena.

The chrome tanning process may be briefly described as follows: The skin is prepared for tannage by the conventional treatments for the removal of its hair, epidermis, and adhering fat and flesh. During this process its component fibrous structure has been "conditioned." The tanning process consists of a preliminary treatment with acid, either sulfuric or hydrochloric, in the presence of salt which is added to prevent swelling. This process is termed "pickling." The object is to bring the skin into a uniform acidic condition and to prevent a too rapid combination between it and the chrome at the start of the tanning process, but the process is not a prerequisite to chrome fixation. To the pickled skin in a revolving wooden drum is then added a solution of basic chromium sulfate or basic chromium chloride. Skin and tan liquor are then agitated until tannage is completed. In all cases the tanning solution is highly acid. (The term "basicity" is used in tanning terminology to indicate the proportionate relation of chromium and acid radical in the chrome solution employed. Thus normal chromium sulfate, $Cr_2(SO_4)_3$, has a basicity of

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

zero, and chromium hydroxide is 100 per cent basic.) This process is termed "one bath" and is the procedure to be discussed in this article. There is also the "two-bath" process which consists of the impregnation of the skin with chromic acid (CrO_3), which is then reduced to chromium sulfate in the skin by treating with a suitable reducing agent.

Questions which have long confronted the leather chemist, and which have been the subjects of extended study may be briefly stated as follows: (*1*) Is the reaction between the protein collagen, composing the mass of fibers and fibrils which is skin, and the chromium compound a stoichiometric reaction or is it an adsorption process, in the modern sense of that term? (*2*) What is the composition of the chrome compound fixed by the skin, and is such composition affected by variations in the character of the liquor employed? (*3*) Are specific parts of the protein molecule involved in the reaction, and if so, which?

In order to understand the present status of these problems, it is necessary to trace some scientific history.

Knapp's hypothesis remained unquestioned for many years. Modern scientific investigation started with Stiasny (7), who, in 1908, stated that the crystalloid acid of the tan liquor penetrates rapidy and is reversibly held by the skin with the subsequent deposition of chrome until an equilibrium is reached. Wood (15), in 1908, suggested the purely chemical nature of tanning and considered the chrome compound as combining with the carboxyl groups of the amino acids of skin collagen to form chrome leather, and vegetable tannins as combining with amino groups to form vegetable leather. Similar views were adopted by Wilson (12) in 1917, when he suggested the combining weight of skin collagen to be 750. Thus "mono-chrome collagenate" would contain 3.38 per cent Cr_2O_3. Thomas and Kelly (8), in 1922, performed a series of experiments in which fixations up to 26.6 per cent Cr_2O_3 were found. They described this as a possible "octochrome collagenate." Thompson and Atkin (10), in 1922, questioned the conception of Wilson, pointing out the difficulty of his premise in view of the fact that both skins and chrome liquor are positively charged during practical tanning and suggested, as an alternative, that certain types of chrome solutions contain negatively charged chrome complexes. Wilson (14) then suggested that, even though the charge of the chrome compound under consideration was predominantly positive, there would be present a small but finite amount of negatively charged bodies which would combine with the skin, and the skin and chrome would continue to ionize and combine until equilibrium was reached. Seymour-Jones (6) found that chrome solutions containing no negatively charged compounds combined with skin to form leather. Thomas and Kelly (9) deaminized skin substance and found it to fix less chrome than before such treatment. They interpreted this to mean that the amino groups play an important and direct part in chrome fixation. Gustavson (3) also studied the decreased chrome fixation of deaminized collagen and suggested the possibility of its lessened capacity for combining with acid being responsible for lowered cationic chrome fixation. Freudenberg (2) called attention to the tendency of the chromium atom to saturate itself coördinatively with nitrogen compounds and suggested this as a possible explanation of chrome tanning. Stiasny and Gustavson, in a long series of publications and experiments, have applied the theories of Werner to the constitution and behavior of chromium compounds. Their work may be summarized as follows: Stiasny believes that the migratory direction of the chrome complex is of no great importance, since a liquor containing only cathodic or only anodic complexes may tan equally well. He considers the composition of the chrome complex, its instability when dissolved in water, and its degree of dispersion to be of much more importance. As stated, he interprets the behavior of chrome tanning compounds in the light of Werner's coördination theory, and he pictures changes in the degree of dispersion of the chrome complex as resulting from the union of two or more chromium nuclei containing hydroxyl groups, resulting in the formation of an enlarged nucleus, in which the hydroxyl groups are balanced between chromium atoms and are thus more firmly held. Stiasny terms this phenomenon "olation." He considers the reaction between chrome and skin to rest on an auxiliary valence action of the hydroxyl groups in the chrome complex with the peptid groups of the skin collagen. Gustavson's views, as a result of his many experimental studies, in which he also interprets chrome tanning in the light of Werner's coördination theory, are in many ways similar to Stiasny's. Gustavson does not believe, however, that the degree of dispersion of the chrome compound is of great importance. He believes that cationic complexes combine with the carboxyl groups of the skin and anionic complexes with the amino groups. Elod and Siegmund (1) showed the general relation between acid take-up from the tanning solution by the skin and the subsequent deposition of chrome. They repeatedly tanned skin after removal by electrodialysis of the acid it had adsorbed from the chrome solution. In this way they were able to fix up to 32 per cent Cr_2O_3, but found no evidence of the chromium collagenates which Thomas and Kelly had postulated. Wilson (13) has recently suggested the possible explanation of chrome tanning as a covalent combination between certain nitrogen atoms of the skin and chromium atoms of the complex chromium cations. In view of the present meager knowledge of the molecular structure of collagen, and since opinions still vary as to the exact atomic structure of chromium, the value of this interesting speculation remains a matter for future knowledge to decide. Interesting speculations have also been advanced by D. Jordan-Lloyd (4) as to the mechanism of tanning, based upon her views of protein structure and in connection with recent x-ray investigations.

The reader will recognize from the foregoing review the seeming complexity of the problem and also its state of confusion. Confining ourselves to the consideration of one-bath basic chrome tanning, since the bulk of all chrome leather is tanned by that procedure, several pertinent facts are apparent. (*1*) Only those chrome compounds capable of hydrolyzing, resulting in the formation of acid and a more highly basic chrome salt, will tan. (*2*) Only one basic chrome sulfate has been definitely isolated,—the water-insoluble $66\frac{2}{3}$ per cent basic compound $Cr_2SO_4(OH)_4$ reported by Werner (11). Basic compounds between the normal $Cr_2(SO_4)_3$ and $Cr_2SO_4(OH)_4$ are still a matter of conjecture, as are also compounds in the range from $Cr_2SO_4(OH)_4$ to hydrous Cr_2O_3. (*3*) Cr_2O_3 (hydrous) has been shown to have tanning properties. (*4*) Tanned leather is generally conceded to contain a chrome compound, acid SO_4 combined with this compound and acid SO_4 combined or associated with the protein of the tanned skin. (*5*) The deposited chrome complex has not been shown to be crystalline. (*6*) The presence of a colloidal fraction in the original tan liquor has not been proven to play a significant part in the tanning reaction. (*7*) A minimum of approximately 3.4 g. of chrome, expressed as Cr_2O_3, is required to produce a stable tannage, but the presence of that amount of chrome does not necessarily indicate that tannage has resulted. (*8*) Hydrolysis of chrome sulfate to basic chrome sulfate in aqueous solution is distinctly influenced by temperature.

The authors (5) inaugurated, in 1934, a series of experimental studies which have, we believe, cleared up many of the disputed points and give a simple and quantitative explanation of the process.

Our procedure has been to tan portions of a uniformly prepared hide substance under carefully regulated conditions and to correlate results obtained after the liquors and leathers had been subjected to analysis. For example, samples of prepared skin containing 25 g. of actual hide substance were treated with 250 cc. of solution. Chrome sulfate of suitable basicity and quantity was in solution in the 250-cc. volume. Tannage was accomplished by rotating continuously in closed jars in a constant-temperature bath at 90°F. for forty-eight hours, a time period found to be long enough to establish tannage equilibrium for the conditions involved.

The tanned samples, after removal from the spent liquor, were either washed in running water for forty-eight hours or squeezed in a laboratory hydraulic press to remove spent liquor mechanically held in the skin, dried, ground in a Wiley mill, and analyzed. For some purposes the spent liquors were analyzed, but the most significant results were obtained from analysis of the tanned specimens.

With regard to the analytical procedures involved it is to be noted that, owing to the nature of the materials, there are certain physical conditions which demand careful attention to details of experimental procedure and analytical methods.

Important variables to be considered are quantity of chrome used per unit weight of actual hide substance, volume of liquid used per unit weight of hide substance, temperature maintained during tanning, and basicity of the chrome sulfate liquor. For most of our work the chrome sulfate used was the same as used industrially, and was prepared in the conventional manner by reducing a sodium dichromate–sulfuric acid mixture with glucose, although in special cases some liquors were prepared in the laboratory. Discrepancies arising from the use of the technical liquors, containing sodium sulfate, small amounts of organic acids, and decomposition products from the glucose, as compared with strictly C.P. chrome sulfate appeared to be minor, and for our purposes the variations involved did not justify the time and effort necessary to produce the required quantities of pure chrome sulfate.

Figure 1 shows grams of chrome, conventionally expressed as Cr_2O_3, deposited in skin, plotted against grams of chrome remaining free in the spent liquor. The spent liquor is that portion of solution actually outside the skin, plus the liquor mechanically held by the skin. It is to be noted that this mechanically held liquid can be removed by subjecting the samples to pressure and is not the fraction of water, or solution, actually combined with the protein as water of hydration.

Figure 2 shows these same values plotted on a logarithmic scale. For any specific liquor basicity the experimental points fall on a straight line, and with a series of liquors of different basicities a family of parallel lines is obtained.

Figure 3 shows a second series of four liquors.

From a study of the curves shown in figures 2 and 3 it would appear that there should be some common denominator for all of them, and that the factor required to bring these curves to a common level is one dealing with basicity or proportion of acid SO_4 to Cr in the tanning compound. It is therefore not surprising to find that the mechanism for fixation of chrome by hide substance is essentially as follows:

1. The chrome sulfate complex is capable of hydrolyzing to give a solution containing some free sulfuric acid and a dissolved chrome sulfate complex of a slightly higher basicity. Removal of acid from the system, by any suitable means, promotes hydrolysis with the resulting condition where an insoluble basic chrome complex is precipitated.

2. The hide substance has an affinity for acid and, when exposed to the action of a suitable chrome liquor, the fibers and individual fibrils of the skin remove acid from that film of liquor with which they are in intimate contact. The basicity of that portion of liquor is thereby raised to a point where the basic chrome complex is thrown out of solution and deposited

in, on, and among those fibers and fibrils, until an equilibrium condition is reached and the acid combining capacity of the now tanned protein is satisfied, and no further chrome deposition occurs.

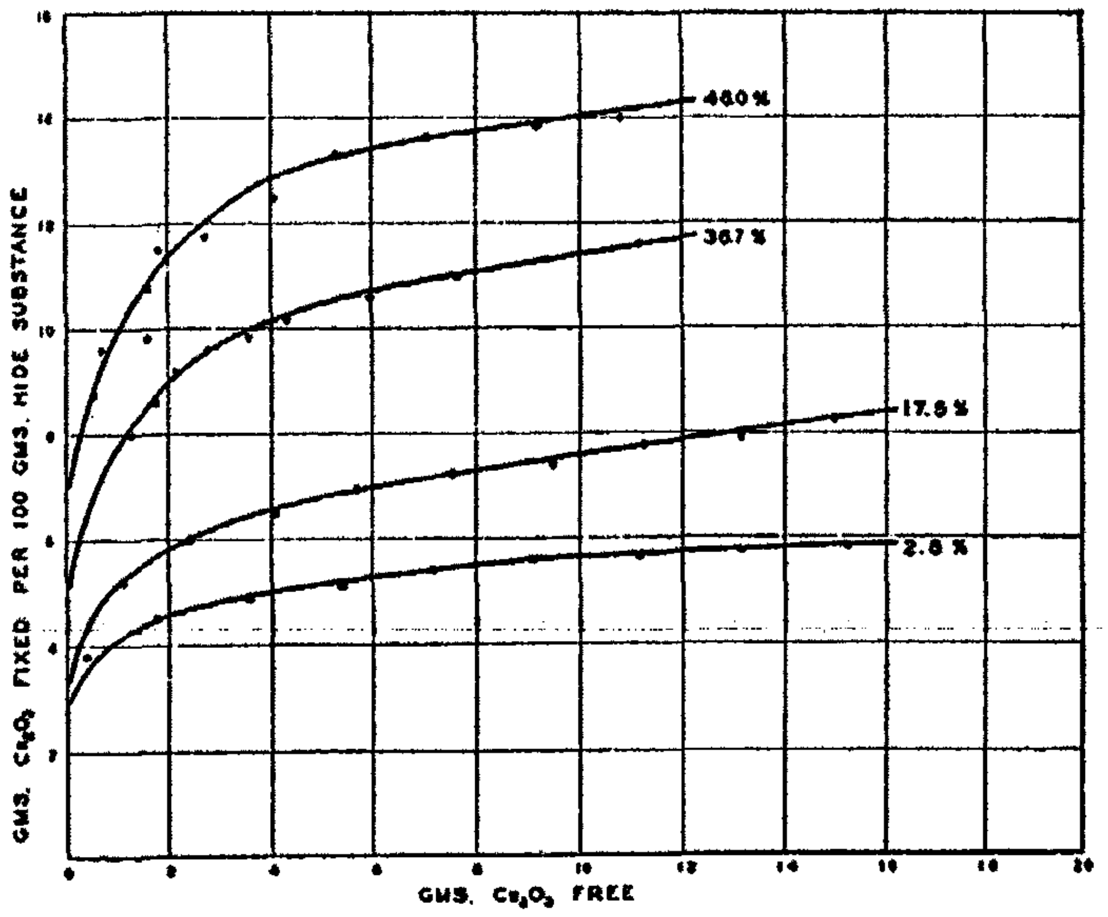

FIG. 1. Grams of Cr_2O_3 deposited in skin plotted against grams of Cr_2O_3 remaining free in the spent liquor.

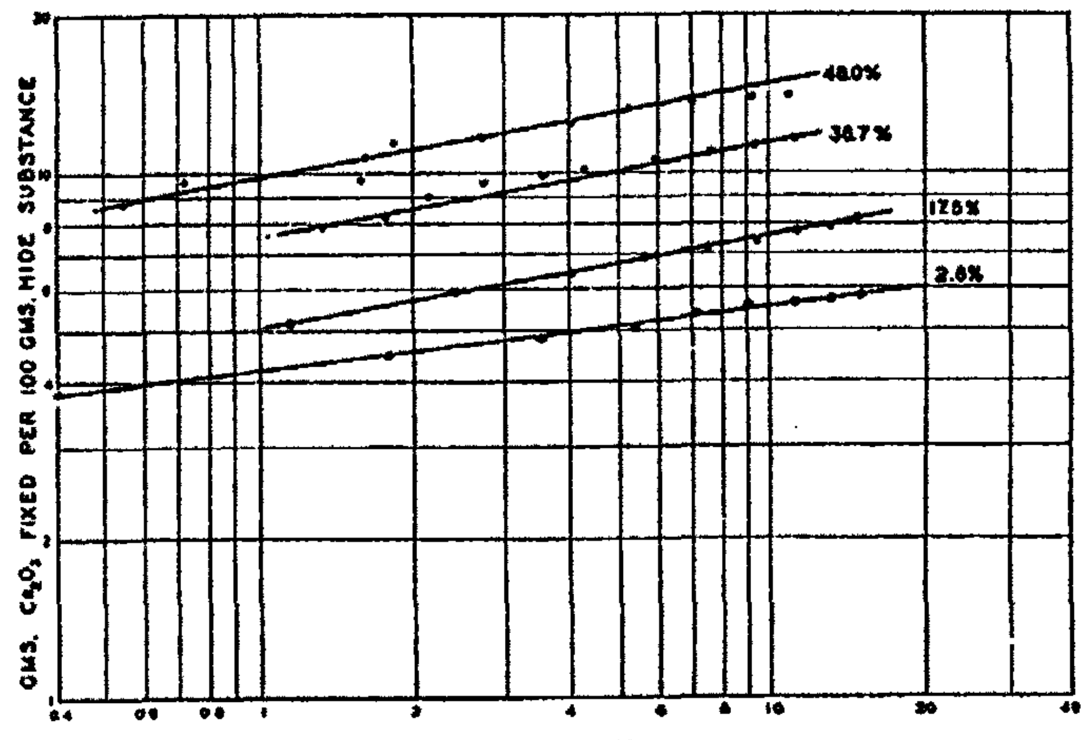

FIG. 2. Same values as in figure 1 plotted on a logarithmic scale

3. The total acid SO_4 of the system is now divided between the protein, the deposited chrome complex, and the spent liquor. The sum of the protein-bound acid and chrome-bound acid can be determined by analyt-

ical methods. Direct methods for quantitatively separating these two fractions have not been successful, but indications are that under at least some conditions, the deposited chrome complex may be in the neighborhood of 66⅔ per cent basic.

Applying an indirect method, assuming that the deposited chrome is a 66⅔ per cent basic compound, and using this factor as the common denominator for data presented in tables 1 and 2, we can calculate values for the "protein-bound" acid present in the skin. Values of deposited chrome are determined by direct analysis. Values for total combined acid SO_4 in the skin may be determined by direct analysis, or, this value may be derived by calculation, since the basicity of the tanned leather is invariably the same as the basicity of the tan liquor employed. Deducting from the total acid SO_4 fixed by the tanned skin that amount required to bring the deposited chrome to 66⅔ per cent basicity, the "protein-bound" acid SO_4 is derived. Deducting the total acid SO_4 bound by the skin from the total available acid given, the available acid in the spent liquor is derived.

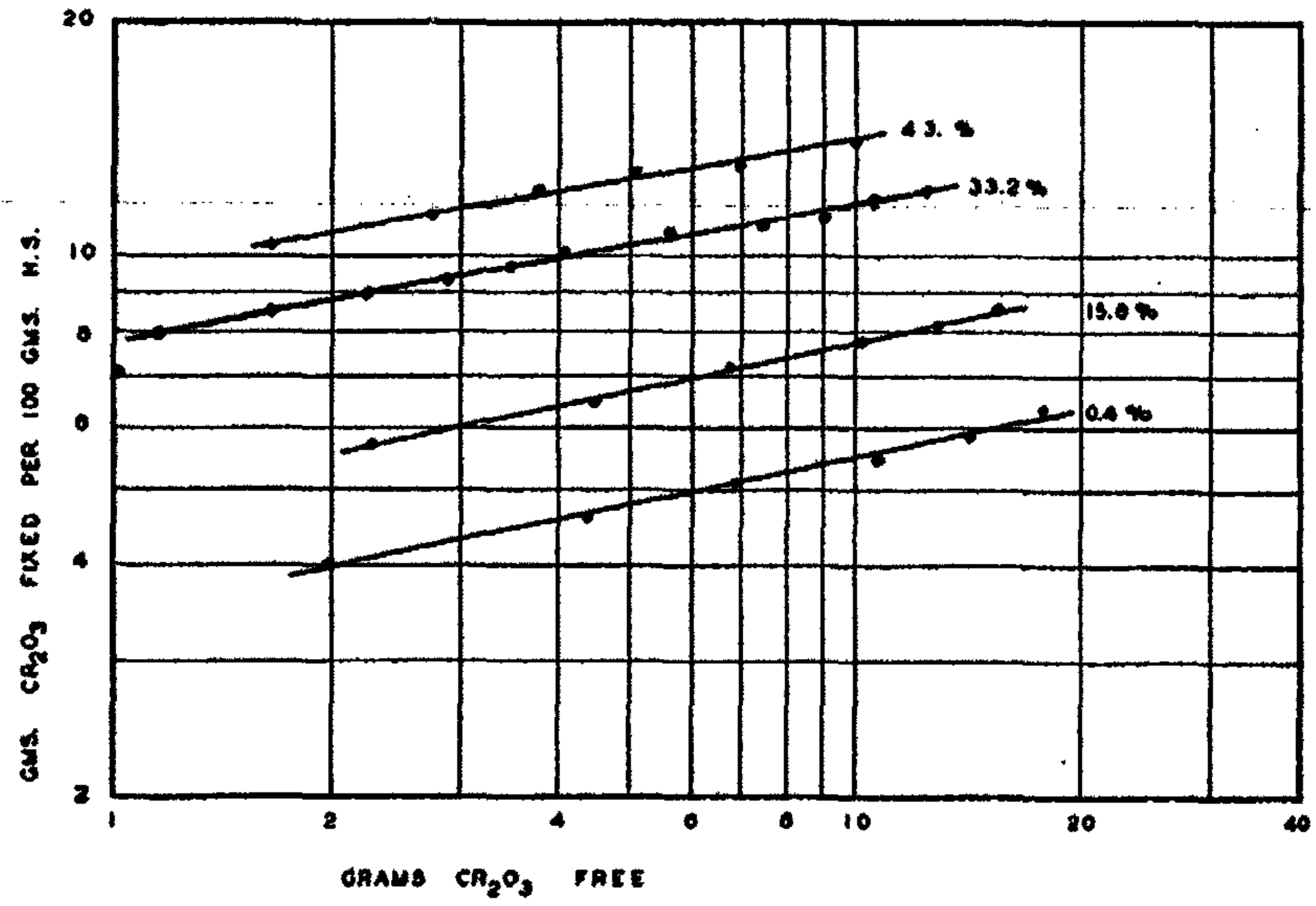

Fig. 3. Plot of a second series of four liquors

Since we wish to show values for the distribution or equilibrium of acid SO_4 between the tanned skin protein and the acid SO_4 of the spent liquor, we find that in the spent liquor the *total* acid SO_4 is not available for reaction with the protein. Only that fraction of acid available by hydrolysis of the basic chrome compound can be considered, and this easy hydrolysis

TABLE 1

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
2.8 per cent basic									
4.22	3.82	0.40	7.77	2.66	5.11	7.04	2.41	4.63	0.48
6.32	4.52	1.80	11.64	3.99	7.65	8.32	2.85	5.47	2.18
8.45	4.87	3.58	15.55	5.33	10.22	8.96	3.07	5.89	4.33
10.55	5.12	5.43	19.41	6.65	12.76	9.42	3.23	6.19	6.57
12.63	5.42	7.21	23.23	7.96	15.27	9.97	3.42	6.55	8.72
14.77	5.62	9.15	27.20	9.32	17.88	10.35	3.54	6.81	11.07
16.85	5.66	11.19	31.00	10.63	20.37	10.41	3.57	6.84	13.53
18.95	5.75	13.20	34.90	11.95	22.95	10.59	3.63	6.96	15.99
21.10	5.82	15.28	38.80	13.30	25.50	10.71	3.67	7.04	18.46
17.5 per cent basic									
6.36	5.21	1.15	9.94	4.01	5.93	8.14	3.29	4.85	1.08
8.45	6.00	2.45	13.20	5.33	7.87	9.37	3.78	5.59	2.28
10.58	6.49	4.09	16.54	6.67	9.87	10.14	4.09	6.05	3.82
12.67	6.94	5.73	19.80	7.99	11.81	10.85	4.38	6.47	5.34
14.81	7.23	7.58	23.14	9.34	13.80	11.30	4.56	6.74	7.06
16.90	7.40	9.50	26.40	10.65	15.75	11.56	4.67	6.89	8.86
19.04	7.76	11.28	29.72	12.00	17.72	12.13	4.89	7.24	10.48
21.12	7.90	13.22	33.00	13.32	19.68	12.35	4.98	7.37	12.31
23.28	8.22	15.06	36.37	14.67	21.70	12.85	5.18	7.67	14.03
36.7 per cent basic									
9.30	7.98	1.32	11.35	5.86	5.49	9.56	5.03	4.53	0.96
10.36	8.58	1.78	12.41	6.53	5.88	10.28	5.41	4.87	1.01
11.39	9.22	2.17	13.65	7.18	6.47	11.05	5.81	5.24	1.23
12.41	9.64	2.77	14.87	7.82	7.05	11.55	6.08	5.47	1.58
13.44	9.83	3.61	16.10	8.47	7.63	11.78	6.20	5.58	2.05
14.50	10.16	4.34	17.37	9.14	8.23	12.18	6.41	5.77	2.46
16.55	10.58	5.97	19.84	10.43	9.41	12.68	6.67	6.01	3.40
18.65	10.98	7.67	22.34	11.75	10.59	13.16	6.93	6.23	4.36
20.70	11.32	9.38	24.80	13.05	11.75	13.56	7.14	6.42	5.33
22.80	11.61	11.19	27.31	14.37	12.94	13.91	7.32	6.59	6.35

(a) Grams Cr_2O_3 given.
(b) Grams Cr_2O_3 fixed.
(c) Grams Cr_2O_3 unfixed.
(d) Total grams acid SO_4 present.
(e) Grams acid SO_4 to make (a) 66⅔ per cent.
(f) Grams available acid SO_4, (d) − (e).
(g) Acid SO_4 to make (b) same basicity as original liquor.
(h) Acid SO_4 to make (b) 66⅔ per cent.
(i) Protein-bound acid SO_4, (g) − (h).
(j) Unfixed acid SO_4 in system, (f) − (i).

TABLE 1—*Concluded*

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
46 per cent basic									
9.30	8.75	0.55	9.51	5.86	3.65	8.94	5.52	3.42	0.23
10.33	9.61	0.72	10.56	6.51	4.05	9.82	6.06	3.76	0.29
11.35	9.76	1.59	11.60	7.16	4.44	9.98	6.16	3.82	0.62
12.37	10.75	1.62	12.65	7.80	4.85	10.99	6.78	4.21	0.64
13.35	11.50	1.85	13.65	8.42	5.23	11.75	7.25	4.50	0.73
14.47	11.75	2.72	14.80	9.13	5.67	12.02	7.41	4.61	1.06
16.51	12.45	4.06	16.89	10.41	6.48	12.73	7.85	4.88	1.60
18.56	13.29	5.27	18.99	11.70	7.29	13.59	8.38	5.21	2.08
20.66	13.65	7.01	21.11	13.03	8.08	13.95	8.61	5.34	2.74
22.70	13.86	9.23	23.21	14.31	8.90	14.17	8.74	5.43	3.47
24.76	13.99	10.77	25.31	15.61	9.70	14.30	8.82	5.48	4.22

practically ceases with the separation and precipitation of the 66⅔ per cent basic compound.

By plotting these derived values for protein-bound acid SO_4 and potentially available acid SO_4 on a logarithmic scale, we find that, regardless of the basicity of the liquor employed, the points fall on a common line, as shown in figure 4. This experimental evidence seems conclusive proof that the deposited chrome complex actually is a 66⅔ per cent basic compound.

With this important fact established it is quite apparent that the critical factor involved, or the primary regulatory force for tannage, is the ability of protein to combine with acid, for an acid equilibrium is reached—protein-bound acid in equilibrium with potentially available acid in the spent liquor—with a resulting chrome equilibrium determined and regulated by the acid equilibrium.

It follows then that any procedure which will change this acid equilibrium will change the quantity of deposited chrome; this has been demonstrated experimentally. Adding alkali to the liquor system raises the level of chrome fixation. The addition of acid lowers the level of chrome fixation, and a complete detanning has been accomplished by repeated extractions with sulfuric acid and sodium sulfate solutions, the sodium sulfate being used to repress the protein swelling that occurs as the tannage is reversed. It is also of interest to note that in every instance the final effect produced in chrome fixation, adequate time being allowed to establish equilibrium, is the effect of the total acid-chrome ratio in the system regardless of the order of addition of extra acid or alkali to the chrome liquor.

This behavior shows clearly that the combination between chrome and hide substance is readily reversible, and is therefore in accord with the

TABLE 2

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
0.4 per cent basic									
6.00	4.01	1.99	11.31	3.78	7.53	7.56	2.53	5.03	2.50
9.00	4.61	4.39	16.96	5.67	11.29	8.70	2.91	5.79	5.50
12.00	5.12	6.88	22.61	7.56	15.05	9.66	3.23	6.43	8.62
16.00	5.44	10.76	30.16	10.09	20.07	10.26	3.43	6.83	13.24
20.00	5.84	14.16	37.70	12.60	25.10	11.01	3.68	7.33	17.77
24.00	6.33	17.67	45.25	15.12	30.13	11.94	3.99	7.95	22.18
15.8 per cent basic									
8.00	5.72	2.28	12.75	5.04	7.71	9.12	3.61	5.51	2.20
11.00	6.48	4.52	17.55	6.94	10.61	10.33	4.09	6.24	4.37
14.00	7.22	6.78	22.31	8.83	13.48	11.51	4.55	6.96	6.52
18.00	7.82	10.18	28.70	11.35	17.35	12.46	4.93	7.53	9.82
21.00	8.14	12.86	33.50	13.25	20.35	12.97	5.13	7.84	12.41
24.00	8.58	15.42	38.30	15.14	23.16	13.68	5.41	8.27	14.89
33.2 per cent basic									
8.16	7.08	1.08	10.31	5.14	5.17	8.96	4.47	4.49	0.68
9.18	8.03	1.15	11.60	5.78	5.82	10.15	5.06	5.09	0.73
10.20	8.55	1.65	12.90	6.43	6.47	10.81	5.40	5.41	1.06
11.20	8.96	2.24	14.16	7.06	7.10	11.33	5.65	5.68	1.42
12.25	9.34	2.91	15.50	7.72	7.78	11.80	5.89	5.91	1.87
13.25	9.77	3.48	16.75	8.35	8.40	12.35	6.16	6.19	2.21
14.27	10.19	4.08	18.05	9.00	9.05	12.88	6.42	6.46	2.59
16.32	10.67	5.65	20.63	10.29	10.34	13.49	6.73	6.76	3.58
18.35	10.90	7.45	23.20	11.57	11.63	13.78	6.88	6.90	4.73
20.40	11.28	9.12	25.80	12.86	12.94	14.25	7.11	7.14	5.80
22.45	11.88	10.57	28.40	14.15	14.25	15.02	7.49	7.53	6.72
24.50	12.12	12.38	31.00	15.45	15.55	15.32	7.64	7.68	7.87
43 per cent basic									
12.00	10.35	1.65	12.95	7.57	5.38	11.16	6.52	4.64	0.74
14.00	11.25	2.75	15.11	8.83	6.28	12.14	7.09	5.05	1.23
16.00	12.17	3.83	17.27	10.10	7.17	13.13	7.67	5.46	1.71
18.00	12.87	5.13	19.44	11.35	8.09	13.88	8.12	5.76	2.33
20.00	12.98	7.02	21.60	12.61	8.99	14.00	8.19	5.81	3.18
24.00	13.95	10.05	25.90	15.14	10.76	15.15	8.79	6.36	4.40

(a) Grams Cr_2O_3 given.
(b) Grams Cr_2O_3 fixed.
(c) Grams Cr_2O_3 unfixed.
(d) Total grams acid SO_4 present.
(e) Grams acid SO_4 to make (a) 66⅔ per cent.
(f) Grams available acid SO_4, (d) − (e).
(g) Acid SO_4 to make (b) same basicity as original liquor.
(h) Acid SO_4 to make (b) 66⅔ per cent.
(i) Protein-bound acid SO_4, (g) − (h).
(j) Unfixed acid SO_4 in system, (f) − (i).

current conceptions of adsorption reactions. This is contrary to the prevailing assumption which has frequently been presented as evidence that adsorption was not involved in chrome fixation.

As further proof that in chrome tanning we are dealing with a reversible adsorption, there may be cited the fact that if equal quantities of skin substance are tanned with equal quantities of basic chrome sulfate but the chrome is given in single concentration in one case and double in the other, more chrome will, of course, be fixed by the double concentration. However, if water is now added to the system so that the double concentration is diluted to single, and tanning is again run to equilibrium, the skin substance will lose fixed chrome until this value equals that of the original single concentration.

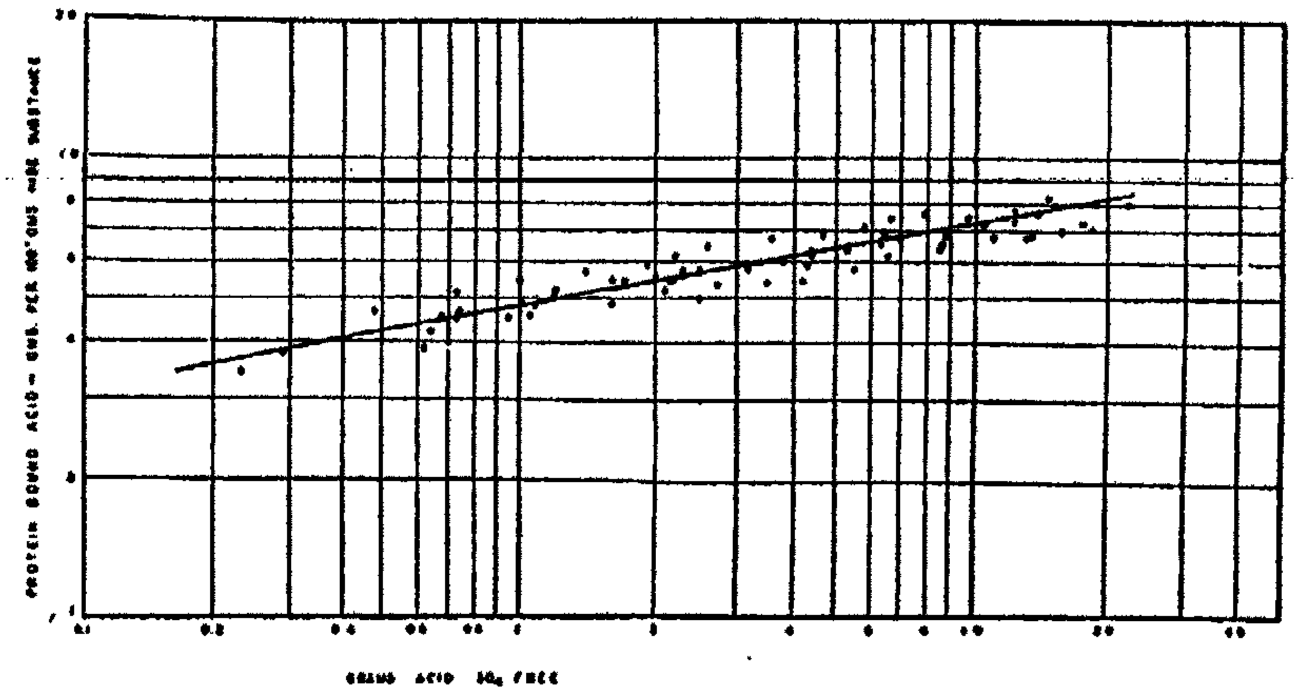

FIG. 4. Derived values for protein-bound acid SO_4 and potentially available acid SO_4 plotted on a logarithmic scale.

The conditions arising from the plant practice of pickling with acid prior to subjecting skins to the action of chrome liquors is no exception to the conditions outlined above, although upon first thought it does not seem reasonable to expect protein that has taken up a maximum amount of acid to be able to take up further amounts and function as outlined above. This protein-bound acid comes into equilibrium with free acid in the surrounding solution; when the pickled protein is passed into the chrome liquor, there is an immediate flow of acid from the pickled skin to the liquor, and the liberated acid immediately enters into combination with the chrome, forming a chrome sulfate liquor of a lowered basicity. The net effect is that which would be obtained if the acid were introduced directly to the liquor and not carried into the liquor through the protein.

In connection with the plant practice of pickling, the common practice is to employ sodium chloride with the pickle acid to prevent swelling. The question is immediately raised as to what effect this added salt will have on subsequent chrome fixation. It has been our purpose in these studies to eliminate chloride ions from the system, consequently we have used only sodium sulfate as a neutral salt. In liquors prepared from sodium bichromate there naturally will be one molecule of sodium sulfate for every Cr_2, so when such liquors are used in an experimental series involving increasing amounts of chrome, we unfortunately have two variables. The alternative is to prepare a strictly C.P. chrome sulfate containing no neutral salts, which is a rather tedious process. The fortunate thing, however, is that the presence of any reasonable quantity of sodium sulfate apparently does not materially influence the final acid distribution equilibrium or chrome distribution values discussed above.

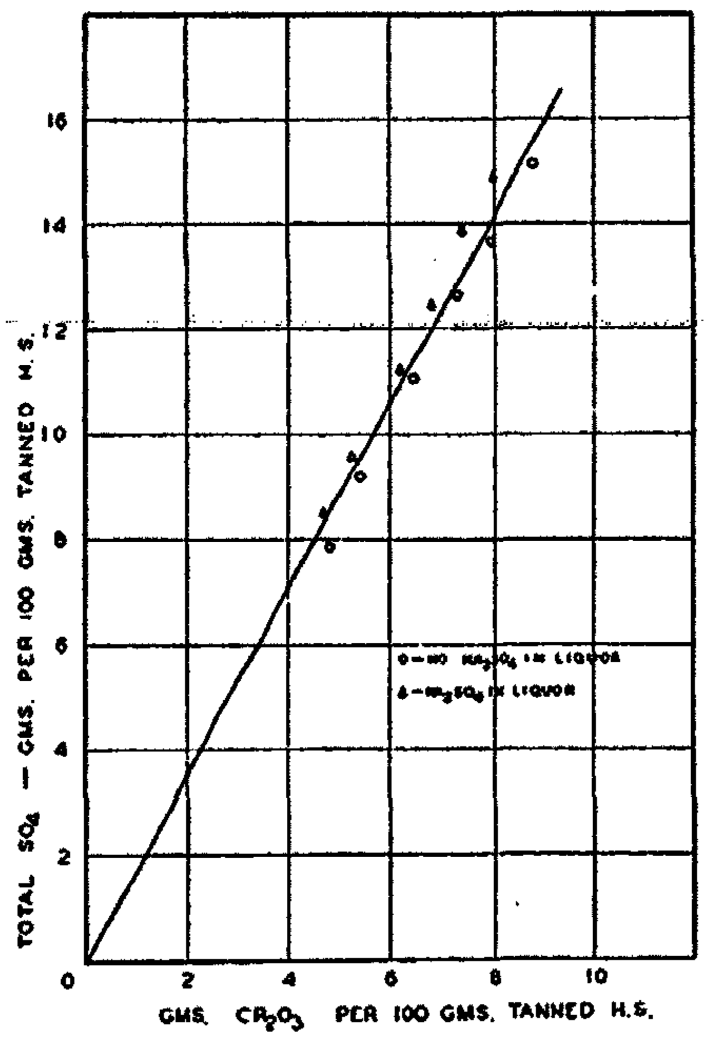

FIG. 5. Experimental results obtained with a pure chrome sulfate liquor and with the same liquor to which anhydrous sodium sulfate had been added.

Figure 5 shows experimental results from a pure chrome sulfate liquor of 7.2 per cent basicity prepared from C.P. chromic acid, sulfuric acid, and hydrogen peroxide compared with a like series with the same liquor to which was added anhydrous sodium sulfate in the proportion of 32 g. per 100 grams of actual hide substance.

From the analytical standpoint, the results are of interest, for while the total sulfate may be extracted from tanned leather and accurately determined, the differentiation between acid sulfate and neutral sulfate is much less satisfactory. Figure 5 shows these values for *total* sulfate, found after the two sets of samples had been removed from the liquor, pressed, dried and analyzed, and plotted against grams of chrome fixed. At least for the conditions involved in this experiment, the sodium sulfate did not function in an important manner with regard to chrome fixation and, further, negligible amounts of the neutral salt were observed remaining in the tanned material after pressing.

SUMMARY

1. Basic chrome sulfate tanning is a typical reversible adsorption process. The amount of chrome which will be fixed by skin under given conditions in tanning may be calculated and predicted as such.

2. When skin is agitated with a basic chrome sulfate solution, the solution diffuses into the skin. The protein of the skin combines with and removes acid from the solution. When sufficient acid is removed, the chrome compound (which requires a certain acid concentration for its solution) becomes insoluble and is deposited in and on the collagen fibers and fibrils which compose the skin.

3. The amount of chrome which will be deposited is quantitatively related to (*a*) the amount of acid which the protein of the skin can remove from the solution and (*b*) the concentration of free or potentially free acid present in the system.

4. Quantitative evidence shows that the acid binding power of the protein of chrome tanned leather is greater than is that of original untanned skin protein. The reason for this is not yet completely understood.

5. The chrome compound fixed by the skin is of $66\frac{2}{3}$ per cent basicity.

6. Despite many published theories on the subject, it is not yet known whether chrome fixation occurs at specific points in the collagen molecule.

In employing the term "adsorption," we are aware that the ultimate differences—if any, and whether of degree or kind—between adsorption and "chemical" processes are not yet clear. Meanwhile, and until such knowledge is available, it is now abundantly clear, however, that chrome tanning is a typical reversible adsorption process rather than what would be termed stoichiometric.

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PROPERTIES OF BUILT-UP FILMS OF BARIUM STEARATE[1]

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In a recent paper Langmuir, Schaefer, and Wrinch (4) described briefly the method which they used to measure the thickness of a monolayer of egg albumin transferred from a water surface to a metal slide. They prepared a chromium-plated slide for this experiment by coating the slide with built-up films of barium stearate which reflected vivid interference colors. They then transferred the monolayer of egg albumin from the water surface to the slide, depositing the albumin on top of the barium stearate, and the change of interference colors produced by the layer of albumin molecules afforded a measure of the thickness of the layer. The thickness was 20 A.U. when the surface pressure exerted on the layer was 30 dynes per centimeter. This paper will describe some of the optical properties of thin films and will show how these properties have been used to obtain very great sensitivity in the method of measuring small increments of film thickness.

The films used in thickness measurements are built by depositing successive monolayers of barium stearate on a chromium-plated slide, by a method which has been described in previous papers (1, 2). The monolayers are formed by spreading stearic acid on water containing a dissolved barium salt, the pH of the water being usually held at about 7.0 by adding a small concentration of potassium bicarbonate to the solution. The layers are transferred from the water surface to the slide by a dipping process, in which one layer is deposited as the slide travels down into the water and the next layer as it rises from the water. Films covering an area of 5 x 2.5 cm. can easily be built at a rate of 20 layers per minute and smaller areas at rates of 40 to 60 layers per minute.

The films are commonly built in a series of steps of increasing thickness, several steps being built on one slide. This is done by controlling the depth to which the slide is dipped into the water. For example, a series of eleven steps having 35, 37, . . . 55 layers is used as a color gauge in many types of measurement, since this series reflects the interference colors

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

which range from yellow at 35 layers through red at 45 layers to a green-blue at 55 layers. This series is built on a 7.5 x 2.5 cm. slide by holding the slide with the long edge vertical and dipping it to a depth of 5.5 cm. until 35 layers are built up by repeated dips. The depth to which it is allowed to travel down into the water is then decreased by progressive steps of 0.5 cm. as two more layers are added on each down-and-up journey. The dividing line between neighboring steps is straight and extremely sharp. The entire series can be built in two to three minutes.

The colors of the light reflected by films built on polished chromium are most brilliant when the films are viewed by polarized light at angles near the grazing angle. The increased brilliancy under these conditions is due to multiple reflections in the film and is explained by the curves in figure 1. These curves are a plot of the light intensity reflected by the film as a function of film thickness when the films are viewed by monochromatic polarized light at an angle of reflection of 80°. The curves were drawn from rough estimates of the intensity made by the eye without the use of a photometer. The source of light was a 6000-lumen sodium vapor lamp, $\lambda = 5893$ A.U. It was polarized by means of a screen of polarizing material of the type manufactured by the Land-Wheelwright Co.

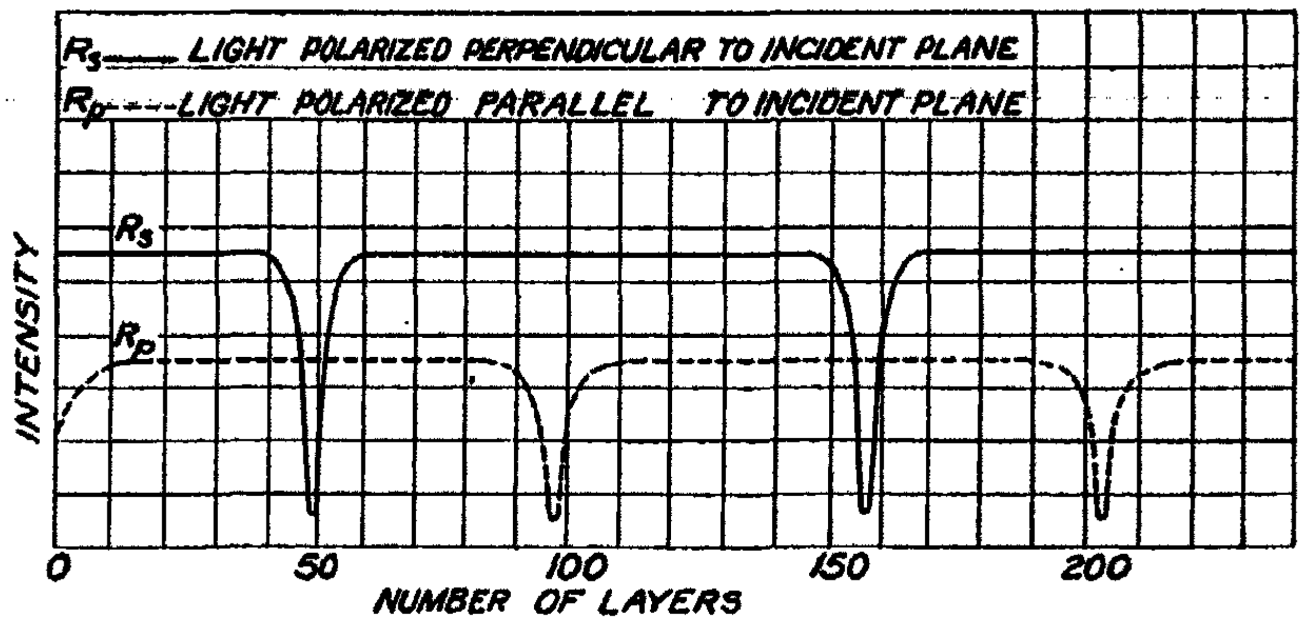

FIG. 1. Intensity minima for monochromatic light reflected from a step-series of barium stearate films built on a polished chromium surface. Angle of reflection is 80°. Wave length of light is 5893 A.U.

The solid line in figure 1 shows the intensity distribution that is seen when a step-series is viewed by light R_s polarized in a plane perpendicular to the incident plane, that is, by light having its electric vector vibrating in a direction parallel to the film surface. The step having 49 layers is very dark, nearly black, and the two neighboring steps having 47 and 51 layers are seen to be much brighter. The sharpness of the minimum depends to a great degree on the angle at which the film is viewed. At angles of reflection of 80 to 83° only about four two-layer steps can be seen on either side of the minimum. Beyond these steps the intensity distribution curve follows a flat maximum and the separate steps are invisible, since it is the contrast between neighboring steps which renders the steps visible to the eye when monochromatic light is used.

When white light illuminates the steps the minima for the various wave lengths appear at successive film thicknesses. Thus the minimum for blue light of wave length $\lambda = 4500$ A.U. occurs at 37 layers, so that the color of the light reflected by this step is yellow. Since the minima are sharp for each wave length one obtains a high resolving power for the different colors reflected by a series of steps built in two-layer intervals in the region from 35 to 55 layers.

When the direction of polarization of the light is changed so that this series is illuminated by light R_p, polarized parallel to the incident plane, the bright colors disappear and only a yellow tinge is seen in the thicker steps of the series. This condition is represented by the dotted curve in figure 1. The contrast between neighboring steps is then imperceptible in the 35 to 55 layer region, but is very great in the region from 87 to 107 layers. The film thicknesses at which minima occur for the ray R_s are proportional to $\lambda/4$, $3\lambda/4$, $5\lambda/4$, etc., and for the ray R_p are proportional to $\lambda/2$, λ, $3\lambda/2$, etc. The difference between the two series of interference minima arises from the fact that light commonly undergoes a phase change when it is reflected at the boundary between two media. In the case of the ray R_s at large angles of reflection, the phase change occurring where light is reflected from the upper surface of the film is nearly the same as where light is reflected from the lower surface, whereas for the ray R_p the two reflections have a difference of phase of nearly 180°. This difference of phase is equivalent to a path difference of nearly one-half a wave length between the ray reflected from the upper surface and the ray reflected from the lower surface of the film. The path difference between the two rays is

$$d = 2nt \cos r \tag{1}$$

where n is the refractive index, t the thickness of the film, and r the angle of refraction of light in the film. Intensity minima occur at thicknesses given by

$$nt \cos r = m\lambda/4 \tag{2}$$

where m has the values 1, 3, 5, . . . for the R_s ray and 2, 4, 6, . . . for the R_p ray. A more detailed study of this subject has been given in another paper (2).

The sharpness of the intensity minima supplies the means whereby small increments of film thickness can be made visible. When a film of unknown optical thickness is compared with a color gauge built in two-layer steps, the film and the color gauge being built on separate slides, the eye can measure differences of thickness by means of color with a probable error of about 0.5 layer. The thickness of one layer is 24.4 A.U. In order to test one's eyesight for the differences which can be detected it is useful to employ vernier color scales which are built of barium palmitate (C_{16}), barium stearate (C_{18}), and barium arachidate (C_{20}). Since the thickness per layer of these substances is closely in the ratio 16:18:20, they provide three different color scales which may be combined in any desired way for use as verniers.

Greater sensitivity is obtained by illuminating films with sodium light than with white light. Differences of thickness equal to 0.2 layer of barium stearate have been made plainly visible to the eye by the following procedure: When a slide on which films are built is turned so that the angle of incidence i decreases from 80 to 73°, the corresponding angle of refraction ($n = 1.495$) changes from $r = 41°12'$ to $r = 39°46'$, and cos r increases 2.1 per cent in value. Therefore, if the minimum lies exactly at 49 layers when seen at 80°, as shown in curve II of figure 2, it shifts to 48 layers at 73° in accordance with equation 2. The neighboring steps having 47 and 49 layers on curve I then match exactly. The intensities of these steps are shown by the open circles on curve I. If an increment of thickness equal to 0.2 layer is added to the film, these neighboring steps no longer match at 73°, the 49.2-layer step being brighter than the 47.2-layer step. Their intensities are shown on the curve by solid circles. If the slide is turned to an angle slightly greater than 73°, the steps again match exactly. It is always possible to find an angle at which two neighboring steps match. The accuracy with which small increments can be detected is usually greater when the method of curve I is employed, in which the minimum lies halfway between two steps, than when the minimum lies at one of the steps as shown in curve II and the series of three steps shown by squares is used to estimate small displacements of the minimum.

The experiment in which known differences of thickness equal to 0.2 layer of barium stearate were observed was performed in the following manner: A step-series of barium stearate was built in two-layer intervals by dipping the slide in the usual way with the long edge of the slide perpendicular to the water surface. The slide was then turned and dipped with the long edge horizontal while three steps of barium arachidate having 2, 4, and 6 layers were built on top of the stearate layers, a part of the stearate being left untouched. The boundaries of the arachidate films therefore ran at right angles to the stearate boundaries, forming a checkerboard of color. The steps which contained 45 and 47 layers of stearate plus 2 layers of arachidate had thicknesses equal to 47.2 and 49.2 layers of stearate. Similarly in the second row, having 4 layers of arachidate, the 43- and 45-layer steps of stearate were increased to 47.4 and 49.4, and in the third row there were steps equal to 47.6 and 49.6 layers. The slide was held at an angle at which the 47- and 49-layer steps of the uncoated stearate matched exactly. It could then be seen that the 47.2 and 49.2 steps did not match exactly, the 49.2 being slightly brighter than 47.2, and the contrast was progressively greater in the rows having the 0.4- and 0.6-layer increments. The contrast was sufficiently great to make it possible to estimate thicknesses having a value halfway between these successive increments. This means that adsorbed layers of molecules or atoms having an optical thickness of 5 A.U. or more can be made visible to the eye without the aid of optical apparatus, and can be measured with a probable error of about 2.5 A.U. By the use of a microphotometer to measure the intensities of the steps as a function of the angle of incidence, the accuracy of measurement of thickness could undoubtedly be increased at least tenfold.

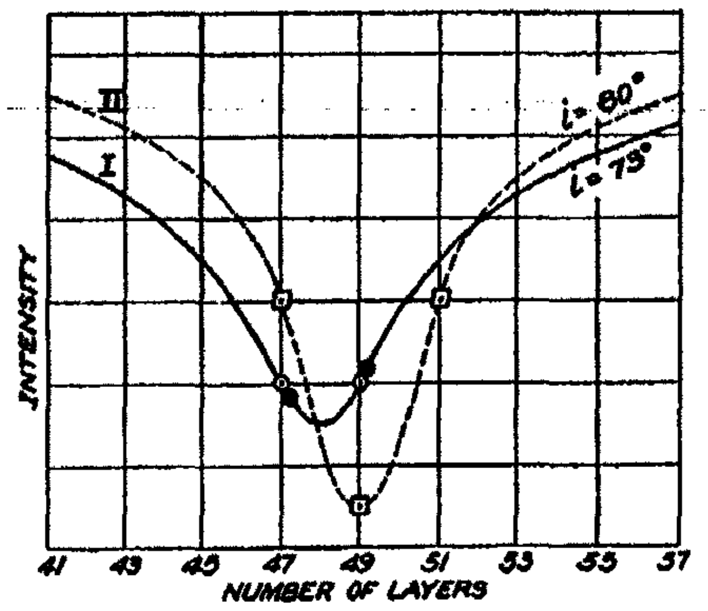

FIG. 2. Intensity minimum for step-series of films of barium stearate built on polished chromium. Films seen by ray R_s of sodium light at angles of incidence $i = 80°$ and 73°.

The term "optical thickness" is defined as the product of actual thickness and refractive index of the film. The thickness measured by means of interference colors is the optical thickness given by the product nt in equation 2, and the refractive index is also used to calculate values of cos r in equation 2 from observed values of the angle of incidence i. Therefore, in order to determine the actual thickness it is necessary to know the refractive index. Fortunately the refractive indices of built-up films of many organic substances do not vary greatly from the refractive index of barium stearate.

Built-up films of barium stearate are birefringent, the refractive index of the ordinary ray, which is the R_s ray, being 1.495 for sodium light. The intensity minima seen with the extraordinary ray R_p are not ordinarily used for interference measurements, since the refractive index of this ray increases with increasing angles of incidence, the film being a positive crystal. The refractive index of a series of ten monolayers of egg albumin was found to be the same as that of the ordinary ray of barium stearate, within a possible error of 0.5 per cent.

The method by which refractive indices are measured is illustrated in figure 3. The graphs show the series of interference minima and maxima which are observed when the films are built on glass. The intensity distribution curve for films on glass does not have the sharp minima and flat maxima seen in the case of films on chromium, but follows a sine or cosine curve. The films are seen best by perpendicular light. If the refractive index n_g of the glass is greater than the refractive index n_l of the film, the intensity minima occur at thicknesses which are odd multiples of $\lambda/4n_l$ and the series of alternating minima and maxima is called an α-series.[2] If $n_g = n_l$ the film is invisible, and if $n_g < n_l$ the order of the fringes is reversed and the minima occur at even multiples of $\lambda/4n_l$, the series in this case being a β-series.

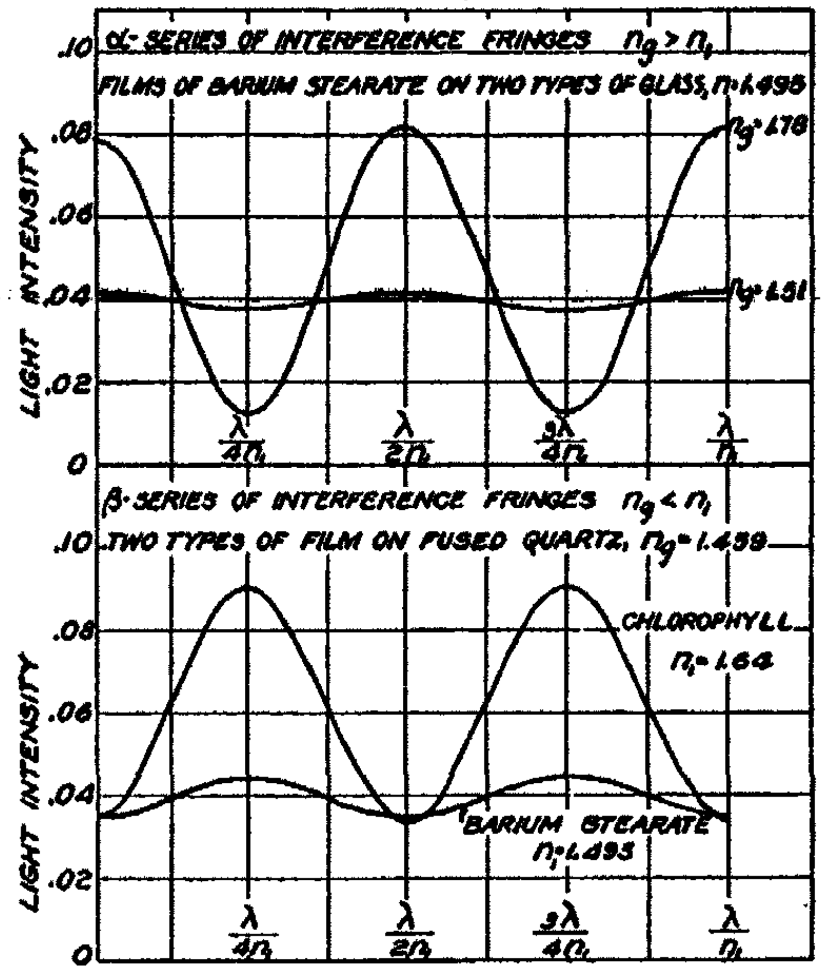

FIG. 3. Interference fringes seen with step-series of films built on glass. Refractive indices of glass, n_g, and of film, n_l, are measured for $\lambda = 5893$ A.U. Films reflect α-series when $n_g > n_l$ and β-series when $n_g < n_l$.

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[2] The notation α and β is used in this paper in place of A and B in a previous paper.

The upper graph in figure 3 shows two examples of the α-series. They represent the light reflected by films of barium stearate built on ordinary microscope slide glass, $n_g = 1.51$, and on glass of very high refractive index, $n_g = 1.78$. The contrast between minima and maxima is 1:6.56 for the glass with $n_g = 1.78$ and 1:1.11 for the glass with $n_g = 1.51$. The lower graph shows the β-series obtained when films of barium stearate and of chlorophyll are built on fused quartz, $n_g = 1.459$. Films of chlorophyll can be built quite readily, a film containing 640 layers having been built with little difficulty. Chlorophyll was found to have a refractive index of 1.64 for sodium light, which is much greater than that of any other substance of which films have been built. However, even in the case of chlorophyll the difference in refractive index from that of barium stearate is only about 10 per cent.

The refractive index of a film is determined by building the film on a series of glasses of known refractive index in steps which reflect successive minima and maxima for sodium light. In the case of barium stearate these steps have 41, 81, 121,... layers when built for use with perpendicular light. When a film is seen to reflect an α-series on one glass and a β-series on another glass, it is known that the refractive index of the film lies between those of the two glasses, and by means of the contrast shown by the maxima and minima in each series it is possible to calculate the difference in refractive index between that of the film and that of the glass.

COPPER USED TO MAKE FILMS DURABLE

In many experiments with substances such as proteins the process of building films requires that the slide be lowered or raised through a surface of water on which no film is spread (4). It was therefore necessary to test barium stearate color gauges to learn whether they could be dipped repeatedly in and out of water through a clean water surface without suffering loss of thickness. The tests showed that when films were built from a water solution containing only barium acetate and potassium bicarbonate, pH = 6.8, the steps suffered a loss of about one layer when dipped for the first time into and out of distilled water. The layer was lost on the up-trip of the slide, the loss being due to the action of the edge of the water surface on the slide as the slide rose through the surface. Repeated dips caused further loss, and after about one hundred dips approximately fifteen layers had been scrubbed off the film by the water edge. Also the surface had been roughened, which was shown by the fact that it scattered light. This difficulty was remedied satisfactorily by adding a small amount of a copper salt to the water. The solution was then $10^{-4}\,M$ in barium acetate, $2 \times 10^{-4}\,M$ in potassium bicarbonate, and $2 \times 10^{-6}\,M$ in copper acetate; the pH was 6.8 to 7.0. After stearic acid was spread on the surface of this solution, it was necessary to wait for

3 to 5 min. before commencing to build stearate films in order to allow sufficient copper to diffuse to the surface. Larger concentrations of copper should be avoided, since a concentration of 10^{-5} M added to a barium solution at a pH of 6.8 will always make the film so rigid that it will not form built-up layers, and usually layers can not be built at a concentration of 5×10^{-6} M.

Optical measurements of barium stearate films built from solutions containing only barium salts and potassium bicarbonate have given the result that the thickness per layer is 24.4 A.U. (2). This thickness is not altered by the presence of copper in a concentration of 2×10^{-6} M. Other substances such as zinc salts dissolved in small concentrations in the water often alter the thickness by 1 to 2 per cent, and in some cases by a larger amount, the thickness being increased in the case of zinc. If a number of films are built from the same solution on different chromium slides, the spacing per layer is the same for all the films, but when the steps are examined by monochromatic light it is seen that the thickness at which the first minimum occurs varies for the different slides within a range of about ± 0.5 layer from the values given in figures 1 and 2. This is a result of the phase change which occurs at the film–chromium boundary, which causes a ray of light R_a to be reflected with the phase which the ray would have if it had penetrated into the chromium to a distance equivalent to 5.7 layers of barium stearate at $i = 80°$. The quantity $N_0 = 5.7$ layers is affected to a small extent by variations in the condition of the chromium surface. Therefore the position of the first minimum is always subject to small variations corresponding to different values of N_0, which tend to displace the curves in figures 1 and 2 slightly to the right or left. For this reason when one wishes to measure the thickness per layer of films of any substance the measurements should be made by studying the *change* in thickness produced by adding a known number of layers to a film prepared on a chromium surface, this change of thickness being wholly independent of N_0.

SKELETON FILMS

Previous papers (2, 4) have described skeleton films which were formed by building up composite layers containing a mixture of barium stearate and stearic acid, and then removing the stearic acid by soaking the film in benzene. The film which remains after this treatment is a skeleton of barium stearate filled with air spaces which have the dimensions of the stearic acid molecule. It has been pointed out that a film of this type could be used as a molecular sieve.

A skeleton film is studied by means of the color of the light which it reflects. When a film which initially contains 50 per cent neutral barium stearate and 50 per cent stearic acid is soaked in benzene until all the stearic acid is removed, the thickness of the film remains the same but the refractive index is greatly lowered, since the spaces initially occupied by stearic acid, having a refractive index of 1.51, are occupied by air. The interference colors reflected by the film show a corresponding change. If the pores of the film are filled with a mineral oil such as Nujol, the color returns to the color of the original film. If a vapor such as octane vapor is brought into contact with the film, the extent to which the color returns toward the original color is a measure of the amount of octane taken up by the film.

A film may be skeletonized by being heated. A previous paper (1) described experiments in which films of barium stearate built at a pH of 8.5 showed a "decrease in thickness" of 10 per cent after being baked for 10 min. in an oven at 100°C. Recent experiments have shown that films baked in this way suffer a decrease only in *optical* thickness, due to a decrease in refractive index. Evidently the stearic acid is removed from the film by evaporation. Films skeletonized by baking are quite imperfect in structure, which is shown by the fact that the films scatter light, whereas films treated with benzene show no appreciable scattering of light.

The speed with which the stearic acid dissolves out of a film is greatly increased by adding a small amount of ethyl alcohol to the benzene. A solution consisting of 1 per cent alcohol and 99 per cent benzene gives good results; larger concentrations of alcohol are apt to injure the film, leaving it fogged in appearance.

The relative percentages of stearic acid and neutral barium stearate (3) contained in a monolayer are fixed by the pH and barium content of the water on which the layer is spread. An attempt was made to form skeleton films by spreading a mixture consisting of 50 per cent stearic acid (or palmitic acid) and 50 per cent cetyl alcohol on water containing barium salts at a pH of 9.0. At this pH all the stearic acid was converted to neutral stearate. Built-up films could be built quite easily, but when these films were soaked in benzene, acetone, and several other solvents for cetyl alcohol the skeleton of barium stearate collapsed, giving a whitish film that was nearly opaque and reflected no interference colors. When it was soaked in alcohol the film remained transparent but shrank at least 10 per cent in actual thickness. Therefore when the pores of the skeleton were filled with oil the increase of optical thickness which was observed was not sufficient to restore the film to its original color.

The process of skeletonizing films can be used as a useful method of analyzing the film for its content of stearic acid or barium stearate. For example, when layers of the type called X-layers are built up, which are deposited only when the slide is lowered into the water through a surface film, no layer being deposited on the up-journey, it has been found that a change takes place in the barium content of the film during the time that the film remains under water. The experiment was made with a solution at a pH of 8.2 that was 10^{-4} M in barium acetate and 3×10^{-3} M in potassium bicarbonate, and to which potassium cyanide was added in a concentration of 5×10^{-5} M to remove possible traces of copper from the water, since Mr. Schaefer has found that X-films are not built if copper is present. When a slide is dipped rapidly through a stearate film spread on this solution, layers of the type called Y-layers are built up, i.e., a layer is deposited as the slide descends and another as it ascends. If the slide remains for 5 to 10 sec. under water after each down-trip, the layers are X-layers. Films containing equal numbers of Y-layers and of X-layers were built on a fused quartz slide, and both types showed a β-series of intensity maxima and minima in accordance with figure 3, the refractive index of X-layers being the same as that of Y-layers. The slide was then immersed in an alcohol–benzene solution, and when it was withdrawn the Y-films were found to have changed to an α-series, indicating a decrease in refractive index to a value less than that of fused quartz, whereas the X-films showed no change. The refractive index of the Y-films was graded from the upper to the lower boundary of the film, the change being greatest near the upper boundary, which was the part of the film which spent only a fraction of a second under water on each up-and-down trip. The decrease in refractive index in this area of the film corresponded to a removal of about 12 per cent of the film. The test shows that the proportion of the film converted to neutral stearate increased from about 88 to 100 per cent during a few seconds' time under water, and that this change was accompanied by a change from the Y- to the X-type of film.

SUMMARY

The use of interference colors to measure small changes of film thickness is described. Films of barium stearate built on a chromium plate in a series of steps having a difference in thickness of two molecular layers between successive steps form an accurate color gauge with which the thickness of monolayers of other substances can be measured. A method is described whereby monolayers having a thickness of 5 A.U. or more are made visible to the eye and can be measured with a probable error of 2.5 A.U. without the use of optical apparatus.

The properties of barium stearate films containing copper and some properties of skeleton films are discussed.

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BUILT-UP FILMS OF PROTEIN AND OF STEROL[1]

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Stimulated by the work of Blodgett (1) on the deposition of fatty acid films on solid slides, the author attempted to deposit films of egg albumin directly on solid surfaces, but without success. The effort was then made to deposit a highly purified preparation of the corn protein, zein.[3] This has been accomplished. Zein was dissolved in 85 per cent ethyl alcohol and spread on a paraffin waxed glass bath containing pure water. A waxed silk thread was used to separate the protein film from the castor oil which was the source of compression (15 dynes per centimeter). A highly polished chromium slide was raised slowly through the protein film by means of a windlass. Deposition was complete, but the slide emerged wet and had to be dried in an oven at a gentle heat. Deposition was again complete when the slide was lowered through the protein film. The slide had always to be dried upon being raised from the bath. Deposition of one hundred layers was accomplished in this manner. They exhibited beautiful colors which, when compared with the colors of a slide on which fatty acids had been deposited, allowed an estimate of the thickness of the protein films to be made. This was calculated to be about 14 A.U. per protein film deposited.

The author is not aware of any surface balance studies done on zein but Hughes and Rideal (2) found a thickness of 12 A.U. for a gliadin film spread on a phosphate buffer at a pH of 5.9. The most remarkable feature about the zein films is that they are strongly hydrophilic, being completely wet by water. This is especially curious when it is remembered that zein is usually considered to be one of the most hydrophobic proteins.

Built-up films of cholesterol were also deposited on polished chromium. The bath was pure water, castor oil was used to compress the surface film,

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[2] With the technical assistance of Mr. Alvin Berman.

[3] By courtesy of Dr. R. A. Gortner.

and the cholesterol was dissolved in petroleum ether. The first film was dried on, and subsequent films deposited rapidly, both with the slide raised or lowered through the surface, and without drying. The films yielded color, but were never as clear and as brilliant as the zein or fatty acid films, being somewhat foggy. They were strongly hydrophobic.

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CERTAIN COLLOIDAL REACTIONS OF CELLULOSE MEMBRANES[1]

40A-18

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Plant cell walls, of which one of the primary constituents is cellulose and in which there are no appreciable accumulations of such materials as lignin or suberin, are referred to as "cellulose membranes." This name is not definitely descriptive, for the cellulose membrane, from the botanical standpoint, is a complex structure both physically and chemically.

The cellulose portion of the cell membranes from various parts of the plant kingdom has been shown to be remarkably uniform in its determined properties. Its relative proportion to the non-cellulosic constituents is, however, highly variable. In certain cells of some of the lower forms the cellulose is present in such slight amounts that its identification requires special adaptations of the usual techniques. The difficulties encountered have their basis not only in the large amounts of non-cellulosic material which prevent the penetration of the reagents to the cellulose, but also in the variable nature of the membrane material with which the cellulose is associated. Efforts to remove the cellulose from these membranes must avoid both its chemical alteration and its loss during the necessary manipulations. The success which usually follows the careful application of these methods has its basis in the comparatively inert and reactive natures of the cellulosic and non-cellulosic constituents, respectively.

A combination of microscopic and microchemical techniques is valuable in obtaining our present information concerning physical relationships of the materials which make up cellulose membranes. The observation of many types of walls of widely differentiated living cells has had a great advantage. It is through the study of a wall in which the relative proportion of cellulosic to non-cellulosic materials is small that we gain the clearest conception of the basic principles of cellulose membrane construction. The membrane of this type is seen to consist of a dense, homogeneous, colloidal mass in the inner regions of which are embedded numbers of uniform sized, ellipsoid particles of cellulose. The difference in the refractive indices of the cellulose particles and of the material which

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

surrounds them is not great, and it is only with carefully adjusted optical equipment that the two membrane components may be clearly distinguished. Magnifications in the neighborhood of 1000 X with lenses of the best quality, microscope slides of colorless glass not more than 0.6 mm. in thickness, carefully arranged specimens, No. 0 cover glasses, and critical illumination with a light beam of low intensity are not merely desirable but necessary for clear definition.

In the living cell the water content of this colloidal portion of the membrane is less than that of the viscous cytoplasm which it surrounds. The approximate amount of water which the membrane contains is shown by its shrinkage during drying. Its hydrophilic properties are, in general, those described by the botanists of the last century as characteristic of "pectic" materials. It is very unlikely that in final chemical analysis all of its basic constituents will meet the requirements of the modern chemical concept of pectic substance.

In comparison with the clear, jell-like appearance of this colloidal portion of the membrane, the cellulose particles are more nearly opaque; and their double refraction in polarized light as well as their ability to diffract x-rays shows that they possess an orderliness of molecular arrangement characteristic of crystalline substances. They are oriented in the membrane almost invariably with their long axes parallel to the surface of the protoplast. In any of the membranes which we have examined they show also a definite orientation with respect to each other. This careful orientation in at least two planes brings about sufficient regularity in crystalline arrangement to produce a weak double refraction of the entire membrane in polarized light, although the particles which are responsible for this effect are surrounded and partially masked by the thick mass of non-doubly refractive colloidal material.

In cellulose membranes in which the proportion of cellulose particles to colloidal wall material is great, the densely packed particles are arranged in single rows, end to end, to form a cellulose fibril in which the particles themselves are no longer distinguishable. In the cotton fiber over 90 per cent of the membrane material may be identified as cellulose. The colloidal matrix so abundant in the type of membrane first described is reduced to a minimum. A thin layer surrounds the entire fiber; thinner layers alternate with the layers of cellulose fibrils in the wall; and determinations resulting from both mechanical and chemical disintegrations of the fibrils show the presence of an even thinner layer around each individual particle. In a membrane so constructed, the colloidal matrix, abundant in the former type of cell, is so greatly reduced in quantity that it takes on the rôle of a cementing material which holds together the particles to form the fibril, and the layers of fibrils, in turn, to form the membrane.

Separate fibrils dissected mechanically from the membrane of the young fiber break down into their constituent particles as a result of further mechanical treatment or through treatment with reagents which are also observed to remove the outer limiting membrane. The surfaces of particles separated mechanically react positively to stains with which the outer limiting membrane stains, and in polarized light they are weakly doubly refractive. When separated by treatment with chemical reagents, as a result of which the surface coating of colloidal material is removed, they no longer react to the same stains and their brightness in polarized light, as well as the sharpness of their outline in ordinary light, is definitely improved. Prolonged treatment with the same fibril-disintegrating reagents shows no effect upon the cellulose particles which we have been able to measure. These observations form the basis of our belief that a comparatively small amount of colloidal material forms a continuous matrix in the membrane of the cotton fiber in which the barely discontinuous mass of particles making up the cellulose component of the membrane is embedded.

The progressive drying of the cotton fiber both before and after the time of the opening of the boll renders the membrane much more resistant to both mechanical and chemical disintegration. The breaking down of the fiber wall may be brought about by many types of reagents. Some of these degrade the colloidal matrix and leave the cellulose particles unaltered. Others bring about the degradation of both the cellulose particles and the colloidal membrane constituents. The successive stages of these reactions may be followed microscopically.

The behavior of the membrane in hydrochloric acid (sp. gr. 1.19) is typical of the first group. Native cotton fibers which have been subjected previously only to mechanical cleaning can be disintegrated into particles with one or more treatments of eighteen to twenty-four hours' duration. Purified cotton linters whose membranes have been rendered less resistant during the purification process react much more quickly to this same treatment. In both instances the membrane materials other than the particles are removed. The ellipsoid shape, size, and microchemical reactions are unchanged (4). The x-ray diffraction pattern is that of native cellulose (5). The use of hydrochloric acid of a slightly higher specific gravity shows that this treatment is on the borderline of cellulose particle hydrolysis. The method as described, however, will furnish large quantities of particles freed from their surrounding materials. The microscopic mounts at the end of the process show merely the cellulose particles in random arrangement, with no evidence of their previous relationships with one another or with the other membrane constituents in the untreated fiber.

Strong sulfuric acid (75 per cent) removes the colloidal phase of the membrane and hydrolyzes the cellulose particles as well. The treatment is drastic and the result almost instantaneous. This hydrolyzed cellulose turns blue in the presence of iodine, and the combined reactions constitute one of our standard tests for cellulose in plant material. If the sulfuric acid is very strong and is applied quickly, the hydrolysis and even the blue coloration are only fleeting. With more careful application (3), the various steps of removal of the inter-particle material, scattering and disarrangement of the particles, and finally the gradual hydrolysis and coloration of the particles can be followed microscopically.

As a result of treatment with both hydrochloric acid and sulfuric acid, the colloidal matrix of the membrane is no longer visible. Phosphoric acid has a decided advantage because of the fact that it merely swells and does not destroy the colloidal matrix and at the same time produces a hydrolysis of the particles, not so rapid as that produced with sulfuric acid. The microscopic appearance of a membrane so treated is more representative of the original membrane components. When iodine is added to a membrane previously treated with 30-60 per cent phosphoric acid, the particles turn blue in the presence of the swollen cementing material which surrounds them.

The information which forms a basis for this description is corroborated by the observed process of membrane formation from the particles which originate in the living cytoplasm. Cellulose particles, surrounded by a thin layer of colloidal material and identical with those described in the mature membrane, occur separately in the cytoplasm of the young cotton fiber. During the process of fiber development, fibrils are formed from single rows of these particles arranged end to end. The fibrils, closely appressed, form the successive layers of the cell membrane of the mature fiber. This general procedure is characteristic of cellulose membrane formation in all of the cells which we have examined in any part of the plant kingdom (1, 2). The many types of physical differentiations found in the various cells appear to be, therefore, the result of different styles of architecture rather than different building materials. Throughout the process of wall formation, the relationship between the cellulose particle and its colloidal coating remains unchanged. The combined groups of observations relating to membrane formation and disintegration constitute the basis for the conception that in the living cell, throughout the cytoplasm as well as the cell membrane, there exists, in varying degrees of density, thickness of layers, and admixture with other materials, a continuous colloidal ground substance in which the various activities peculiar to the life processes of a cell take place.

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PLATE I

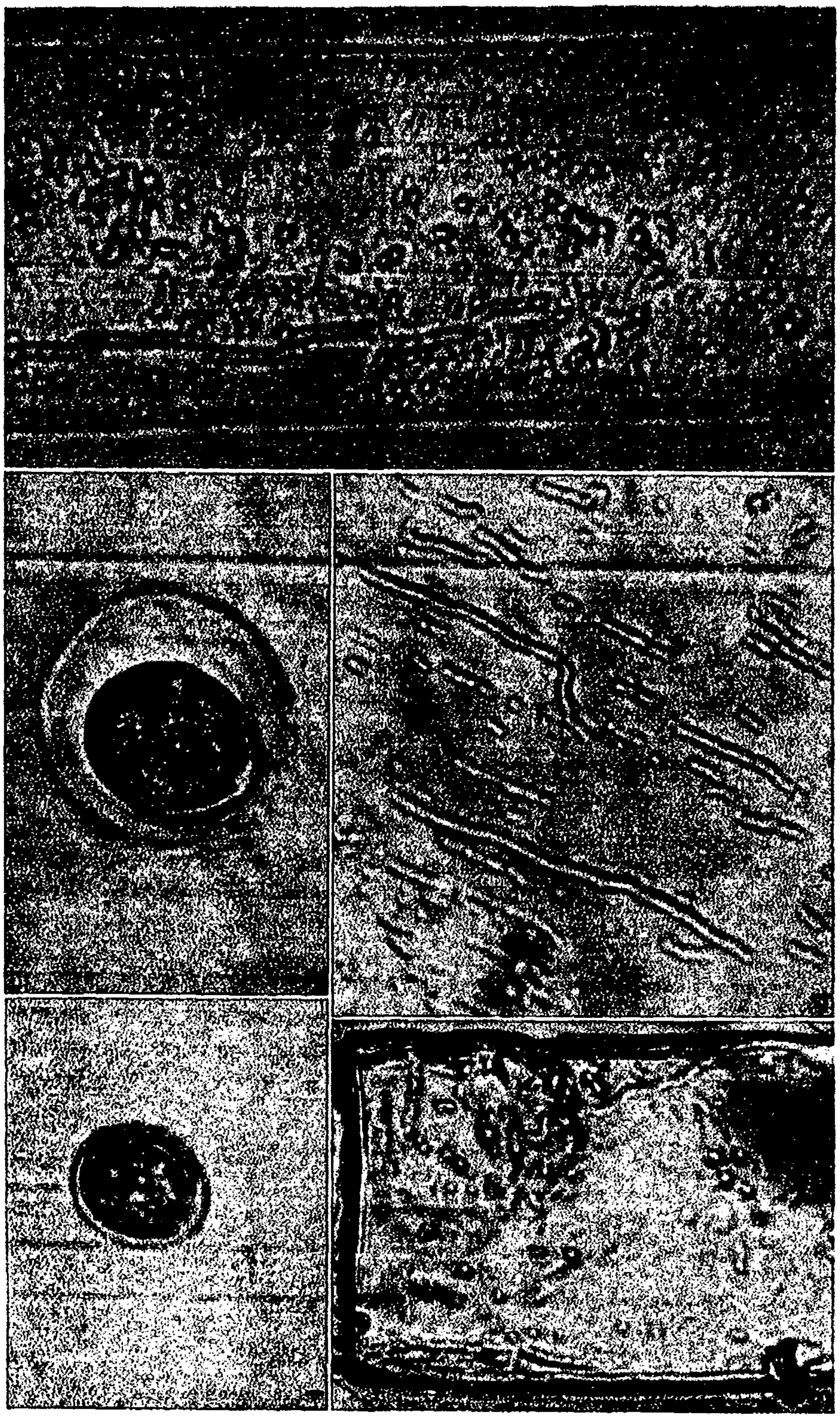
Fig. 1. A single-celled alga (*Chlamydomonas* sp. ?) showing thick layer of colloidal material upon its surface. In the inner regions of this colloidal mass a few layers of cellulose particles are embedded. × 1380.

Fig. 2. The cell shown in figure 1 after careful treatment with phosphoric acid, sulfuric acid, and iodine in potassium iodide. Swelling uniform in protoplast and colloidal matrix. Separated cellulose particles more clearly visible. × 1380.

Fig. 3. Young cell of *Oedogonium* (sp. ?). Cellulose particles and chains of particles in the living cytoplasm. Thinner band of colloidal material upon surface stained with ruthenium red. × 1380.

Fig. 4. Cellulose particles and fibrils dissected mechanically from the membrane of a young cotton fiber. × 1500.

Fig. 5. Very young cotton fiber showing separate cellulose particles, fibril formation from rows of cellulose particles, one layer of the developing cellulose membrane, and the very thin layer of colloidal material which covers the fiber. × 1500.



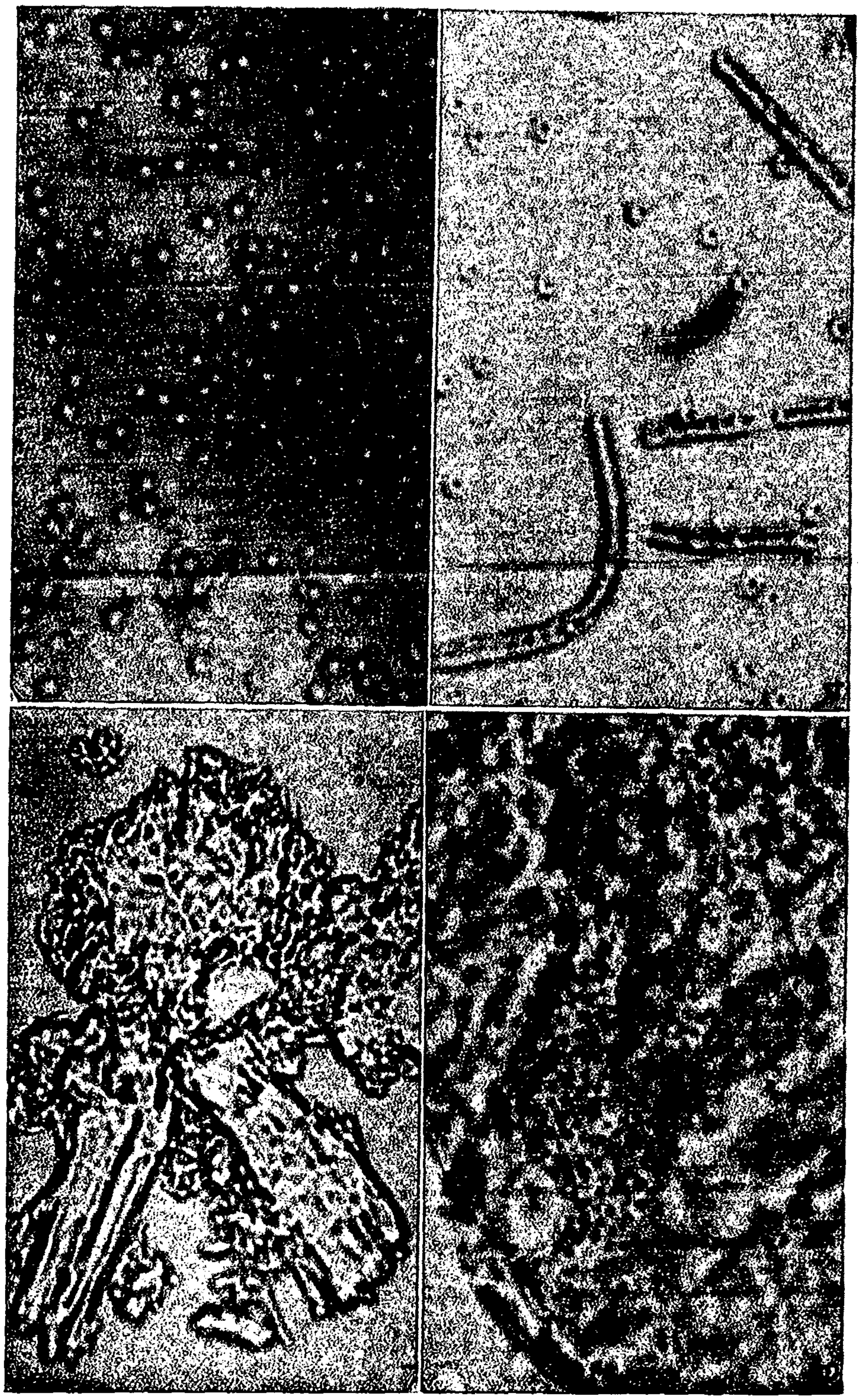


PLATE II

Fig. 1. "Purified cotton linters," during the process of removal of the colloidal matrix by treatment with hydrochloric acid (sp. gr. 1.19), show the disintegration into fibrils and the fibrils, in turn, into particles.

Fig. 2. Early stages of hydrolysis of cellulose particles through treatment with sulfuric acid. Colloidal matrix of the membrane removed bringing about separation of particles.

Fig. 3. Mature cotton fiber treated with phosphoric acid and iodine in potassium iodide. Colloidal matrix swollen and hydrolyzing cellulose particles turn blue in presence of iodine in potassium iodide.

Fig. 4. Single fibrils and cellulose particles dissected mechanically from the membrane of a young *Valonia ventricosa* cell, and treated with phosphoric acid and iodine in potassium iodide. Swelling of colloidal matrix and hydrolysis of the cellulose particles as indicated by their swelling and blue coloration with iodine.

(× 920, enlarged to 1380)

COLLOID CHEMISTRY IN PAPER MAKING[1]

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The paper-makers' composition of cellulose fibers, water, rosin size, and alum, together with such additional components as may be present, including fillers, starch, color, hard water constituents, etc., affords a complexity of colloidal effects which are strongly reflected in the characteristics of the finished product, and much scientific effort is currently being devoted to separating and studying the variables involved.

Given a suspension of cellulose pulp in water, and adding certain of the other materials one by one, it is possible to describe certain consequences as indicated in figure 1, illustrating the system water-pulp-rosin size-alum, the components being added in that order.

In this scheme the interpendence of the several components is illustrated. The relative amounts of free rosin, aluminum resinate, and aluminum oxide present before the furnish reaches the paper machine are to a considerable extent dependent upon the nature of the pulp present, as well as upon time effects; and the relative amounts of the several materials which remain in the finished paper after the filtering action on the machine wire has occurred depend upon many colloidal factors. It is of great technical importance to recognize further that the system as represented in figure 1 is not fixed as to composition. Without going into details, it need only be mentioned that the "white water" (filtrate) from the paper machine is constantly returning to the system, partly to the beater where the paper-making operation itself begins, and partly to the system shortly before it flows to the machine. Such constituents in the system as may become selectively adsorbed in a specific manner, and such of them as may be held to the fibers through electrostatic effects and, finally, such of them as may be flocculated and held by filtering action during sheet formation, will leave a constantly varying filtrate to be returned as make-up water. To the extent to which these variables occur, corresponding variations result in the product, i.e., the finished paper.

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

[2] Research Associate, Institute of Paper Chemistry, Appleton, Wisconsin.

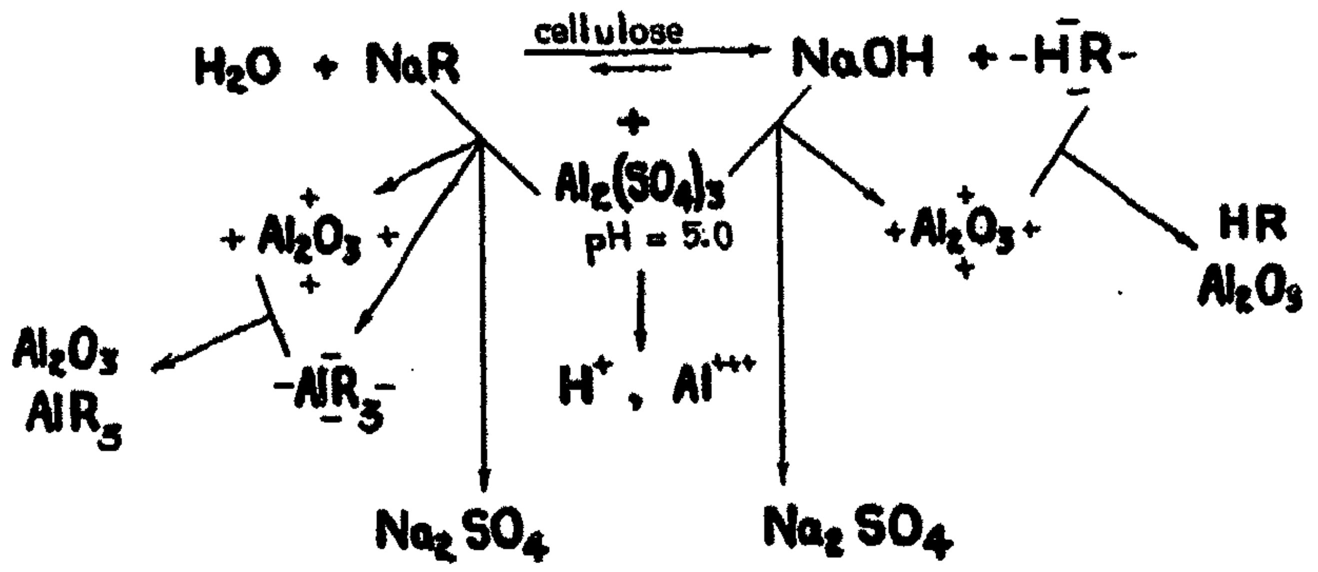

FIG. 1. The system water-pulp-rosin size-alum

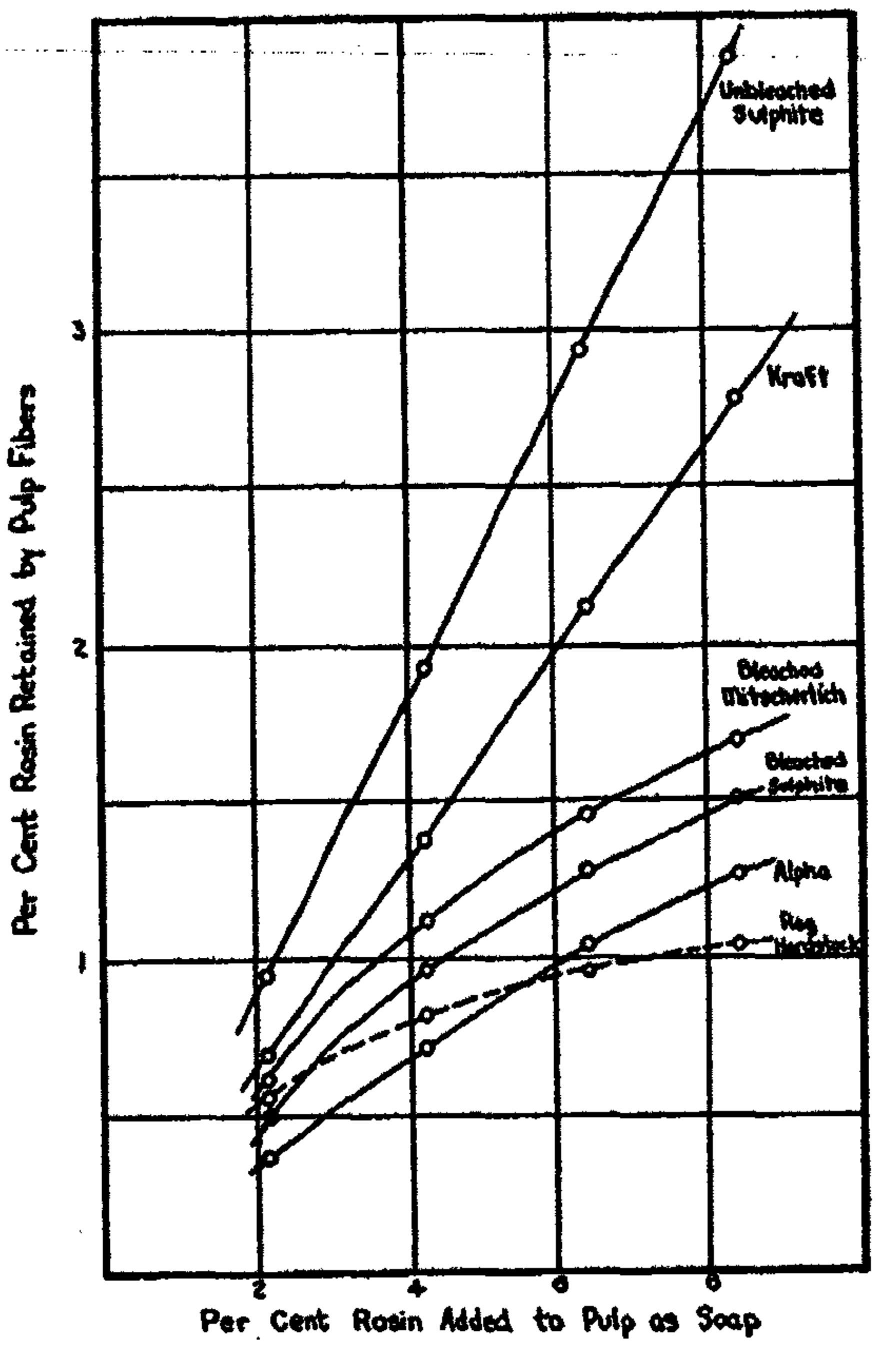

FIG. 2. The action of commercial pulp fibers on dilute rosin soap solutions

HYDROLYSIS OF ROSIN SOAP

In this scheme it is indicated that the pulp itself will extend the hydrolysis of sodium resinate. It is stated by Haug (8) and by Ivanoff (9) that under conditions of great dilution, such as occur in paper sizing ($N/1000$ to $N/100$), sodium resinate is almost, if not completely, hydrolyzed. Employing several independent methods of investigating this point, including the method of conductance and the *nitrosotriacetoneamine* method of Francis (7), Bialkowsky (3) showed in our laboratory that purified sodium resinate in a concentration of 0.01 N is less than 1 per cent hydrolyzed at 30°C. and that in a $N/300$ solution it was only 4.3 per cent hydrolyzed at 56°C. These data are in accord with those of Beedle and Bolam (2) and with those of McBain (15) on the soaps in general, who found that soaps were not greatly hydrolyzed even under conditions of great dilution.

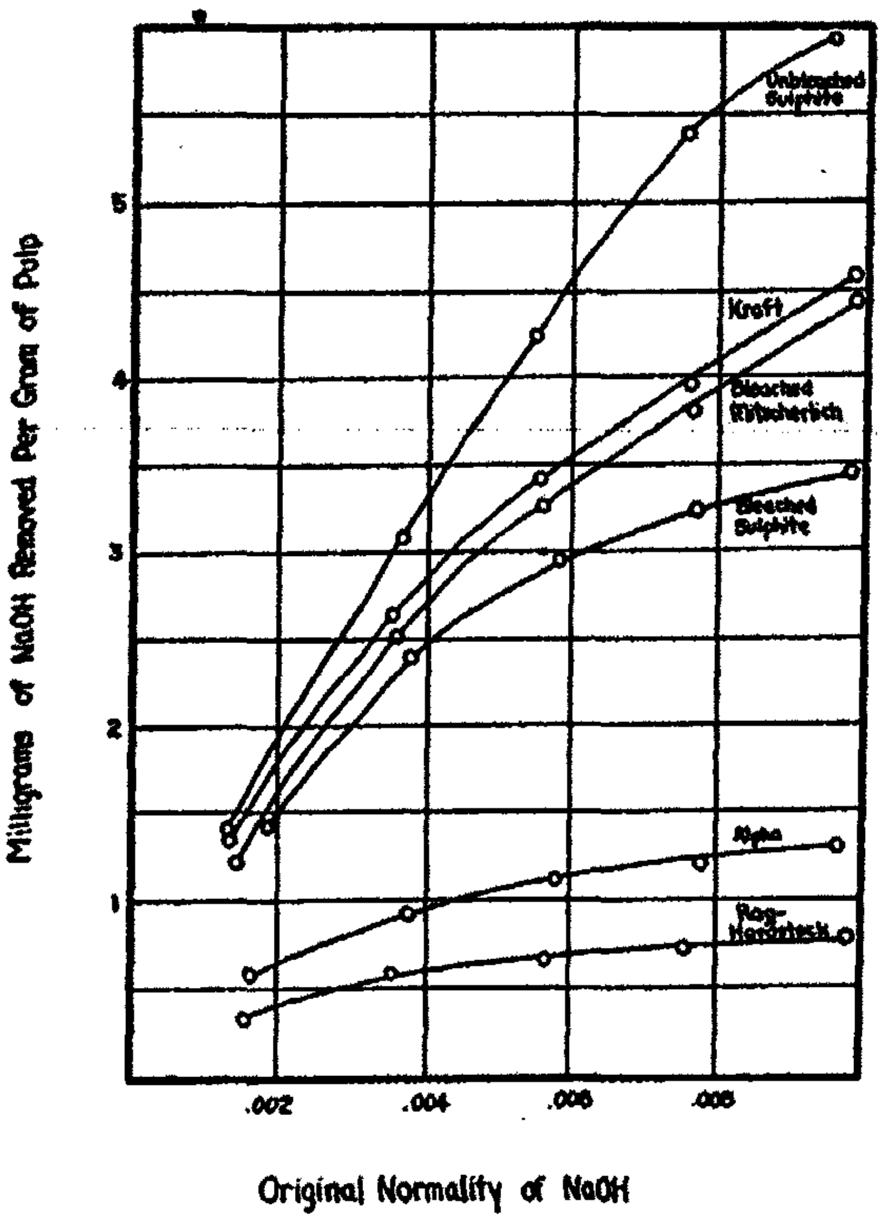

FIG. 3. Alkali removal from dilute sodium hydroxide solutions by commercial pulps.

Extending the investigation further we have found, through determinations of hydrolysis constants of sodium abietate in the presence of various kinds of cellulose pulps, that a pronounced shift in hydrolysis toward the liberation of free rosin acid occurs. The magnitude of the effect depends upon a number of circumstances, including the nature of the pulp fibers, presumably owing to their impurities. The result is a marked increase in the hydrolysis of sodium abietate solutions, as shown in figure 2. These data were obtained through a determination of the amount of rosin remaining in pulp fibers after standing in contact with dilute solutions of sodium abietate for twenty-four hours at 25°C. The fibers were then filtered off and extracted with ether after drying.

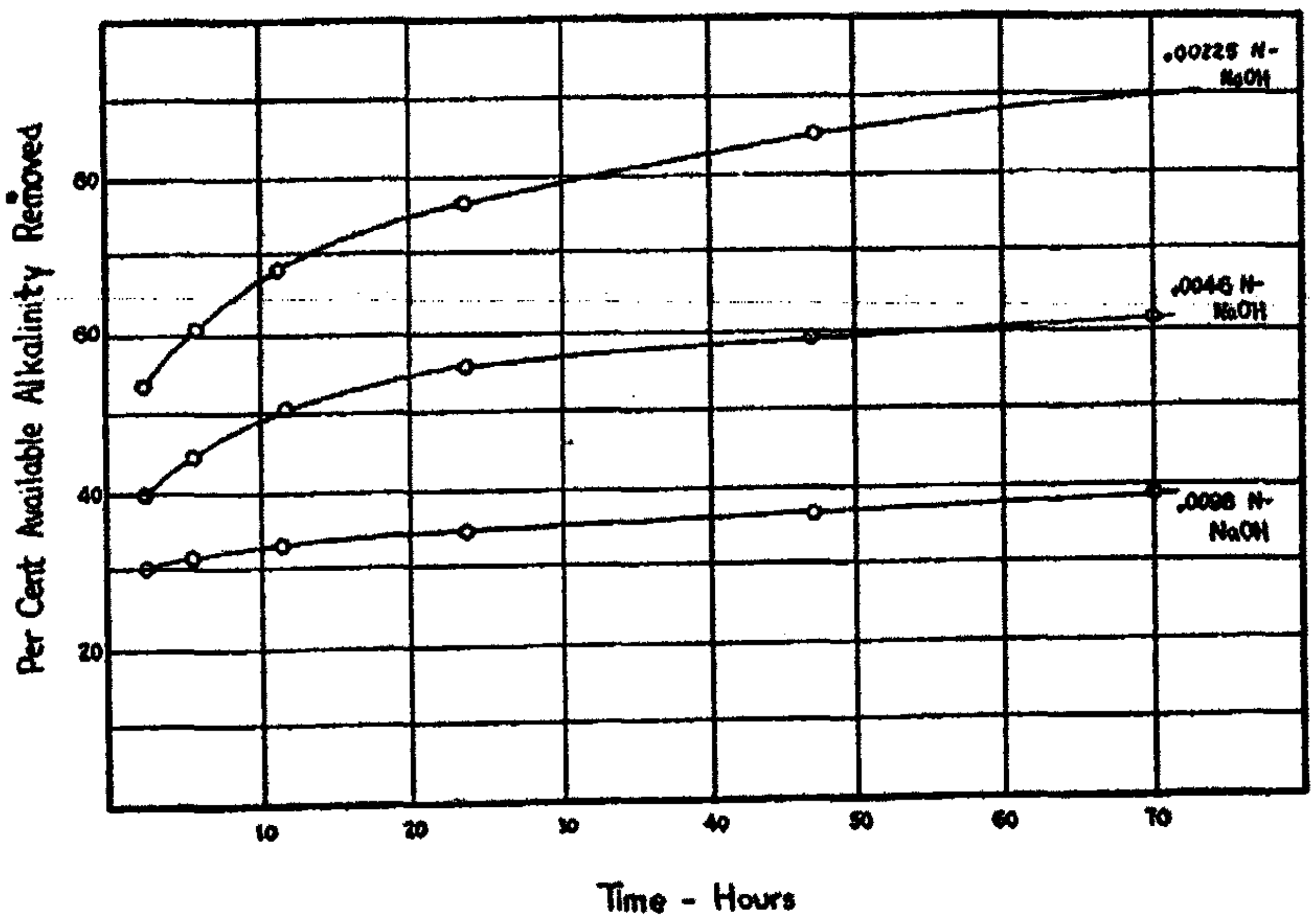

FIG. 4. Removal of alkali by pulp from dilute sodium hydroxide solutions with time.

The mechanism of the effect is obviously due to a hydrolytic selective fixation of alkali by the pulp. In figure 3 are shown similar results in the absence of rosin soap. In this instance the data were obtained by the method of nitrosotriacetoneamine decomposition, as described by Clibbens and Francis (5), as a measure of hydroxyl-ion concentration within the concentration range of our experiments. It will be observed that the relative activity of the pulps is the same in their alkali-binding power on the one hand, and their hydrolyzing power for dilute sodium abietate on the other.

ALKALI BINDING BY CELLULOSE

Figure 4 shows the effect of time on the amount of alkali binding by bleached sulfite pulp. Apparently, a large part of the total action occurs within relatively short intervals of time, this point being a matter of considerable technical interest. Figure 5 shows the behavior of this particular sample of bleached sulfite in increasing concentrations of alkali, the points on the curve indicating equilibrium values. A similar curve for "alpha" (a pulp purified by alkali extraction of impurities) is also shown. The strong resemblance of these curves to adsorption isotherms is apparent.

In regard to the behavior of cellulose in dilute alkali, Kanamaru (10, 11, 12) accounts for adsorption of electrolytes by cellulose through the mechanism of H^+ and $(OH)^-$ layer formation along the surface of fibers, and states that the behavior of fibers in this respect is greatly influenced by washing, acid treatment, electrodialysis, and deterioration, such as would lead to the formation of oxycellulose, which he believes to have a greater power for binding alkali.

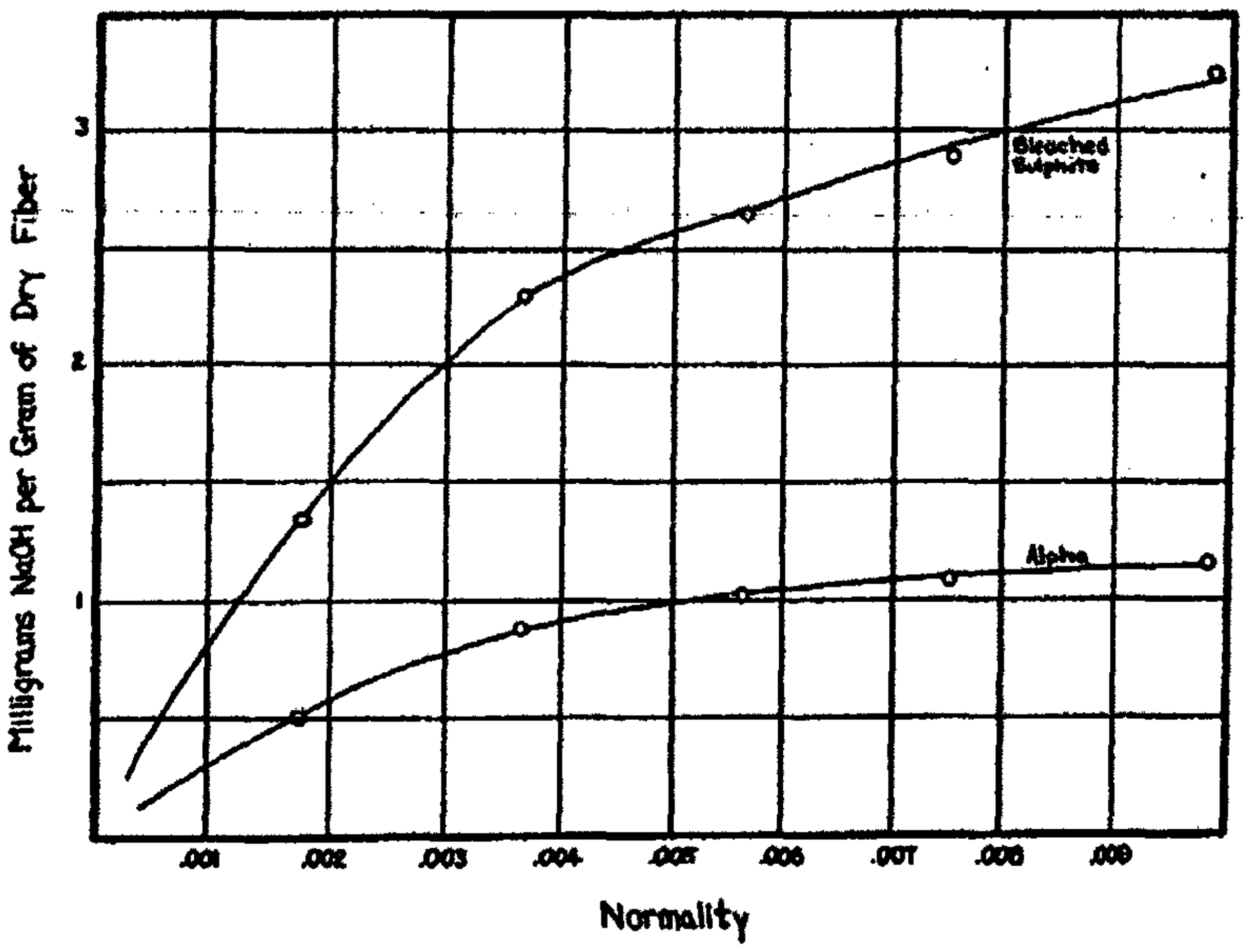

FIG. 5. Removal of alkali by pulp versus concentration

Much of the work reported in the literature on the binding of alkali by cellulose relates to higher alkali concentrations than those considered here. Bancroft (1) in summarizing this work finds that, even in mercerizing concentrations of alkali, there is no evidence to show the formation of definite compounds between cellulose and alkali.

Downs (6) has investigated in our laboratory the nature of alkali binding by various types of cellulose fibers. He studied a number of factors, including pH, ash constituents, pentosan content, and other extractives, such as uronic acid. The pulps examined were those studied by Bialkowsky and possessed wide differences in chemical composition. The evidence at hand seems to show that, in the case of the less pure pulps, alkali binding is due largely to chemical combination with the acidic impurities, such as lignin and products of cellulose decomposition. In the case of the more purified pulps, such as rag and alpha, the alkali binding, although less in extent, seems to be more nearly a physical adsorption. No evidence was found to favor an exchange adsorption, although the ash of the pulp fibers before and after treatment with dilute alkali was studied extensively.

THE EFFECT OF ALUM

Thus far, no consideration has been given to alum as a component in the system. The addition of alum to pH around 5.0 brings to a conclusion the hydrolysis of the alkali-binding rosin soap, with the establishment of an extremely different set of conditions. Not only is the unhydrolyzed soap converted into aluminum resinate, but hydrous alumina is also formed, along with sodium sulfate and an acid condition of the system. It will be observed, however, that if sodium resinate were added to a substantially neutral pulp and allowed to stand for an appreciable period of time, say one-half to three-quarters of an hour before the alum is added, the relative amounts of free rosin and aluminum resinate available for sizing will, to a certain extent, be dependent upon the extent to which free rosin has been liberated by the pulp.

It is of interest to note that the order of arrangement of the various pulps in figures 1 and 2 is substantially that of the ease with which they are sized in the commercial operation, the alpha and rag pulps being the most difficult. Without pressing this coincidence unduly, it may be considered as new evidence in favor of the free rosin sizing theory, as opposed to the aluminum resinate theory. Theory suggests that a more finely divided free rosin, as well as a more intimately distributed rosin, will result if liberated through the alkali adsorption-hydrolysis mechanism, than if produced by adding a relatively coarse free rosin dispersion as such. It may happen that such rosin as is liberated at the pulp fiber surfaces by the hydrolytic action of the cellulose is extremely finely divided and may be deposited on the fiber surface in this condition.

The addition of alum brings to a conclusion all chemical reactions within the system, converting the unhydrolyzed soap into aluminum resinate, and liberating alumina and sodium sulfate. The relative amounts of free rosin, aluminum soap, and alumina which finally appear in the finished paper depend not only upon the amounts of these substances available, but also upon such adsorption, electrostatic, and flocculating factors as may be present.

Robinson (17) has shown in our laboratory that when excess alum is added to dilute sodium abietate solutions in the absence of cellulose fibers, only the neutral aluminum abietate is formed, thus confirming the work of Schutz and Klauditz (19). The other possibility of a physical coprecipitate mixture of alumina and free rosin was not observable, presumably owing to the low degree of hydrolysis of dilute sodium abietate. In the presence of fibers of various character, however, free rosin acids were found precipitated on the fibers in amounts as anticipated according to the varying capacities of the different pulps to hydrolyze dilute sodium abietate solutions.

HYDROUS ALUMINA

The retention of free rosin, starch, filler, and color in the paper sheet is doubtless influenced in large measure by colloidal alumina and by the electrostatic effects involved. This has been applied commercially by the writer (18) to improve the effectiveness of starch in paper making. The work of Lee (13) shows that rosin in paper does not exist as films on fiber surfaces, but rather as microscopically visible particles distributed through the sheet structure. Some of the rosin is no doubt mechanically caught, but in all probability some, perhaps most of it, is attached to the fibers through the agency of colloidal alumina acting, as Lorenz (14) puts it, in the sense of an electrostatic cement, binding negative fibers to negative rosin particles. No doubt other factors are involved in the retention of rosin by fibers. Olsen and Gortner (16) have shown that the ash content of pulps, pH conditions, and degree of hydrolysis of alum employed play important rôles. It is difficult, however, to reconcile the photomicrographs of Lee with the process of rosin adsorption without assuming that rosin can be adsorbed in the form of surface films not resolvable in the microscope. It would be interesting to know in such a case how large rosin particles could be and still be held to the fibers essentially through surface adsorption forces.

It appears probable, however, that colloidal alumina plays an important part in the fixation of rosin on fibers. The aged alum solutions employed by Gortner to show the contrast with the results obtained with fresh alum solutions exhibit the influence of increased amounts of alumina in producing a relatively higher rosin retention at higher pH values. These results coincide well with commercial experience, which has taught that sizing may be improved under conditions of lower acidity by enriching the system with alumina through the addition of an alkali or sodium aluminate. Presumably, the binding of alkali by pulp will not impoverish the system with respect to alumina; in fact, upon the addition of alum there may be alumina formed in reaction with alkali bound at the fiber surface to produce a very desirable electropositive surface film to which negative materials may readily adhere. Moreover, as pointed out by Weiser (21), fibers which absorb aluminum oxide will promote the hydrolysis of aluminum salts. It may thus be supposed that the hydrolytic action of fibers on sodium resinate may be extended to cover the hydrolysis of alum; in the first case the action is due to selective ion adsorption and in the second, to selective adsorption of alumina. Thus, those pulps exhibiting greater alkali binding may be more readily sized by rosin, not only through a greater power of liberating free rosin and alumina, but also through the localization of hydrous alumina formation at their surfaces.

ION EFFECTS

Among the ions formed in the system are hydrogen, aluminum, sulfate, and sodium ions, and traces of extraneous ions. All of these ions exert their influence on the electrostatic conditions at the several interfaces and modify the colloidal relations between them.

It is generally considered that, in contact with water, cellulose bears a negative electrostatic charge, and that alumina may serve as a mordanting agent under such circumstances. The intensity of the negative condition at fiber surfaces, however, may be greatly reduced by hydrogen ions, and may even become positive in the presence of aluminum ions in very low concentration, according to Briggs (4). Meanwhile, adsorption of hydrogen ions and possibly aluminum ions by the alumina tends to intensify the positive nature of the latter. As a consequence, changes in pH as established by alum in such a system may, and, under conditions of commercial operation, do result in important alterations of the finished product.

The concept of the isoelectric point as applied to cellulose is not entirely satisfactory, at least with reference to pH. If an isoelectric point exists, it must occur under conditions of very strong acidity, as pointed out by Stamm (20). The combined action of hydrogen and aluminum ions, however, would seem to bring a charge reversal on the fiber surface within the conditions of the paper-making system. Opposed to these influences, the action of sulfate ions would tend to keep the fiber negative and to reduce the intensity of the positive nature of alumina. The effect of an accumulation of sulfate ions in diminishing the flocculating power of alumina for such materials as rosin, clay, and starch explains the often experienced necessity of adding more and more alum to the system in actual operation in order to maintain consistent results. In the most troublesome cases, it becomes necessary to drain away the white water and begin with a fresh system.

DRYING THE SYSTEM

When the sheet of paper is formed, a part of all the components of the system passes to hot dryer rolls where water is gradually and almost completely removed. An entirely new set of conditions is now established, owing to concentration, abstraction of a certain portion of soluble components, temperature elevation, and pH changes. These changes induce further chemical and colloidal reactions, including the formation of what has, perhaps erroneously, been termed a basic aluminum resinate, and the formation of β-aluminum oxide, which bears an important relation to the stiffness of the sheet and its receptivity for printing ink.

Of particular interest to manufacturers of permanent paper for documents is the possibility of liberation of acid from alumina sols when heated, since acid so liberated would be deleterious to the life of paper. We have not been able to find these effects in paper drying (22) and, if such acid be liberated, it must again combine with other materials present.

CONCLUSION

An attempt has been made to point out the interdependence of the several constituents in the paper-making system and to describe such of the colloidal effects as have been investigated. It will be all too obvious that much remains to be learned about the colloidal complexity of the system; if the discussion leaves much confusion, such has not been wholly intentional. No attempt has been made to emphasize the great technical consequences of the colloidal phenomena involved.

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THE BONDING FORCE OF CELLULOSIC MATERIALS FOR WATER (FROM SPECIFIC VOLUME AND THERMAL DATA)[1]

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An attempt was made in a previously reported research (14) to determine the volumetric contraction occurring in the water adsorbed by cellulosic materials. Apparent density measurements of wood and cellulose containing various amounts of adsorbed water were made in benzene. Benzene causes no swelling of cellulosic materials, indicating that its affinity for cellulosic materials is small. This, together with the fact that the internal surface of contact is relatively small, would make the adsorption compression of benzene negligible. It is questionable, however, that benzene penetrates the void structure of the dry cell walls completely. For this reason the benzene can be relied upon as a displacing medium only when the moisture content of the cellulosic material is sufficiently high for water to have opened up or itself filled all of the void structure. It was shown that the volumetric contraction occurring in the adsorbed water could be calculated down to a moisture content of about 6 per cent from the measurements in benzene. Below this point accurate data for the true density of the cellulosic material are required to make the calculations.

Howard and Hulett (6) have determined the density of carbon in helium and have shown that at room temperatures the helium is practically non-adsorbed. Davidson (3) similarly concluded that helium is non-adsorbed on cellulose. Because of its low molecular weight it should further penetrate the void structure completely. Hence measurements of the density of the same cellulosic materials used in the previous investigation were made in helium.

The essential features of the apparatus used for making the density measurements are shown in figure 1. A and B are two Pyrex glass bulbs of about 200-cc. capacity, separated by a stopcock S_1. The sample bulb

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

[2] Maintained at Madison, Wisconsin, in coöperation with the University of Wisconsin.

A can be removed at the ground-glass joint J and filled with the cellulosic material by removing the stopcock. S_1, S_2, and J are provided with mercury seals to prevent leaks. M is a mercury manometer, which was read with a cathetometer to 0.005 cm. L is a 200-cc. bulb used to keep the mercury level in the right-hand arm of M at the same point for all the measurements by adjusting the pressure over L with stopcocks S_3 and S_4. This made unnecessary any volume corrections. The whole apparatus was immersed in a thermostatically controlled water bath at 30°C. ± 0.01°.

The volume of A was determined by calibration with water. With A empty the apparatus was completely evacuated, helium was admitted to B, the pressure determined, and then the pressure was again determined after expansion into A. The volume of B plus the connecting tubes could then be calculated from the volume of A and the two pressures, using the perfect gas law. The same procedure was followed in determining the void space in A when filled with a sample of wood or cellulose. The material was oven-dried at 105°C. prior to filling the bulb and then vacuum-dried at 105°C. for about twenty-four hours after assembly of the apparatus by surrounding the bulb with a heating coil jacket. A final vacuum of about 10^{-4} mm. of mercury was attained. The system was then brought to 30°C. and held for about half a day before making the measurements, to insure thermal equilibrium. Weighings of the sample bulb were made at atmospheric pressure just after the vacuum drying and again after a series of expansions.

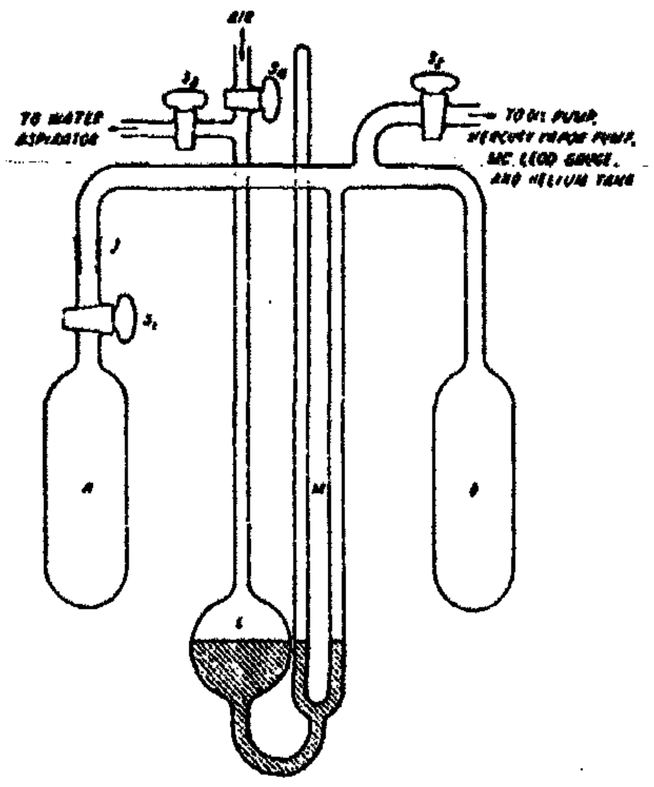

FIG. 1. Apparatus for determining the void volume of cellulosic materials by gas displacement.

Density measurements were also made in water and benzene in 200-cc. plate-top pycnometers. The air was removed from the submerged materials in the half-filled pycnometers by carefully applying a vacuum and releasing until no sign of air bubbles was obtained up to a vacuum which caused boiling of the liquid when the pycnometers were immersed in an ice bath.

The densities of the following materials determined in helium, water, and benzene, are given in table 1: benzene–alcohol extracted white spruce sawdust of 40 to 60 mesh; the same in the expanded aerogel form (8); standard cotton linters alpha-cellulose; a normal spruce sulfite pulp and the same after beating for twenty hours; and spruce and maple lignin prepared by the modified sulfuric acid method of the Forest Products Laboratory (11). The expanded aerogel was prepared according to the method of Kistler (8), using methanol and acetone as intermediate replacing agents. Measurements on control blocks showed that a large proportion of the normal shrinkage occurred in the final expansion step, regardless of the technic used. Because of this shrinkage the density value for the expanded wood determined in benzene, although greater than the corresponding density value for the unexpanded wood, was not so great as the density value determined in helium. In all cases the density values determined in helium are intermediate between those determined in water and those determined in benzene, as has been previously reported (3, 12). The difference between the helium and benzene values for the cotton is practically the same as that found by Davidson (3).

TABLE 1

Densities of wood, cellulose, and lignin substance at 30°C.

SUBSTANCE	HELIUM DISPLACEMENT			WATER DISPLACEMENT			BENZENE DISPLACEMENT		
	Density	Average error	Number of determinations	Density	Average error	Number of determinations	Density	Average error	Number of determinations
Extracted white spruce..	1.4603	0.0005	10	1.5332	0.0002	2	1.444	0.007	2
Expanded aerogel from extracted white spruce..............	1.4604	0.0004	4	1.530		1	1.450	0.005	2
Standard cotton linters..	1.585	0.0012	7	1.6028	0.0003	2	1.571	0.0005	2
Spruce sulfite pulp:									
Unbeaten.............	1.570	0.0024	6	1.590	0.0005	2	1.555		1
Beaten................	1.593	0.0022	6	1.616	0.0008	2	1.578		1
Spruce lignin (modified sulfuric acid method)	1.377	0.0008	10	1.399	0.0010	2	1.366		1
Maple lignin (modified sulfuric acid method)	1.406	0.0011	6	1.422	0.0007	2	1.388		1

The volume contraction occurring in the cellulosic material-adsorbed water system was calculated from the previously determined data in benzene (14), using the newly found density values in helium as the true densities of the cellulosic materials. The external pressure P in kilobars that would be required to cause this volume change Δv per gram of water, on the basis of the volume change occurring entirely in the water phase, was then calculated from the following compressibility relationship for water given by Gibson (5):

$$\Delta v = 0.307 \log \frac{2.923 + P}{2.923} \tag{1}$$

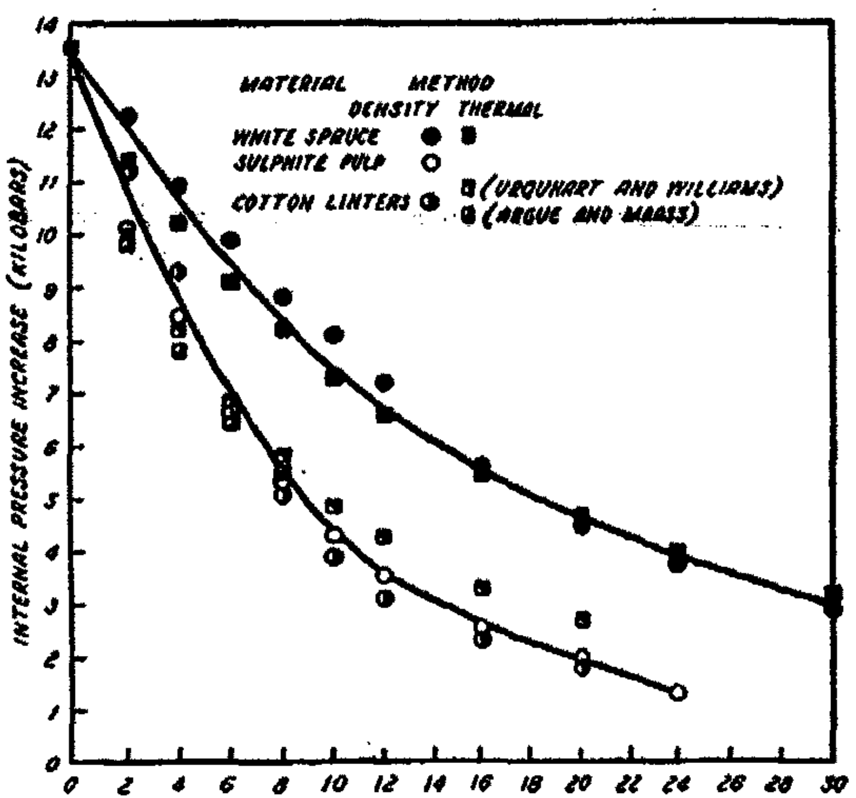

FIG. 2. The external pressure that would cause a compression of water equal to the volumetric contraction occurring on its adsorption by wood, cotton, and pulp, or the equivalent internal pressure change that causes the contraction for different moisture contents determined from both density and thermal data.

The values for white spruce, cotton, and sulfite pulp are plotted in figure 2. The values for the beaten and the unbeaten pulp were so nearly identical that only the average value is plotted.

Campbell and Russell (2) have doubted whether helium completely penetrates the void structure of cellulose, because they obtained density values for swollen cellulose in benzene by replacement of water with alcohol and of alcohol with the benzene that were slightly greater than the helium values. This difference, it seems, can be better explained by assuming that a small amount of water was not replaced in their measurements, rather than by assuming that the helium fails to penetrate the cellulose completely. In order to meet these investigators' objections, however, it seemed advisable to attempt determining the compression effect by an entirely different method.

Katz (7) has shown that a qualitative proportionality exists between the initial heat of solution or the heat of swelling of binary aqueous systems and the accompanying volume change. He gives values for the ratio $\bar{C}_0/\bar{H}_0$ ranging from 1 to 3 × 10^{-3} for a series of solutions and swelling systems in which $\bar{C}_0$ is the volume change in cubic centimeters and $\bar{H}_0$ is the heat of solution or swelling in gram-calories resulting when 1 g. of water is added to an infinite amount of dry solute or swelling material. It is apparent that this relationship cannot be general, as there should be a greater change in volume per unit thermal change for a more compressible liquid than for a less compressible liquid. It thus seemed logical to substitute the change in internal pressure $\bar{P}_e$, which causes the change in volume, for the change in volume and thus compare values of the differential ratio $\bar{P}_e/\bar{H}$. Partial differential values are used, as compression may occur in both constituents of the liquid–liquid systems considered.

Gibson (5) gives the relationship between the specific compression of water, the internal or intrinsic pressure change, and the externally applied pressure which can be expressed in the following partial differential form:

$$-\frac{\overline{\Delta pv}}{x_1} = 0.307 \log \frac{2.923 + \bar{P}_e + P}{2.923 + \bar{P}_e} \qquad (2)$$

where $\frac{\overline{\Delta pv}}{x_1}$ represents the partial compression of the water per gram of water resulting from the partial internal pressure change of the water $\bar{P}_e$ in kilobars caused by the presence of the solute and the external pressure change P in kilobars. The partial specific compression can be obtained by plotting the compression per gram of solution against the weight fraction of the water and drawing tangents to the curve. The intercept of the water axis gives the partial specific compression for water in a solution the composition of which is represented by the point of tangency (9).

The external pressure P that would cause the same volume change in the solvent as occurs in the process of solution can be calculated from equation 1 expressed in a partial form

$$v_1 - \bar{v}_1 = 0.307 \log \frac{2.923 + \bar{P}}{2.923} \qquad (3)$$

in which v_1 is the specific volume of the water and $\bar{v}_1$ is the partial specific volume of the water in the system, obtainable in a similar way to the partial specific compression.

Gibson (5) gives data for both the specific volume and the compressibility of a sulfuric acid–water system. From these data the external pressure required to give the partial specific volume change of the water can be calculated, using equation 3, and the change in the internal pressure that causes the change in compressibility can be calculated, using equation 2. These values are given in table 2. The data show that the internal pressure change of water in the solutions is equal to the external pressure required to cause an equal change in volume in the water alone. It is thus valid to consider the pressure changes in figure 2 equivalent to internal pressure changes.

Table 3 gives the ratios of the partial internal pressure change to the partial heat of solution of water in aqueous solutions of organic compounds, inorganic acids, bases, and salts, and salts of organic acids all of which dissolve with the evolution of heat. The partial internal pressure changes were calculated from specific volume data only (*International Critical Tables*), as specific compression data were available only for the sulfuric acid solutions. The heat of solution data with the exception of that for sulfuric acid (10) were also obtained from the *International Critical Tables*. Because of the difficulty of obtaining accurate graphical values for $\bar{v}_1$ and for $\bar{H}$ at high concentrations of water, the values for the ratio $\bar{P}_e/\bar{H}$ could not be determined at concentrations higher than those given in table 3 with any degree of accuracy. In all cases where miscibility is complete, the ratios of $\bar{P}_e/\bar{H}$ for zero concentration of water are about equal, the average deviation from the average value 12.5 being 4 per cent. The same constancy exists for all the data at high concentrations of water. In some cases the agreement is good over the whole concentration range, whereas in other cases, such as that of sulfuric acid, the ratio decreases at intermediate concentrations. In the case of the salts and bases the agreement is good up to concentrations approaching saturation.

TABLE 2

Change in partial internal pressure of water in aqueous sulfuric acid solutions calculated from the specific volumes and from the specific compressions

SOLUTE	WEIGHT FRACTION OF H_2O (x_1)	SPECIFIC VOLUME MINUS PARTIAL SPECIFIC VOLUME OF H_2O ($v_1 - \bar{v}_1$)	EXTERNAL PRESSURE ON H_2O TO GIVE VOLUME CHANGE (P)	PARTIAL SPECIFIC COMPRESSION OF H_2O PER KILOBAR $\left(-\frac{\overline{\Delta pv}}{x_1}\right)$	CHANGE IN PARTIAL INTERNAL PRESSURE OF H_2O ($\bar{P}_e$)
			kilobars		*kilobars*
H_2SO_4	0.0	0.308	26.8	0.0048	26.0
	0.0723	0.283	21.3	0.0055	21.0
	0.1365	0.193	9.3	0.0110	8.7
	0.2167	0.093	3.0	0.0225	2.5
	0.4048	0.038	0.95	0.0312	0.85
	0.6699	0.012	0.28	0.0367	0.25
	0.7333	0.008	0.17	0.0380	0.13
	0.8734	0.004	0.08	0.0390	0.04

TABLE 3

Relationship between the change in the partial internal pressure of water and the partial heat of solution of water in the formation of various aqueous solutions

SOLUTE	WEIGHT FRACTION OF H_2O (x_1)	SPECIFIC VOLUME MINUS PARTIAL SPECIFIC VOLUME OF H_2O ($v_1 - \bar{v}_1$)	CHANGE IN PARTIAL INTERNAL PRESSURE OF H_2O ($\bar{P}$)	PARTIAL HEAT OF SOLUTION OF H_2O ($\bar{H}$)	RATIO $\left(\frac{\bar{P}}{\bar{H}}\right)$
			kilobars	*kilojoules*	
Glycerol	0.0	0.040	1.00	0.081	12.3
	0.1	0.028	0.69	0.056	12.3
	0.2	0.023	0.55	0.043	12.8
	0.3	0.019	0.45	0.037	12.2
	0.4	0.012	0.28	0.027	10.4
	0.5	0.010	0.22	0.021	10.5
	0.6	0.0075	0.16	0.014	11.4
	0.7	0.004	0.09	0.008	11.2
Glycol	0.0	0.053	1.40	0.100	1.40
	0.1	0.044	1.15	0.0865	13.3
	0.2	0.035	0.88	0.065	13.5
	0.3	0.026	0.63	0.049	12.9
	0.4	0.019	0.45	0.0375	12.0
	0.5	0.014	0.325	0.029	11.2
	0.6	0.009	0.20	0.022	9.1
	0.7	0.005	0.11	0.0125	8.8
	0.8	0.002	0.045	0.0035	12.8
HNO_3	0.0	0.198	10.2	0.90	11.3
	0.1	0.190	9.3	0.80	11.6
	0.2	0.163	7.0	0.59	11.8
	0.3	0.136	5.0	0.39	12.8
	0.4	0.086	2.7	0.22	12.0
	0.5	0.058	1.6	0.13	12.3
	0.6	0.036	0.9	0.08	11.2
	0.7	0.011	0.25	0.02	12.5
H_3PO_4	0.0	0.129	4.80	0.43	11.2
	0.1	0.093	3.00	0.37	8,1
	0.2	0.068	1.95	0.25	7.8
	0.3	0.038	1.00	0.14	7.1
	0.4	0.028	0.70	0.08	8.7
	0.5	0.021	0.50	0.05	10.0
	0.6	0.010	0.23	0.02	11.5
	0.7	0.006	0.13	0.015	11.5
H_2SO_4	0.0	0.306	26.5	1.92	13.8
	0.05	0.292	23.0	1.75	13.1
	0.10	0.260	17.5	1.50	11.7
	0.15	0.182	8.5	1.12	7.6
	0.20	0.106	3.6	0.78	4.6
	0.30	0.052	1.4	0.43	3.3
	0.40	0.0355	0.92	0.26	3.5
	0.50	0.0265	0.64	0.14	4.6
	0.60	0.0170	0.40	0.08	5.0
	0.70	0.0095	0.22	0.04	5.5
	0.80	0.0045	0.10	0.015	6.7
	0.90	0.0025	0.05	0.004	12.5

TABLE 3—*Concluded*

SOLUTE	WEIGHT FRACTION OF H_2O (x_1)	SPECIFIC VOLUME MINUS PARTIAL SPECIFIC VOLUME OF H_2O ($v_1 - \bar{v}_1$)	CHANGE IN PARTIAL INTERNAL PRESSURE OF H_2O ($\bar{P}$)	PARTIAL HEAT OF SOLUTION OF H_2O ($\bar{H}$)	RATIO $\left(\frac{\bar{P}}{\bar{H}}\right)$
			kilobars	*kilojoules*	
KOH	0.425	0.115	4.00	0.420	9.5
	0.5	0.083	2.57	0.255	10.1
	0.6	0.045	1.20	0.110	10.9
	0.7	0.014	0.33	0.027	12.2
	0.8	0.0075	0.17	0.014	12.1
NaOH	0.6	0.104	3.50	0.295	11.9
	0.7	0.068	1.95	0.140	13.9
	0.8	0.023	0.55	0.040	13.7
$KC_2H_3O_2$	0.4	0.038	0.97	0.075	12.9
	0.5	0.027	0.66	0.053	12.4
	0.6	0.018	0.43	0.035	12.3
	0.7	0.008	0.175	0.013	13.5
	0.8	0.0015	0.032	0.0022	14.5
	0.9	0.0005	0.013	0.001	13.0
$NaC_2H_3O_2$	0.7	0.006	0.13	0.010	13.0
	0.8	0.002	0.045	0.0035	12.8
	0.9	0.0005	0.013	0.001	13.0
$CaCl_2$	0.6	0.044	1.15	0.096	12.0
	0.7	0.020	0.48	0.038	12.6
	0.8	0.009	0.20	0.015	13.3
$MgCl_2$	0.7	0.032	0.80	0.070	11.4
	0.8	0.012	0.28	0.025	11.2
$ZnCl_2$	0.4	0.052	1.4	0.130	10.8
	0.5	0.039	1.0	0.087	11.5
	0.6	0.024	0.58	0.048	12.1
	0.7	0.017	0.40	0.033	12.1
	0.8	0.009	0.20	0.018	11.1
	0.9	0.004	0.09	0.008	11.2
LiCl	0.7	0.014	0.33	0.095	3.6
	0.8	0.009	0.20	0.018	12.0
	0.9	0.004	0.09	0.007	12.8
$CuCl_2$	0.6	0.032	0.80	0.055	14.5
	0.7	0.022	0.52	0.036	14.4
	0.8	0.009	0.20	0.016	12.5

This relationship fails to hold for exothermic solutions. The expansion accompanying the absorption of heat is invariably too small, and in some cases there is a slight contraction accompanying the absorption of heat. The relationship also fails in cases where the constituent other than water is more compressible than water. As neither of these cases applies to cellulose–water systems, it seemed justifiable to apply the ratio $\bar{P}_e/\bar{H} =$ 12.5 kilobars per kilojoule in the calculation of $\bar{P}_e$ from thermal data. Values of $\bar{P}_e$ for the wood and cotton calculated from the heat of swelling data (13) that were obtained from vapor pressure data (13, 15) and from direct heat of swelling data (1) are plotted in figure 2, together with the values of P obtained from adsorption compression. The agreement is good. It tends to substantiate the contention that true density values for cellulosic materials can be obtained in helium and strengthens the validity of the calculated internal pressure values.

The values of $\bar{P}_e$ represent the increase in the internal pressure of water, so that the normal internal pressure of water, which is about 12.5 kilobars, should be added to these values to obtain the total internal pressure. The data thus show that the initial bonding force of cellulosic materials for water is about twice that of water for itself. This seems much more reasonable than the value of sevenfold to eightfold greater calculated from the data of Filby and Maass (4), especially in the light of the fact that the initial attractive force of sulfuric acid for water is only three times that of water for water (see table 3). It is of interest to note that the surface-bound water corresponding to the inflection point of the moisture content–relative vapor pressure curves, 5 to 6 per cent for wood and about 3 per cent for cotton, exhibits the same internal pressure of about 22.5 kilobars for both wood and cotton. The average force with which all the water is held below the fiber-saturation point varies for the different cellulosic materials: 15.5 kilobars for the wood, 14.7 for the cotton, and 13.5 for the pulp, or 24, 17, and 8 per cent greater than the force with which water holds water.

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STUDIES IN DROP FORMATION AS REVEALED BY THE HIGH-SPEED MOTION CAMERA[1]

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Measurements of the weight of drops, or of drops formed from a given volume of liquid, have long been used for the calculation of surface tension at liquid–vapor interfaces, and for the determination of interfacial tensions between liquids.

Many investigators (notably Tate, Worthington, and Rayleigh) have attempted the formulation of theoretical equations to make possible the calculation of surface tension from the volume or weight of a drop detaching itself from a tip of given size. Unfortunately, most of these equations were based on plausible but false assumptions.

The drop-number method proposed by Traube (2, 4) gives only rough approximations, and its results are unreliable. W. D. Harkins and F. E. Brown (3) have developed an excellent technique for obtaining self-consistent data on the surface tension of liquids by the drop-weight method, and in 1918 they presented empirical curves which make the accurate determination of surface tension possible.

Preliminary investigations conducted a year ago in these laboratories with the aid of the high-speed motion picture camera (4) seemed to show the value of direct observation of the mechanism of drop formation in surface tension research.

The empirical surface tension correction curves offered by Harkins and Brown are very interesting, in that they show a distinct minimum followed by a maximum (figure 1). It was hoped that actual observation of the formation of drops from tips of various diameters might throw some light on the cause of the peculiar shape of the surface tension correction curve.

For this purpose, a set of twenty-three brass and copper tips was constructed by methods similar to those described by Harkins and Brown. These tips are shown in section and their dimensions are tabulated in figure 2.

In order to time the falling of the drops closely enough to photograph

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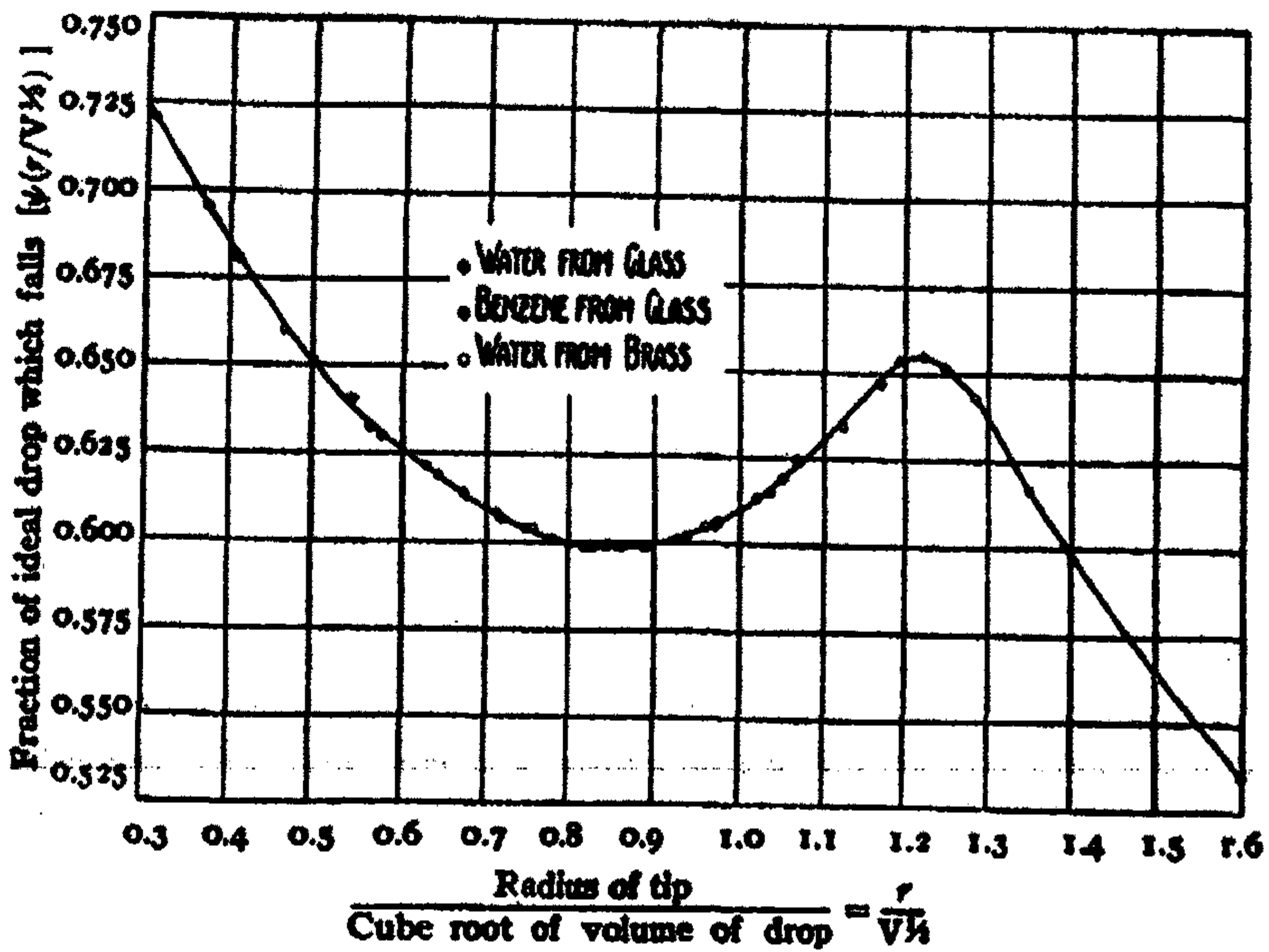
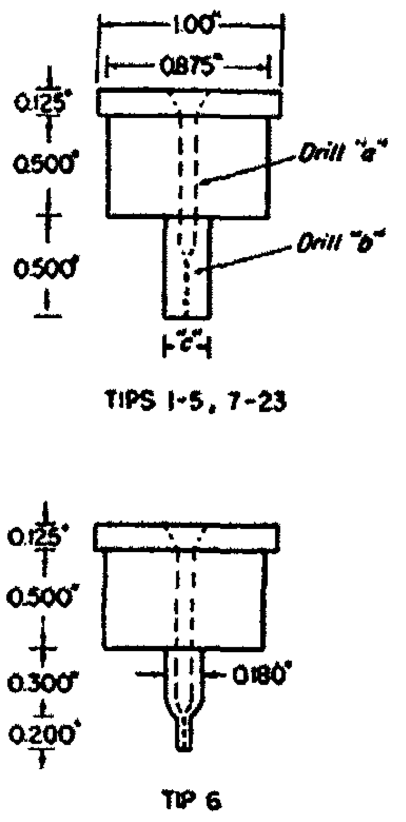
[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.



Drop-weight corrections. (Note: Point 1 does not belong on the curve since the benzene crawled up the side of the tip.)

FIG. 1. Empirical surface tension correction curves of Harkins and Brown



TIP	MATERIAL	DRILL "a"	DRILL "b"	"c" Inches	"c" Centimeters
1	Copper	50	80	0.173	0.439
2	Copper	40	80	0.224	0.569
3	Copper	40	80	0.275	0.699
4	Copper	30	78	0.324	0.823
5	Copper	30	77	0.377	0.958
6	Brass	50	80	0.075	0.191
7	Brass	50	80	0.100	0.254
8	Brass	50	80	0.135	0.343
9	Brass	40	80	0.200	0.508
10	Brass	40	80	0.268	0.681
11	Brass	40	79	0.295	0.749
12	Brass	30	78	0.315	0.800
13	Brass	30	77	0.355	0.902
14	Brass	30	76	0.395	1.003
15	Brass	30	73	0.473	1.201
16	Brass	30	72	0.512	1.300
17	Brass	30	70	0.551	1.400
18	Brass	30	70	0.570	1.448
19	Brass	30	69	0.596	1.514
20	Brass	30	68	0.607	1.542
21	Brass	30	67	0.635	1.613
22	Brass	30	64	0.711	1.806
23	Brass	30	60	0.791	2.009

FIG. 2. Details of stalagmometer tips

them during the single second that it is practical to run the high-speed camera, the stalagmometer shown in figure 3 was constructed. Full-sized drops were formed on the tips and then suddenly detached by a slight turn of the thumb screw. This method, while not suitable for precise quantative determinations, introduced relatively small errors in the actual weight of the drops formed.

Three series of pictures were taken. The first series was taken for the purpose of attempting to determine the reasons for the peculiar shape of the surface tension correction curve. Conductivity water was used for these tests. The second series was made to discover whether the minimum in the curve of surface tension versus concentration of certain organic chemicals in aqueous solutions (as described by McBain, Ford, and Wilson (5)) may be observed on freshly formed surfaces, or is only developed as the surfaces age. Solutions of sodium oleate in water were used. The

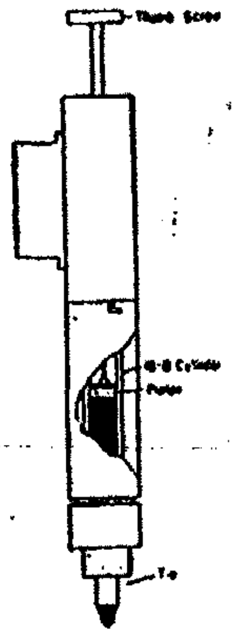


Fig. 3. Stalagmometer

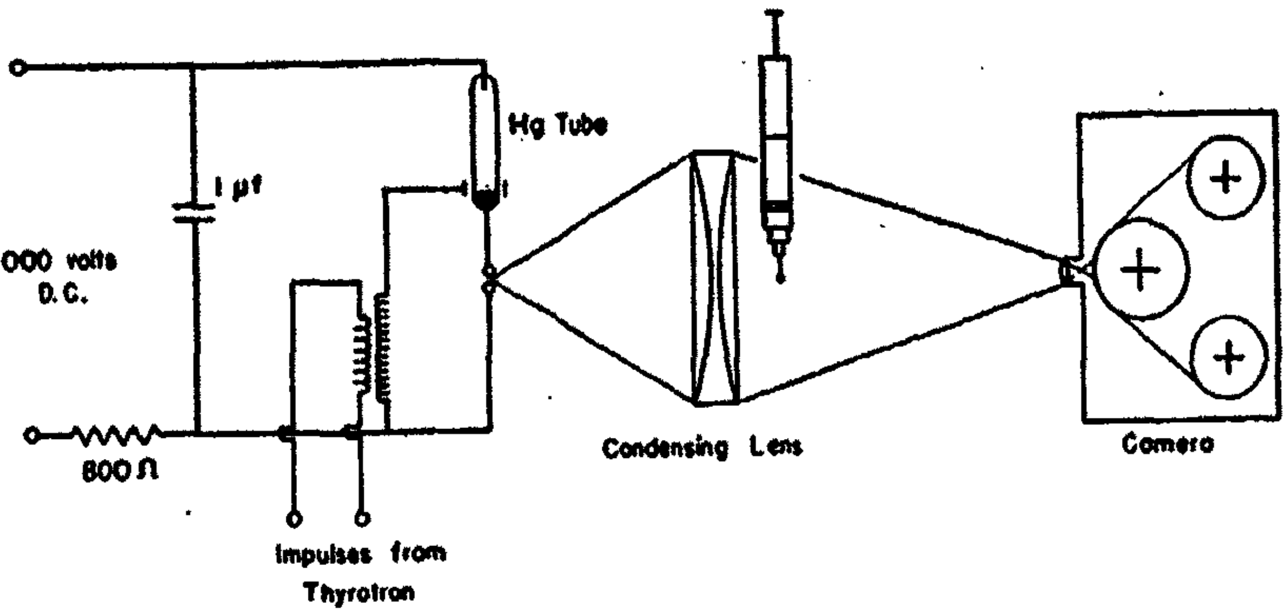


Fig. 4. Apparatus for silhouette photography

third series was undertaken for the purpose of determining whether solutions having identical surface tensions as determined by the du Noüy ring method (using moderately aged surfaces) would all form drops in an identical manner. For this purpose, nitrobenzene and solutions of sodium oleate in water, alcohol in glycerol, and alcohol in water were used.

Motion pictures (see figure 4) were taken at the rate of 800 pictures per second of drops of water falling from each tip. Significant frames were selected from each roll (figures 5, 6, and 7). Measurements of the diameters of all of the primary and secondary drops were made on enlarged photographic prints and are tabulated in table 1. From these measurements the weights of the individual drops were calculated and totaled, and the results were compared with the average drop weights obtained by weighing several sets of ten drops each (see table 2). As may be seen, the calculated values agree rather well with the directly measured values.

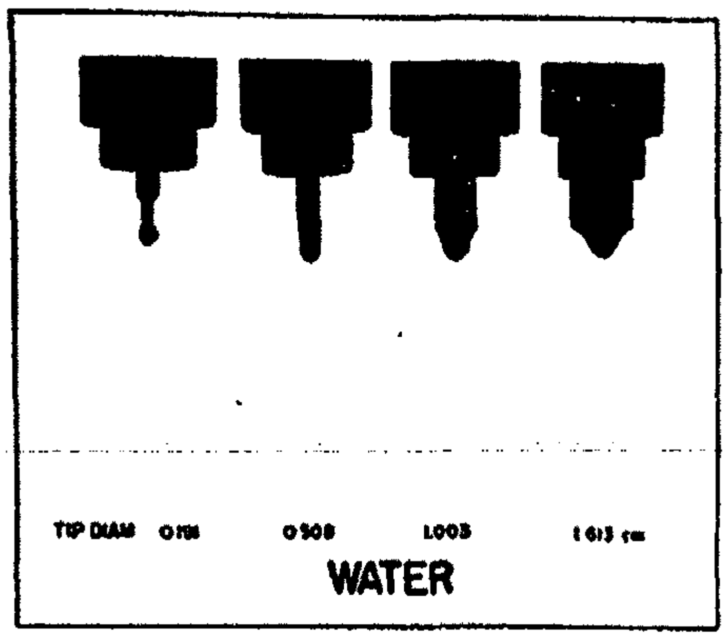


Fig. 5

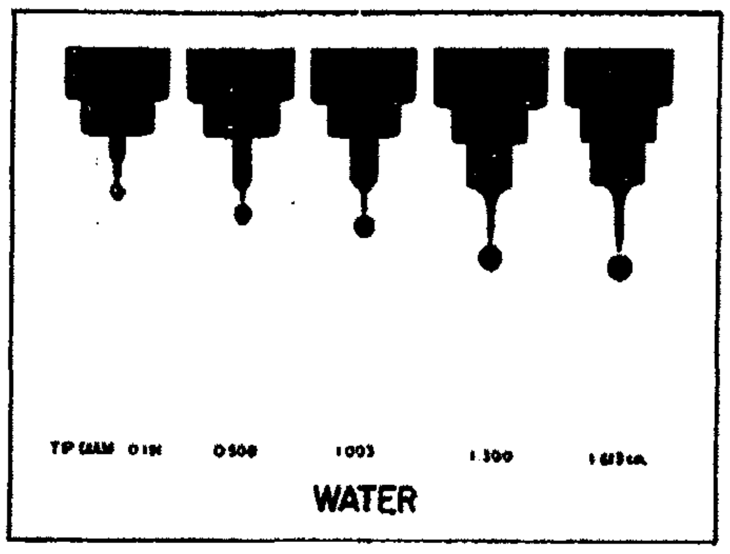


Fig. 6

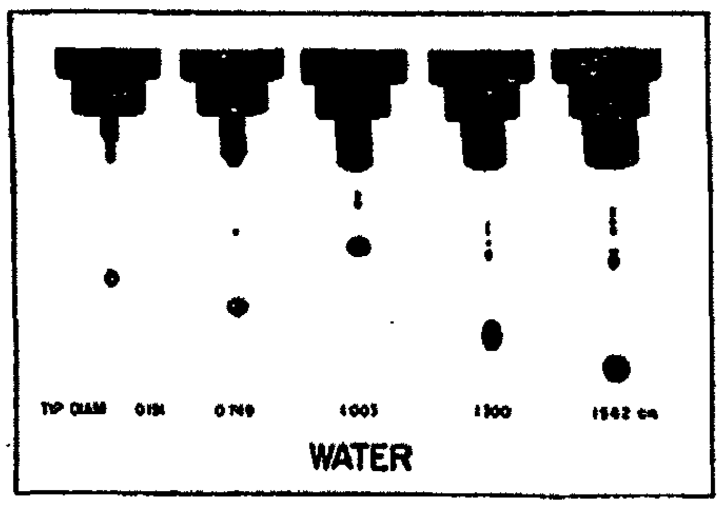


Fig. 7

Figs. 5, 6, and 7. Drops of water falling from tips of various diameters

The stem length at the instant of detachment of the primary drop was also determined from the enlargements.

One of the first points of interest is the variation in shape and size of the pendant drop just prior to the instant that instability sets in. It will be noticed in figure 5 that for tips whose diameter is smaller than 0.5 cm., the pendant drop has a diameter greater than the diameter of the tip. The pendant drop on larger tips has a smaller diameter than the tip on which it is formed.

TABLE 1

Dimensions of drops in centimeters

TIP	DIAMETER	STEM LENGTH	DROP DIAMETERS						
			Primary	Secondary	3	4	5	6	7
6	0.191	0.20	0.40						
7	0.254	0.38	0.42						
8	0.343	0.43	0.46						
9	0.508	0.64	0.52	0.14					
10	0.681	0.84	0.56	0.16					
11	0.749	0.94	0.57	0.17					
12	0.800	0.99	0.59	0.17					
13	0.902	1.07	0.60	0.18					
14	1.003	1.25	0.62	0.19	0.16				
15	1.201	1.63	0.65	0.26	0.16	0.14	0.11		
16	1.300	1.75	0.67	0.26	0.16	0.14	0.14		
17	1.400	1.83	0.70	0.28	0.20	0.14	0.14		
18	1.448								
19	1.514	2.00	0.72	0.32	0.22	0.20	0.18	0.14	0.16
20	1.542	2.03	0.72	0.32	0.22	0.20	0.18	0.14	0.16
21	1.613	2.08	0.72	0.32	0.23	0.20	0.18	0.16	0.14
22	1.806	2.16	0.72	0.32	0.25	0.20	0.18	0.16	0.13
23	2.009	2.24	0.72	0.32	0.25	0.20	0.18	0.16	0.13

Consider a static drop of liquid hanging from a tip. The entire weight of the drop must be supported by adhesion of the liquid to the surface of the tip. In figure 8 the silhouette of a drop is presented. Now suppose an imaginary horizontal plane is passed through a drop at any point. Line a–a represents such a plane drawn through the neck. The sum of the vertical components of all the forces acting at this section must be zero. These forces are (*a*) surface tension around the perimeter, and (*b*) compressive stress in the liquid. Graphical analysis of the drop in figure 8 (surface tension 72 dynes per centimeter) shows a vertical upward component of surface tension at section b–b of 0.103 g., 0.038 g. of water hanging from this plane, and a resultant net compressive force of 0.427 g. per cm^2. over the area of the section. Similar analysis at a–a shows the vertical component of the surface tension of 0.095 g., 0.0682 g. of water hanging from the plane, and a resultant net compressive force of 0.236 g. per cm^2. At the surface of the tip the component due to surface tension is 0.104 g., 0.094 g. of water is supported, and the net compressive force is 0.0574 g. per cm^2. This is therefore a stable drop. The difference in hydrostatic head between the tip and a–a is 0.179 cm. of water, and the difference in net compressive force is 0.178 g. per cm^2., a good check. The hydrostatic head between a–a and b–b is 0.192 cm. of water, and the difference in net compressive force is 0.191 g. per cm^2. This agrees with A. M. Worthington's conclusions (6).

TABLE 2

Drop weights calculated from measurements in table 1 as compared with actual drop weights

TIP	CALCULATED DROP WEIGHT	ACTUAL DROP WEIGHT
	grams	*grams*
6	0.034	0.0325
7	0.039	0.0396
8	0.051	0.0522
9	0.074	0.0717
10	0.094	0.0956
11	0.100	0.1033
12	0.110	0.1086
13	0.116	0.1202
14	0.131	0.1388
15	0.156	0.1737
16	0.171	0.1868
17	0.198	0.2071
18		0.2131
19	0.221	0.2201
20	0.221	0.2224
21	0.229	0.2295
22	0.231	0.2257
23	0.231	0.2314

The conditions given above are normal for a stable pendant drop. Additional liquid can be added to the drop until the net compressive force at the neck approaches zero, at which time instability sets in. At this instant the problem changes from one of static forces to one of dynamic motions. Unbalanced forces are opposed by accelerations and viscous drag. It becomes practically impossible to predict the mechanism of detachment on a theoretical basis because of the complexity of the motions of the drop, its stem, and secondary drops. This is illustrated by figure 9, which shows the actual mechanism of drop formation for water falling from a large tip.

It is interesting to note how complicated the drop formation becomes with large tips. Instability first shows itself by a lengthening and reduction in the diameter of the neck. The neck breaks off close to the primary drop, which oscillates as it falls. The neck now begins to break up into segments and detaches itself from the residual fluid remaining on the tip. The segments of the neck now become independent secondary drops, falling after the primary drop at unequal velocities; some of them may coalesce.

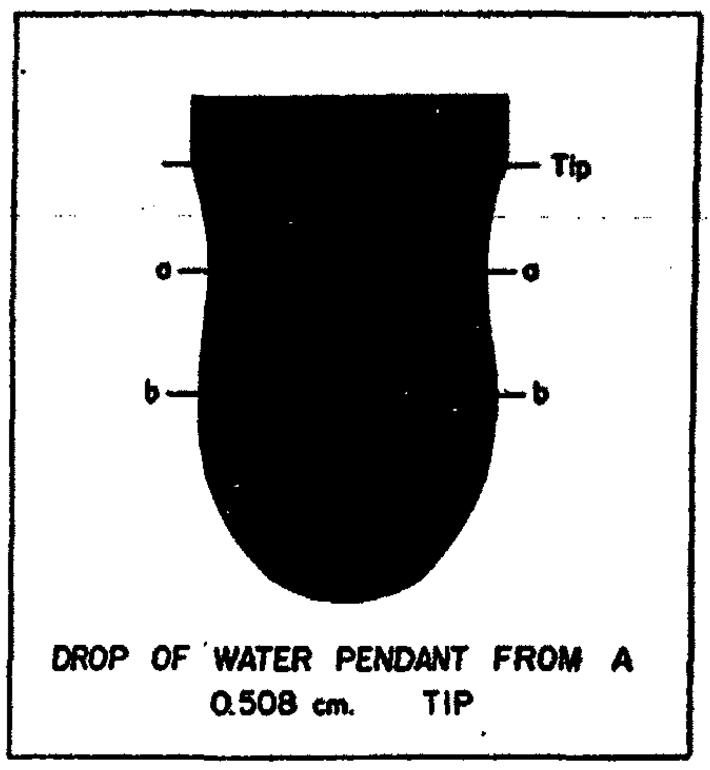


Fig. 8

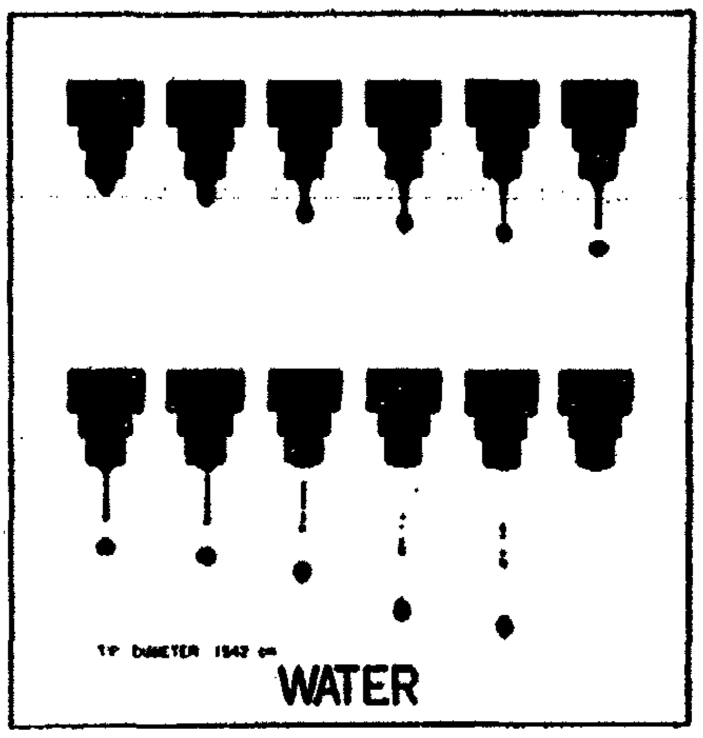


Fig. 9

Fig. 8. Drop of water pendant from a tip having a diameter of 0.508 cm.

Fig. 9. Actual mechanism of drop formation for water falling from a large tip, the diameter of which is 1.542 cm.

Tate assumed that the weight of a drop equaled the product of the surface tension of the liquid by the circumference of the tip on which it formed. This would be true if the wall of the drop were vertical where the liquid joins the tip, if there were no compressive forces across the plane, and if all of the pendant drop actually detached. Unfortunately, this ideal condition is never met in actual practice. The pictures show clearly that it is very rare for the wall of the drop to be vertical at its juntion with the tip, the compressive force is not zero, and there is always a very considerable residual drop left on the tip.

Harkins and Brown have used Tate's law as a point of departure, and contributed an empirical correction curve which makes it possible to determine from a knowledge of the volume of Tate's "ideal" drop the volume of the drop which actually falls. Figure 10 shows this curve, together with pictures of drops formed from various tips. At the left-hand side of the diagram the actual falling drop is a large portion of the ideal drop. The decrease from here to the minimum is due to decrease in diameter of the drop relative to the diameter of the tip. The increase between the minimum point and the maximum is probably due to the increase in the thickness of the stem and the detachment of a greater portion of the pendant drop. At the maximum, the maximum size of primary drop is attained, and although the stem length continues to increase, the increase in the size of secondary drops formed from it is small compared to the increase in circumference of the tip, and the curve falls off rapidly as the tip diameter is increased. This is paralleled by the difficulty of completely wetting large tips effectively. The curve of profile of the pendant drop becomes nearly tangent to the tip at the point of junction. As a result, the main component of the surface tension forces is toward the center of the tip, tending to sweep the liquid toward the center into a drop of smaller diameter and surface. This leaves a thin film of moisture on the tip, which tends to evaporate very rapidly, owing to its practically colloidal dimensions.

McBain, Ford, and Wilson (5) have pointed out that while the addition of small amounts of certain organic chemicals to water causes a reduction in surface tension, a definite minimum surface tension is reached, after which further additions of the organic chemical increase the surface tension. Sodium oleate is such a substance. The experiments on which their results were based were conducted on aged surfaces. As may be noted from the preceding figures, a large amount of new surface is always formed when a drop falls from a surface, and if the drop is formed just prior to the time of detachment, it is possible to study a surface which has aged for only a few hundredths of a second. Drop formation, therefore, presents an excellent method for determining if the minimum surface tension mentioned above is dependent on the rather slow formation of surface structure implied by the usual concept of concentration of a surface-active substance at an interface.

In the paper mentioned above, the minimum surface tension was observed for sodium oleate in water solutions when the concentration reached about 0.1 per cent by weight. Solutions of sodium oleate in water of 0.001, 0.01, 0.1, and 1.0 per cent by weight were used for the experiments. A check on the variation of du Noüy ring surface tensions showed that the 0.1 per cent solution gave the minimum surface tension in accordance with the above reference. The four largest tips in the set were used, since they offered opportunity for the greatest possible variation in the method of drop formation.

Figures 11, 12, and 13 show typical results from this series of tests. The predicted minimum is quite pronounced. Figure 11 shows that the 0.1 per cent solution produced the smallest primary drop and the shortest stem. Figure 12 emphasizes the shortening of the stem. Figure 13 shows the effect of concentration of the sodium oleate on the number of secondary drops formed by segmentation of the stem. This result indicates that, at least with the system under investigation, the appearance of a minimum surface tension does not depend on aging of the surface.

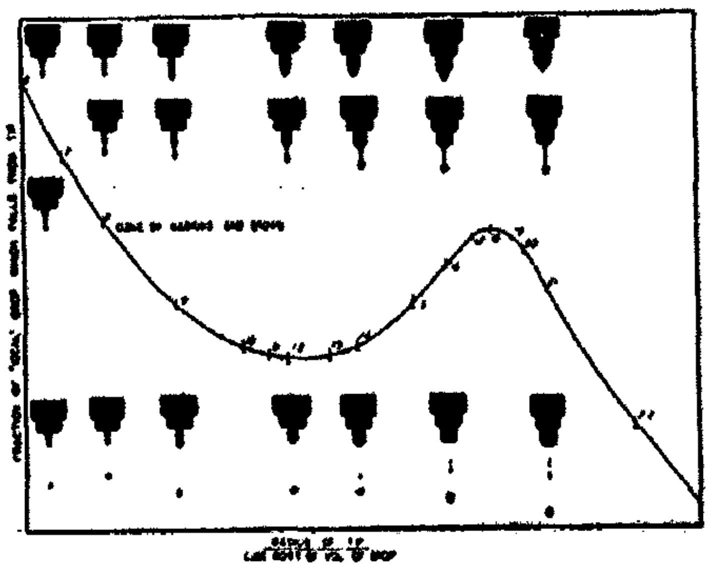


Fig. 10

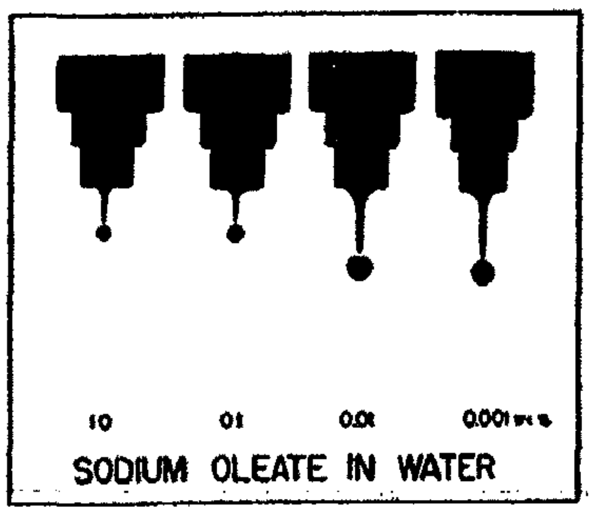


Fig. 11

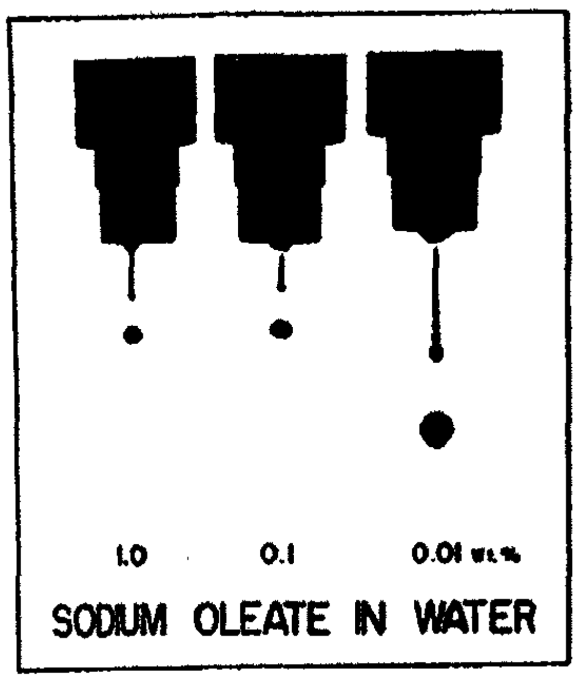


Fig. 12

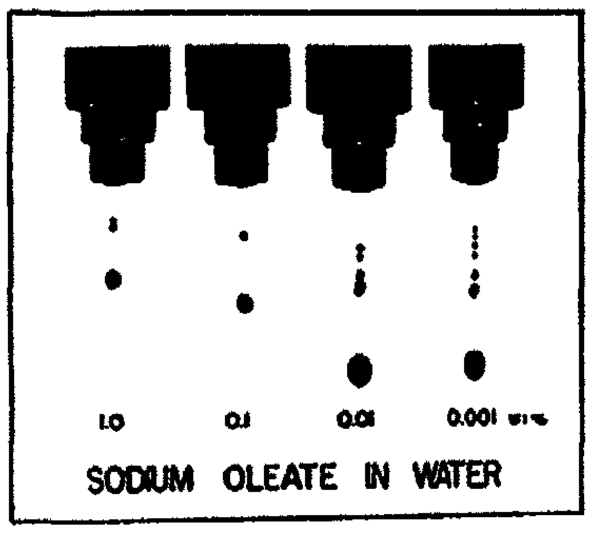


Fig. 13

Fig. 10. Empirical correction curve of Harkins and Brown, together with pictures of drops formed from various tips.

Figs. 11, 12, and 13. Results obtained with sodium oleate solutions

The experiments conducted last year with moderate-sized tips showed that the mechanism of formation of drops of glycerol is markedly different from that of the formation of drops of water, for example, particularly in regard to the length of stem formed and the method of segmentation of that stem. This raises the question of the validity of the measurement of the surface tensions of viscous liquids and of solutions of surface-active materials by the drop-weight method. In order to study the problem, solutions were made which had identical surface tensions as shown by the du Noüy ring method, but which differed widely in their other physical properties. The approximate compositions of the solutions used are given in table 3, but no unusual precautions were taken in preparing the chemicals used. Tips No. 1, 4, 18, and 23 were used with each solution. Typical results are shown in figures 14 to 16. Tips 18 and 23 were, of course, too large to obtain reliable values of surface tension by the drop-weight method with solutions of such low surface tension.

TABLE 3

Solutions having the same surface tension as determined by the du Noüy ring method

SOLUTION	SURFACE TENSION	COMPOSITION	SPECIFIC GRAVITY
Nitrobenzene	48.0	100 per cent commercial nitrobenzene	1.199
Alcohol-water	47.8	85.6 per cent water 13.7 per cent ethyl alcohol 0.7 per cent methyl alcohol	0.973
Sodium oleate-water	48.1	0.00068 per cent sodium oleate 99.99932 per cent water	1.000
Glycerol-water	47.7	90.8 per cent glycerol 9.0 per cent ethyl alcohol 0.2 per cent methyl alcohol	1.219

If the drop-weight, or the drop-number, method were to be reliable, the minimum requirement would be that the shape and size of the pendant drop at the instant instability sets in, and the portion of this drop finally detached from the tip should be the same for each of the liquids (1). Admitting that the drop-weight method as conducted in these experiments, and to some extent regardless of the details of technique, gives the surface tension of fresh surfaces, whereas the du Noüy ring method uses aged surfaces, the sodium oleate in water solution may be excused from conforming with the "normal" liquid, nitrobenzene. The alcohol in water solution is qualitatively similar to the nitrobenzene, but the glycerol is very different. Our conclusion is that the drop-weight and drop-number methods may be reliable for pure liquids, but that their use for determining the surface tension of solutions and of viscous liquids is questionable.

The tenacity of the extremely small filaments of glycerol which are formed as the detached stem segments is remarkable. Many pairs of drops remained joined by practically invisible threads, but these threads contracted and pulled the drops together so that they coalesced. Some

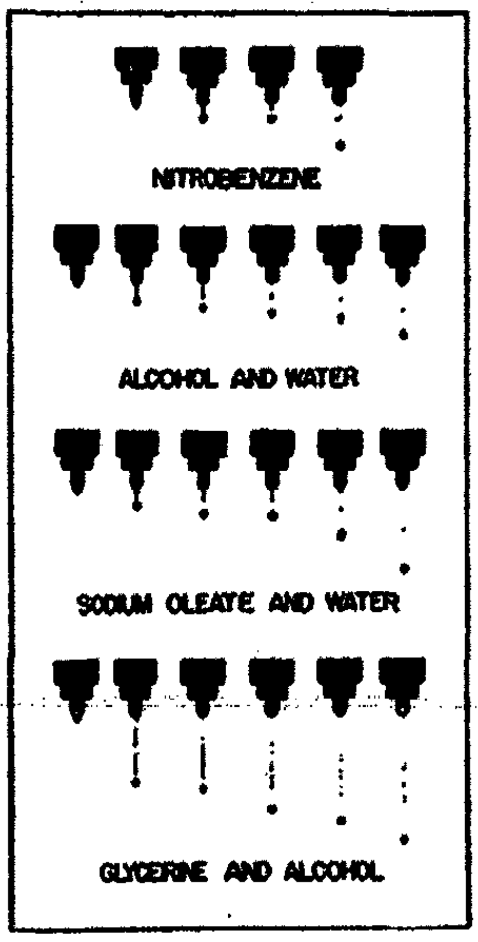


FIG. 14. Drop formation in the case of solutions having the same surface tension

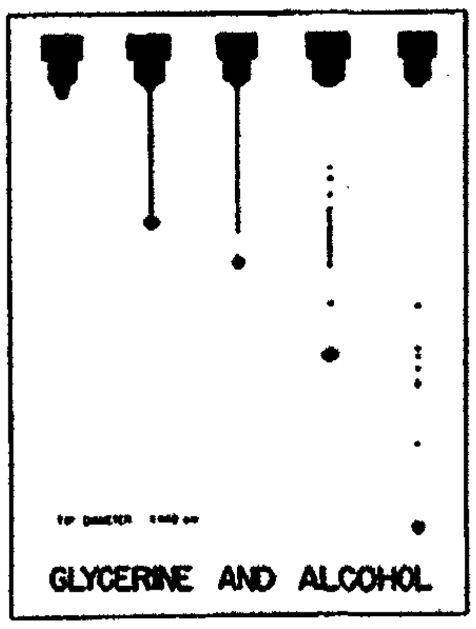


FIG. 15

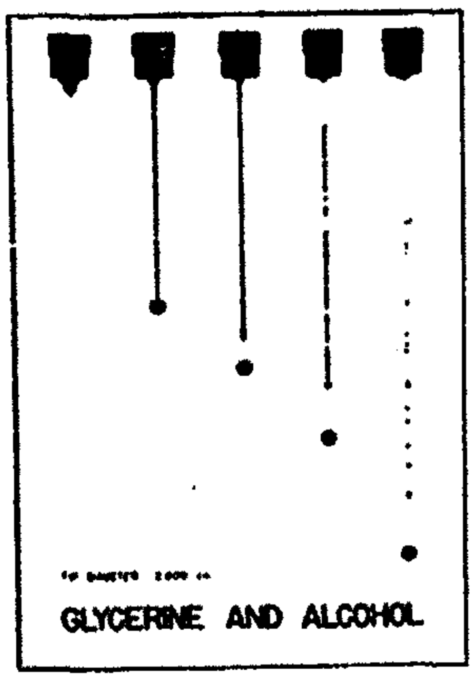


FIG. 16

FIG. 15. Drop formation in the case of a solution of glycerol and alcohol (see table 3), using a tip having a diameter of 1.448 cm.

FIG. 16. Drop formation in the case of a solution of glycerol and alcohol (see table 3), using a tip having a diameter of 2.009 cm.

of these threads showed in the original enlargements, but are lost in subsequent reproduction. Other pairs of drops coalesced which were not joined by visible threads. There is a good chance that these were joined by invisible filaments.

The ability of viscous liquids to form threads may throw new light on the actual nature of viscosity. It is quite conceivable that microscopic or colloidal liquid filaments are formed when an attempt is made to shear or stir a viscous liquid.

SUMMARY

1. Accurate graphical analysis of the stresses in a pendant drop can be made providing a sharp silhouette is available.
2. There are net compressive forces at all planes in a stable drop.
3. The mechanism of drop formation from large tips is very complex, and the use of large tips for surface tension measurements is not advisable.
4. Primary drops from small tips may be of larger diameter than the tip itself, but the primary drops from large tips are small compared to tip size.
5. The number of secondary drops formed by the segmentation of the stem varies both with the tip size and with the nature of the liquid used. Drops formed on the smallest tips detached without the formation of any secondary drops, while fifteen secondaries were formed during the detachment of a drop of an alcohol in glycerol solution from a large tip.
6. The occurrence of a minimum surface tension of soap solutions, as predicted by McBain, Ford, and Wilson, was readily verified by examination of motion pictures of drops of soap solution falling from large tips.
7. It was found that the physical properties of a liquid have a large effect on the mechanism of drop formation. Viscosity and surface activity are both important.
8. Dynamic methods for determining surface tension should be used with extreme caution unless the methods of calculation are known to be applicable to the particular liquid being studied. Static methods are preferable.

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THE MECHANISM OF THE DEHYDRATION OF ZEOLITES[1]

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In recent years calcium sulfate hemihydrate, or plaster of Paris, has been frequently referred to as a zeolite rather than as a definite hydrate. This point of view resulted from the observations (*a*) that the dehydration isobar was continuous and (*b*) that there was little or no change in crystal structure on dehydration. The present investigators have shown that calcium sulfate hemihydrate in the form of submicroscopic crystals (15) prepared by dehydration of selenite, or of macrocrystals (14) prepared by crystallization from a nitric acid solution, is a definite chemical hydrate, giving a stepwise dehydration isobar when care is taken to establish equilibrium at each temperature, and showing characteristic differences in the x-radiogram before and after dehydration. In the light of these observations, it was believed that a similar dehydration and x-ray diffraction study of various zeolites might yield information of interest concerning the mechanism of their dehydration.

The comprehensive reports of Hey (4) and of Hey and Bannister (5) make unnecessary more than a brief mention of how water is thought to be bound in zeolites. Hey (4) considers zeolites to be "a well-defined group, generally regarded as hydrated silicates of aluminum and the alkalis or alkaline earths," with the ratio $O/(Al + Si) = 2$. It is generally considered (12) that their unusual base exchange and dehydration properties are the result of the nature of the crystal lattice, which consists (1, 10) of SiO_4 and AlO_4 anions in a framework containing channels large enough to hold cations and water molecules. Three general theories have been proposed to explain the manner in which water is bound in the zeolite:

(*a*) *Solid solution theory.* The original zeolite is assumed to be a definite hydrate, but upon dehydration the resulting product forms a continuous series of solid solutions with the hydrate. This solid solution theory is intended to reconcile the continuous dehydration isobar for a hydrate with the phase rule.

(*b*) "*Vagabond water*" *theory.* The water molecules are believed to be free to move about in the lattice, and not to occupy definite positions in the

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unit cell. It is not clear from this theory whether or not the zeolites are to be regarded as true hydrates.

(c) *Adsorption theory.* The water is held by adsorption forces within the capillary-like channels of the crystal lattice.

X-ray analysis has shown (16) that water or the constituents of water may be present in the lattice in three ways: (a) H_2O groups arranged around another ion as in coördination compounds like $AlCl_3 \cdot 6H_2O$; (b) OH groups as in definite hydroxides; or (c) H_2O groups held in lattice channels such as exist in the zeolites. To this enumeration there may be added (2, 6) OHO bridges such as are found in diaspore, $AlHO_2$ (2).

It is generally conceded that the changes in the x-ray patterns of zeolites before and after dehydration may be very small. Some writers cite this evidence to show that the lattice changes, and that the water molecules occupy a definite position within the unit cell. On the other hand, other writers use these same facts to show how non-essential the water molecules are to the lattice. These changes, large or small, will be considered in further detail in later paragraphs.

It is the purpose of this paper to report the results of a dehydration and x-ray diffraction study of the following zeolites: scolecite, stilbite, heulandite, thomsonite, analcite, natrolite, mesolite, and chabazite.

EXPERIMENTAL

Preparation of samples

Selected samples of the various zeolites to be studied were ground in an agate mortar to approximately 200 mesh. The ground samples were exposed to the water vapor in the atmosphere for several days, and therefore could be weighed without any special precautions to avoid loss or gain of water during the weighing.

Isobaric dehydration

The dehydration isobars were obtained by methods already described (13, 15). Care was taken to allow the establishment of equilibrium at each temperature point of the isobar. To establish some points, as long as 1200 hours were required. The isobaric dehydration data for the several samples are given in table 1, and are shown graphically in figures 1 to 8 inclusive.

X-ray examination

Samples for x-ray diffraction analysis of each zeolite were taken at various temperatures from separate portions which had been treated in the same way and at the same time as the weighed samples for the dehydration isobars. At all temperatures the samples were sealed off according to a method similar to one already described in detail (15). When the

TABLE 1

Isobaric dehydration data for zeolites

TEMPERATURE IN 0°C.	LOSS OF WEIGHT IN PER CENT																		
	Scolecite			Stilbite		Heulandite		Thomsonite		Analcite		Natrolite			Mesolite		Chabasite	
	A	B	C	A	B	A	B	A	B	A	B	A	B	C	A	B	A	B
30↓	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50↓	0.04	0.04		0.90	0.89	1.36	1.31	0.62	0.61	0.03	0.05	0.07	0.08		0.37	0.39	1.92	1.84
75↓	0.09	0.05		1.25	1.24	1.99	1.87	0.75	0.76	0.05	0.06	0.11	0.08		0.44	0.46	3.11	2.90
100↓	0.12	0.18		2.05	2.08	2.76	2.22	1.03	1.03	0.19	0.13	0.19	0.13		0.54	0.56	5.23	4.92
105↓	0.20														0.70			
120↓				7.84	7.71	5.39	5.34	1.81	2.17		0.38		0.24			0.76	9.47	9.22
134↓	0.28			8.62		5.74		2.08		0.54		0.26			0.78		11.22	
153↓		0.38			9.30		6.50		2.46		0.91		0.56			1.30		10.8
165↓	1.12			10.98		7.19		2.95		1.85		1.62			2.02		12.87	
180↓		1.89			11.71		7.45		2.98		2.01		1.92			2.48		13.0
200↓	4.30	4.42		13.93	13.05	8.06	8.06	3.41	3.39	2.91	2.86	4.23	4.28		3.71	3.68	14.26	14.0
155↑	0.61	0.66		11.19	11.20	6.58	6.54	3.30	2.59	1.07	1.33	0.60	0.72		1.26	1.42	11.30	10.33
25↑	+0.14			3.34		+0.52		+0.12		1.03		+0.12			+1.17		+0.65	
100↓	0.24			6.55				1.74		1.13		0.22			0.98		5.10	
150↓	0.44			10.17		5.96		2.49		1.13		0.47			1.15		10.36	
230↓	4.72			14.70		11.81		4.35		4.62		4.87			5.88		17.19	
255↓		4.75			15.61		12.85		6.02		6.28		5.21			7.27		17.62
280↓		4.90			16.13		13.52		6.83		6.93		6.28			10.99		18.19
300↓			4.76											5.02				
330↓			5.02											6.45				
375↓			10.04											11.01				
400↓			10.26		16.83		14.27		9.25		8.15		10.78			11.88		19.24

zeolite was in equilibrium, as evidenced by the constancy of weight at a definite temperature and pressure, a small portion was placed, still hot, in a preheated Mark tube (a thin capillary tube of Lindemann glass). The Mark tube was then placed beside the sample bottle and heated at the same temperature for at least twenty-four more hours in the event that there had been some displacement in the equilibrium during the transfer; the tube was then carefully sealed off while still hot. X-ray diffraction patterns were obtained for the various samples using Cu K_α x-radiation from a Philips tube; the camera diameter was about 57 mm. Diagrammatic representations of the results of the x-ray analyses are given in figures 1 to 8 inclusive.

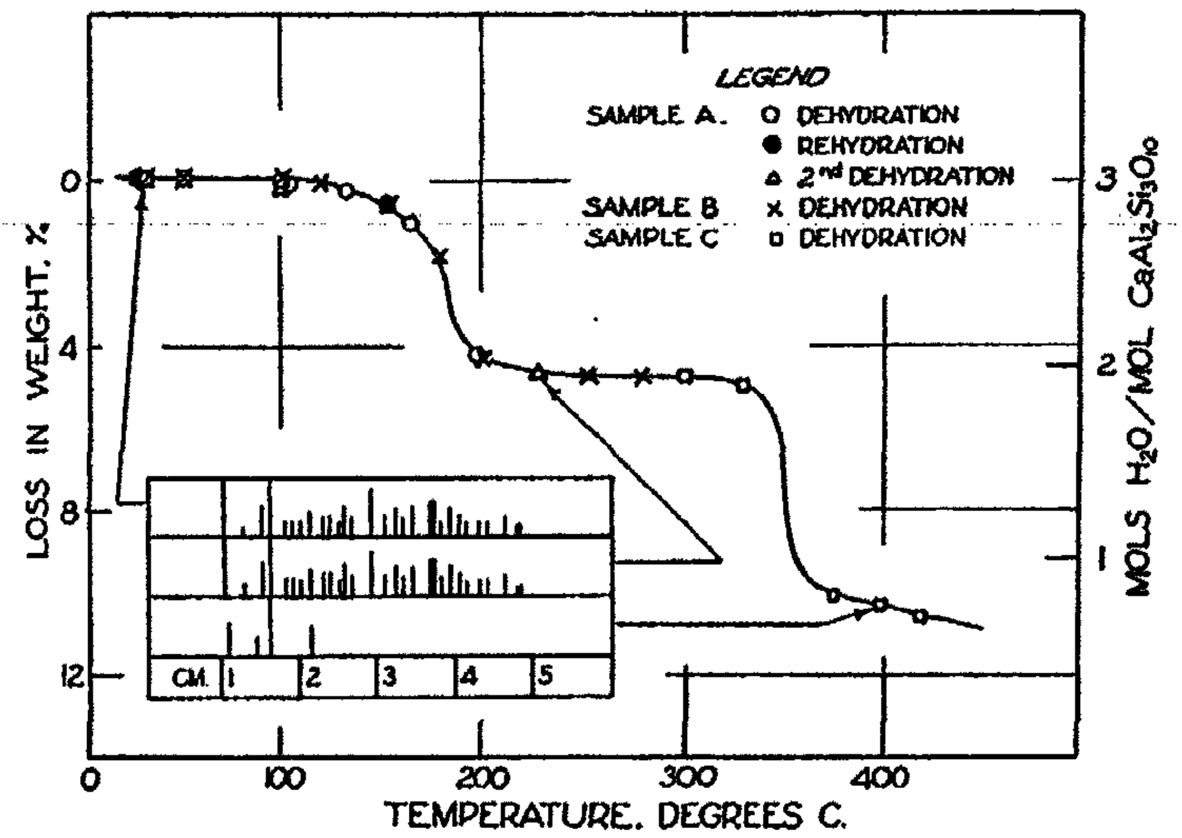

FIG. 1. Dehydration isobar and x-ray diffraction patterns for scolecite

DISCUSSION

Scolecite

The accepted composition of scolecite is $CaAl_2Si_3O_{10} \cdot 3H_2O$, but there is no conclusive evidence as to whether or not this zeolite is a definite hydrate. Pauling (8) and Taylor, Meek, and Jackson (11) concluded from x-ray data that the water is a constituent part of the lattice. Rinne (9) observed alterations in the x-radiogram upon dehydration; on the other hand Kelly, Jenny, and Brown (7) obtained a smooth dehydration isobar. The isobar shown in figure 1 indicates quite clearly that a stepwise curve is obtained for scolecite when care is taken to maintain a constant aqueous vapor pressure and sufficient time is allowed for the establishment of equilibrium at each point. The breaks in the isobar for the tri- and dihydrates of scolecite are quite as sharp as for most hydrates. The x-radiograms, also shown in figure 1, lead to the same conclusion. The differences between the x-radiograms of the tri- and di-hydrates are extremely small. If it is assumed that the crystal merely loses one molecule of water from the channels in the lattice, little alteration would be expected to take place either in the positions of the lines or in their intensities. It should be recalled that the changes in the x-radiograms of calcium sulfate hemihydrate before and after dehydration are not marked, although there are characteristic changes which can be easily detected. After dehydration at 400°C., the scolecite lattice is completely broken down.

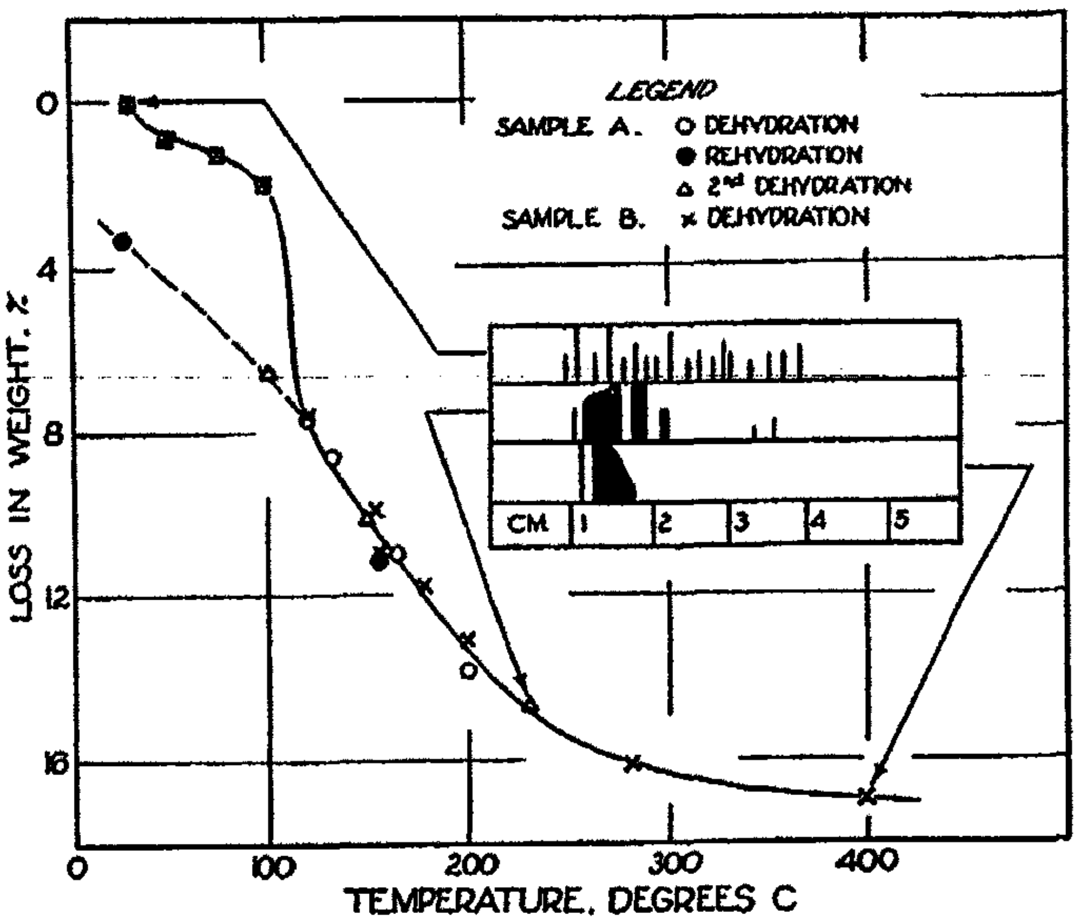

FIG. 2. Dehydration isobar and x-ray diffraction patterns for stilbite

Stilbite

The dehydration isobar (figure 2) for stilbite shows no indication that this zeolite is a definite hydrate. The break in the curve is indicative of the formation of a second modification of stilbite (similar to the two modifications of heulandite, previously recognized). It will be noted that the break in the curve is not reversible. Upon heating stilbite to around 100–120°C., the x-radiogram changes quite markedly; rehydration does not again alter the x-ray diffraction pattern. After the second modification of stilbite is formed, the dehydration–rehydration curve is reversible. Heating to around 400°C. breaks down the lattice.

Heulandite

The dehydration isobars and x-ray diffraction patterns for heulandite, given in figure 3, indicate that this zeolite exists in at least three modifications. The transition at 200–220°C. is well known (4), but the transition at 100–120°C. has not been previously recognized, to the knowledge of the present investigators. The shape of the isobar could be explained by hydrate formation if the breaks had occurred at definite ratios of water to anhydrous mineral. We are of the opinion that heulandite is not a definite hydrate.

Thomsonite

The isobars for thomsonite given in figure 4 show no indication of hydrate formation, and the accompanying x-radiograms show only a slight lattice contraction. The data indicate that thomsonite is not a definite hydrate, but that the water is held by adsorption forces within the channels in the lattice. It should be mentioned that Hey (5) obtained a continuous isobar for the usual variety of thomsonite, but observed a break in the isobar for a special sample. The break was attributed to the formation of a second modification of thomsonite. Since the sample examined by us gave no break in the isobar, our results throw no light on this question.

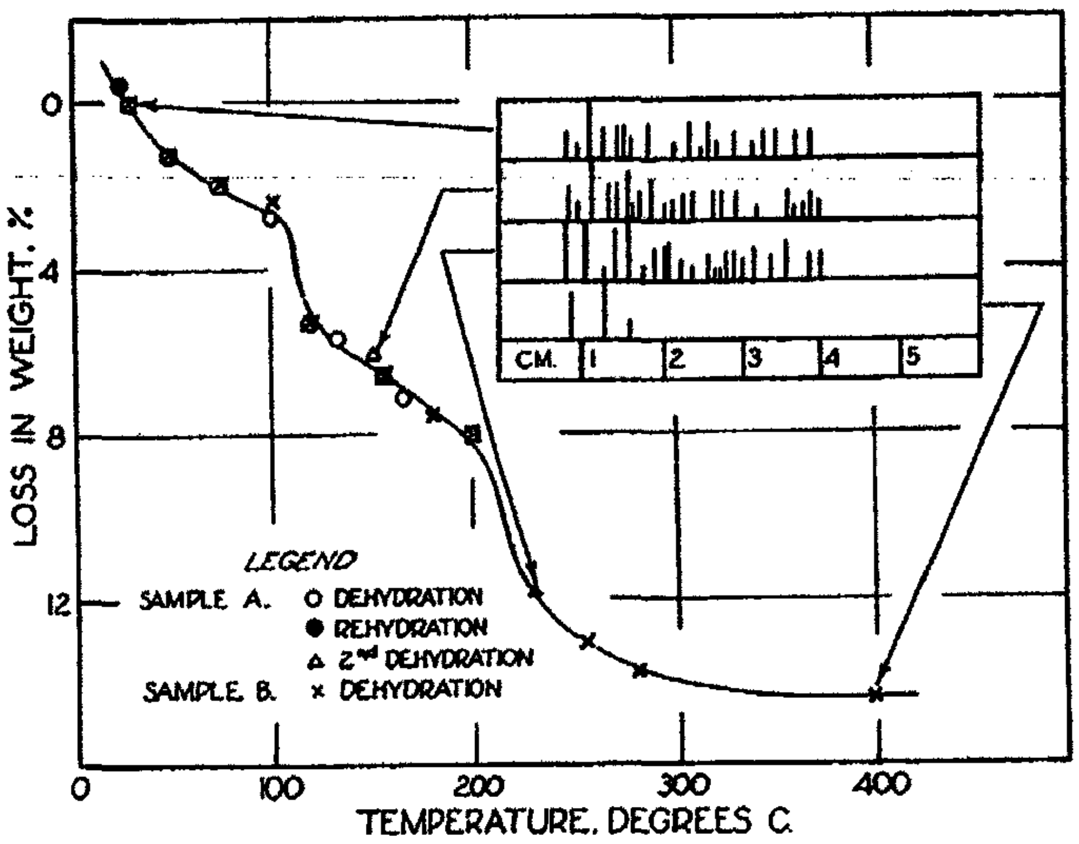

FIG. 3. Dehydration isobar and x-ray diffraction patterns for heulandite

Analcite

Analcite is usually considered to be $NaAlSi_2O_6 \cdot H_2O$. Gruner (3), who observed a slight lattice shrinkage and a slight alteration in intensities after dehydration, suggests that the water is (*a*) "vagabond water," (*b*) contained in a larger lattice complex, or (*c*) adsorbed. His suggestions are apparently based on the fact that the water has little influence on the lattice dimensions. The dehydration isobar given in figure 5 shows no indication of the formation of a hydrate. It is apparent that the analcite

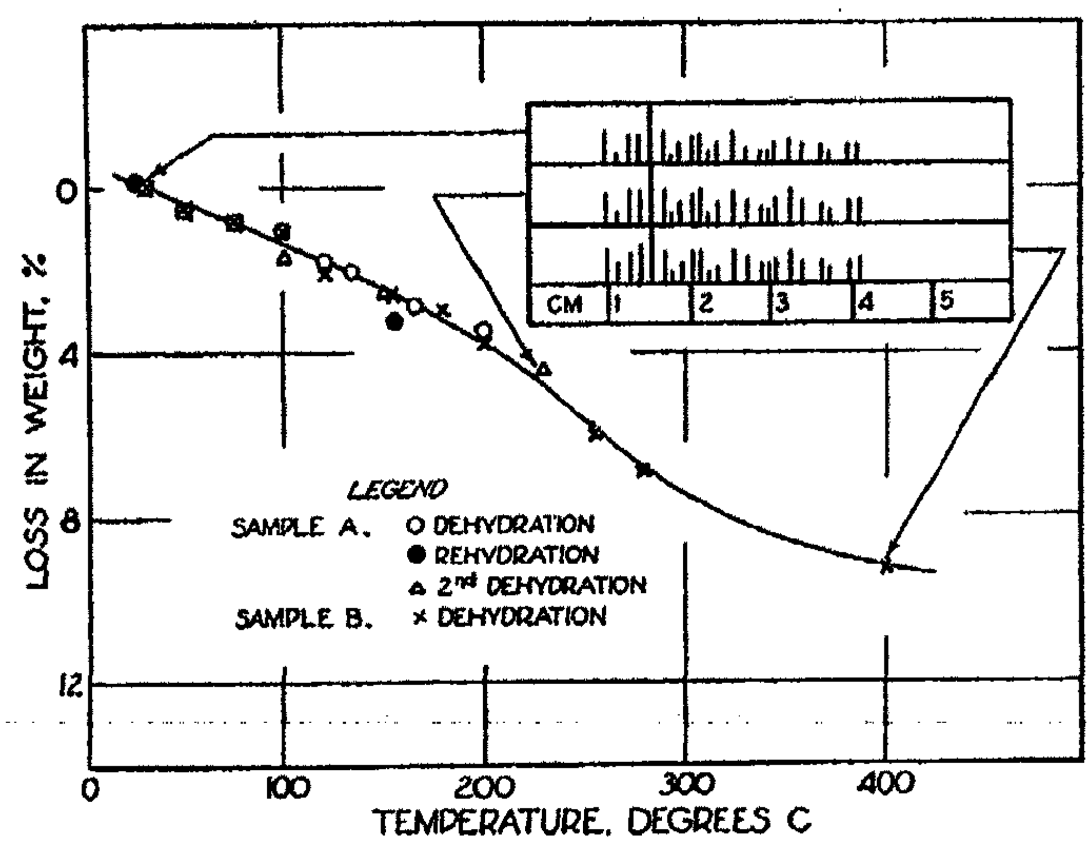

FIG. 4. Dehydration isobar and x-ray diffraction patterns for thomsonite

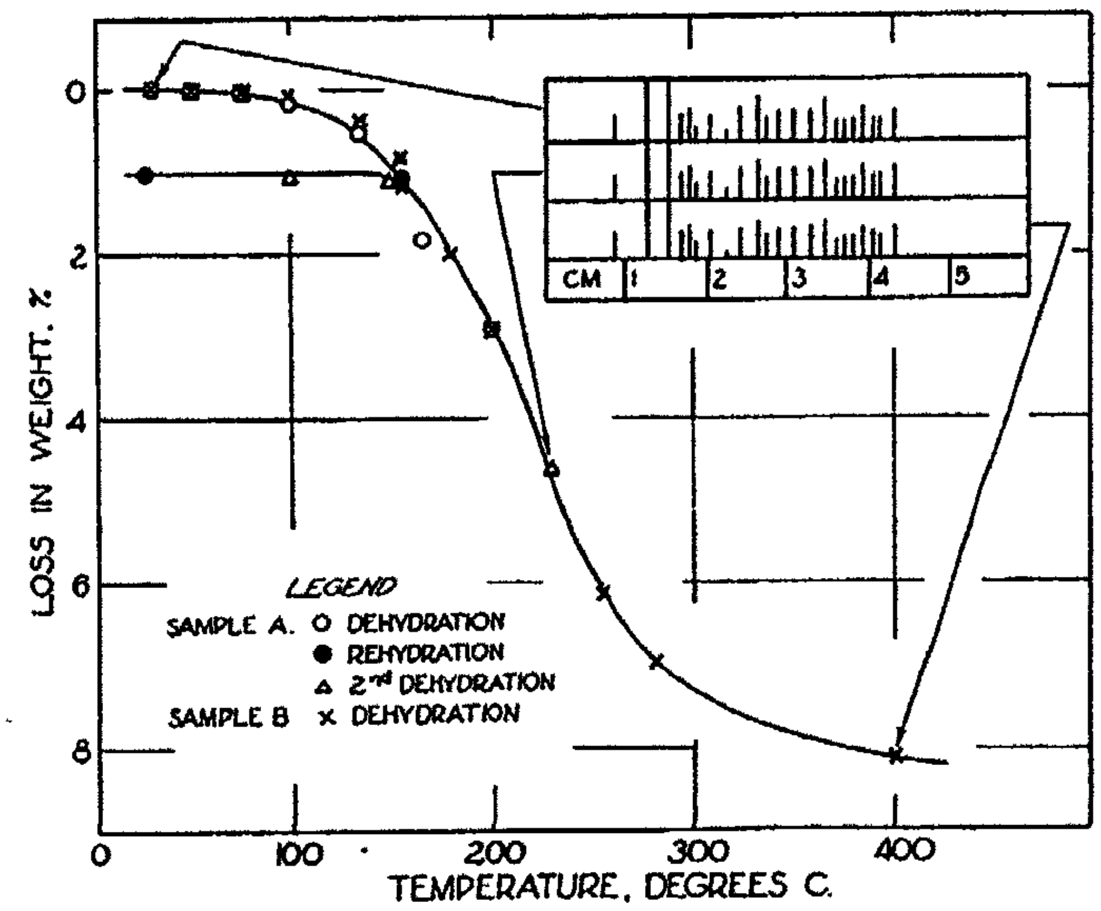

FIG. 5. Dehydration isobar and x-ray diffraction patterns for analcite

isobar is not completely reversible until after the first dehydration. If it should be argued that the original sample is a definite monohydrate, then the same evidence would require the sample upon rehydration likewise to be a definite hydrate having the approximate composition $NaAlSi_2O_6 \cdot 0.9H_2O$. Since this is improbable, one must conclude either that analcite is not a true hydrate or that the structure is based on a lattice much more complex than that of the other zeolites. In the absence of conclusive evidence, the present authors prefer to assume that the water in analcite is held by adsorption forces in the channels within the lattice, and that the irreversibility is the result of the heat treatment. If the analcite had been heated to a higher temperature, such as 400–500°C., a much smaller amount of water would be taken up on rehydration. It was observed that the lattice shrinks only a little on heating from 30° to 230°C. or even to 400°C., in general agreement with Gruner. Heating to a much higher temperature would be expected to break down the lattice completely.

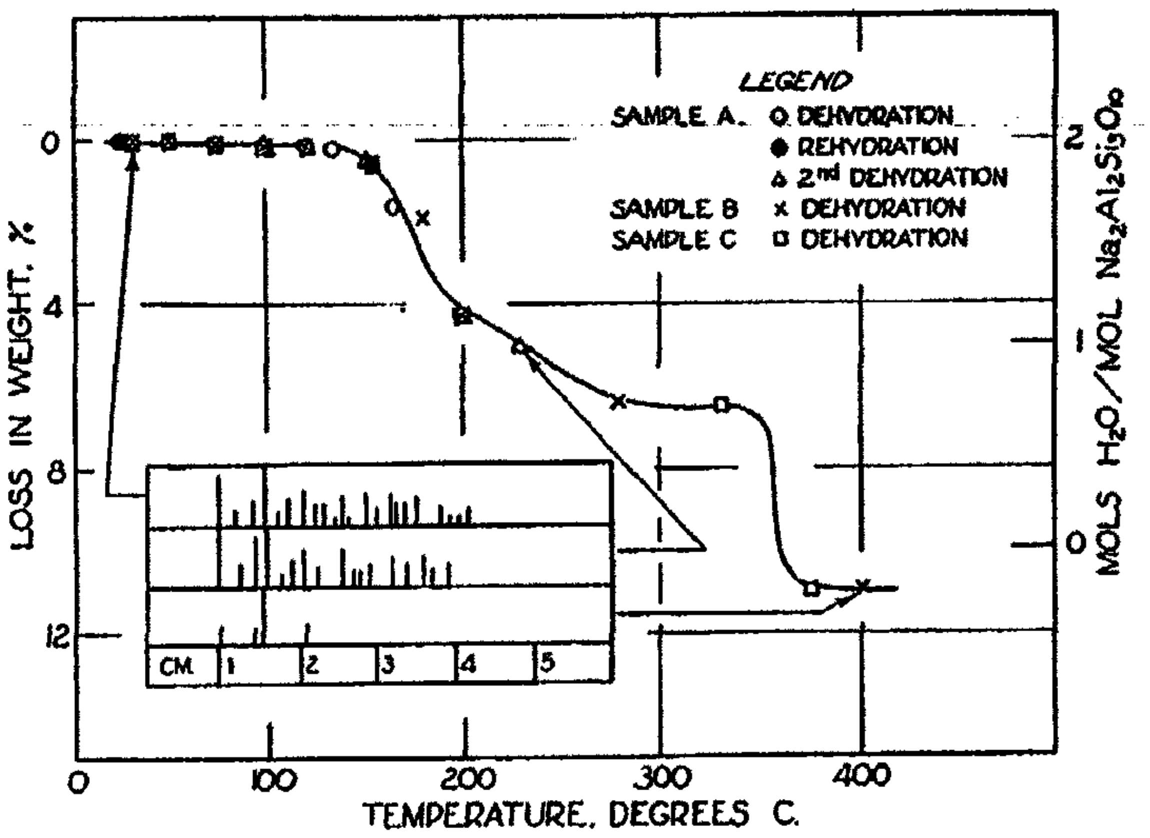

FIG. 6. Dehydration isobar and x-ray diffraction patterns for natrolite

Natrolite

The formula of natrolite is usually written $Na_2Al_2Si_3O_{10} \cdot 2H_2O$. In confirmation of this, the results of isobaric dehydration and x-ray diffraction examination (figure 6) show clearly that natrolite is a dihydrate which decomposes above 160–180°C. to form a monohydrate, stable to around 250°C. The x-radiogram shows a slight but significant change when the first molecule of water is lost, and a pronounced change when the monohydrate breaks down.

Mesolite

Mesolite is thought to be a mixture or a solid solution of varying amounts of scolecite, $CaAl_2Si_3O_{10} \cdot 3H_2O$, and natrolite, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ (3, 20).

X-radiograms of these three zeolites are very much alike for short exposures, and show only small differences on larger exposures. The shape of the dehydration isobar (figure 7) is such as might be expected from a solid solution of scolecite and natrolite. The first break would correspond to the dehydration of the scolecite trihydrate and the natrolite dihydrate to form the respective lower hydrates. The second break, which is not so pronounced, would be interpreted as the point of decomposition of the mixture of lower hydrates to the anhydrous material. The x-radiograms for samples at 30°C. and dehydrated to 230°C. show a slight alteration similar to those obtained when scolecite trihydrate decomposes to the dihydrate. Heating mesolite to 400°C. breaks down the lattice completely.

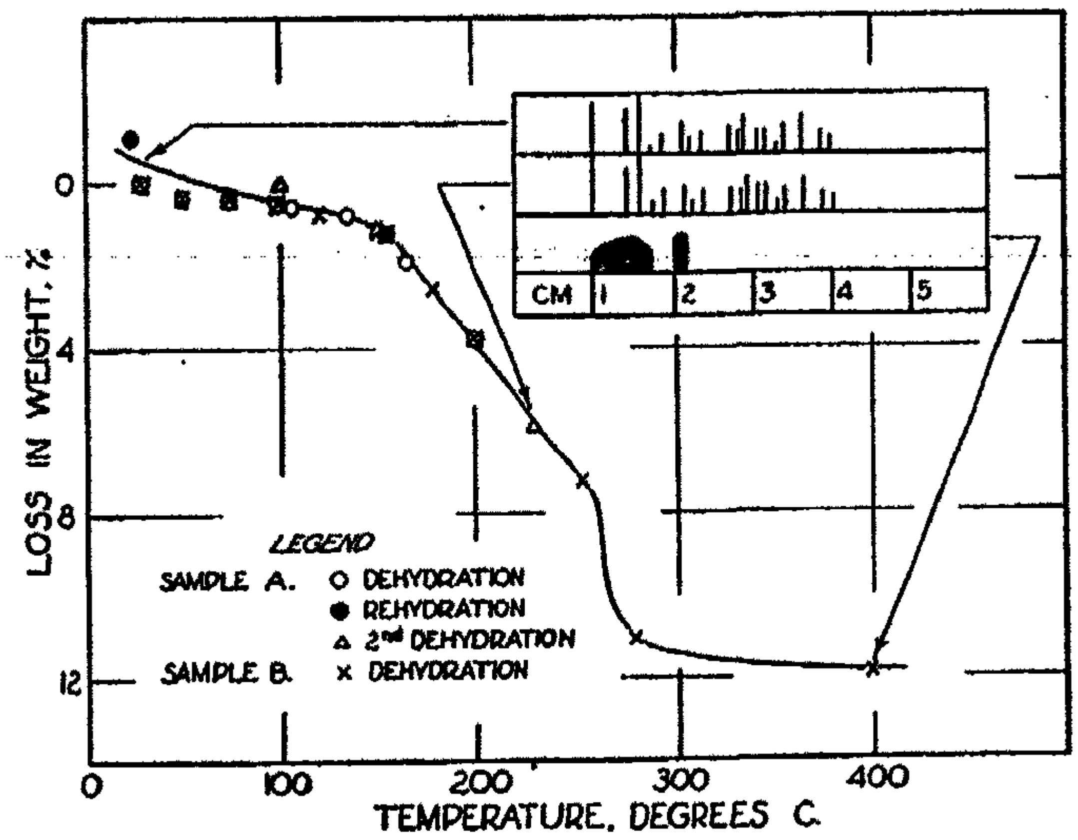

FIG. 7. Dehydration isobar and x-ray diffraction patterns for mesolite

Chabazite

The dehydration isobar for chabazite given in figure 8 is a typical desorption curve showing no indication that a hydrate is formed. There is some evidence of hysteresis at temperatures around 100–150°C. The diagrams of the x-ray diffraction patterns, also given in figure 8, show that the lattice shrinks slightly upon dehydration.

The dehydration mechanism

The results of isobaric dehydration indicate that: (*a*) scolecite and natrolite are definite hydrates; (*b*) mesolite is not a hydrate but a mixture of solid solution of scolecite and natrolite; (*c*) stilbite, heulandite, thomsonite, analcite, and chabazite are not hydrates, but hold water by adsorption forces within channels in the lattice; (*d*) stilbite and heulandite exist in more than one crystalline modification. These results do not disagree with the general view that the zeolite structure consists of a framework of AlO_4 and SiO_4 anions possessing channels large enough to contain sodium or calcium cations, water molecules, or small molecules of various organic liquids.

It is apparent that the binding forces differ from zeolite to zeolite. Thus scolecite and natrolite hold the water by definite chemical forces, as does calcium sulfate hemihydrate, whereas other zeolites, such as analcite, stilbite, heulandite, and chabazite, hold the water molecules by adsorption forces. Since such zeolites as scolecite and natrolite give stepwise dehydration isobars and some significant changes in the x-ray patterns upon dehydration, there seems to be no reason for not considering these materials to be hydrates. Since zeolites such as chabazite give dehydration isobars which are continuous, and also give continuous sorption and desorption isobars (cf. 12) for other vapors, there is no reason to consider these materials to be hydrates.

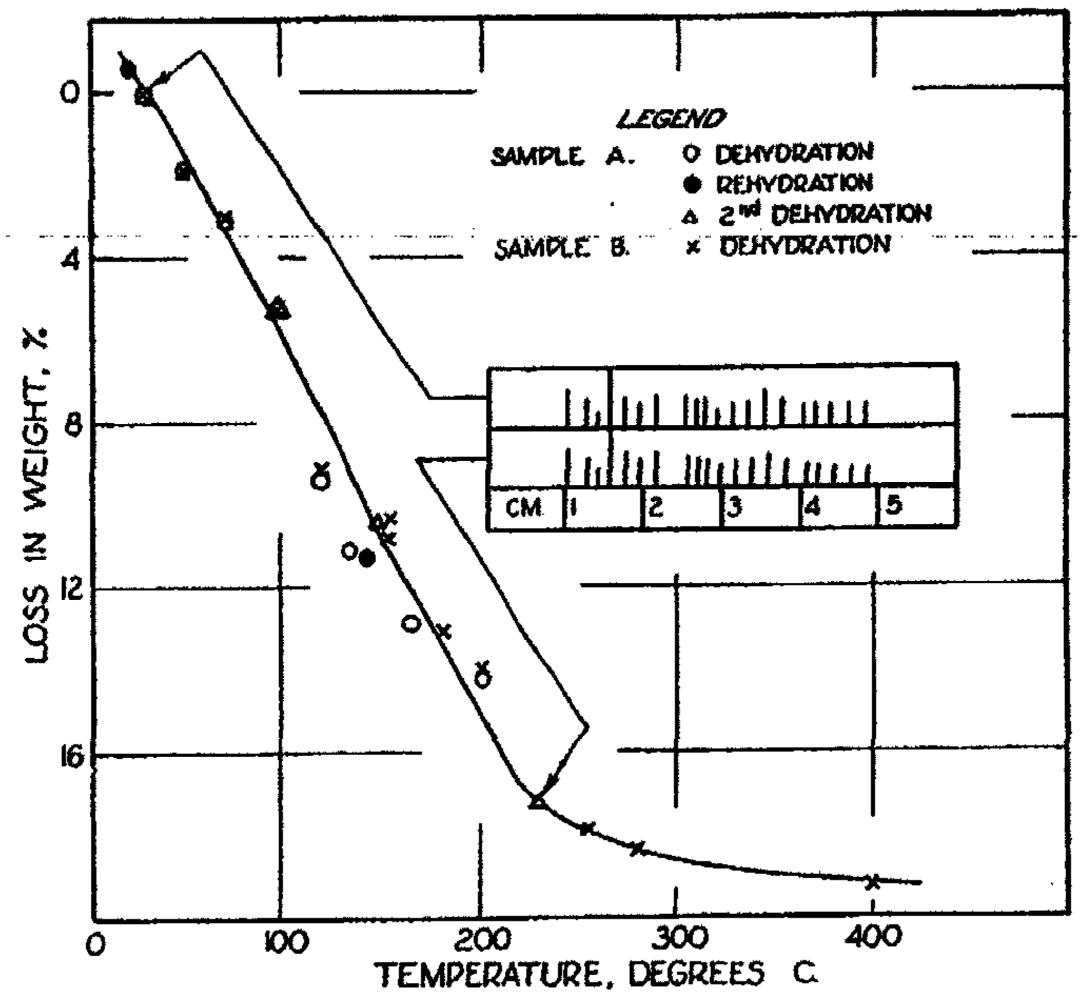

FIG. 8. Dehydration isobar and x-ray diffraction patterns for chabazite

The type of dehydration curve obtained for chabazite or thomsonite cannot be reconciled with the phase rule by assuming the formation of a continuous series of solid solutions between the hydrated material and the anhydrous material. This explanation would account for the continuous course of the isobar after the "decomposition temperature" was reached, but would not account for the absence of a univariant portion of the isobar below the "decomposition temperature."

Since some zeolites are definite hydrates and some zeolites are not definite hydrates, the present writers are of the opinion that there is nothing to be gained by the use of the expression "zeolitic water."

SUMMARY

The following is a brief summary of the results of this investigation:

1. In recent years it has been claimed that the water in calcium sulfate hemihydrate is held in a manner usually described as zeolitic, that is, the water is lost continuously on isobaric dehydration. Since the present investigators have found from x-ray and dehydration studies that calcium sulfate hemihydrate is a definite chemical individual which loses its water stepwise on isobaric dehydration, the question is opened as to the mechanism of the dehydration of the minerals usually designated as zeolites.
2. Scolecite, stilbite, heulandite, thomsonite, analcite, natrolite, mesolite, and chabazite have been investigated by the methods of x-ray diffraction analysis and isobaric dehydration.
3. X-ray diffraction examinations were made on samples dehydrated at fixed temperatures at a constant aqueous vapor pressure of 23.6 mm. After the samples had come to equilibrium they were sealed in tubes of Lindemann glass while still hot to avoid the possibility of rehydration.
4. The dehydration isobars were obtained at an aqueous vapor pressure of 23.6 mm., allowing days or weeks for the establishment of equilibrium.
5. The precautions pointed out in paragraphs 3 and 4 above have been frequently overlooked in the past.
6. Scolecite is a definite trihydrate giving a definite dihydrate upon isobaric dehydration.
7. Natrolite is a definite dihydrate giving a definite monohydrate upon isobaric dehydration.
8. Mesolite is not a hydrate, but a mixture or a solid solution of scolecite and natrolite.
9. Stilbite, heulandite, thomsonite, analcite, and chabazite are not hydrates; the water is bound by adsorption forces within channels in the lattice.
10. Stilbite and heulandite exist in more than one modification.
11. It is confirmed that some zeolites show a significant lattice shrinkage after prolonged or excessive dehydration.
12. Since some zeolites are definite hydrates and some are not definite hydrates, there is nothing to be gained by using the expression "zeolitic water."

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THE SHAPE, STRUCTURE, AND SOLIDITY OF THE AGGREGATES OF NON-SPHERICAL COLLOIDAL PARTICLES

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When spherical colloidal particles coagulate, the aggregate which is formed is isotropic in every respect. On the other hand, the coagulation of non-spherical particles may produce aggregates of anisotropic shape and structure, i.e., the aggregation takes place in a regular manner. A coagulation which leads to such anisotropic aggregates can be described as a "regular" coagulation. These terms are already familiar, but their application rests almost entirely upon experimental work carried out by Freundlich, Schuster, and Zocher (4, 5, 14) on the coagulation of benzopurpurin sols by electrolytes. The following considerations deal with the ferric oxide sol, which in this respect is more simply constituted. By means of coagulation processes of various kinds, the question of the shape and structure of aggregates of non-spherical particles is investigated. Furthermore, the changes brought about in them spontaneously and artificially as well as their solidity are discussed.

METHOD

The particles of ferric oxide sols are plate-shaped, almost uniaxial, small rhombic crystals (1, 8). According to their structure and shape they are double refracting, dichroic, and double diffracting. From the changes in these properties and especially from the changes in the order of magnitude of the properties during coagulation, far-reaching conclusions can be drawn as to the structure of the aggregates formed, and consequently as to the degree of regularity of a coagulation. The following investigations are based upon this principle. Earlier papers must be consulted for details (6, 9).

If particles are oriented, anisotropy appears. In this paper orientation by a magnetic field was chosen, since it is remarkably distinct with ferric oxide sols. Thus a high sensibility can be achieved which is superior to that resulting from electrical or stream orientation.

Magnetic double refraction and double diffraction were determined. As usual, instead of the double refraction the phase difference, δ, is given

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[1] Translated by Hans Neurath.

and instead of the double diffraction the rotation of the plane of polarization, τ, which is produced by it is recorded.[2] $\delta_{spec.}$ refers to a layer 1 cm. thick and an iron concentration of 0.1 per cent. $\delta_{red.}$ is the effect of the undiluted sol for a layer 2.81 mm. thick.

I. AGGREGATES FORMED BY ELECTROLYTE COAGULATION

1. *Influence of the rate of coagulation*

Figure 1 represents the change of double refraction caused by electrolyte coagulation[3] in well-aged, fairly "active" sols (primary particles with strong internal anisotropy). Since such high values of double refraction can be regarded as intrinsic double refraction, the general decrease of the effect proves that the structural anisotropy of the aggregates is smaller than that of the primary particles. After equal time intervals, it is smaller the higher the concentration of the *gegen* ions and, hence, the faster the aggregation takes place.

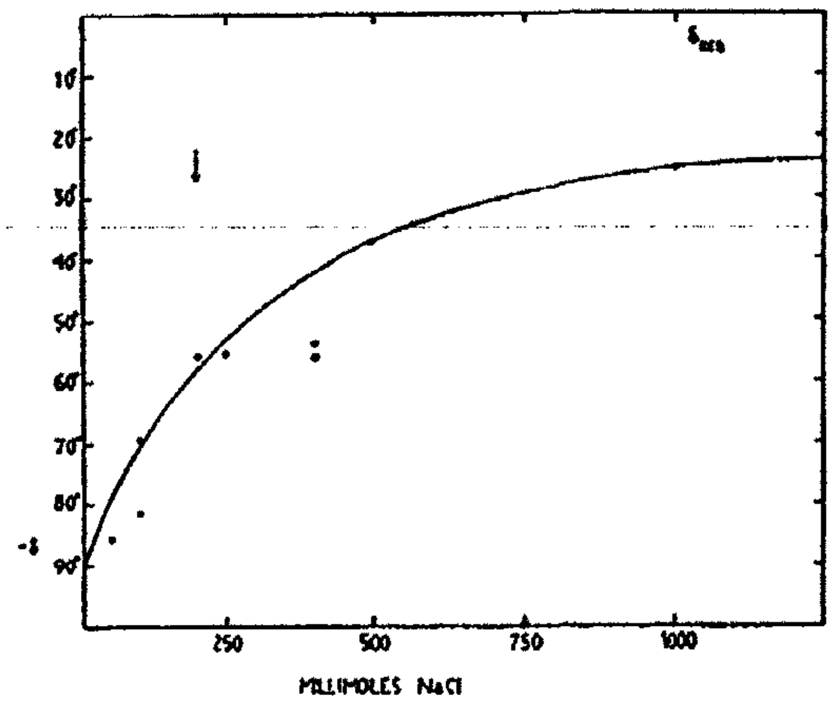

FIG. 1. Change of the double refraction with increasing electrolyte content I. Graham sol, more than fifteen years old. Coagulation value = 250 millimoles of sodium chloride per liter (twenty hours). On the right-hand side of the arrow the sols were coagulated quantitatively at the time of the measurement (one day after adding electrolyte). Intensity H = 25,000 Gauss.

Figure 2 gives the complicated picture of a sol whose primary particles were less anisotropic. The more rapid decrease of the structural anisotropy with higher electrolyte concentration would yield, after equal time intervals, a curve corresponding to figure 1. However, a certain coarsening of the particles, owing to coagulation, with lower electrolyte concen-

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[2] With the sols used, the dichroism can be neglected as relatively very small.

[3] As customary, we are speaking in terms of double refraction and double diffraction, although data given represent only their direct measure.

tration may favor the orientation of the particles in the magnetic field. because the Brownian movement of the coarser particles is less vivid, This influence is only marked when the particles are poorly anisotropic. The superposition of these two effects—decrease of structural anisotropy of the aggregates with higher electrolyte concentration, and better orientation of somewhat larger particles with lower electrolyte concentration—causes the complicated curve in figure 2.

The anisotropy of shape decreases with increasing electrolyte content in the same way as the anisotropy of structure. In this case, a maximum is observed for the slight stream double refraction and likewise for the slight formation of streaks. Below this maximum the particles are too small, above the maximum too spherical, to be oriented by streaming.

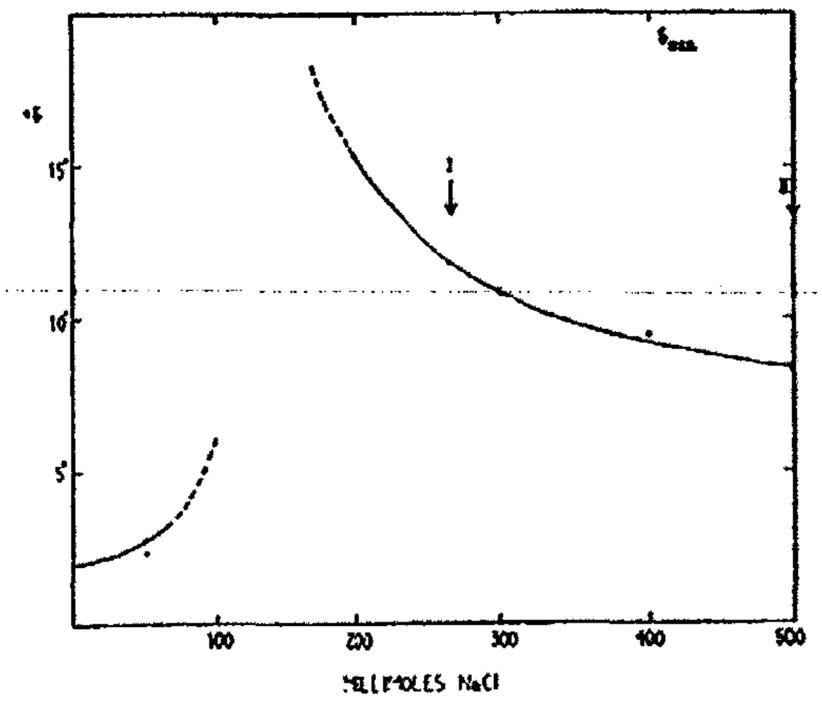

FIG. 2. Change of the double refraction with increasing electrolyte content II. Three months old sol from ferric acetate. Coagulation value = 250 millimoles of sodium chloride per liter (twenty hours). On the left-hand side of the arrow I no coagulation, on the right-hand side partial coagulation. On the right-hand side of the arrow II quantitative coagulation at the time of the measurement (one day after adding electrolyte). $H = 25{,}000$ Gauss.

In aggregates containing somewhat regularly oriented primary particles, the latter might be oriented with their longest axis parallel or perpendicular to the axis of the aggregate. Longitudinal fibrillation was, however, present in all cases dealt with. This was shown by the sign of the stream double refraction being the same before and after coagulation.

2. *Changes of shape and structure of the aggregates during coagulation*

Since the anisotropy of the aggregates formed by electrolyte coagulation is smaller than that of the primary particles, the observed double refraction decreases in the simplest case with progressing coagulation. With sols whose particles are relatively poorly oriented the picture can become complicated, the double refraction passing through a maximum with time (figure 3). Before the maximum is reached, the decrease in Brownian movement of the growing aggregate, which promotes orientation, as mentioned above, prevails. Afterwards, the decrease of the internal and external anisotropy predominates, which diminishes the effect.

The maximum of the δ/z curve (change of the double refraction, δ, with time, z) shows smaller values with higher electrolyte content, and is reached faster. This proves that: (*1*) an accelerated growth of the aggregates by electrolyte coagulation is accompanied by a decrease of their structural anisotropy, and (*2*) the relative acceleration of the decrease of anisotropy is greater than the acceleration of the aggregation. Thus, the aggregates in all degrees of dispersion formed by rapid coagulation possess a smaller structural anisotropy than similar aggregates formed by slow coagulation. The magnitude of the maximum of double refraction with time becomes a relative measure of the regularity of orientation in the aggregates produced by electrolyte coagulation.

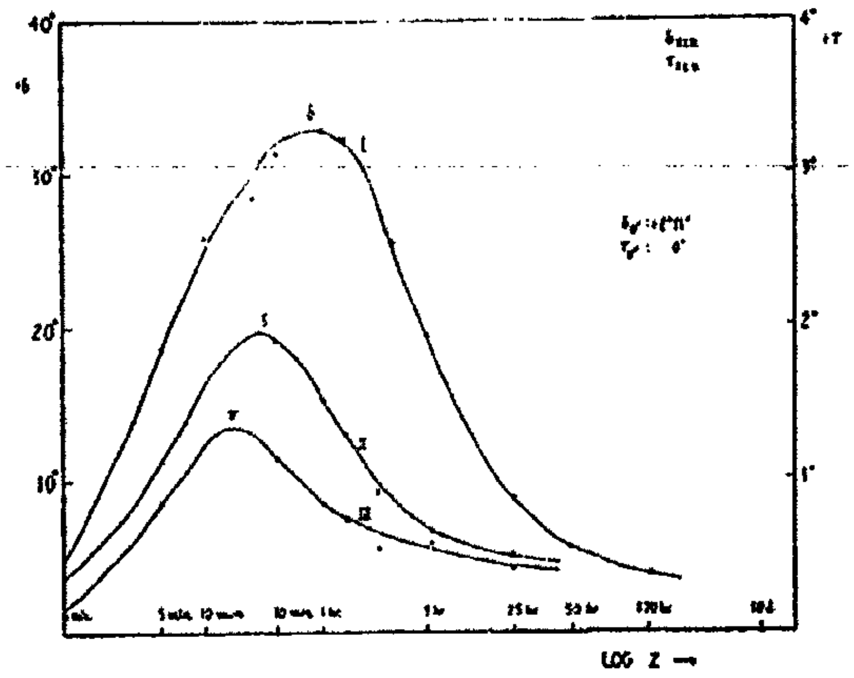

FIG. 3. Change of the double refraction and double diffraction with progressing slow coagulation. Sol from ferric acetate. $H = 25{,}000$ Gauss. I, coagulation value = 2 millimoles of sodium chloride per liter. II and III, coagulation value = 500 millimoles of sodium chloride per liter.

In the course of electrolyte coagulation the sols become double diffracting. A maximum[4] with time, which changes with the size and with the anisotropy of shape of the particles (figure 3, curve III), is also observed in this case. Since the δ/z maximum is already attained before the general turbidity of the sol has reached its maximum (or, in other words, before

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[4] The difference between the shape of the curve of double diffraction and that of double refraction is due to τ depending on the degree of dispersion.

the optimum size for the maximum diffraction and double diffraction is reached), the conclusion can be drawn that the anisotropy of shape of the aggregates of ferric oxide sols decreases with progressive increase of their mass. The observation of a maximum with time of stream double refraction likewise leads to the same conclusion (with sols having rod-shaped particles, however, stream double refraction increases continuously with time, as is known).

3. The influence of the original stability of the sols on the development of the anisotropy of aggregation

Sols of small original stability (flocculating value below 50 millimoles of sodium chloride per liter, in two hours) behave in much the same manner as very stable sols. The regularity of aggregation, however, appears to be considerably less with the unstable than with the stable sols, if the rate of coagulation of the less stable sol is comparable to or even smaller than that of the stable sols.

4. The theory of the formation of aggregates and change of aggregation during the electrolyte coagulation of shape-anisotropic particles

The following facts have been shown by the previous results: (*a*) Nonspherical particles have the tendency to be aggregated regularly. (*b*) This tendency is greater the more slowly coagulation takes place. (*c*) This tendency decreases with progressing coagulation, i.e., with the size of the growing aggregates.

The selective behavior of particles colliding in slow coagulation has been attributed hitherto to differences in the collision energy of the particles.[5] The arrangement of the colliding particles also seemed to be important for the success of a collision. The London interaction energy between two molecules is greater the smaller the distance between the centers of gravity of the particles. In applying London's views on the action between two colloidal particles (10), the conclusion is that the attraction between two shape-anisotropic particles probably is greatest, if they collide in such a way that their longest axis and, at the same time, their largest surface are turned toward each other. Moreover, with such an arrangement the aggregates possess the lowest surface tension with respect to the medium. Now we assume that of particles with relatively high residual charge only those arrangements undergo effective collisions which correspond to or approach the greatest attraction, provided the energy of collision is sufficiently high.

[5] Besides the differences in the total energy of the particles, which are a consequence of the statistical distribution, the differences in the energy vector of the particles approaching each other in the direction of their connecting lines (2) are mainly decisive.

With the coagulation of shape-anisotropic particles, a competition between the rate of orientation and the rate of accumulation has been assumed hitherto. It was supposed that there are two independent variables whose ratio determines the degree of the regularity in the coagulated aggregates. According to the assumption put forward in this paper, such an antagonism does not exist. In every case only a tendency toward regularity exists, whose magnitude is variable. For the reasons mentioned above it is a function of the energy-yield of the collisions and of the anisotropic conditions of the particles.

This assumption leads to the conclusion that the rate of coagulation of sols with plate-shaped particles and likewise that of sols with rod-shaped particles must be distinctly different from that of sols with spherical particles, whereas according to Mueller's theory (13) only sols with rod-shaped particles are excepted. At present no systematic experiments on the rate of coagulation of sols with plate-shaped particles have been carried out which could be used to decide this question.

II. AGGREGATES WHICH ARE FORMED BY MECHANICAL COAGULATION

1. General anisotropic character of the aggregates

The mechanical coagulation by stirring or shaking is in all cases accompanied by a considerable increase of the double refraction and by the development of a very strong double diffraction ($\tau_{\text{spec.}}$ maximum = $-22.5°$). In general, this increase is greater the longer the treatment lasts. In this case the regularity of the aggregates appears to be, as a rule, considerably greater than in the case of electrolyte coagulation. Accordingly, a decrease of the anisotropy of the aggregates with progressing coagulation will be overcompensated at every stage of coagulation by the improvement of their orientation in the field; this is again partly due to the decrease in intensity of the Brownian movement. Both the intrinsic anisotropy of the aggregates and their anisotropy of shape are very marked. This is shown by their strong double diffraction. All mechanically coagulated sols had comparatively high values of stream double refraction.

2. The influence of the original stability of the sols

The increase of anisotropy of a sol by mechanical coagulation appears likewise to be greater the greater its original stability. Double refraction increased to 43.6-fold in a sol with the relatively high coagulation value of 15 millimoles of sodium chloride per liter (7), the maximum degree of coagulation being about 10 per cent. A sol having the relatively very low coagulation value of 2 millimoles of sodium chloride per liter, however, became only 25.7 times more double refracting with the same mechanical treatment, in spite of almost 100 per cent coagulation.

3. The anisotropy of aggregation on addition of electrolyte to mechanically coagulable sols

The increase of double refraction of a sol which is readily coagulable by stirring is less with the same treatment, if a precipitating electrolyte is added. The higher the electrolyte concentration the less is the increase (figure 4, curve I), i.e., we have actually a decrease in double refraction. The same holds for the double diffraction (figure 5, curve I). If, however, in the case of purely mechanical coagulation the degree of coagulation is relatively small, the increase of double refraction and double diffraction, respectively, can be furthered by addition of electrolyte. It passes through a maximum with increase in electrolyte content (curves II and III of figures 4 and 5). The anisotropy of the aggregates which are formed by mechanical coagulation is less, the more the coagulation is promoted by the addition of electrolyte.

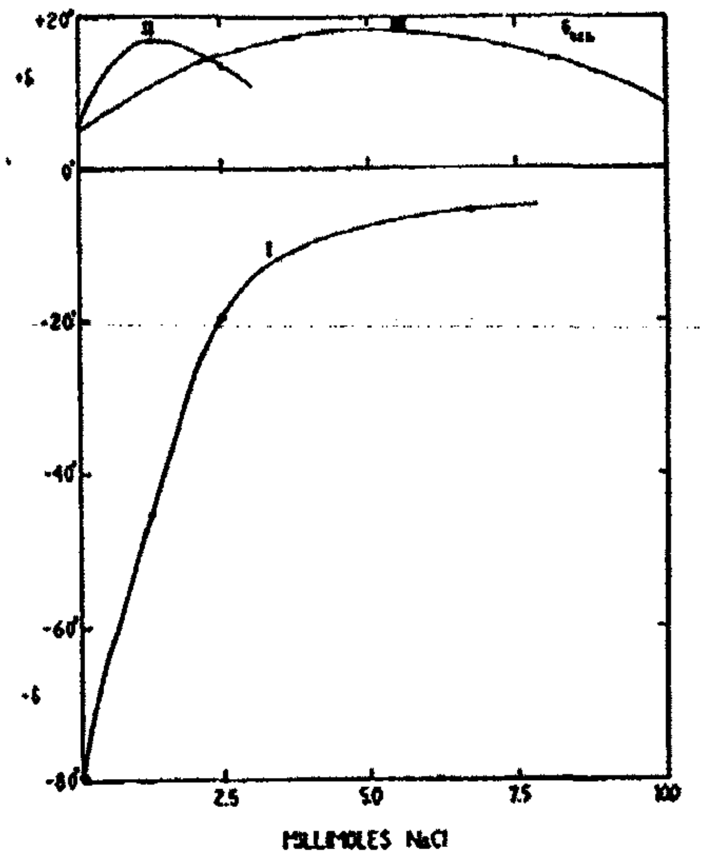

Fig. 4. Influence of electrolyte on the change of the double refraction by mechanical coagulation. I, sol from ferric acetate, coagulation value = 2 millimoles of sodium chloride per liter. II, sol from ferric chloride, prepared by simple dialysis, coagulation value = 15 millimoles of sodium chloride per liter, coarse dispersion. III, Graham sol, coagulation value = 15 millimoles of sodium chloride per liter, fine dispersion. Time of shaking six to seven hours. $H = 25{,}000$ Gauss.

4. Change of the anisotropy of aggregation with the size of the particles

In sols which are coagulated mechanically, the fine aggregates are likewise more anisotropic than the coarser ones. Systematic centrifugation and sedimentation experiments lead to this conclusion. Since after complete sedimentation, especially after strong centrifugation, the magneto-optical effects observed in the residual sol exceed those in the original sols, in many cases, considerable anisotropy must be ascribed to the very fine non-settling secondary particles. A goethite sol, for instance, with $\delta_{spec.}$ of 9°52′ before coagulation, showed after coagulation a specific effect of 45° (τ = 13°); and after subsequent centrifugation, in the course of which 86.1 per cent of the disperse phase was removed, a specific double refraction of the residual sol of 28°33′ (τ = 4°34′).

In no case, however, is the regularity of the aggregates perfect. This conclusion resulted from a comparison of the specific double refraction reached by sufficiently long natural aging of the sol (up to a maximum double refraction of the primary particles of the sol of 400°) with that which can be achieved by mechanical coagulation (up to a maximum double refraction of the aggregates of 290°). The same conclusion is reached by comparing the increase of effect passing from fine to coarse primary particles in naturally heterodisperse sols with the increase of effect passing from primary particles to aggregates in sols which were made heterodisperse by mechanical coagulation.

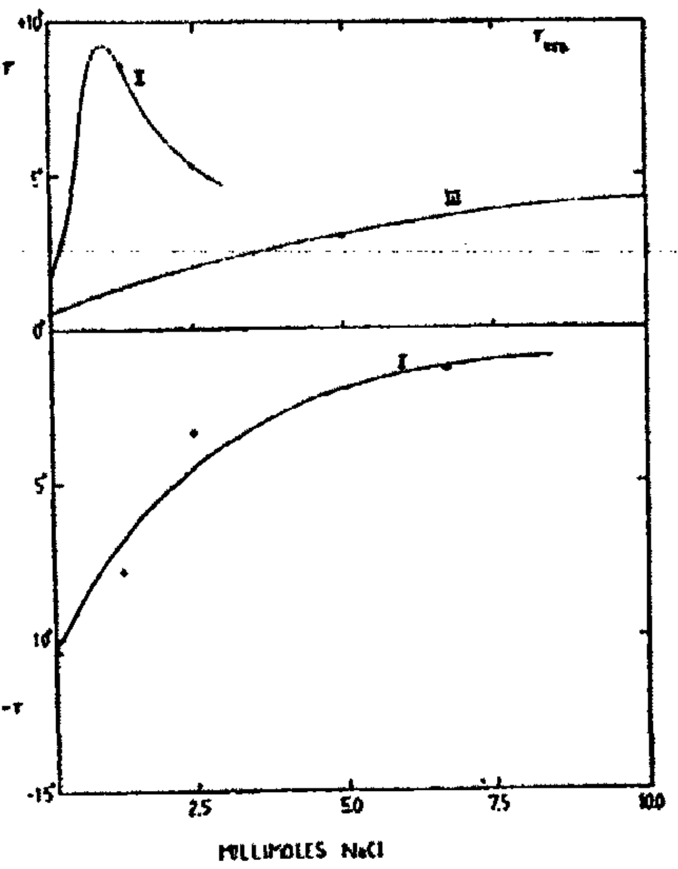

FIG. 5. Influence of the addition of electrolyte on the change of the double diffraction by mechanical coagulation. Conditions identical with those of figure 4.

5. *Influence of the intensity of treatment*

Double refraction increases very greatly, if the intensity of mechanical treatment (stirring or shaking) is increased. In the case of a partially coagulating sol this might be due to an increase in the degree of coagulation. However, the rise occurs even when the degree of coagulation is almost quantitative, applying less intensive treatment. In this case the additional increase can amount to more than twentyfold as to double refraction and more than one hundredfold as to double diffraction. This extraordinary increase can result only from a higher internal anisotropy and a considerably increased anisotropy of shape of the aggregates which are formed by (or exposed to) a more intensive mechanical treatment. The increase of double diffraction, particularly, can not be due to a change of dispersion, since increased intensity of treatment may cause particles to be split off from the aggregates, and not make the latter become coarser; hence double diffraction would tend to decrease, not to increase.

6. The theory of the formation of aggregates in mechanical coagulation

The especially great tendency to form aggregates containing well-oriented primary particles in the case of mechanical coagulation may be due to two causes: a marked influence of the arrangement of the particles during the aggregation process and a subsequent orientation of imperfectly oriented primary particles due to the stretching of the aggregate by mechanical treatment.

The second cause, the deformation of the aggregates in the direction of their longest axis when streaming, has to be regarded as characteristic of the mechanical coagulation. This deformation increases with the rate and the turbulence of streaming and causes an increase of the internal anisotropy of shape of the aggregates (part II, section 5). The longitudinal deformation of the aggregates is accompanied by an orientation of their elementary particles comparable in principle with the processes of stretching of gels.[6]

This oriented stretching requires that a force vector acts preferably in the direction of the longitudinal axis of the aggregate, which lies in an angle toward the direction of streaming (11, 15). This condition is fulfilled sufficiently, if the streaming gradient is high enough.

III. THE SOLIDITY OF AGGREGATES

1. The solidity of aggregates coagulated by electrolyte

When influencing by shaking the electrolyte coagulation of very stable sols (coagulation value for sodium chloride higher than 100 millimoles per liter), that are not mechanically coagulated, larger magnetoöptical effects are observed than in the case of pure electrolyte coagulation. Since

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[6] There is, however, a considerable difference, since we are dealing here with an irreversible deformation, the development of permanent optical anisotropy of the gel, in contrast to a reversible deformation and temporary optical anisotropy of very elastic gels and gel suspensions, respectively; see, for instance, W. Kuhn (12).

violent shaking causes in this case not an increase in the degree of coagulation, but rather a decrease (see part III, section 2), it is clear that in electrolyte coagulation, too, mechanical treatment promotes the anisotropy of aggregation. The solidity of the aggregates appears to increase with increasing electrolyte concentration. Hence the aggregates formed by mechanical coagulation, where the electric charge of the primary particles has not been reduced at all by adding electrolyte, have probably the loosest structure. This would agree with the facts mentioned above (part II, section 5), that the magnetoöptical effects increase so enormously with the intensity of mechanical treatment.[7]

2. The mechanical splitting of aggregates

A splitting of aggregates is likewise possible, if the aggregates are sufficiently soft and the mechanical treatment sufficiently strong. This can be proved easily by comparing the sedimentation velocity of coagulated sols before and after subsequent mechanical treatment. The mechanical peptization of sols which had been coagulated by electrolytes, already observed by Freundlich and Basu on vanadium pentoxide and gold sols (3), may be related to this mechanical splitting of aggregates.[8] The degree of coagulation, especially in the case of very stable ferric oxide sols, is less after equal time intervals, if, instead of a pure electrolyte coagulation, an electrolyte coagulation with simultaneous violent shaking is carried out. It is even possible for the supernatant liquid to be water clear after electrolyte coagulation, whereas in the other case a concentrated residual sol is still present. Here, possibly, differences in the aggregates as to their power to adsorb play a rôle.

3. The change in solidity of the aggregates with time

The increase in anisotropy which is observed when sols coagulated by electrolytes are shaken is less, the longer the time interval until shaking was begun. The solidity of the aggregates increases accordingly with their age.

IV. THE SPONTANEOUS CHANGE OF THE STRUCTURE OF AGGREGATES WITH TIME

1. Mechanically coagulated sols

The question arises as to whether a change in the orientation of the primary particles takes place simultaneously with their approach to each

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[7] The process of coagulation is, therefore, different from that which was described in part II, section 3.

[8] In the case of weak shaking, however, the electrolyte coagulation seems to be rather promoted (13). Since in this case neither a deformation nor a splitting of aggregates is possible, other coagulating influences due to shaking may predominate.

other in the aggregate. This would be most likely to happen in the case of the loosest aggregates, i.e., those which are formed by mechanical coagulation (see part III, section 1). We have studied the change in magneto-optical behavior in the course of one month after the coagulation in a ferric oxide sol prepared from iron carbonyl, which was coagulated mechanically up to 8.3 per cent. The observed development of the anisotropy with time showed rather conclusively that the internal anisotropy of such aggregates increases with time, owing to a spontaneous improvement of the orientation of the primary particles. It might be concluded from this fact that the regular state represents the one poorer in free energy.

A spontaneous increase in the orientation of the primary particles in the aggregates is indicated also by another observation, which was made with a mechanically coagulated sol about one year after its coagulation. The coagulate contained macroscopically large aggregates of somewhat irregular oblong shape which showed, under the polarization microscope, a uniform extinction as if they consisted of single crystals.

2. Electrolyte coagulated sols

In the case of aggregates formed by electrolyte coagulation it is not easy to decide whether a further change is due to the action of the flocculating electrolyte or to a spontaneous process. If the change in double refraction is investigated for a period of two weeks after coagulation has been accomplished, it is observed that the magnetoöptical effects do not drop to zero, but that there remains a considerable, fairly constant, residual value of double refraction and double diffraction. This is indicated already by figure 3, which is confined to a rather short time interval. Thus an aggregate formed by slow electrolyte coagulation of a stable sol keeps a considerable residue of permanent anisotropy. The anisotropy of shape is specially important, since the final value of double diffraction is, as a rule, only about 50 per cent smaller than the maximum value observed at all.

SUMMARY

1. The non-spherical particles of ferric oxide sols tend to aggregate into regular formations when coagulated. They form oblong aggregates in which the particles are oriented parallel to the long axis of the aggregate. The degree of regularity of the aggregate decreases with the rate of coagulation and likewise with the number of aggregated primary particles. In the case of rapid coagulation, aggregation is completely irregular.

2. The tendency to aggregate regularly is explained by the assumption that the attraction of shape-anisotropic particles and the probability of collision are presumably the greatest, if the particles turn their longest axis towards each other when colliding. In the case of slow coagulation

not only a selectivity of the collision effect, due to differences of the collision energy, is taken into account, but also a selectivity determined by the arrangement of the particles. The importance of the "arrangement factor" decreases as the particles become more nearly spherical and likewise when their electrical charge is reduced.

3. When mechanically coagulated the aggregates are as a rule far more regular than when coagulated slowly by electrolytes. The anisotropy of shape, particularly, is remarkably high. As in paragraph 2 the arrangement of the colliding particles is regarded as essential for successful collision. It is shown that the regularity of the aggregates is in mechanical coagulation largely due to their deformation by the streaming gradient caused by stirring or shaking the sols.

4. The structure and the shape of the aggregates formed by coagulation change spontaneously for a long time even after the coagulation is apparently completed. In some cases there seemed to be a tendency for a subsequent improvement in the regularity of the aggregates.

5. A comparison of the magnetoöptical effects in pure electrolyte coagulation with those in electrolyte coagulation coupled with shaking allows conclusions to be drawn as to the deformation and the solidity of the aggregates. Their solidity increases with the rate of aggregation and likewise with the age of the aggregates.

6. Particularly loose aggregates are split by violent shaking. This mechanical peptization is supposed to be indirectly responsible for the stabilization by violent shaking of sols coagulated by electrolytes.

I wish to express my most sincere thanks to Professor H. Freundlich for his great interest in these investigations.

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A STUDY OF THE COMPOSITION OF THE LIQUID PHASE IN AQUEOUS SYSTEMS CONTAINING STRONG ELECTROLYTES OF HIGHER VALENCE TYPES AS SOLID PHASES

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INTRODUCTION

During the last fifty years there has accumulated in the chemical literature an enormous amount of data on phase equilibria in concentrated, aqueous solutions of strong electrolytes of all valence types. These data have not as yet been subjected to a systematic theoretical study, and our present knowledge of the whole field is almost entirely empirical. However, in order to be able to calculate the solubility curve for a given solid phase as obtained from these data a general equation applicable to strong electrolytes of all valence types has previously been suggested (3, 2; cf. also 4) and also tested with regard to its accuracy in the case of a number of systems containing uni-univalent strong electrolytes. Therefore it was considered to be of some interest to pursue this study a little further and to apply the general equation to the data available for systems containing electrolytes of higher valence types. Although most of them probably should be considered as weak electrolytes and the number of systems where our formulas are applicable thus could be expected to be quite limited, nevertheless a large number of cases have been found where these formulas seem to apply with high accuracy.

Since this study might be said to represent the application of an idea, rather than exactly proved and theoretically valid equations, known minor deviations of the fundamental concepts employed from certain experimental data for very dilute solutions will not be considered. In the cases studied these deviations seem to have an entirely negligible influence at higher concentrations, and would at any rate be impossible to trace using the solubility data alone. As will be shown in the following, in the case of a number of different systems, within the accuracy of the data available, the equations employed appear to give an exact representation of the actual conditions. The fact that the general equation mentioned above summarizes with considerable precision the solubility data for a considerable number of systems has been regarded as sufficiently interesting to justify this paper.

GENERAL CONSIDERATIONS

The general equation for the solubility of highly soluble, strong electrolytes in mixed solutions operates with the known activity coefficient γ_R of a reference electrolyte R of the same valence type as that of the pure electrolyte forming the solid phase. In the case of homoionic electrolytes the equation has the following form:

$$\log \gamma_{R(\mu_T)} + k_1\mu_T + k_2(\mu_T - \mu_x) + \frac{\nu_1}{\nu_1 + \nu_2} \log \left[\frac{\nu_3(\mu_T - \mu_x)}{n_2} + \frac{\nu_1 \mu_x}{n_1} \right]$$

$$+ \frac{\nu_2}{\nu_1 + \nu_2} \log \frac{\nu_2 \mu_x}{n_1} = \log \gamma_{R(\mu_s)} + k_1\mu_s + \log m_s(\nu_1^{\nu_1} \nu_2^{\nu_2})^{\frac{1}{\nu_1+\nu_2}} \qquad (1)$$

In equation 1 the total ionic strength of the liquid phase is designated by μ_T, the ionic strength of the electrolyte forming the solid phase by μ_x, and the solubility of the solid phase in the pure solvent is denoted by m_s. It is assumed to dissociate into ν_1 positive and ν_2 negative ions and has the ionic strength factor n_1. The co-solute is considered as homoionic with respect to its ν_3 positive ions and it has the ionic strength factor n_2.

The constant k_1 gives the slope of the linear variation of the logarithm of the ratio of the activity coefficients of two strong electrolytes of the same valence type in pure aqueous solutions as plotted against their concentrations in ionic strength. As will be shown later in the case of uni-bivalent strong electrolytes, at higher ionic strengths the relationship given by k_1 might be valid, with an added constant, for the logarithm of the ratio of the activity coefficients of electrolytes of different valence types.

The constant k_2 gives the slope of the linear variation of the logarithm of the activity coefficient of a strong electrolyte in binary solutions of constant total ionic strength as plotted against its partial value of the latter. Its value varies from system to system, but it is independent of any reference electrolyte. The use of k constants of higher order for polycomponent systems is unnecessary since, as has been shown previously in the case of uni-univalent electrolytes, the total effect of an arbitrary number of components is obtained by adding the individual effects expressed by the k_2 constants. In the case of certain systems it has been found that k_2 varies linearly with the concentration of the co-solute. Thus by changing the k_2 term to $[k_2 - k_3(\mu_T - \mu_x)]\ (\mu_T - \mu_x)$, these cases also may be expressed by the general equation, as will be shown below.

Obviously it is impossible to test the constancy of k_1 in more than a very few cases, and the fact that it may be found to be valid within the experimental errors in these few cases does not prove that it would hold for all possible cases and outside the concentration ranges employed. The generalization made is thus a pure assumption which, however, if true, would be extremely useful. We shall therefore present a few of the data on which the assumed constancy of k_1 has been based.

If three electrolytes A, B, and C are given and it is proved that B and C with respect to A follow the rule, it must be true that B with respect to C also follows the same. Robinson and Frank (14; cf. also 16), using sodium bromide as reference electrolyte, find that sodium and potassium chlorides in their test of the rule employing data for integral heats of dilution give curves very different from straight lines. However, if we apply a similar test to all three of these electrolytes, using the E.M.F. data available and hydrochloric acid as reference substance, the result given in table 1 is obtained.[1] The observed activity coefficients for sodium and potassium chlorides and for sodium bromide are compared with the values calculated using the k_1 constants indicated. As a test case for uni-bivalent electrolytes the same comparison has been given for barium chloride with calcium chloride as reference electrolyte. The differences between observed and calculated activity coefficients are without any exceptions well within the probable experimental errors of the data used and, thus far in the cases studied, the constancy of k_1 has been proved.

The ideal gas laws have a very fundamental importance, although an actual gas that follows these laws exactly at any pressure or temperature does not exist. The usefulness of the ideal gas laws is founded upon the fact that under ordinary circumstances a large number of gases in their behavior follow these laws very closely. Similarly, our quantitative treatment of heterogeneous equilibria of strong electrolytes is based on one very simple empirical rule, which is not exact in the true sense of the word and which can not be tested for all possible cases, but there are indications that it represents in a number of cases a close approximation to the actual conditions. Therefore this empirical rule is a very powerful tool as a means for describing in a simple manner and with considerable precision the equilibria in saturated solutions of strong electrolytes.

In the case of uni-univalent electrolytes hydrochloric acid has previously always been used as reference substance, since its activity coefficient at 25°C. is known accurately over a large concentration range. The highest concentration for which the activity coefficient of any uni-bivalent electrolyte is measured with precision is only 1.70 molal, which range is entirely insufficient for our purposes. However, if we plot the logarithm of the activity coefficients of a uni-univalent and a uni-bivalent electrolyte, let us say hydrochloric acid and calcium chloride, respectively, against the total ionic strength, we find that with increasing concentration the curve obtained very rapidly changes over to a straight line, as shown

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[1] For supplementary tables order Document 1012 from Science Service, 2101 Constitution Ave., Washington, D. C., remitting twenty-five cents for microfilm form, or forty cents for photocopies readable without optical aid.

TABLE 1

Observed activity coefficients for sodium and potassium chlorides and sodium bromide with the corresponding calculated values using hydrochloric acid as reference substance; observed and calculated activity coefficients of barium chloride with calcium chloride employed as reference substance

m	γ_{HCl}	SODIUM CHLORIDE, $k_1 - 0.088$			SODIUM BROMIDE, $k_1 - 0.068$		
		$\gamma_{obsd.}$	$\gamma_{calcd.}$	Difference	$\gamma_{obsd.}$	$\gamma_{calcd.}$	Difference
0.00	1.000	(1.000)	1.000		(1.000)	1.000	
0.10	0.796	0.782	0.780	0.002	0.784*	0.784	0.000
0.20	0.767	0.736*	0.736	0.000	0.742	0.743	0.001
0.30	0.757	0.712	0.712	0.000	0.722	0.722	0.000
0.40	0.754	0.695	0.695	0.000	0.708	0.708	0.000
0.50	0.757	0.684	0.684	0.000	0.700	0.700	0.000
1.00	0.809	0.661	0.661	0.000	0.692	0.692	0.000
1.50	0.898	0.660	0.663	0.003	0.701	0.710	0.009
2.00	1.013	0.675	0.679	0.004	0.737	0.741	0.004
2.50	1.151	0.695	0.693	0.002	0.778	0.778	0.000
3.00	1.318	0.721	0.718	0.003	0.828	0.824	0.004
3.50	1.519	0.755	0.751	0.004	0.877	0.878	0.001
4.00	1.760	(0.796)	0.783		0.939	0.941	0.002

m	POTASSIUM CHLORIDE, $k_1 - 0.118$			m	γ_{CaCl_2}	BARIUM CHLORIDE, $k_1 - 0.0915$		
	$\gamma_{obsd.}$	$\gamma_{calcd.}$	Difference			$\gamma_{obsd.}$	$\gamma_{calcd.}$	Difference
0.00	(1.000)	1.000		0.00	1.000	(1.000)	1.000	
0.10	0.774*	0.774	0.000	0.10	0.515	0.479	0.483	0.004
0.20	0.722	0.725	0.003	0.20	0.481	0.424*	0.424	0.000
0.30	0.693	0.696	0.003	0.30	0.482	0.400	0.399	0.001
0.40	0.671	0.675	0.004	0.40	0.496	0.386	0.385	0.001
0.50	0.658†	0.659	0.001	0.50	0.519	0.380	0.378	0.002
1.00	0.610†	0.614	0.004	0.60	0.548	0.376	0.375	0.001
1.50	0.589†	0.593	0.004	0.80	0.622	0.374	0.375	0.001
2.00	0.581†	0.583	0.002	1.00	0.715	0.378	0.380	0.002
2.50	0.576	0.577	0.001	1.25	0.863	0.390	0.391	0.001
3.00	0.578	0.576	0.002	1.50	1.047	0.406	0.406	0.000
3.50	0.578	0.577	0.001					
4.00	0.588	0.583	0.005					

* Reference point; † mean of freezing-point and E.M.F. values.

Data for hydrochloric acid: Randall and Young, J. Am. Chem. Soc. **50**, 989 (1928); Harned and Ehlers, J. Am. Chem. Soc. **55**, 2179 (1933). For sodium chloride: Harned, J. Am. Chem. Soc. **51**, 416 (1929); Harned and Nims, J. Am. Chem. Soc. **54**, 423 (1932). For sodium bromide: Harned, J. Am. Chem. Soc. **51**, 416 (1929). For potassium chloride: Harned, J. Am. Chem. Soc. **51**, 416 (1929); Spencer, J. Am. Chem. Soc. **54**, 4490 (1932); Redlich and Rosenfeld, Landolt-Börnstein's Physikalisch-Chemische Tabellen, 5th edition, 2nd. Erg., Part 2. For calcium chloride: Scatchard and Tefft, J. Am. Chem. Soc. **52**, 2265, 2272 (1930). For barium chloride: Tippetts and Newton, J. Am. Chem. Soc. **56**, 1675 (1934); cf. also Lucasse, J. Am. Chem. Soc. **47**, 743 (1925). All measurements have been carried out at 25°C.

graphically in figure 1 using the data of Randall and Young (12) and of Harned and Ehlers (8) for the former at 25°C. and those of Scatchard and Tefft (17) for calcium chloride and of Tippetts and Newton (18) for barium chloride, also at 25°C. Above an ionic strength of 2 the curves in figure 1 give the following equation for the activity coefficient of calcium chloride:

$$\log \gamma_{CaCl_2} = \log \gamma_{HCl} - 0.0167\mu - 0.216$$

The last term in this equation might be of some interest. Its value is independent of the choice of reference electrolyte or the particular electrolyte considered.

With regard to the application of the rule just discussed for the k_1 values of uni-bivalent electrolytes to those of still higher valence types, the data available do not give any conclusive evidence. Thus the data of LaMer and Parks (11) and those of Robinson and Jones (15) for cadmium sulfate go very far apart, although for both sets of measurements quite high accuracy is claimed. On the other hand, the data of Robinson and Jones for magnesium sulfate agree fairly well with the values obtained from solubility data, as is shown by the following comparison:

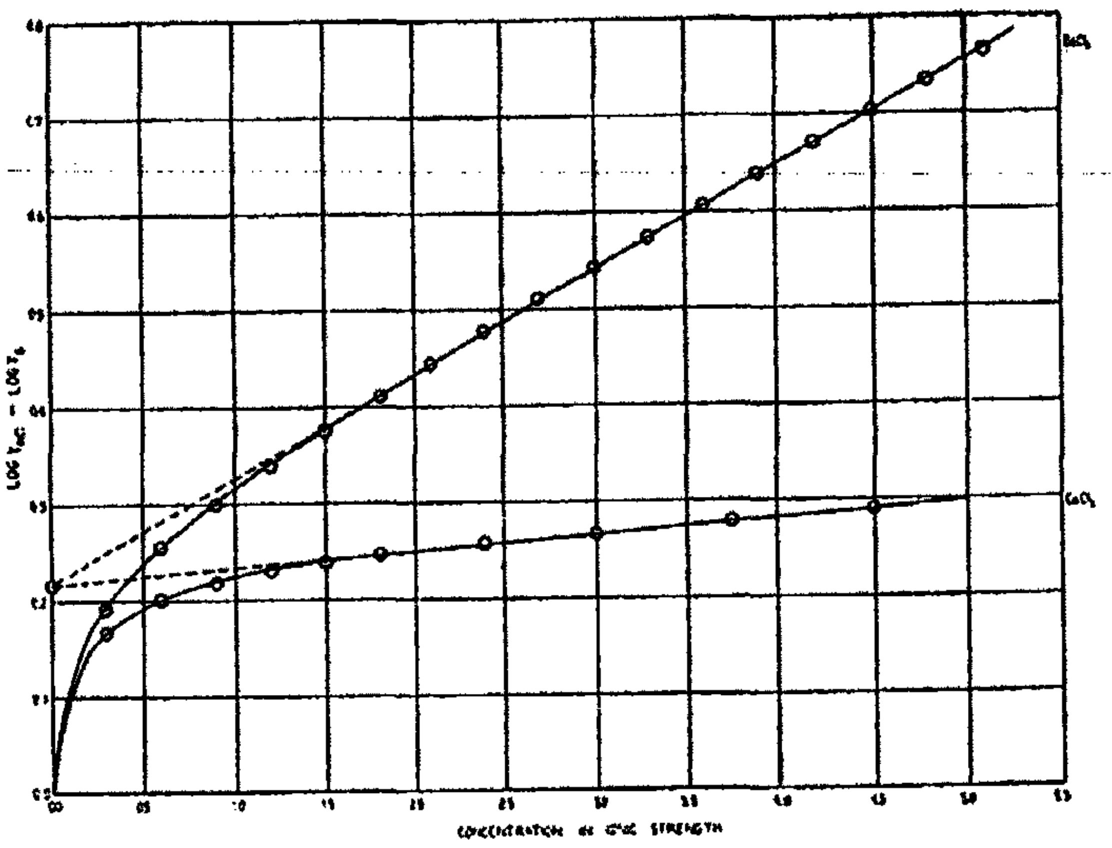

FIG. 1. Curves for the logarithm of the ratio of the activity coefficients of barium and calcium chlorides to that of hydrochloric acid at 25°C.

$MgSO_4$ μ	VALUES OF k_1 OBSERVED BY ROBINSON AND JONES	k_1 CALCULATED FROM SOLUBILITY DATA	DIFFERENCE
4	0.0635	0.056	−0.007
6	0.0559	0.058	0.002
8	0.0545	0.060	0.005
10	0.0573	0.061	0.004
12	0.0644	0.058	−0.006

Considering that in the case of the solubility data an error in the value of the activity coefficient of the reference electrolyte introduces a very much larger error in the values calculated for magnesium sulfate, the differences shown are probably within the experimental errors of the data used.

THE APPLICATION OF EQUATION 1 TO SPECIAL CASES

Before we apply equation 1 to the first test case, we shall consider the changes that take place at the transition point of one hydrate to another or to the anhydrous form. In the liquid phase the curve for the activity coefficient of the electrolyte forming the solid phase will be assumed to be continuous in its own supersaturated solution and independent of the number of moles of solvent bound in the solid phase. The activity of a hydrated solid phase, however, is given by the product of the activity of the electrolyte in the solution and the n^{th} power of that of the solvent, if n is the number of moles of crystal water. Apparently it would be a complicated matter to calculate separate values for the activities of both electrolyte and solvent, and in most cases all the experimental data necessary are not available. Since in going from one hydrate to another the total change of the ionic strength will in most cases be relatively small, the changes of the activity of the solvent are also small; we may, however, obtain a great simplification of our problem by assuming that as a first approximation the logarithm of the activity of the solvent varies linearly with the concentration of the co-solutes to the electrolyte forming the solid phase. The k_2 values employed will appear to be changed by a certain amount, depending on the change of the activity of the solvent, and

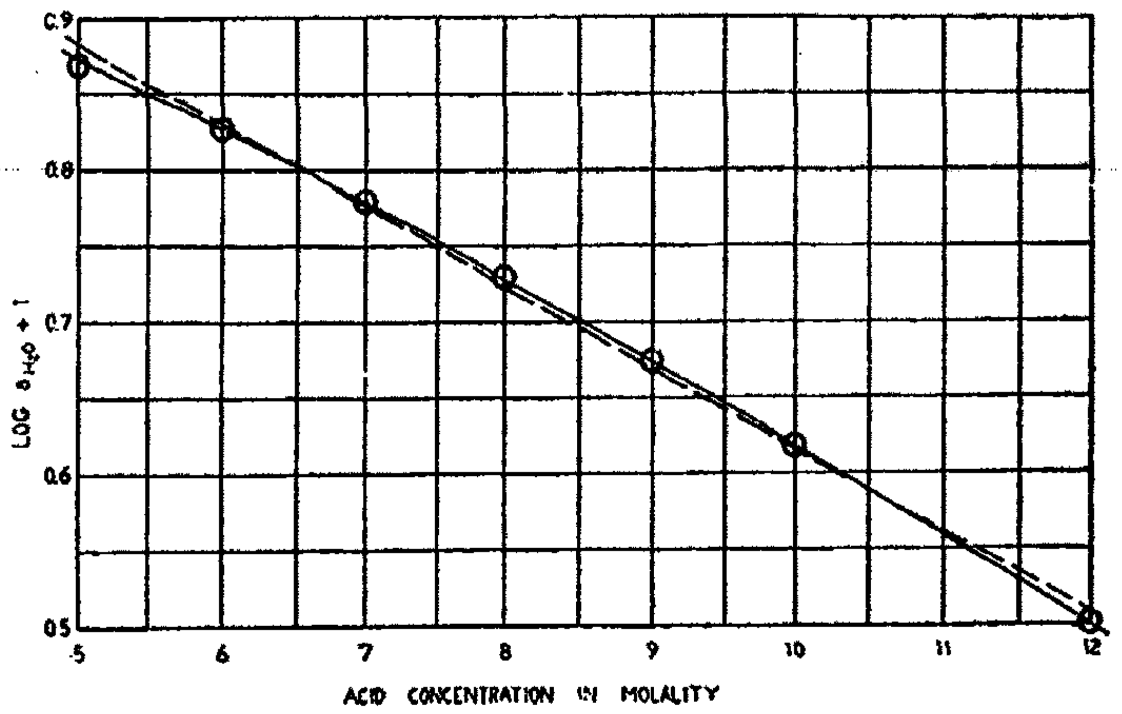

FIG. 2. Curve for the variation of the logarithm of the activity of water in pure aqueous solutions of hydrochloric acid from 5 to 12 molal at 25°C., according to data of Randall and Young (loc. cit.).

their correct values will be obtained only in the case of anhydrous solid phases. As an illustration of the variation of the logarithm of the activity of water with the concentration of an electrolyte present, figure 2 gives the curve for hydrochloric acid between 5 and 12 molal according to the data of Randall and Young. In the ternary systems to be discussed below the changes of the total ionic strength are small, and the assumption of a linear variation of the logarithm of the activity of the solvent appears to introduce a negligible error.

THE SYSTEM SODIUM SULFATE-SODIUM CHLORIDE-WATER AT 25°C.

Solid solutions or double salts are definitely absent and only three different solid phases are formed:—the decahydrate, anhydrous sodium sulfate, and sodium chloride. The changes of the composition of the liquid phase are shown graphically in figure 3. The solubility curves for the solid phases are the calculated ones. A few of the experimental points found in the literature which obviously were seriously in error have been excluded. The equation used for the calculation of the solubility of sodium chloride has the following form:

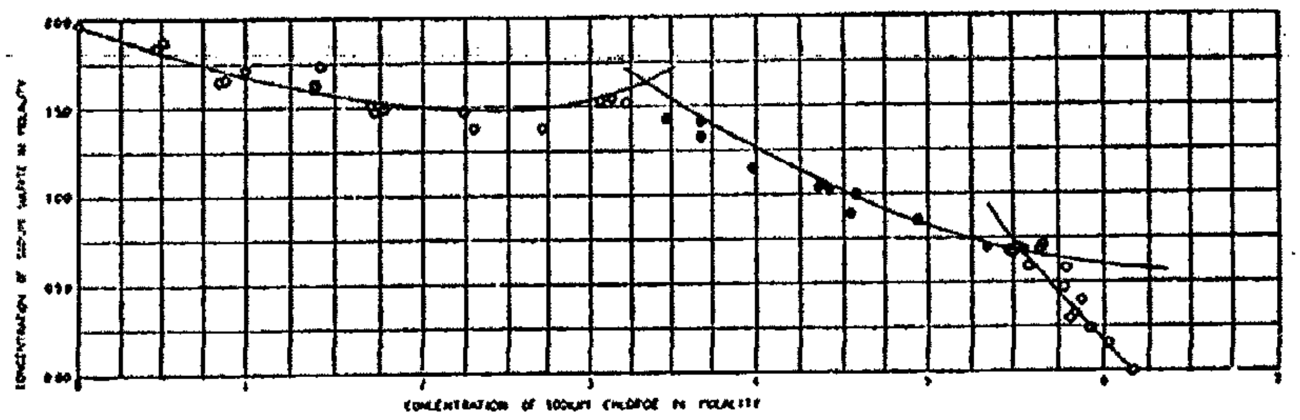

FIG. 3. The calculated curves for the composition of the liquid phase in the system sodium sulfate-sodium chloride-water at 25°C. in the presence of sodium chloride, anhydrous sodium sulfate, and its decahydrate as solid phases. Experimental points according to a table by D'Ans (Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen, Verlag Ackerbau, Berlin, 1933).

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.088\mu_T + 0.0321(\mu_T - \mu_x) + 1/2 \log (2\mu_T + \mu_x)/3 + 1/2 \log \mu_x = 0.777 \qquad (2)$$

where μ_x is the desired ionic strength of sodium chloride. The value employed for the solubility of sodium chloride in pure water at 25°C. was 6.162 molal. The solubility curve for anhydrous sodium sulfate present as solid phase was computed from the equation:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.188\mu_T + 0.038(\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log (\mu_T - \mu_x/3) = 0.0056 \qquad (3)$$

where μ_x is the desired ionic strength of sodium sulfate. Equation 3 has two mathematical solutions for every value of the total ionic strength. Within the concentration range limited by the two triple points between the different phases, both of these solutions correspond to actual solubility values. The solubility curve for the decahydrate may be obtained by solving the following system of equations for different sodium chloride concentrations:

$$\log \gamma_{HCl(\mu_T)} - 0.188\mu_T + 0.038(\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log (\mu_T - \mu_x/3) + 10 \log a_{H_2O} = \text{constant} \qquad (4a)$$

$$\log \gamma_{HCl(\mu_T)} - 0.088\,\mu_T + 0.0321\mu_x + 1/2 \log (\mu_T - \mu_x) + 1/2 \log (\mu_T - \mu_x/3) = \log a_{NaCl} \qquad (4b)$$

$$N_{NaCl}\, d \log a_{NaCl} + N_{Na_2SO_4}\, d \log a_{Na_2SO_4} + N_{H_2O}\, d \log a_{H_2O} = 0 \qquad (4c)$$

where a denotes activities, N mole fractions, and μ_x is the desired ionic strength of sodium sulfate. Solution by successive approximation would involve a very large amount of labor; but by assuming a linear variation of $\log a_{H_2O}$ with the sodium chloride concentration, practically the same result is obtained in a far simpler manner using the following equation:

$$\log \gamma_{HCl(\mu_T)} - 0.188\mu_T + 0.001(\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log (\mu_T - \mu_x/3) = -\,0.118 \qquad (5)$$

where μ_x is the desired ionic strength of sodium sulfate. The value employed for the solubility of sodium sulfate in pure water at 25°C. was 1.963 molal. The calculated k_1 value was -0.188, while the E.M.F. measurements of Harned and Hecker (9; cf. also 1) give the value -0.195. The difference between the two values is well within the experimental errors of the results used for their computation. Considering the scattering of the experimental points, the calculated solubility curves shown in figure 3 seem to give a good representation of the system studied.

THE SYSTEM MAGNESIUM CHLORIDE–MAGNESIUM SULFATE–WATER AT 25°C.

In our second test case, we shall calculate the composition of the liquid phase in this system with the latter electrolyte present as a solid phase in the form of its heptahydrate. According to van't Hoff, at very high concentrations of magnesium chloride the sulfate is present as its hexahydrate and finally also as the monohydrate (kieserite). Our calculations, however, do not cover the range where the latter two phases may exist. The solubility of magnesium sulfate in aqueous solutions of magnesium chloride has been calculated, employing the following equation:

$$\log \gamma_{HCl(\mu_T)} - 0.123\mu_T + 0.0277(\mu_T - \mu_x) + 1/2 \log \mu_x/4 + 1/2 \log (4\mu_T - \mu_x)/12 = 0.240 \qquad (6)$$

where μ_x is the desired ionic strength of magnesium sulfate. The values given in the literature for the solubility of magnesium sulfate in pure water at 25°C. show a large spread, and it is rather uncertain which ones should be considered as most reliable. The value 3.025 molal has been used as the average of the determinations which agreed best with each other. A graphical comparison between calculated and experimental values is shown in figure 4. We find that, as in the case of anhydrous sodium sulfate, equation 6 has for each value of the total ionic strength two mathematical solutions corresponding to actual points on the solubility curve.

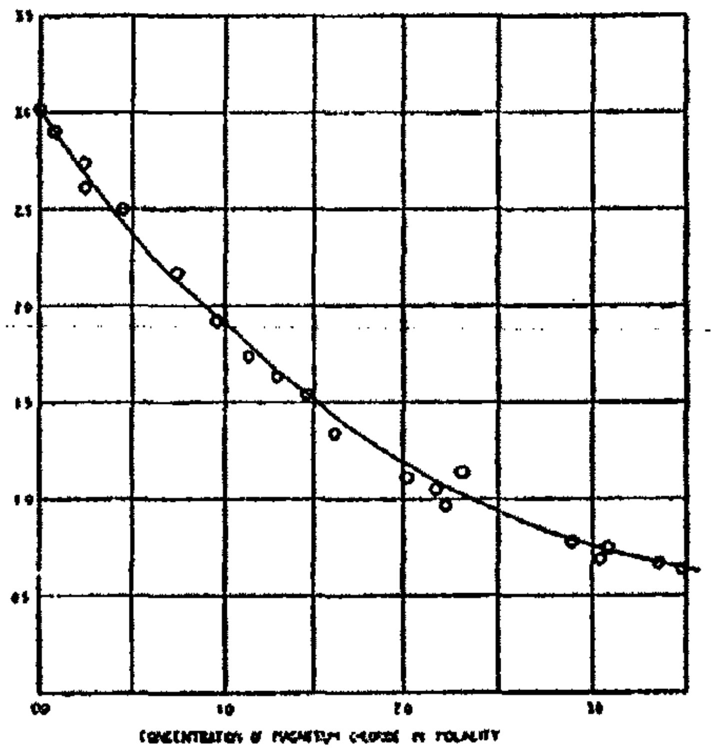

FIG. 4. The calculated curve for the composition of the liquid phase in the system magnesium sulfate–magnesium chloride–water at 25°C. with the heptahydrate of magnesium sulfate present as solid phase. Experimental points according to a table given by D'Ans (loc. cit.).

THE QUATERNARY SYSTEM SODIUM CHLORIDE–MAGNESIUM SULFATE–WATER AT 25°C.

This system is far more complicated than the two already treated, since not only are both hetero- and homo-ionic electrolytes present simultaneously but also seven different solid phases may appear. The possible solid phases are the sodium and magnesium chlorides and sulfates and the three double salts astrakanite, loeweite, and vanthoffite. To treat the whole system in detail would be quite laborious, and we shall limit ourselves to the calculation of the solubility curve for sodium chloride in the presence of astrakanite as coexistent solid phase. The experimental data available for the 25°C. isotherm seem to indicate that within the analytical errors the concentration of magnesium sulfate in the liquid phase is practically constant and on the average equal to 0.905 molal in the presence of sodium chloride as solid phase. Therefore we shall assume in the following that this really is the case. Using the values previously employed for the k_1 constant and the activity of the solid phase of sodium chloride, the equation obtained for its solubility curve has the form:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.0875\mu_T + 0.025(\mu_T - \mu_s - 3.62) - 0.022\cdot 3.62 + 1/2 \log \mu_s + 1/2 \log (2\mu_T + \mu_s - 7.24)/3 = 0.777 \qquad (7)$$

where μ_s is the desired ionic strength of sodium chloride. A graphical comparison with the experimental data is shown in figure 5. To judge from this figure, experimental and calculated curves should just about coincide. In a similar manner as described for sodium chloride, the solubility curves for the other solid phases appearing in the system might be treated.

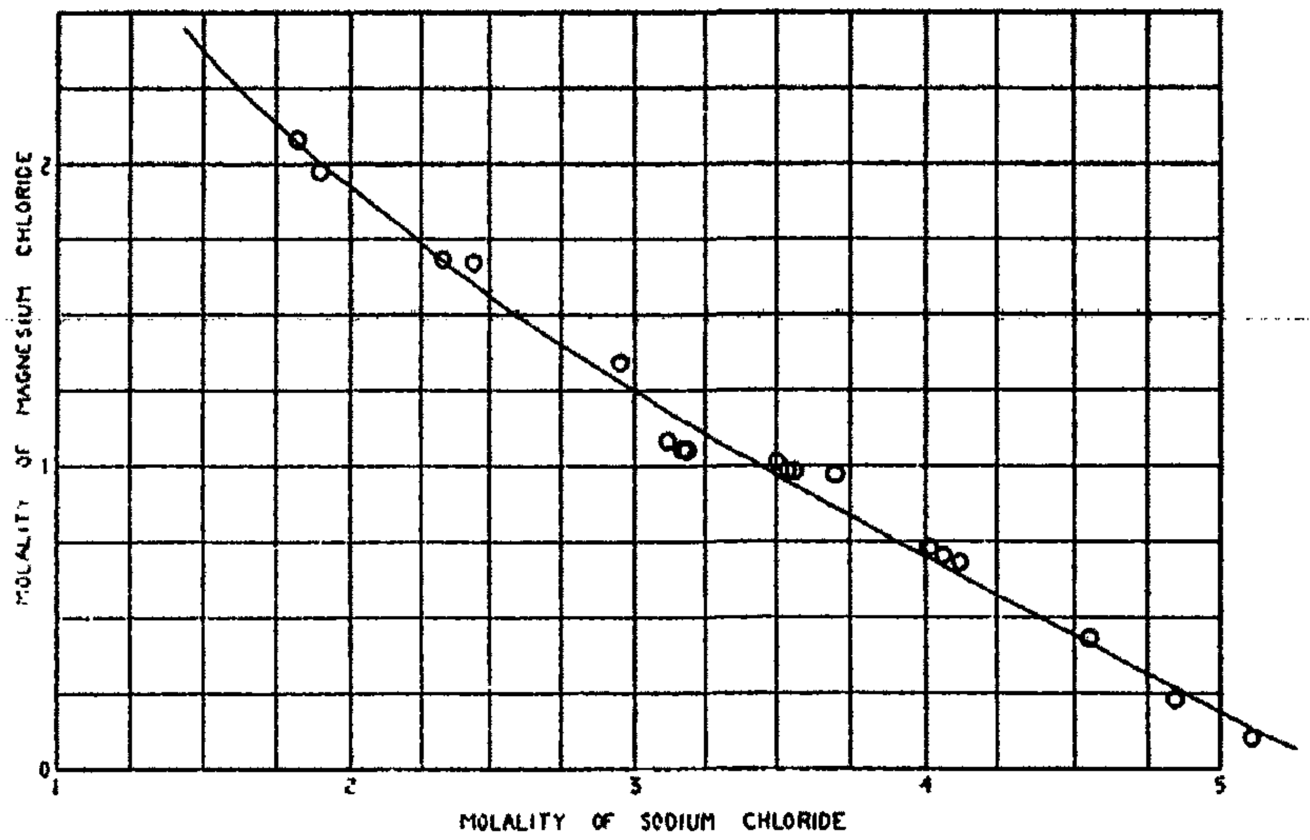

FIG. 5. Calculated curve for the solubility of sodium chloride in the quaternary system sodium chloride–magnesium sulfate–water in the presence of astrakanite as coexistent solid phase.

THE SOLUBILITY CURVE FOR SODIUM CHLORIDE IN THE QUINARY SYSTEM SODIUM CHLORIDE–POTASSIUM CHLORIDE–MAGNESIUM CHLORIDE–MAGNESIUM SULFATE–WATER AT 25°C.

Technically, and for the question of the formation of oceanic salt deposits, this system is of exceptional importance. The 25°C. isotherm has been studied in considerable detail. With sodium chloride continuously present as solid phase, not less than thirteen other different solid phases may appear by varying the three independent variables,—the concentrations of potassium and magnesium chlorides and of magnesium sulfate.

The three different k_3 values needed for the calculation of the solubility curve for sodium chloride, which correspond to three separate ternary systems, are given in the data for the preceding system discussed and in some earlier calculations. Thus we obtain the following equation:

$$\log \gamma_{HCl(\mu_T)} - 0.0875\mu_T - 0.021\mu_{KCl} + 0.025\mu_{MgCl_2} - 0.022\mu_{MgSO_4} + 1/2 \log \mu_x + 1/2 \log (\mu_x + \mu_{KCl} + 2/3\mu_{MgCl_2}) = 0.777 \quad (8)$$

where μ_x indicates the desired ionic strength of sodium chloride. It should be noted that all constants in this equation are derived from experimental data which are entirely independent of any measurements for the quinary system. Therefore a comparison between measured and observed solubilities of sodium chloride should be of great interest. However, owing on one hand to the slowness with which true equilibrium is reached and the large analytical difficulties of studying a quinary system accurately, and on the other hand to the inaccuracies caused by the accumulated errors in the constants employed, we would expect to find differences between observed and calculated solubility values of the order of magnitude of about 5 per cent.

TABLE 2

Comparison between observed and calculated values for the solubility of sodium chloride in the quinary system sodium chloride–potassium chloride–magnesium chloride–magnesium sulfate–water at 25°C.

KCl m	$MgCl_2$ m	$MgSO_4$ m	$NaCl$ m		SOLID PHASES BESIDES $NaCl$
			Obsd.	Calcd.	
0.71	3.79	0.28	0.38	0.48	KCl; $MgSO_4$, 4 and 5 H_2O
0.63	3.73	0.28	0.64	0.54	KCl; $MgSO_4$, 4 and 5 H_2O
1.02	2.49	1.04	1.28	1.31	KCl; $MgSO_4 \cdot 6H_2O$; schoenite
1.47	1.69	0.75	1.92	1.98	KCl; leonite
1.13	1.28	1.05	2.45	2.62	$MgSO_4 \cdot 7H_2O$; astrakanite; schoenite
1.76	1.03	0.64	2.91	2.70	KCl
1.17	0.92	1.03	3.05	3.13	$MgSO_4 \cdot 7H_2O$; astrakanite; schoenite

In table 2 is given a comparison between observed and calculated solubilities of sodium chloride in the quinary system, using experimental values taken at random from the data in the literature collected by D'Ans. The large deviations found in the case of the first two values are without any doubt due entirely to experimental errors, since the concentrations of the three co-solutes are practicaly the same in both cases. However, the following values show in comparison an astonishingly good agreement between observed and calculated solubilities. In principle, similar calculations could be carried out for every one of the possible solid phases appearing in the quinary system, naturally taking care that the proper existence limits are determined.

THE SYSTEM POTASSIUM SULFATE–MAGNESIUM SULFATE–WATER AT 25°C.

At this temperature only three different solid phases may appear in the system: anhydrous potassium sulfate, the double salt schoenite (K_2SO_4, $MgSO_4,6H_2O$), and the heptahydrate of magnesium sulfate. It is only at considerably higher temperatures that other double salts like leonite and langbeinite begin to appear as solid phases. Since the magnesium sulfate phase covers only a comparatively short concentration range, we shall limit ourselves to the study of the composition of the liquid phase in the presence of potassium sulfate and schoenite as solid phases. Solid solutions seem to be definitely absent.

The solubility of potassium sulfate in pure water at 25°C. is equal to 0.6905 molal, which value is an average of all of the more reliable determinations found in the literature. The activity coefficient of potassium sulfate in pure aqueous solutions at the same temperature has been measured by Åkerlöf. At corresponding concentrations, the activity coefficient of potassium sulfate is slightly lower than that of sodium sulfate, giving a k_1 value of about -0.200 with hydrochloric acid as reference substance. Using equation 1 we thus obtain:

$$\log \gamma_{HCl(\mu_T)} - 0.200\mu_T + 0.0325(\mu_T - \mu_x) + 2/3 \log 2\mu_x/3 + 1/3 \log (3\mu_T + \mu_x)/12 = -0.361 \qquad (9)$$

where μ_x is the desired ionic strength of potassium sulfate. A graphical comparison with the experimental points is shown in figure 6.

The activity of a hydrated double salt may be expressed as the product $(a_A)^{n_A} (a_B)^{n_B} \ldots (a_{H_2O})^{n_{H_2O}}$ where A, B, . . . represent the single components present and n their numbers. In the case of schoenite present as solid phase the following equation would thus be valid:

$$\log a_{K_2SO_4} + \log a_{MgSO_4} + 6 \log a_{H_2O} = \text{constant} \qquad (10)$$

Combining the expressions required for the activities of potassium and magnesium sulfates we thus obtain:

$$3[\log \gamma_{R(\mu_T)} + k_1^*\mu_T + k_2^*(\mu_T - \mu^*) + 2/3 \log 2\mu^*/3 + 1/3 \log (3\mu_T + \mu^*)/12] + 2[\log \gamma_{R(\mu_T)} + k_1^{**}\mu_T + k_2^{**}(\mu_T - \mu^{**}) + 1/2 \log \mu^{**}/4 + 1/2 \log (4\mu_T - \mu^{**})/12] + 6 \log a_{H_2O} = \text{constant} \qquad (11a)$$

where the index * denotes potassium sulfate and ** denotes magnesium sulfate. Introducing the previously made assumption of a linear variation of $\log a_{H_2O}$ and simplifying, equation 11a gives:

$$5/6 \log \gamma_{R(\mu_T)} + k_{1(d)}\, \mu_T + k_{2(d)}\, \mu^* + 1/3 \log 2\mu^*/3 + 1/3 \log(3\mu_T + \mu^*)/12 + 1/6 \log(\mu_T - \mu^*)/4 = \text{constant} \qquad (11b)$$

where the subscript d refers to the double salt as a whole. Using the experimental data for schoenite as solid phase the following formula is obtained:

$$5/6 \log \gamma_{\mathrm{HCl}(\mu_T)} - 0.049\mu_T - 0.175\,\mu_z + 1/3 \log 2\mu_z/3 + \\ 1/3 \log (3\mu_T + \mu_z)/12 + 1/6 \log (\mu_T - \mu_z)/4 = -0.874 \qquad \text{(11c)}$$

where μ_z is the desired ionic strength of potassium sulfate. Figure 6 shows that observed and calculated values for the composition of the liquid phase in the presence of schoenite show very good agreement over the entire concentration range between the triple points.

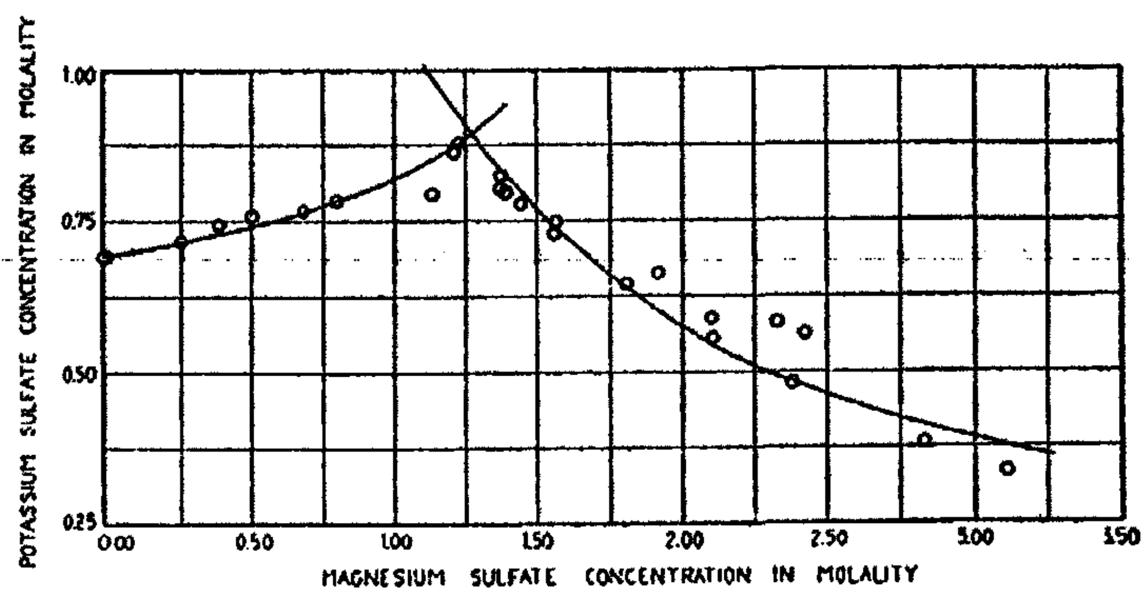

FIG. 6. The calculated curves for the composition of the liquid phase in the system potassium sulfate–magnesium sulfate–water at 25°C. in the presence of potassium sulfate and of schoenite as solid phases. Experimental points according to a table given by D'Ans (loc. cit.).

SYSTEMS CONTAINING UNI-TRIVALENT STRONG ELECTROLYTES AS SOLID PHASES OF CO-SOLUTES

Although a number of studies of such systems have appeared in the literature, none seems to give data sufficiently accurate for our purposes. Therefore the solubility of potassium chloride in solutions of ferric chloride and of potassium ferricyanide in solutions of potassium chloride has been determined at a number of concentrations of the co-solutes. Since the measurements were carried out in a manner very much the same as the one previously employed for earlier similar studies, experimental details may be omitted. All salts used were analytical reagents. Only the potassium chloride was recrystallized once and then dried at 500°C. The latter salt in the ferric chloride system was determined as the perchlorate. With the procedure adopted, duplicate analysis gave as a rule checks within one part in 5000. The ferricyanide concentration was determined by evaporation of the samples at 70°C. and then heating the dry residue at 130–140°C. for twenty-four hours. The same method, applied to the determination of the potassium chloride concentration, gave checks to one part in 10,000. The amount of decomposition of the ferricyanide residue due to the heating seemed to be entirely negligible, since addition of water gave a practically clear solution and excellent checks were obtained from duplicate samples. A summary of the experimental data is given in table 3.

TABLE 3

Experimental data for the solubility of (1) potassium ferricyanide in solutions of potassium chloride and (2) potassium chloride in solutions of ferric chloride at 25°C.

(1) POTASSIUM FERRICYANIDE		(2) POTASSIUM CHLORIDE	
KCl *m*	$K_3Fe(CN)_6$ *m*	$FeCl_3$ *m*	KCl *m*
0.0000	1.437	0.0000	4.826
0.5019	1.283	0.2256	4.548
1.0017	1.139	0.4684	4.237
1.5023	0.9915	0.7587	3.892
2.0060	0.8541	1.0139	3.584
2.4933	0.7344	1.3218	3.328
2.9923	0.6180	1.657	3.105
3.4920	0.5217	2.024	2.928
3.9961	0.4274	2.427	2.817
4.4927	0.3518	2.872	2.792
		3.365	2.871

Applying equation 1 to the data for the ferricyanide system in table 3 the following formula is obtained:

$$\log \gamma_{HCl(\mu_T)} - 0.135\mu_T + 0.0133(\mu_T - \mu_x) + 1/4 \log \mu_x/6 + 3/4 \log (\mu_T - \mu_x/2) = 0.200 \tag{12}$$

where μ_x denotes the ionic strength of potassium ferricyanide. Equation 12 gives a very close agreement between observed and calculated solubility values with a maximum difference of a few tenths of 1 per cent, as is shown graphically in figure 7.

The experimental data for the ferric chloride system do not fit the formula required by equation 1, as also was to be expected since ferric chloride, like most heavy metal salts of higher valence types, is without much doubt a weak electrolyte. Just for this reason, however, a study of the deviations of this system from the composition giving the formula expected would be very interesting, but before doing this we shall first discuss a considerably simpler system, that of sodium chloride-sodium nitrate-water at 25°C., where similar deviations occur. This system has been studied by Reinders (13) and by Cornec and Chretien (7). Their data are shown graphically in figure 10.

Using the previously employed k_1 value for sodium chloride, a numerical analysis of the experimental data shows that the k_3 value for this salt present as solid phase varies linearly with the sodium nitrate concentration, and thus the following equation is obtained:

$$\log \gamma_{\mathrm{HCl}(sT)} - 0.088\mu_T - [0.0466 - 0.00221(\mu_T - \mu_z)](\mu_T - \mu_z) + 1/2 \log \mu_z + 1/2 \log \mu_T = 0.777 \qquad (13)$$

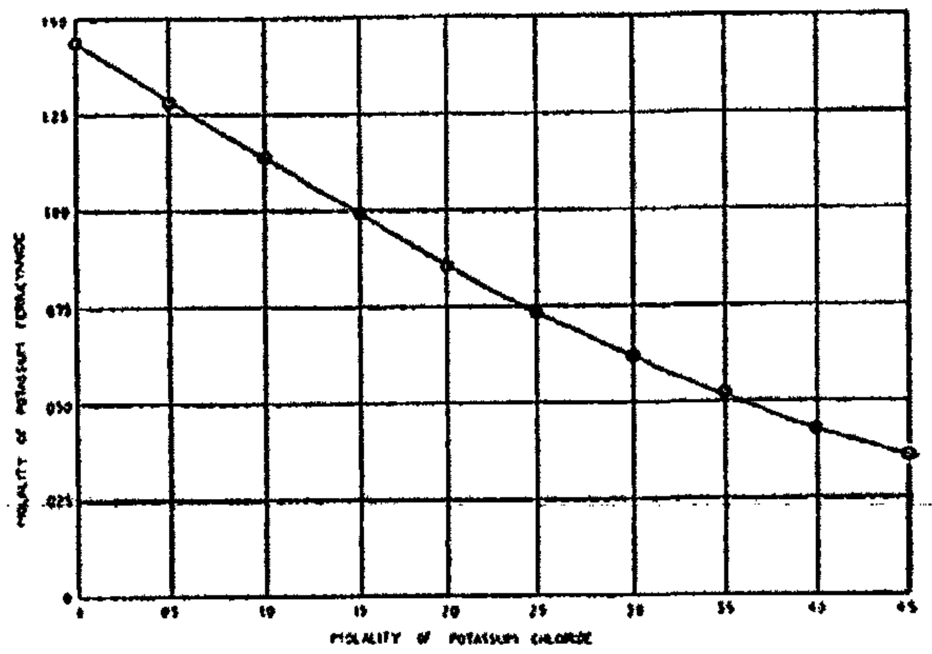

FIG. 7. Calculated curve for the solubility of potassium ferricyanide in solutions of potassium chloride.

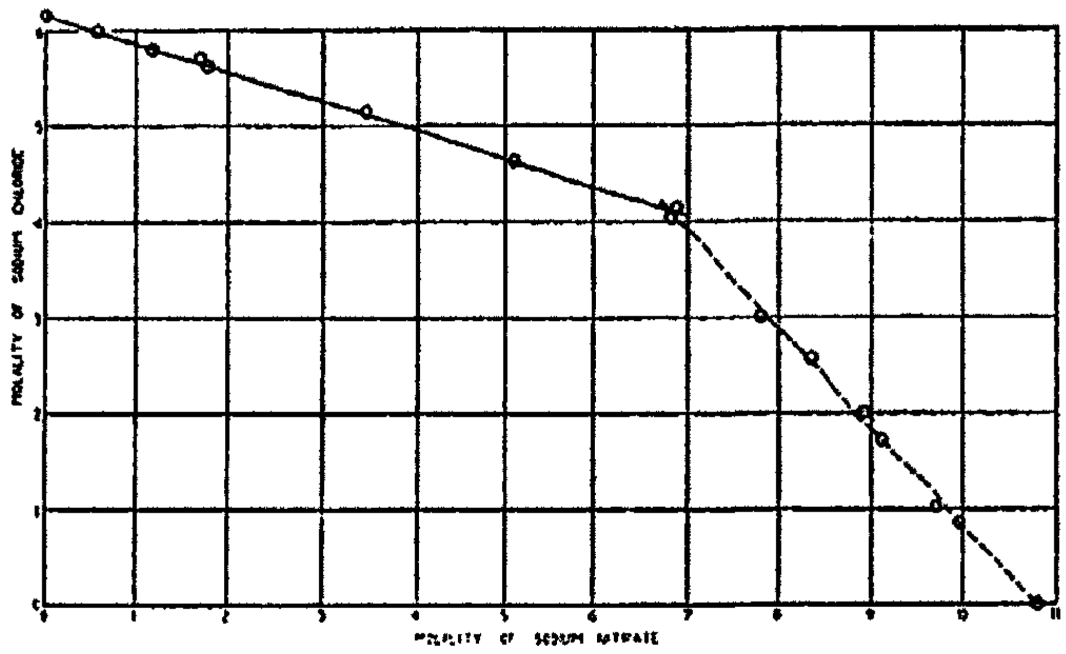

FIG. 8. Calculated curve for the solubility of sodium chloride in solutions of sodium nitrate (dotted line, sodium nitrate solubility curve). Experimental points by Reinders (13) and by Cornec and Chretien (7).

where μ_z denotes the ionic strength of sodium chloride. Equation 13 apparently gives an accurate description of the composition of the system, as is shown graphically in figure 8 by the close fit of the experimental points to the calculated curve for the solubility of sodium chloride.

Analogous to the change adopted for the k_3 term in equation 13 the experimental data for the potassium chloride-ferric chloride system show that also in this case the corresponding term in the equation required might be changed in the same manner. This would give the following formula:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.118\mu_T - [0.0204 - 0.0017(\mu_T - \mu_x)](\mu_T - \mu_x) + 1/2 \log \mu_x + 1/2 \log (\mu_T + \mu_x)/2 = 0.466 \qquad (14)$$

where μ_x designates the ionic strength of potassium chloride. Up to an ionic strength of about 14, equation 14 fits the experimental data shown graphically in figure 9, well within the probable errors of the constants employed. At higher ferric chloride concentrations the uncertainty of these constants is too large for a safe judgment, if the differences found between observed and calculated solubilities are real or not.

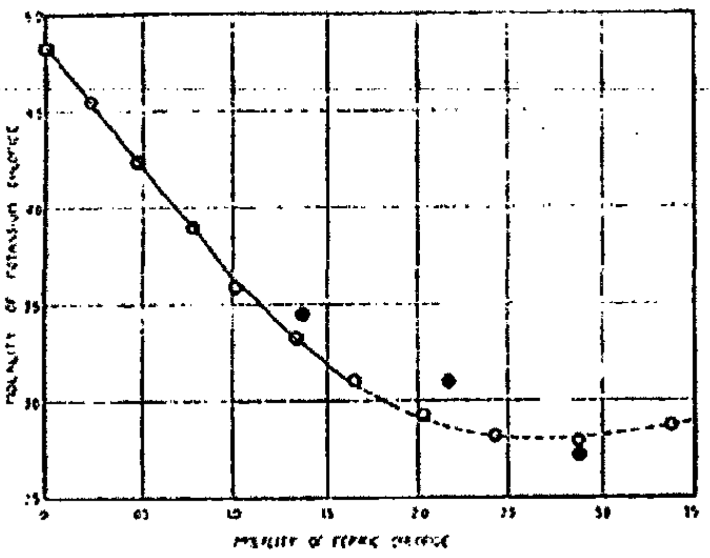

FIG. 9. Calculated curve for the solubility of potassium chloride in solutions of ferric chloride (dotted section purely experimental). Black dots, data of Malquori (Gazz. chim. ital. **58**, 891 (1928)).

THE SOLUBILITY OF BARIUM NITRATE IN SOLUTIONS OF SODIUM BROMIDE, BARIUM BROMIDE, BARIUM CHLORIDE, BARIUM HYDROXIDE, SODIUM NITRATE, ALUMINUM NITRATE, AND THORIUM NITRATE AT 25°C.

As already shown in the case of the last two systems discussed, the k_2 term in the equation required for the solubility of the solid phases had to be changed by allowing a linear variation of k_2 with the concentration of the co-solute. Therefore it is of considerable interest that for some barium nitrate systems studied the experimental data, summarized in table 4, fit the formulas required by equation 1 very well indeed without changing the k_2 term, while for others this is not the case. The author is indebted to Father F. C. Hickey for the measurements with barium chloride and barium hydroxide as co-solutes, which he carried out with rather unusual precision.

With regard to experimental details, previously given descriptions of

TABLE 4

Experimental data for the solubility of barium nitrate at 25°C. in solutions of (1) sodium bromide, (2) barium bromide, (3) barium chloride, (4) barium hydroxide, (5) ferric chloride, (6) sodium nitrate, (7) aluminum nitrate, (8) thorium nitrate, and (9) mixed solutions of sodium and aluminum nitrates of constant total stoichiometrical ionic strength

(1) SODIUM BROMIDE		(2) BARIUM BROMIDE		(3) BARIUM CHLORIDE		(4) BARIUM HYDROXIDE	
NaBr m	$Ba(NO_3)_2$ m	$BaBr_2$ m	$Ba(NO_3)_2$ m	$BaCl_2$ m	$Ba(NO_3)_2$ m	$Ba(OH)_2$ m	$Ba(NO_3)_2$ m
0.0000	0.3922	0.0000	0.3922	0.0000	0.3922	0.0000	0.3922
0.5130	0.4123	0.1740	0.3647	0.3059	0.3656	0.0883	0.4029
0.9994	0.4184	0.3649	0.3520	0.5975	0.3626	0.1940	0.4179
1.9963	0.4163	0.5840	0.3390	0.9083	0.3657	0.3245	0.4382
3.0174	0.3977	0.8250	0.3317	1.193	0.3704	0.3237	0.4353
4.0089	0.3823	1.0948	0.3286	1.485	0.3840	0.3070*	0.3054
5.0606	0.3608	1.417	0.3290	1.783	0.3992	0.2953*	0.2138
6.0532	0.3465	1.770	0.3345	1.824	0.4016	0.2742*	0.0000
		2.173	0.3468	1.842	0.4003		
		2.671	0.3714				
		3.251	0.4220				

(5) FERRIC CHLORIDE		(6) SODIUM NITRATE		(7) ALUMINUM NITRATE		(8) THORIUM NITRATE	
$FeCl_3$ m	$Ba(NO_3)_2$ m	$NaNO_3$ m	$Ba(NO_3)_2$ m	$Al(NO_3)_3$ m	$Ba(NO_3)_2$ m	$Th(NO_3)_4$ m	$Ba(NO_3)_2$ m
0.000	0.392	0.0000	0.3922	0.0000	0.3922	0.0637	0.339
0.225	0.384	0.4963	0.2650	0.1772	0.2330	0.1315	0.287
0.468	0.341	0.9977	0.2025	0.3682	0.1269	0.2037	0.237
0.759	0.298	1.9956	0.1465	0.5748	0.0810	0.2808	0.191
1.014	0.255	2.9967	0.1339	0.7990	0.0572	0.3632	0.151
1.322	0.215	3.9844	0.1321	1.043	0.0397	0.4517	0.122
1.657	0.174	4.968	0.1337	1.310	0.0315	0.5467	0.100
2.024	0.142	5.974	0.1366	1.603	0.0259	0.6491	0.082
2.427	0.105	6.975	0.1401	1.926	0.0229	0.7601	0.069
2.872	0.077	7.980	0.1435	2.284	0.0208	0.8800	0.059
3.365	0.053	8.984	0.1472	2.683	0.0189		

(9) MIXED SOLUTIONS OF SODIUM AND ALUMINUM NITRATES			
$NaNO_3$ μ	$Al(NO_3)_3$ μ	$Ba(NO_3)_2$ m	$\log \gamma_s / \gamma_0$
0.000†	6.000†	0.0416†	−0.2722
1.000	5.000	0.0565	−0.3625
2.000	4.000	0.0714	−0.4359
3.000	3.000	0.0871	−0.4996
4.000	2.000	0.1027	−0.5547
5.000	1.000	0.1195	−0.6048
6.000†	0.000†	0.1366†	−0.6500

* Barium hydroxide solid phase.

† Interpolated solubility value.

similar solubility measurements may be sufficient. All salts used were analytical reagents and they were not subjected to further purification except for barium nitrate, which was recrystallized once and then dried at 150°C. for a couple of days. Sodium bromide, sodium nitrate, and the barium salts present as co-solutes, except barium hydroxide, were determined by weighing the dry residue of their pure solutions. All determinations were carried out in duplicate, and checks better than one part in 10,000 were obtained quite easily. In the case of systems containing sodium, aluminum, or thorium nitrate, barium was determined as sulfate according to standard procedure, with all the samples diluted in the ratio one to ten. However, even with the greatest care it was as a rule impossible to get checks better than 0.1 to 0.2 per cent, and precipitates from the most concentrated thorium nitrate solutions showed variations up to 0.5 per cent. Keeping the solutions with the precipitate practically at the boiling point overnight seemed to decrease the error. According to Balcar and Stegeman (5), thorium chloride in pure solutions increases the solubility of barium sulfate very rapidly. In the case of thorium nitrate solutions with sulfuric acid present in excess this does not need to be the case, but can not as yet be predicted with certainty. The barium sulfate precipitates from the ferric chloride solutions were very faintly yellow and after heating were slightly reddish. A correction of 1 per cent was considered justifiable and was applied to all the determinations. Duplicate samples gave checks of 0.1 to 0.2 per cent.

The solubility curve for barium nitrate with either barium bromide and barium chloride or sodium bromide present as co-solute follows apparently within the experimental errors the formula required by equation 1. Thus we obtain from the experimental data the following formulas:

(1) solubility of barium nitrate with sodium bromide present as cosolute:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.220\mu_T + 0.1059(\mu_T - \mu_x) + \log \mu_x/3 + 2/3 \log 2 = -0.5326 \qquad (15a)$$

(2) solubility of barium nitrate with barium chloride present as cosolute:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.220\mu_T + 0.0520(\mu_T - \mu_x) + 1/3 \log \mu_T/3 + 2/3 \log 2\mu_x/3 = -0.5326 \qquad (15b)$$

(3) solubility of barium nitrate with barium bromide present as cosolute:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.220\mu_T + 0.0597(\mu_T - \mu_x) + 1/3 \log \mu_T/3 + 2/3 \log 2\mu_x/3 = -0.5326 \qquad (15c)$$

In these equations μ_x indicates the ionic strength of barium nitrate. As is evident from the preceding discussion, below an ionic strength of about

2.2 a correction should be applied to the logarithm of the activity coefficient of hydrochloric acid, owing to the non-linearity of the ratio between the logarithms of the activity coefficients of a uni-univalent and a unibivalent strong electrolyte in more dilute solutions. The calculated curves with the experimental points are shown in figure 10.

In the case of sodium or thorium nitrate present as co-solute, the formulas required by equation 1 do not fit the experimental data but give excellent agreement by allowing for a linear variation of k_2 with the concentration of the co-solute. Curiously enough, the solubility data for the aluminum nitrate and ferric chloride systems follow very accurately the formulas required by equation 1 without changing the k_2 term. Thus we obtain the following equations:

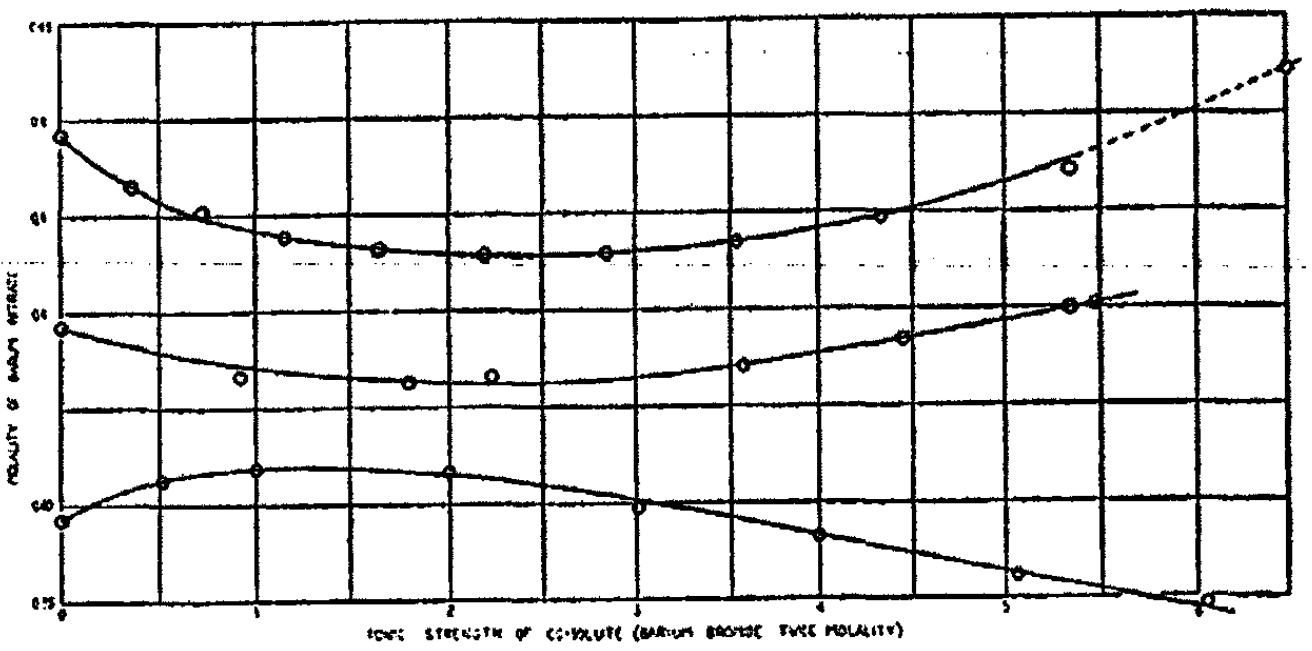

FIG. 10. Calculated curves for the solubility of barium nitrate in solutions of (1) sodium bromide, (2) barium chloride, and (3) barium bromide (dotted extension not calculated).

(4) solubility of barium nitrate with sodium nitrate present as co-solute:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.220\mu_T - [0.0159 - 0.0047(\mu_T - \mu_x)]\,(\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log (3\mu_T - \mu_x)/3 = -0.5326 \qquad (15d)$$

(5) solubility of barium nitrate with thorium nitrate present as co-solute:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.220\,\mu_T + [0.0552 + 0.0013(\mu_T - \mu_x)](\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log (12\mu_T + 8\mu_x)/30 = -0.5326 \qquad (15e)$$

(6) solubility of barium nitrate with aluminum nitrate present as co-solute:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.220\mu_T + 0.0710(\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log (3\mu_T + \mu_x)/6 = -0.5326 \qquad (15f)$$

(7) solubility of barium nitrate with ferric chloride present as co-solute:

$$\log \gamma_{HCl(\mu_T)} - 0.220\mu_T + 0.1244(\mu_T - \mu_x) + \log \mu_x/3 + 2/3 \log 2 = -0.5326 \qquad (15g)$$

The data given in table 4 for the solubility of barium nitrate in mixed solutions of sodium and aluminum nitrates agree fairly well with the values calculated according to the formula derived from the previously developed equations for the composition of arbitrary mixtures, but a more thorough experimental study is necessary before the applicability of these equations to this and similar cases can be decided. The solubility curves are shown in figure 11.

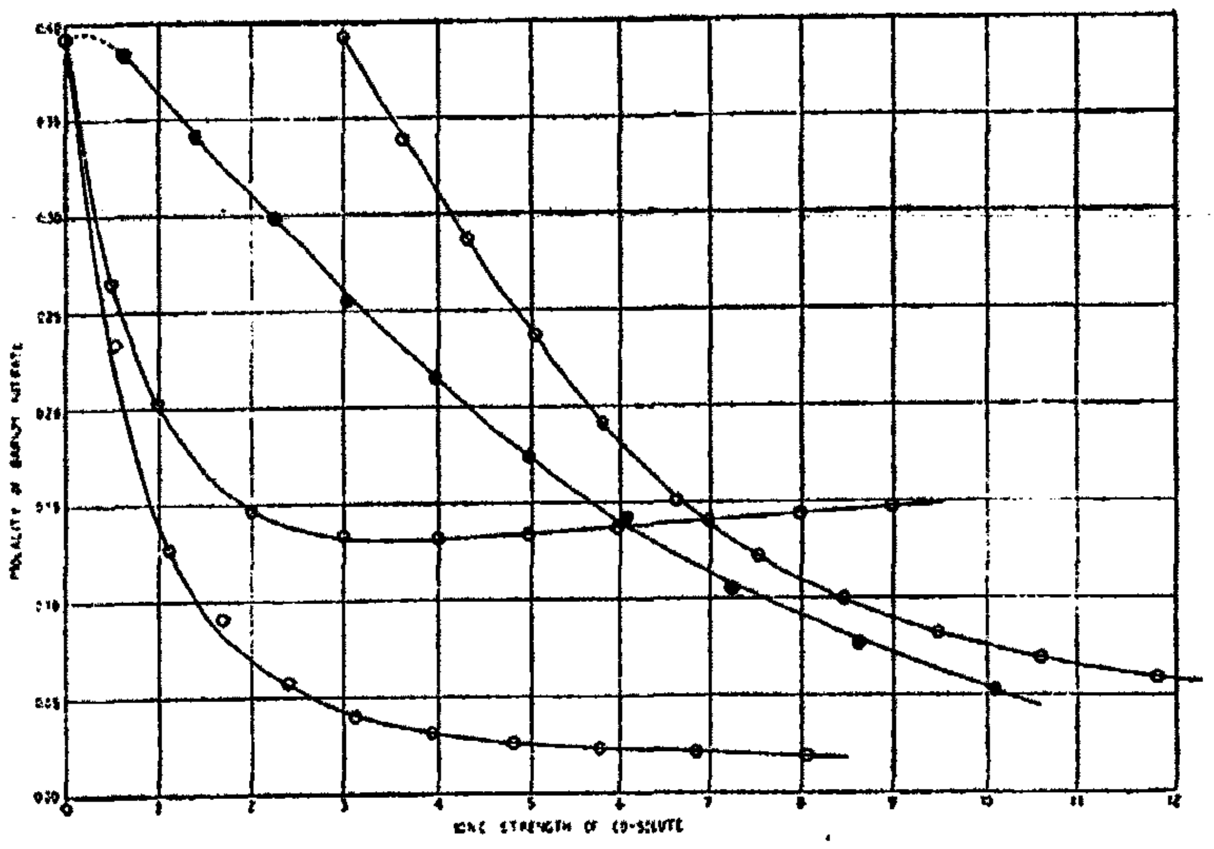

FIG. 11. Curves for the solubility of barium nitrate in solutions of (1) aluminum nitrate, (2) sodium nitrate, (3) ferric chloride (black dots), (4) thorium nitrate. To avoid confusion the last curve has been moved three spaces to the right.

THE SOLUBILITY OF CUPROUS AND MERCURIC CHLORIDES IN SOLUTIONS OF ALKALI CHLORIDES

It would be possible to examine in the same manner as described above a practically endless series of systems similar to those already discussed, and in all probability in every case the solubility curves of the solid phases could be calculated using formulas derived from equation 1. The meaning of the constants employed for these calculations is self-evident in the case of systems containing only typical strong electrolytes like the alkali halides, but their significance in the presence of heavy metal salts is lost. An instance where this is particularly apparent is in the case of systems containing alkali halides with cuprous or mercuric halides present as solid phases. Cuprous chloride decomposes in pure water and its properties can not be studied directly. Mercuric chloride behaves in its pure aqueous solutions practically like a non-electrolyte with a dissociation constant of about 10^{-14}. With this in mind we are going to apply equation 1 to the solubility data of Brønsted (6) for cuprous chloride in solutions of potassium chloride and of Herz and Paul (10) for mercuric chloride in solutions of lithium and calcium chlorides. The following formulas are obtained:

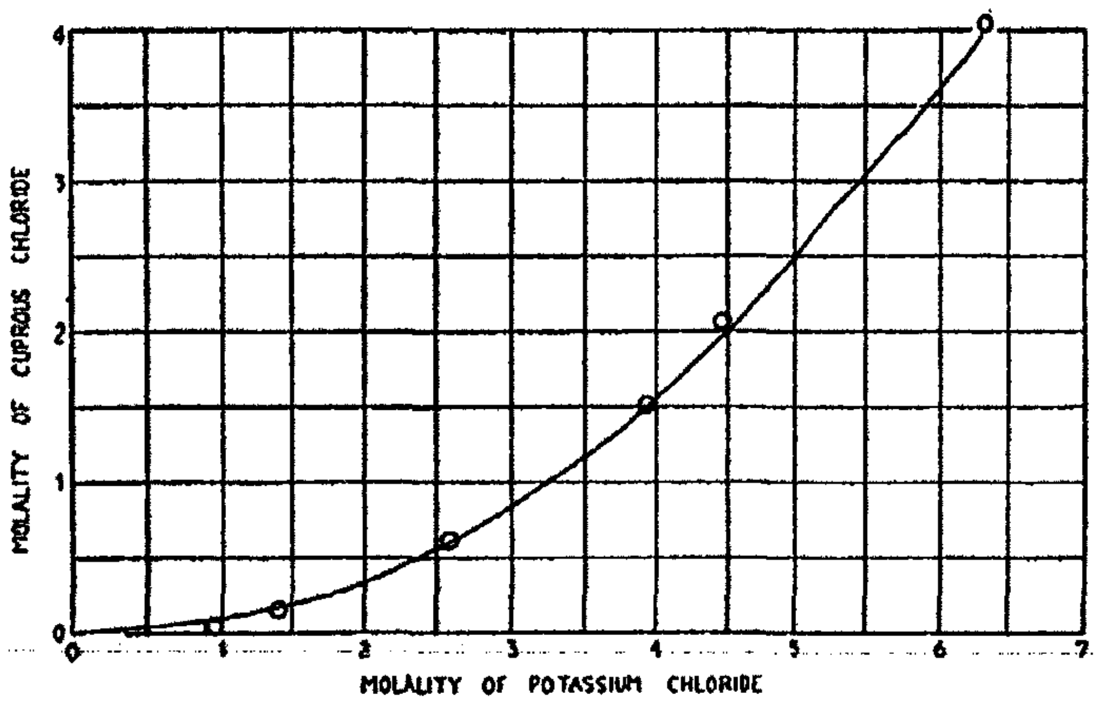

Fig. 12. Calculated curve for the solubility of cuprous chloride in solutions of potassium chloride. Experimental points according to Brønsted.

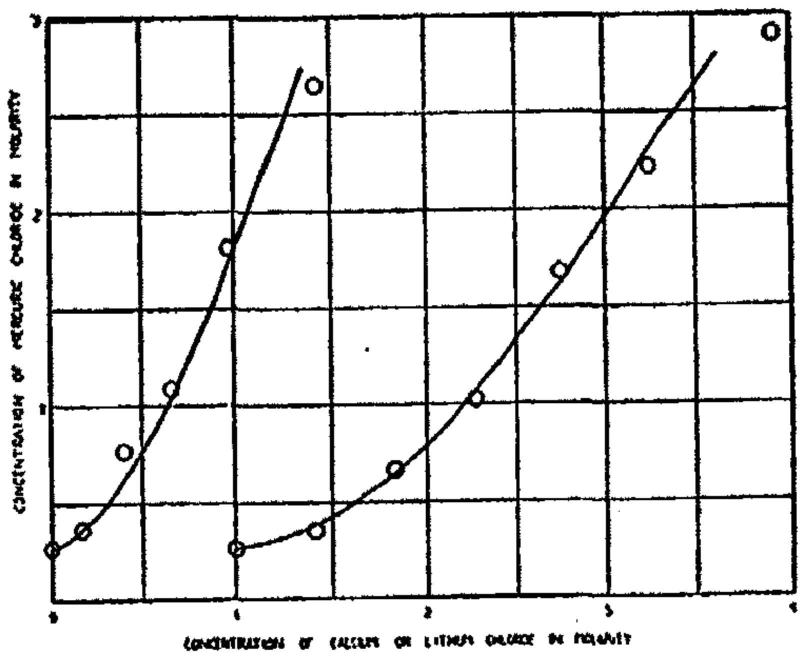

Fig. 13. The calculated curves for the composition of the liquid phase in the systems (1) mercuric chloride–lithium chloride–water and (2) mercuric chloride–calcium chloride–water at 25°C. in the presence of mercuric chloride as solid phase. The curve for the first system has been moved to the right to avoid confusion of the experimental points.

(1) solubility of cuprous chloride with potassium chloride present as cosolute:

$$\log \gamma_{\mathrm{HCl}(\mu_T)} + 0.180\mu_T - 0.767(\mu_T - \mu_x) + 1/2 \log \mu_x + 1/2 \log \mu_T = -1.140 \qquad (16)$$

(2) solubility of mercuric chloride with lithium chloride present as cosolute:

$$\log \gamma_{R(\mu_T)} + 0.143\mu_T - 0.830(\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log (\mu_T - \mu_x/3) = -0.799 \qquad (17a)$$

(3) solubility of mercuric chloride with calcium chloride present as cosolute:

$$\log \gamma_{R(\mu_T)} + 0.143\mu_T - 0.572(\mu_T - \mu_x) + 1/3 \log \mu_x/3 + 2/3 \log 2\, \mu_T/3 = -0.799 \qquad (17b)$$

In these equations μ_x indicates the stoichiometrical ionic strength of cuprous or mercuric chloride. In the latter case all concentrations are calculated as moles or ionic strength per liter of solution. As reference electrolyte sodium sulfate has been used, assuming mercuric chloride to be a uni-bivalent electrolyte. As required for a typical strong electrolyte the same k_1 value has been used for both lithium and calcium chlorides as cosolutes.

A graphical comparison between calculated solubility curves and the experimental points is shown in figures 12 and 13. Herz and Paul indicate that at high concentrations new solid phases appear, but we find that up to an ionic strength of about 8.5 the agreement between observed and calculated solubility values is quite good and their differences well within the experimental errors. However, the k_1 value obtained for mercuric chloride does by no means account for its behavior in pure aqueous solutions, since it would make this compound as strong an electrolyte as strontium chloride. Similarly, cuprous chloride would appear to be much stronger an electrolyte than hydrochloric acid.

DISCUSSION

The most striking aspect of the study presented above is the very large variety and number of systems to which equation 1 probably may be applied successfully, if we are willing to drop the original significance of the constants employed. As already stressed, only in systems containing typical strong electrolytes do the constants employed agree according to their definition with the thermodynamic behavior of the compounds present. However, even if the true meaning of the constants employed is lost, those obtained seem to be characteristic of the compound studied, as was shown for the k_1 value of barium nitrate in eight different systems;

even for mercuric chloride its apparent k_1 value was independent of the nature of the co-solute in a number of cases studied.

The k_2 values vary with the co-solute present, but in polycomponent systems they should be independent of the co-solutes present. The study of the solubility of sodium chloride in a quaternary and a quinary system undoubtedly made it very probable that this is the case for typical strong electrolytes. A few measurements with barium nitrate in mixed nitrate solutions seemed to indicate that this might be true even for polycomponent systems containing heavy metal salts, but a thorough experimental study of this point is necessary since there are no suitable data available.

Previously it has been shown that for strong uni-univalent electrolytes their k_1 and k_2 values may be related to each other in a rather simple manner. If these values for a number of electrolytes having a common co-solute were plotted, straight lines were obtained and the slopes of these lines varied linearly with the k_1 value of the co-solute. The pursuance of such a rule for uni-univalent electrolytes with uni-bivalent electrolytes as co-solutes was one of the objects of this study, but as it turned out, neither were the experimental data available sufficiently accurate, nor was the number of systems covered large enough. The value of finding such a rule is easily apparent. It would be possible to describe the solubility curve of an electrolyte present in its pure solid phase in any aqueous polycomponent system containing electrolytes to which this rule applies, provided one characteristic constant were known for each one of the co-solutes.

SUMMARY

The solubility has been determined for barium nitrate at 25°C. in solutions of sodium bromide, barium bromide, barium chloride, barium hydroxide, ferric chloride, sodium nitrate, aluminum nitrate, and thorium nitrate. A few measurements have also been carried out with mixed solutions of sodium and aluminum nitrates. The solubility has further been determined at 25°C. for potassium chloride in solutions of ferric chloride and for potassium ferricyanide in solutions of potassium chloride.

The solubility data for the systems mentioned and also for the following systems have been studied, using a general solubility equation: sodium chloride–sodium sulfate–water; magnesium chloride–magnesium sulfate–water; sodium chloride–magnesium sulfate–water; sodium chloride–potassium chloride–magnesium chloride–magnesium sulfate–water; potassium sulfate–magnesium sulfate–water; sodium chloride–sodium nitrate–water; cuprous chloride–potassium chloride–water; mercuric chloride–lithium and calcium chlorides–water.

It was found that in every one of the cases studied the solubility curves for the solid phases could be calculated accurately using the general solubility equation. The differences between observed and calculated solubility values for large concentration ranges seemed always to be within the probable errors in the constants employed or due to the experimental data. In a few cases the k_2 term was slightly modified.

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DIFFUSION OF LITHIUM IONS THROUGH QUARTZ IN AN ELECTRIC FIELD

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It has long been known that ions of lithium and sodium can be transported through certain glasses and quartz in an electric field (9,8; see also 3). The transport in quartz is not isotropic, but is in the direction of the principal axis of the crystal (10,4). Although the transport in glasses is electrolytic in the sense that there is a replacement of the cations of the glass, in quartz, which is obtainable in a very pure state naturally, it seems that the process must be one of simple diffusion.

Figure 1 shows a projection of the structure of quartz on a plane perpendicular to the principal axis. There is one "pore" or tunnel running through the crystal parallel to the principal axis for each unit cell (corresponding to one pore per 20 (A.U.)^2). Since the ionic transport is always found to occur in the direction of these tunnels, it has plausibly been assumed that the ions move through these tunnels (2). This is further supported by the fact that the radius of a tunnel is about 1 A.U., from the x-ray measurements and assigned O^{--} sizes. The usually accepted values of the ion radii for Li^+, Na^+, and K^+ are 0.75 A.U., 1.00 A.U., and 1.33 A.U. It is experimentally found that Li^+ and Na^+ can be transported but that K^+ cannot (10).

It occurred to the authors that thin crystals of quartz might well serve as simple Graham's law diffusion membranes for use in concentrating $_3Li^6$ and, as a result, the mechanism of the transport of Li^+ through the quartz has been investigated in some detail.

EXPERIMENTAL

The cell used, shown in figure 2, is essentially like that described in reference 10. The following materials were used in the anode and cathode compartments:

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	Anode	*Cathode*
(I)	LiCl, H_2O	Hg
(II)	LiCl, pyridine	Hg
(III)	Li, Hg	Hg
(IV)	$LiNO_3$	Hg
(V)	$LiNO_3$	NH_4HSO_4

I and II (used in an all-glass cell with quartz diaphragm and nickel electrode) showed no transport. Measurable transport was obtained in cases III, IV, and V, with a potential drop across the cell of 5 to 125 volts.

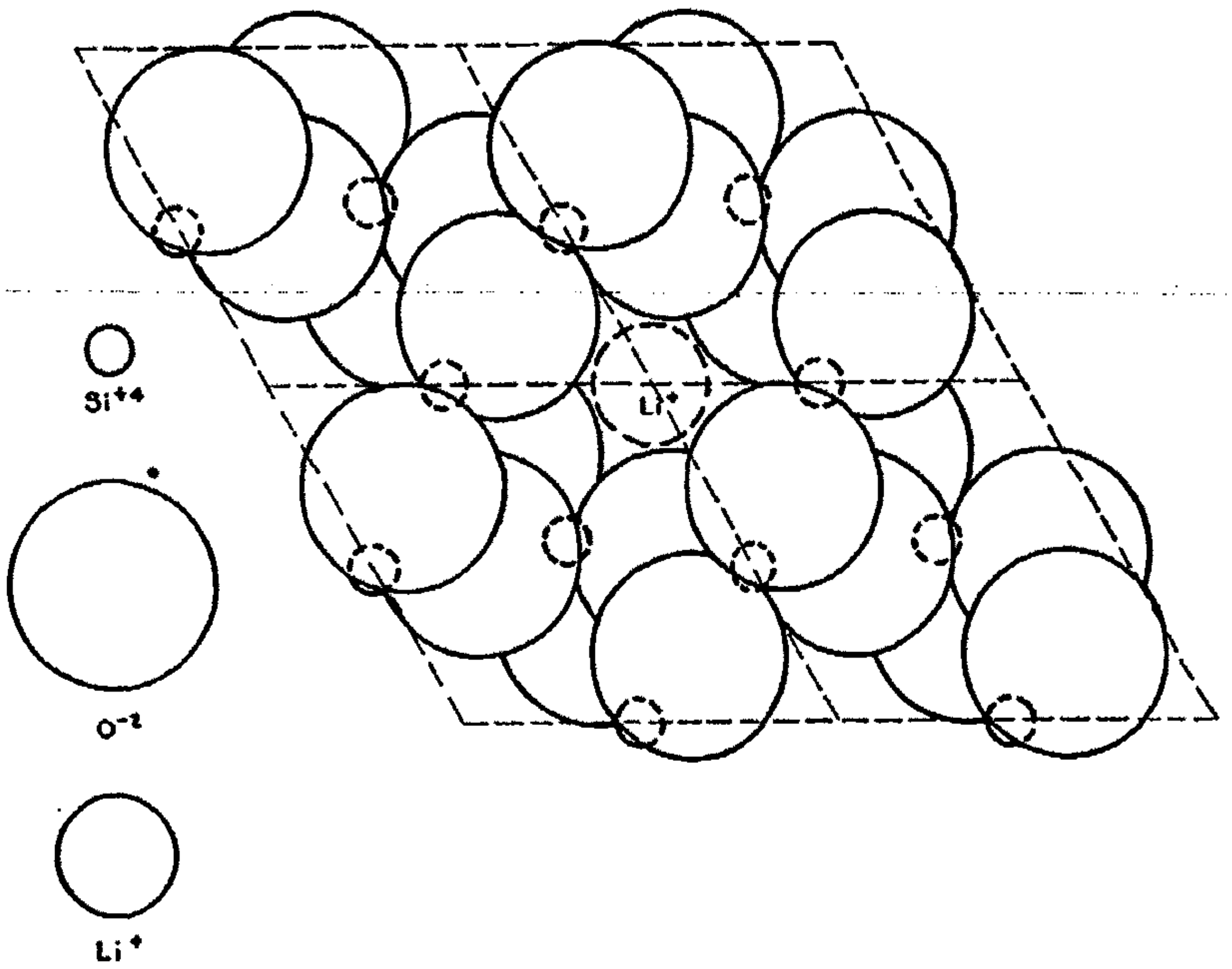

FIG. 1. Projection of structure of α-quartz on basal (0001) plane

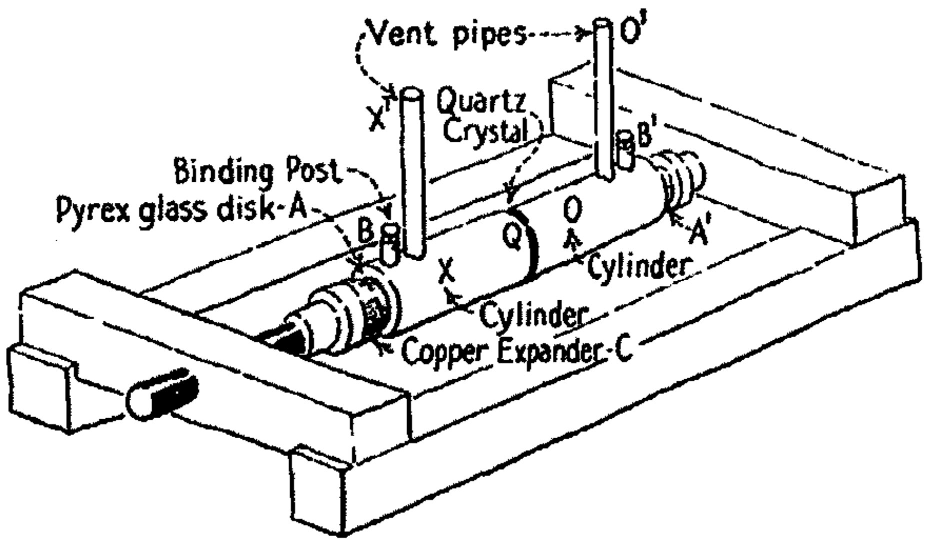

FIG. 2. The cell

The following schedule of experiments was set up: (*a*) Electrolysis was maintained at 55 volts during the entire period of the experiment except when cell characteristics were determined. (*b*) Measurements of cell current with potential drop of 5 to 125 volts across the cell, at 10-volt intervals, were made hourly. These measurements required only about five minutes of the hour. The electrolysis was continued until three successive hourly sets of data checked each other within experimental error. (*c*) Similar sets of data were obtained for each crystal at each of a set of different temperatures providing the crystal was not damaged during the experiment. The cell was heated in a well-insulated electric oven, the temperature of which was manually controlled within ± 1°C. (*d*) Such data were obtained for a number of specimens of quartz, both of different thicknesses and from different specimens of the mineral.

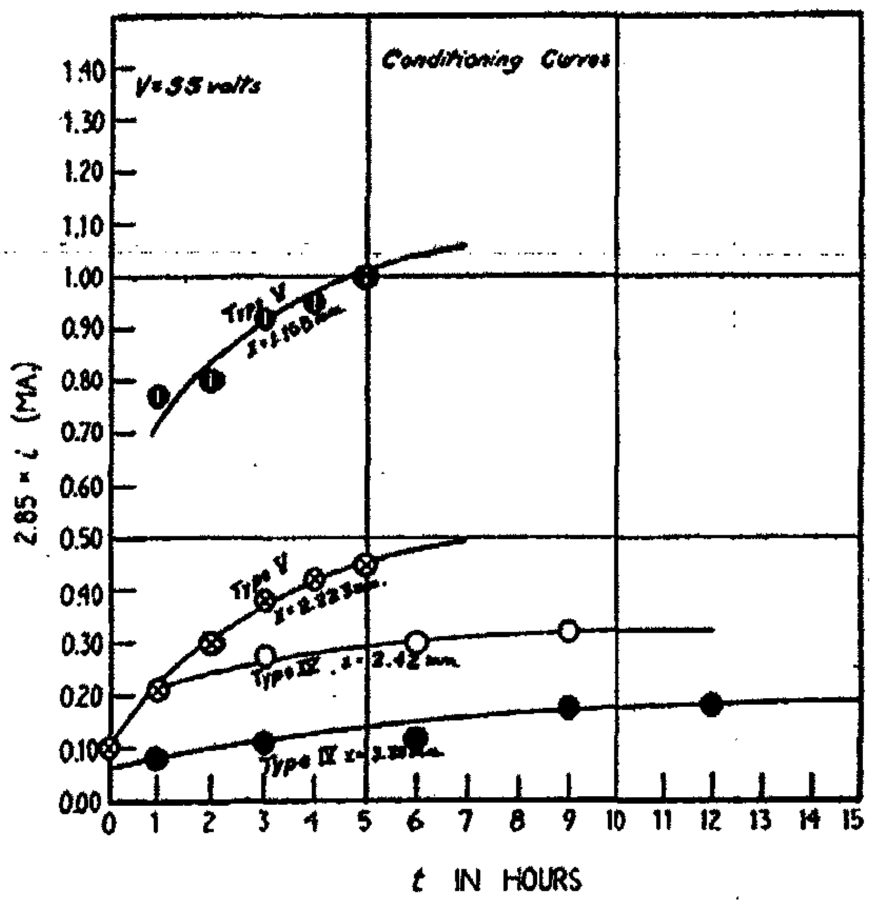

FIG. 3. Variation of current with time at a selected potential drop of 55 volts for cells of type *III*, IV, and V.

RESULTS

Figure 3 shows the variation of current with time at a selected potential drop of 55 volts for cells of type III, IV, and V. It is clear that a conditioning period is required before consistent data may be obtained. This phenomenon is believed to be due to a necessity of obtaining a wetting of the crystal face and of freeing the pores of the quartz of any foreign ions which may be present.

Figure 4 shows the variation of log i with $1/T$ for several voltages for several cells. These data may be accurately represented by the equation:

$$i = Se^{\frac{-W}{RT}}$$

The work function W takes on values given in table 1. It seems to approach an asymptotic value of about 17 kg-cal. per mole of Li^+ transported. The current during electrolysis of crystals of potassium chloride, sodium chloride, etc., has been found also to be given by such an expression (4).

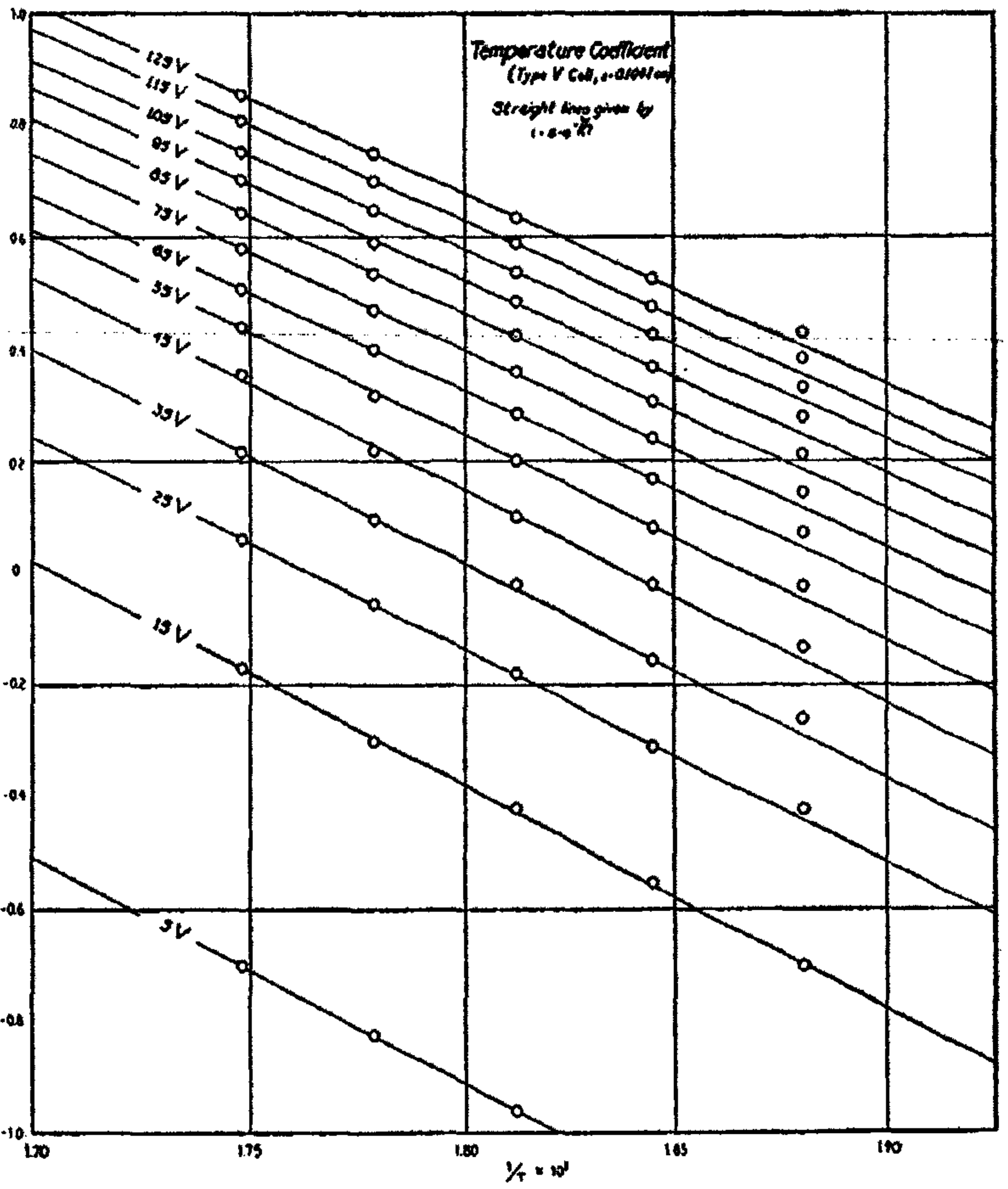

FIG. 4. Temperature dependence of cell current

It is of interest to note that the measurements on the alkali halides were made at very small current densities corresponding to values of W at low voltages and that the value of W so obtained is the same as that obtained here at such current density within experimental error, i.e., about 20 kg-cal. per mole. The lack of transport in water, etc., may be ascribed either to solvation or to the fact that at room temperature not enough ions have sufficient energy to make the current measurable.

The quantity, W, has been interpreted by Jost (5) as the work necessary to liberate a cation in a crystal field. In the case treated here one seems forced to attribute to W the value of the work necessary to evaporate a mole of Li^+ from the anode compartment into the crystal. Since the ion is being removed from not too dissimilar environments in the two cases, the interpretation is essentially the same.

TABLE 1

Variation of values of W and S with potential drop

POTENTIAL DROP IN VOLTS	W IN KG-CAL. PER MOLE (x = 0.222 CM.)	LOG S (x = 0.222 CM.)	W IN KG-CAL. PER MOLE (x = 0.1041 CM.)	LOG s (x = 0.1041 CM.)
5	18.3?	6.98	16.9	
15	19.8	6.76	17.9	6.26
25	18.3	6.41	17.4	6.30
35	17.6	6.25	17.4	6.46
45	17.3	6.27	16.7	6.28
55	17.9	6.55	16.6	6.34
65	17.6	6.53	15.9	6.17
75	17.9	6.73	15.9	6.24
85	17.7	6.60	15.9	6.21
95	17.6	6.70	15.6	6.24
105	17.6	6.79	15.5	6.24
115	17.1	6.63	15.6	6.35
125	17.3	6.73	15.6	6.38

As to the quantity S, one may naïvely interpret it as a collision factor which counts the chance that an ion, in a layer within a free path of the crystal, may make a collision with a crystal pore. One does not know, well, how to make a calculation of S on such an interpretation. However, taking over from the kinetic theory of gases the expression (7)

$$Z = N\sqrt{\frac{RT}{2\pi M}}$$

(where Z is the number of ions striking 1 cm.^{2} of surface per second, N is the number of ions per cm.^{3}, and M is the molecular weight), and considering the target area of pores in the quartz, the number of ions striking pores per square centimeter of surface per second is about 6×10^{24}. If one selects a value of W = 20 kg-cal., one obtains a maximum current density of 30 milliamperes per square centimeter.

This corresponds to the saturation current and is of the right order of magnitude. It suggests that it would be worthwhile to determine saturation currents as a function of the temperature.

Figure 5 shows typical curves for i versus V. It is clear that Ohm's law is not obeyed. A plot of log i versus log V is instructive. In figure 6 curve (1) is a plot of Ohm's law and curve (2) is a plot of the Langmuir equation (6,1) for infrasaturation currents in a hot cathode vacuum tube

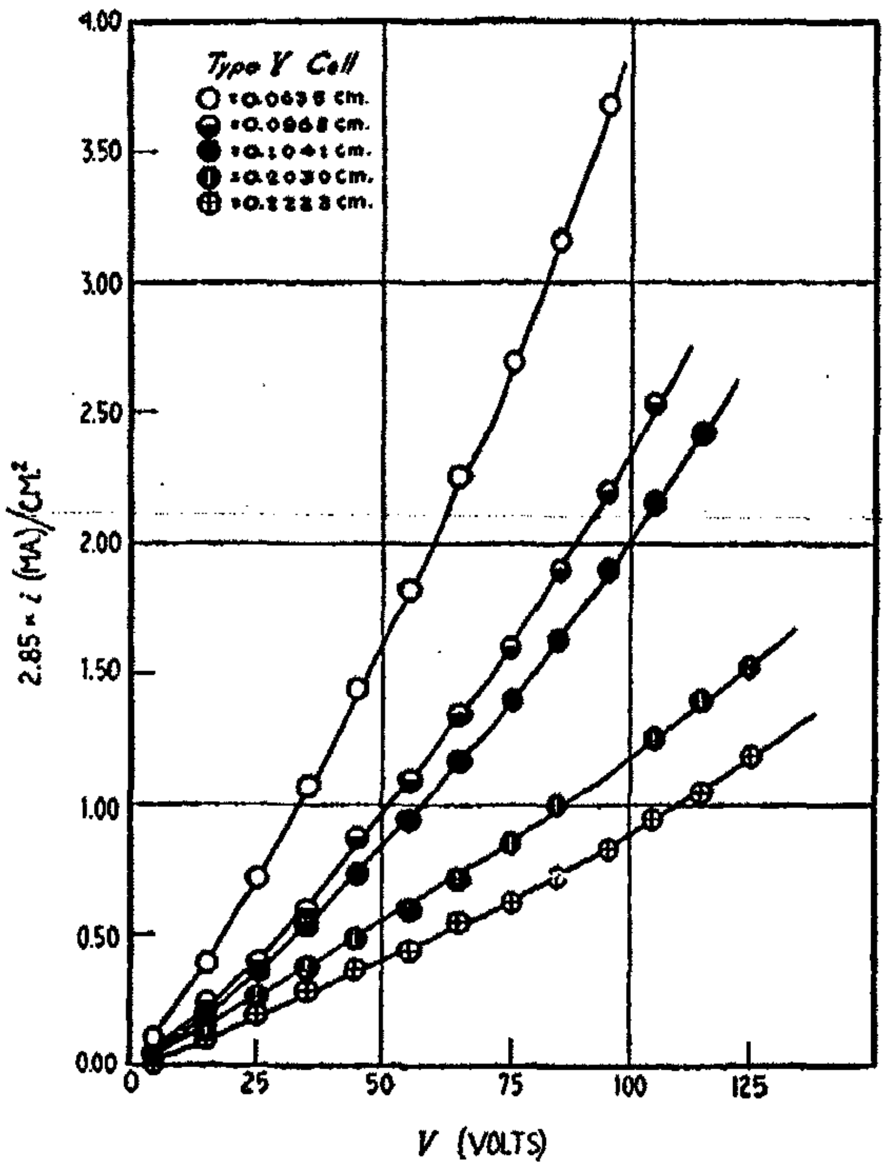

FIG. 5. Voltage variation of cell currents for different thicknesses of crystals

$$i = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{V^{3/2}}{x^2}$$

where i is the anode current, V is the anode potential, x is the distance between anode and cathode (treated as parallel plates), and e and m are the charge and mass of the electron, respectively. The other curves in figure 6 are based on a set of experimental data.

The experimental data are represented well by the equation:

$$i = C \cdot V^{1.175}$$

in which C is a function of the crystal thickness. This is, suggestively, a case lying between Ohm's law and Langmuir's equation.

We have proceeded on the assumption that an "in-between" interpretation may be given, physically, in a rather naïve fashion.

If one sets νeV, where ν is the valence of the ion, νe its charge, and V the potential of the field, equal to the energy of the ion in the field and in turn sets this equal to the kinetic energy of the ion plus the work done by the ion on the crystal, one may obtain the expression:

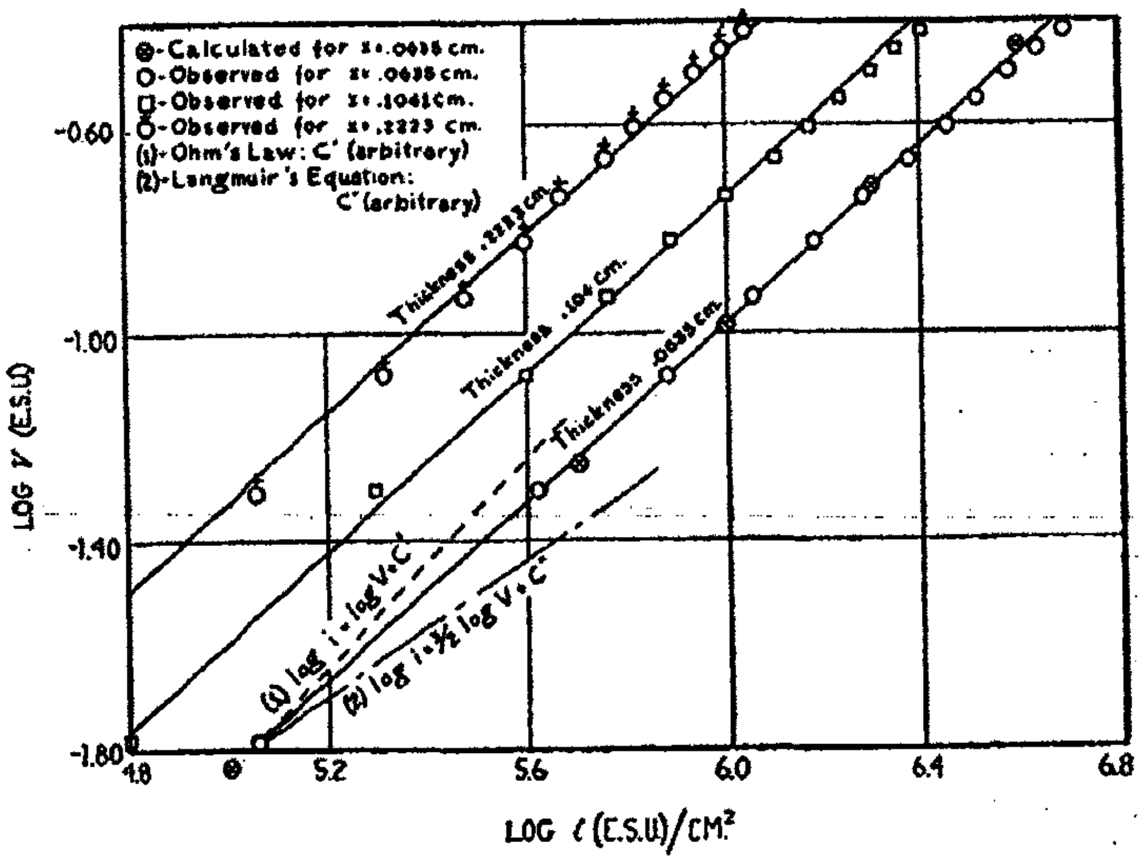

FIG. 6. Observed and calculated cell characteristics

$$\nu eV = 1/2\ mv^2 + kvx$$

where kv is, perhaps, the force from Stokes' law, and m is the mass of the ion, v is the velocity of the ion, and x is the distance the ion has moved. This presumes that the initial velocity of the ions is negligible, which is not exact, as is shown by the temperature coefficient.

Setting $k = r_0 \nu e \rho$ and $v = i/\rho$, where ρ is the volume change density, one obtains the dimensionally homogeneous equation

$$\nu eV = \frac{mi^2}{2\rho^2} + \nu e i r_0 x \qquad (1)$$

Eliminating between equation 1 and the one-dimensional form of Poisson's equation,

$$\frac{d^2V}{dx^2} = \frac{4\pi\rho}{K} \qquad (2)$$

where K is the dielectric constant, one obtains

$$\frac{d^2V}{dx^2} = \frac{2\pi i}{K}\sqrt{\frac{2m}{ve}}\,(V - ir_0x)^{-1/2} \tag{3}$$

On integration, using suitable boundary conditions, this yields

$$(V - ir_0x)^{3/2} - \frac{3r_0^2}{a}i(V - 2ir_0x) - 9/16\,aix^2 = 0 \tag{4}$$

where

$$a = \frac{8\pi}{K}\sqrt{\frac{2m}{ve}}$$

The two constants r_0 and a were determined from experimental data for V and i for a crystal of thickness $x = 0.0635$ cm. by choosing values of r_0 and finding a value of a which would cause equation 4 to vanish simultaneously for two sets of V, i values. The values of the constants $r_0 = 6.0 \times 10^{-7}$ and $a = 4.25 \times 10^{-6}$ E.S., C.G.S. units which caused equation 4 to vanish for different sets of V and i values, were thus obtained. These values of the constants correspond to $r_0 = 5.4 \times 10^6$ ohm-cm. and $K = 1.30$ (to be compared with $K = 5$ for quartz).

The value of the dielectric constant thus is to be attributed to an ion immersed in one of the pores of the quartz. It seems reasonable to the authors that this should be little greater than that for a vacuum, since the average charge density in this portion of the crystal is very nearly zero. The fact that a reasonable value of the dielectric constant is obtained leads one to put some faith in the validity of equation 4 other than of a purely empirical character. In figure 6 the calculated points marked ⊕ show the reasonably good fit that this equation gives.

This treatment should apply to currents developed in high tension insulators in which, after ions are formed, space charge undoubtedly plays a part.

It is believed that this work has developed a method for the investigation of the kinetics of collision and attendant "free volume" in electrolytic solutions (i.e., by use of solutions of, say, lithium nitrate in potassium nitrate). One of the authors plans to continue certain phases of this work. When results become available on the isotopic concentration efficiency, they will be separately reported.

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SUGAR ALCOHOLS. IX

A PHYSICOCHEMICAL STUDY OF THE ERYTHRITAN-BORIC ACID COMPLEX

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INTRODUCTION

In previous communications the authors (5, 4) studied the influence of certain of the sugar alcohols and their anhydrides upon the dissociation constant of boric acid. In one study (4) it was demonstrated that erythritan, 1,4-anhydroerythritol, was unique among the compounds investigated, inasmuch as its downward displacement of the titration curve of boric acid was greater than that of any other compound. This interesting property of erythritan prompted the present physicochemical investigation of the erythritan-boric acid complex.

MATERIALS AND METHOD

The boric acid was of buffer quality. The erythritan was prepared from erythritol by dehydration with sulfuric acid (3,1). The calculated values for its composition are as follows: carbon, 46.15 per cent; hydrogen, 7.69 per cent. Analysis gave the following composition: carbon, 46.02 per cent; hydrogen, 7.58 per cent. The levulose employed was Merck's crystals.

The pH was determined electrometrically at 24°C.±1°, using the Wilson-type (7) hydrogen electrode.

EFFECT OF ERYTHRITAN-BORIC ACID RATIO ON pH

In former studies the pH of a 4 per cent erythritan solution in one-tenth molar boric acid was found to be 2.6. The following studies were instituted to determine the influence of varying concentrations of erythritan upon the pH of a solution of boric acid of fixed concentration. The results are set forth in figure 1, curve A.

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EFFECT OF DILUTION UPON THE pH OF THE ERYTHRITAN-BORIC ACID COMPLEX

It is well known that dilution plays an important rôle in the dissociation of polyhydric alcohol-boric acid complexes as evinced by a diminution in the hydrogen-ion concentration upon the addition of water. In order to determine this effect quantitatively with respect to the erythritan-boric acid complex the following experiments were performed, in which a solution of equal quantities of 0.5 molar erythritan and 0.1 molar boric acid was employed. The results are set forth in figure 1, curve B.

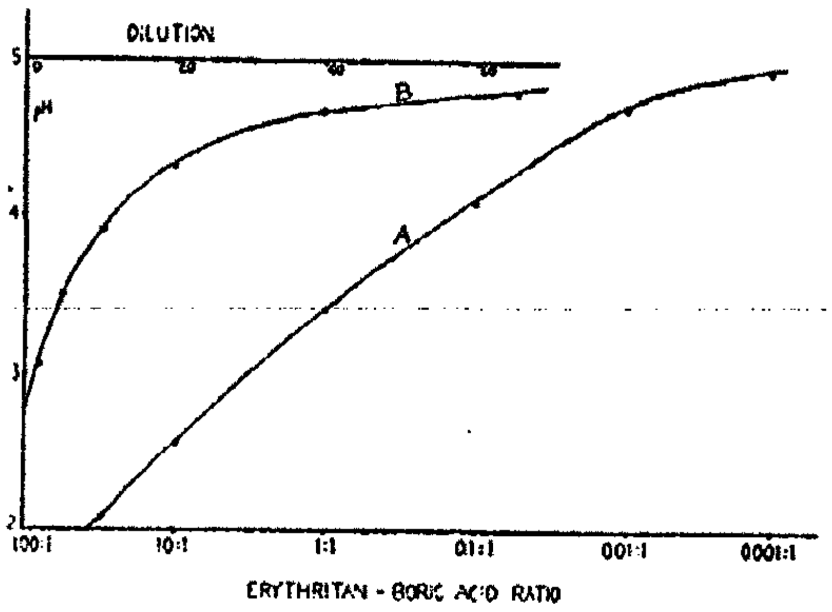

FIG. 1. The effect of the erythritan-boric acid ratio upon pH (curve A) and the effect of dilution upon the pH of the erythritan-boric acid complex (curve B).

EFFECT OF TIME AND TEMPERATURE UPON THE DISSOCIATION OF THE ERYTHRITAN-BORIC ACID COMPLEX

The complex was prepared in 1:1 ratio in 0.1 molar concentrations Portions of the solution were kept at 6°, 25°, and 60°C., respectively, over a period of five hours. During this time the pH was determined hourly, the temperature of the sample for determination having been brought to 25°C. The pH of the complex was 3.01. The fifteen determinations did not vary by more than the error of the experiment, i.e., ±0.05 pH.

DETERMINATION OF THE NUMBER OF MOLECULES OF ERYTHRITAN COMBINED WITH ONE MOLECULE OF BORIC ACID IN THE COMPLEX

Using the mathematical expression of Böeseken (2) in which D represents the polyalcohol and n the number of moles of it combined with one molecule of boric acid, HB,

$$\log[\mathrm{HB}] + n \log [\mathrm{D}] + K = -2\mathrm{pH}$$

and

$$1/2 \log [\mathrm{HB}] + \frac{n}{2} \log [\mathrm{D}] + K_1 = -\mathrm{pH}$$

Assuming that the polyalcohol-boric acid complex is completely dissociated and, further, that the hydrogen-ion concentration produced by boric acid is negligible compared with the concentration produced by the

TABLE 1

Values of n for polyol-boric acid complexes

RATIO OF POLYOL BORIC ACID	pH	a	ΔpH	n
		A. Levulose (Böeseken)		
4:1	3.01	$\frac{4:1}{3:1}$	0.14	2.3
3:1	3.15	$\frac{3:1}{0.5:1}$	0.79	2.0
1:1	3.60	$\frac{4:1}{0.5:1}$	0.93	2.1
0.5:1	3.94	$\frac{4:1}{1:1}$	0.59	2.0
		B. Levulose		
4:1	2.86	$\frac{4:1}{3:1}$	0.09	1.4
3:1	2.95	$\frac{3:1}{0.5:1}$	0.52	1.3
1:1	3.27	$\frac{4:1}{0.5:1}$	0.61	1.4
0.5:1	3.47	$\frac{4:1}{1:1}$	0.41	1.4
		$\frac{3:1}{1:1}$	0.32	1.3
		$\frac{1:1}{0.5:1}$	0.20	1.3
		C. Erythritan		
4:1	2.56	$\frac{4:1}{3:1}$	0.08	1.3
3:1	2.64	$\frac{3:1}{0.5:1}$	0.50	1.3
1:1	2.94	$\frac{4:1}{0.5:1}$	0.58	1.3
0.5:1	3.14	$\frac{4:1}{1:1}$	0.38	1.3
		$\frac{3:1}{1:1}$	0.30	1.3
		$\frac{1:1}{0.5:1}$	0.20	1.3

complex, the hydrogen-ion concentration is a measure of the concentration of the complex.

$$[H^+] = [BD'n]$$

In two solutions of different concentrations of the polyalcohol and the same concentration of boric acid, the ratio of the concentrations of the polyalcohol is proportional to the change in pH.

$$\Delta\text{pH} = \frac{n}{2}\log a$$

$$n = \frac{2\Delta\text{pH}}{\log a}$$

in which a is the ratio of polyalcohol to boric acid in the two solutions. In accordance with this hypothesis, the authors attempted first to obtain the same value for n found by Böeseken for the levulose–boric acid complex as shown in table 1, A.

Using Merck's crystals of levulose, the values ±0.02 pH which we obtained, at 22°C. with a hydrogen electrode previously standardized against 0.05 molar potassium acid phthalate, are set forth in table 1, B.

We are unable to account for the differences between the results of our investigations and those of Böeseken. Comparing these with the pH values obtained for the levulose–boric acid complex by Mellon and Morris (6) in 1:4 ratio, we find that our values agree well and show a greater hydrogen-ion concentration of the complex than Böeseken observed.

A similar experiment was made to determine the value of n for the erythritan–boric acid complex. The results are shown in table 1, C.

The fact that n is not an integer points to the likelihood of the presence of more than one complex compound of the polyalcohol in combination with one molecule of boric acid or the presence of a very complex molecule.

CONCLUSIONS

1. Increasing the ratio of erythritan–boric acid potentiates the hydrogen-ion concentration of the complex.
2. The effect of dilution on the hydrogen-ion concentration of the complex has been quantitatively studied.
3. Time and temperature have no permanent effect on the dissociation of the complex.
4. The value of n in the levulose–boric acid complex and for the erythritan–boric acid compound is approximately 1.3.

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THE THERMAL DECOMPOSITION OF DIMETHYL SULFITE[1]

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The thermal decompositions of organic compounds studied, especially during the past ten years, in the search for simple homogeneous unimolecular reactions have added considerably to our knowledge of the mechanism of numerous pyrolyses. The enormously different behavior found in the decomposition of methyl nitrite (6) and of its isomer nitromethane (7)—the former essentially simple, the latter extraordinarily complex—is but one illustration of the variety which confronts the worker in this field, especially where little is known of the bond strengths in the compounds used.

A search of the literature on organic sulfites shows but one reference to their thermal stability or to the products formed on pyrolysis. Prinz (4) states that diethyl sulfite boils with decomposition at 200°C., giving sulfur dioxide and ethyl ether. It was on the basis of such a possible simplicity that this investigation was undertaken. The choice of the methyl compound was made solely for its lower boiling point and with the knowledge that methyl ether, if formed, should be relatively stable at such low temperatures. As is later shown, however, the reaction is by no means so simple, at any rate for the methyl derivative, and there appears to be a distinct possibility that Prinz may actually have been working with the isomer, ethyl ethylsulfonate.

The dimethyl sulfite was prepared by the method of Arbusow (1). Two moles of freshly distilled thionyl chloride was allowed to drip slowly into four moles of dry methyl alcohol. During the early stages the mixture must be cooled below 20°C., otherwise the yield of sulfite is negligible. Hydrogen chloride was carried off in a stream of nitrogen bubbling through the reaction mixture, which was thus kept effectively stirred. After the first violent reaction subsided the mixture was allowed to warm up and was finally refluxed on a water bath for two hours to remove all hydrogen chloride. Fractionation of the product yielded a sample boiling between

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[1] Abstract of a thesis submitted by Richard C. Wood in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1936.

125.8 and 126.1°C. It has an odor very similar to that of acetone, without any trace of the sharpness characteristic of sulfur dioxide. Samples of the sulfite were allowed to stand in glass-stoppered bottles for some months during the course of the work, but on distillation gave no evidence of sulfur dioxide and showed no change in boiling point.

To determine the general course of the pyrolysis and the products of decomposition, the sulfite vapor was passed through a Pyrex tube maintained at 550°C. The temperature used resulted from experience of the extent of decomposition occurring during the very short time of contact. The vapors passed through three traps on issuing from the furnace, the first at room temperature, the second in ice, and the third in a dry ice–toluene mixture. All gases escaping beyond this were collected over water.

The products in the first trap proved, on distillation, to consist primarily of unchanged sulfite, together with a lower boiling fraction with a very disagreeable odor markedly resembling, by comparison, that of dimethyl disulfide. The quantity did not permit an accurate determination of the boiling point, which, however, was less than 110°C. The residue from this distillation on standing yielded white needles similar to those observed on the cooler parts of the pyrolysis tube just outside the furnace. After recrystallization from alcohol, a mixed melting point determination at 109°C. proved them to be dimethyl sulfone.

TABLE 1

Analysis of the exit gases

SAMPLE	SO_2	CO	H_2	CH_4
1	24.2	22.4	13.6	35.0
2	26.8	22.0	17.0	27.2
3	27.4	21.4	16.6	27.8
4	32.8	29.2		

The second trap (in ice) was empty. The third trap (at −78°C.) contained a quantity of liquid which analysis showed to be sulfur dioxide. Specific tests showed the absence of sulfur trioxide, mercaptans, and hydrogen sulfide.

A small amount of a yellow solid was observed in the connecting tubes between the traps. It did not volatilize at room temperature but was not sulfur. It proved to be highly unstable and in the presence of dilute nitric acid gave off copious quantities of sulfur dioxide. The quantity being small, further identification was not attempted.

The gases collected over water were analyzed in a Fisher gas analyzer. The absence of oxygen, carbon dioxide, and unsaturated hydrocarbons, and the presence of carbon monoxide, hydrogen, and methane were first demonstrated. With a view to determining the relative amounts of these gases in comparison with the sulfur dioxide formed, a complete analysis was made of the exit gases without freezing out the sulfur dioxide. The analyses in table 1 were found.

If the decomposition were to be represented as:

$$(CH_3)_2SO_3 \rightarrow SO_2 + CO + CH_4 + H_2$$

the analyses given in table 1 would prove to be somewhat low in carbon monoxide and still lower in hydrogen. The presence of considerable amounts of dimethyl sulfone would involve a reduction as follows:

$$(CH_3)_2SO_3 \rightarrow (CH_3)_2SO_2 + 1/2\ O_2$$

which might account for the hydrogen lacking in the analysis. No explanation of the low carbon monoxide values can be offered other than incomplete absorption in the analyses, where it will be observed that the totals also are less than 100 per cent.

Having thus obtained some knowledge of the products of the decomposition, measurements of the rates under varying conditions of temperature and pressure were attempted by a static method. The reaction vessel was a 235-cc. Pyrex flask mounted in an electric furnace, manually operated, the temperature of which, measured by a platinum resistance thermometer, could be controlled to half a degree. The flask was connected by capillary tubing to a mercury manometer, a storage supply of sulfite, and a Hyvac pump. The connecting capillaries were heated to a temperature around 130°C. to prevent condensation during an experiment and to maintain a reasonably high vapor pressure of the sulfite. This involved also maintaining one stopcock at this temperature. A stopcock lubricant with a Dammar gum base was found satisfactory.

The temperature range covered was from 340 to 390°C. At 340°C. and 350°C., where the reaction rate was quite slow, only a search for possible evidence of an induction period in the reaction was made. No such evidence was found even at low pressures.

The pressures of sulfite initially present covered the range from 10 to 250 mm. In view of the large pressure increase the latter figure was the practical upper limit with the apparatus employed. It was found that the rates of reaction on a clean surface were always high and erratic. When the reaction vessel had been evacuated for from five to fifteen minutes after a run and a second run then made, the rate of reaction was lowered and could be more easily reproduced. Such a pumping procedure was standardized for all runs, data for which are given in table 2. The products of the reaction appeared to be without effect on the rate, but undoubtedly a clean surface is poisoned during a run although, as will be seen later, not sufficiently to suppress completely a heterogeneous reaction.

Data of a typical experiment are given in table 2.

An attempt to calculate unimolecular velocity constants from the rate of pressure change directly observed, gave values which rapidly decreased during a single run. The constants given in table 3 are therefore the values at zero time extrapolated from readings at 15-second intervals over the first two to five minutes of reaction.

Included in table 3 are data obtained using the reaction vessel packed with short lengths of Pyrex tubing with fire-polished ends, whereby the surface to volume ratio was increased about elevenfold. The rate is seen to be increased by a factor of two, indicating definitely some heterogeneity. If the homogeneous and heterogeneous reactions are independent of each other and the calculated elevenfold increase in surface may be relied upon, this doubling in the rate should correspond to about 11 per cent of the total reaction being heterogeneous. A study of the actual rate of pressure change on the increased surface showed that the rate falls off faster than the rate on the original surface. The increased surface, in other words, causes a marked acceleration only in the early stages. This might seem to suggest a progressive poisoning of the increased surface. The results, however, were quite reproducible, and more prolonged seasoning was without effect. Furthermore, the percentage pressure change on the increased surface was slightly less than on the original surface. This latter value, however, was variable with temperature, increasing with increasing temperature from 240 to 260 per cent at temperatures from 360 to 390°C. These values are not too reliable, since on very long standing a small pressure decrease, sometimes amounting to as much as 5 per cent, was observed. This was undoubtedly due to a diffusion of some of the products from the reaction vessel and condensation on the cooler connecting tubes. The reaction vessel at all times was perfectly clean, but a black deposit

TABLE 2

Data of a typical experiment

Temperature, 370°C.; initial pressure, 140 mm.

TIME	PRESSURE INCREASE	TIME	PRESSURE INCREASE
minutes	*mm.*	*minutes*	*mm.*
1	19	25	220
2	37	30	238
3	52	40	266
5	78	50	287
7	100	60	303
10	128	80	328
15	165	100	340
20	196	120	344

collected in the capillaries which could be distilled along them leaving a clean surface behind.

The above data are plotted in figure 1 as log K_0 against log P. Over the pressure range covered the points lie on straight lines, showing an increase in K_0 as the pressure increases. The slopes of the lines are the same, namely 0.115, indicating the reaction to have an overall order slightly higher than the first. It might appear that the reaction was pseudo-unimolecular, but already in a pressure range where the equilibrium quota of activated molecules was not maintained. What is probably more likely, however, in view of the complexity of the products, is that the reaction

TABLE 3

Complete decomposition data in velocity constants at zero time

TEMPERATURE, 362°C.		TEMPERATURE, 370°C.	
Initial pressure	$K_0 \times 10^3$	Initial pressure	$K_0 \times 10^3$
mm.	*sec.* $^{-1}$	*mm.*	*sec.* $^{-1}$
23	5.52	17	8.19
24	6.15	32	8.97
33	5.92	50	9.01
75	6.25	98	9.83
96	6.62	140	10.2
186	6.82	201	11.4
251	7.08	257	11.1

TEMPERATURE, 380°C.		TEMPERATURE, 390°C.	
Initial pressure	$K_0 \times 10^3$	Initial pressure	$K_0 \times 10^3$
mm.	*sec.* $^{-1}$	*mm.*	*sec.* $^{-1}$
13	13.8	11	27.9
22	16.1	27	30.2
27	17.6	28	30.2
65	17.7	42	34.8
120	18.6	72	34.2
184	19.4	121	37.4
235	21.1	153	37.1

TEMPERATURE, 370°C.; INCREASED SURFACE	
Initial pressure	$K_0 \times 10^3$
mm.	*sec.* $^{-1}$
23	16.9
33	17.1
126	20.8
165	21.3
234	22.0

proceeds by a free radical mechanism involving several simultaneous reactions.

That the reaction is not a chain reaction, or, if a chain reaction, is of very short chain length was demonstrated by attempting to induce sulfite decomposition at 300°C. by free methyl radicals from azomethane. In table 4 are given the actual pressure change data for two mixtures of the sulfite and azomethane.

It will be seen that the rate of pressure change roughly parallels that found for azomethane and shows no indication of any decomposition of the sulfite whatsoever, since the pressure increase observed is approximately 100 per cent of the azomethane initially present, whereas had the sulfite also decomposed the total pressure would have risen to well over 1 atmosphere in the second case above. It may be remarked that no particular effort had been made to purify the azomethane, though its ability to induce decomposition in other substances was demonstrated.

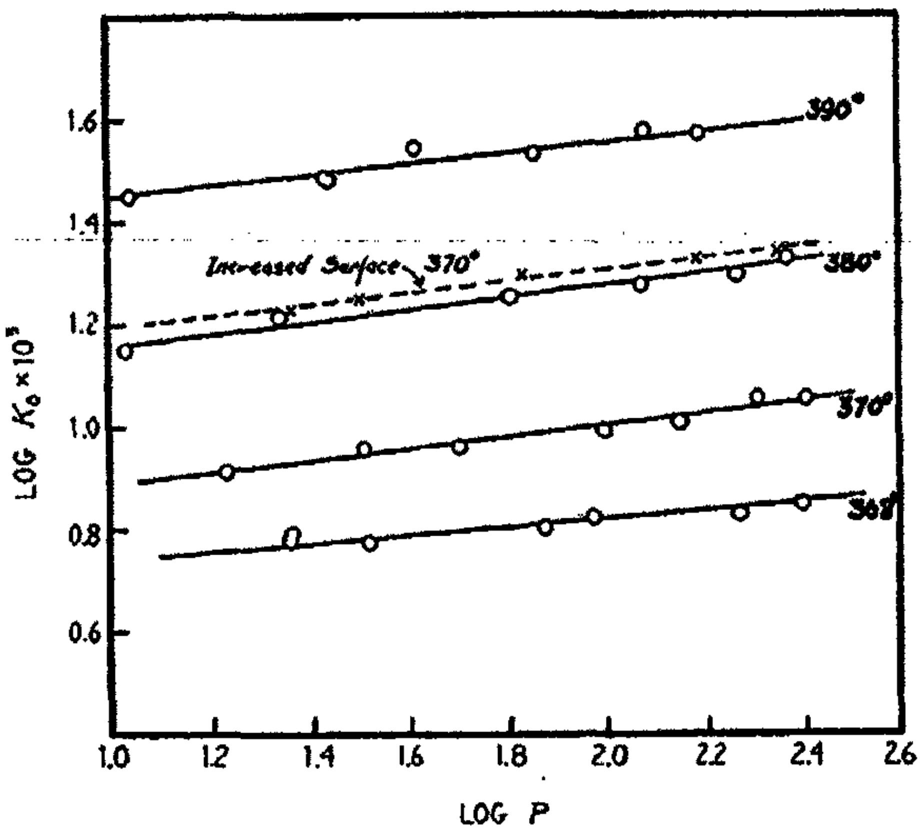


FIG. 1. Change of initial rate with change in pressure

Since the data plotted in figure 1 show parallel lines, the energy of activation is independent of pressure over the pressure range studied. From the temperature coefficient of these lines an average energy of activation of 55,000 cal. was calculated.

The effect of added gases on the initial rate of reaction was determined for nitrogen and for the products of the decomposition. It was found that traces of oxygen in the nitrogen caused a considerable acceleration of the rate of pressure change. On removing these traces, however, no effect for nitrogen alone could be found, the results duplicating those found in its absence. The effect of the products was tested by allowing a small amount of the sulfite to decompose completely and then adding a fresh amount of sulfite whose rate of decomposition was then carefully followed. This was done for varying ratios of sulfite to product at both high and low total pressures. The results obtained were always in agreement with the data found in the absence of added products within the experimental error. Details therefore need not be given.

TABLE 4

Decomposition in the presence of azomethane

Temperature, 300°C.

INITIAL SULFITE............39 mm. INITIAL AZOMETHANE.......20 mm.		INITIAL SULFITE............300 mm. INITIAL AZOMETHANE....... 20 mm.	
Time	Pressure	Time	Pressure
min.	*mm.*	*min.*	*mm.*
0.5	61	0.5	321
1	62	1	322
2	64	2	324
3	65	3	325.5
4	66.5	4	326.5
5	68	5	327.5
10	72	10	332.5
15	75	15	336
20	77	20	337
30	79	30	339
40	79.5	40	341

DISCUSSION OF RESULTS

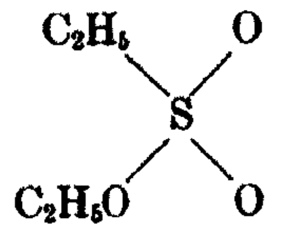
The work of Prinz previously referred to and the major products of the reaction here found would suggest that the initial decomposition is a split of the sulfite into methyl ether and sulfur dioxide, followed by a decomposition of the ether into methane, carbon monoxide, and hydrogen. Against this, however, are the following facts: (*1*) that every effort to find methyl ether among the products failed; (*2*) that methyl ether alone decomposes at a reasonable rate around 450 to 550°C. (2); and (*3*) that the energy of activation of methyl ether, even in this temperature range, is 58,500 cal. (2).

Since the energy of activation here found for dimethyl sulfite is only 55,000 cal., the probability of an initial decomposition into an already activated methyl ether molecule, which would facilitate its decomposition, seems small, unless the reaction

$$(CH_3O)_2SO \rightarrow CH_3OCH_3 + SO_2$$

were fairly highly exothermal. Lacking any absolute data, this would not appear reasonable. On the contrary it might be expected that the reaction was actually endothermal.

Reverting to Prinz's statement, it is now known that diethyl sulfite, $(C_2H_5O)_2SO$, boils at 167°C., whilst the isomer, the ethyl ester of ethylsulfonic acid, $C_2H_5SO_3C_2H_5$, boils at 206°C. It would appear probable, therefore, that Prinz was working with the latter compound. This is the more reasonable, too, in view of the two coördinate linkages in the latter compound.



It is hoped that a report on this compound may shortly be made.

The only remaining possibility for a mechanism of the decomposition of the sulfite would seem to involve free radicals. It is a relatively simple matter to work out a scheme which will yield the observed products. It is not so simple, however, to see how such schemes should fail to yield chain reactions of chain length at least comparable to those suspected (3,5) in methyl ether, unless such a reaction as

$$2CH_3 + SO_2 \rightarrow (CH_3)_2SO_2$$

were a very efficient chain-breaking step. No specific estimate was made of the amount of dimethyl sulfone formed during the reaction, though the quantity was quite considerable. As suggested earlier, however, there is no reason to suppose that the presence of the sulfone may not be due to a reduction of the sulfite. The sulfone boils at 238°C. and shows a marked resistance to both oxidation and reduction and might therefore conceivably be stable in the temperature range 360 to 390°C. used here. It seems probable that this was the product condensing in the capillaries during an experiment and, judging from the end points on the increased surface, may be the product responsible for the small heterogeneity observed.

There would appear to be nothing to gain in considering specific free radical schemes, in the absence of more information. It is anticipated that an investigation of the sulfonate isomer may shed more light on the complexities here found in the sulfite.

SUMMARY

The decomposition of dimethyl sulfite, studied in the temperature range 360 to 390°C. and at pressures from 10 to 250 mm., yields methane, carbon monoxide, sulfur dioxide, hydrogen, and dimethyl sulfone as principal

products by a reaction of order slightly higher than the first, which is not, however, entirely homogeneous. It is presumed that the reaction involves free radicals, but it is shown that if it is a chain reaction, it has only short chains. The overall energy of activation is 55,000 cal.

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PROPOSED MECHANISM FOR THE ADSORPTION OF ACIDS AND BASES BY PROTEIN MATERIALS WITH SPECIAL REFERENCE TO THE SYSTEM HYDROGEN CHLORIDE-HIDE PROTEIN

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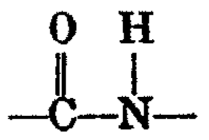
In a previous paper (2) it was shown, from phase rule considerations, that the equilibrium established between hydrogen chloride and hide protein and between ammonia and hide protein resulted in the formation of an adsorption complex, rather than a true chemical compound. In order to account for the adsorption, a mechanism based on equilibrium data for the system hydrogen chloride-hide protein and on the known structure of protein has been developed. Before presenting the proposed mechanism a few words concerning the structure of hide protein will be given.

When hide substance is hydrolyzed by acid or alkaline solution the protein breaks down into simpler molecules. The hydrolysis proceeds in steps and yields, in succession, proteoses, peptones, polypeptides, and finally amino acids. Conversely, there is evidence for the belief that the proteins are the end products of the condensation of many molecules of amino acids (3). Briefly, for instance, two molecules of α-amino acid would react to form a dipeptide thus,

$$RCHNH_2COOH + NH_2CH_2COOH \rightarrow RCHNH_2CONHCH_2COOH + H_2O$$

The —COOH group or the —NH_2 group of this dipeptide could react with a basic group or acid group, respectively, from another amino acid, to form a polypeptide and so on to yield peptones, proteoses, and proteins.

As a result of such condensations there will be, in addition to the characteristic amino acid groups, —NH_2 and —COOH, the following structure



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$$

and others, depending on the nature of the groups entering into the condensation. The presence of acid and basic groups in the same molecule accounts for the amphoteric nature of the protein, and the different basic groups will vary in their ability to form salts with acids.

Concerning the nature of the union of the polypeptide residues, Conant (1) states, "Many believe.... that the forces which unite the polypeptide residues are different from the usual valences which hold the atoms together in the simple organic compounds." This implies the idea of primary valences within the polypeptides, together with the existence of secondary or residual valence forces to combine these polypeptides into peptones, proteoses, and proteins. The validity of such a picture appears to be borne out by the relative ease of hydrolysis of proteins to proteoses and peptones, compared to the hydrolysis of the latter to polypeptides and amino acids.

The nature of the adsorption complex will be considered from the standpoint of the secondary or residual valence forces existing between the polypeptide residues. While these residues undoubtedly have a preferred orientation in the protein molecule, it seems plausible to assume that the protein molecules themselves have a random orientation with respect to each other. Such random orientation could result in the secondary valences of one group in a given molecule of protein being so situated with respect to the secondary valence field of another group from a different molecule that the resultant residual valence would be zero. Or, the orientation might be such that two groups from different molecules, with residual valence of like sign, would be in close proximity to each other, thereby producing an adsorption area more conducive to adsorption than either one alone. Other orientations might arise, producing active centers of varying adsorptive power between these two extremes.

For instance, the ability of $—NH_2$ or $—CH_2NHCH_2—$ to add hydrogen chloride would be modified if the orientation were such that one or more carboxyl groups were in its immediate vicinity. The resultant affinity of hydrogen chloride for a given basic group could vary between the extremes of no affinity, to the case where the basic group in question could accommodate one molecule of hydrogen chloride. Two basic groups in close proximity to each other, but modified by carboxyl groups, might produce a field of residual valence that could accommodate but one molecule of hydrogen chloride. Less probable would be the case where three basic groups were so modified by carboxyl that they could share but one or two molecules of hydrogen chloride between them. *Likewise the affinity of the carboxyl group,* $—COOH$, *for bases would be modified by the close proximity of the basic groups occurring in the molecule.*

From this standpoint, there could be no stoichiometric relationship between protein and acids or between protein and bases.

Consider now what would happen when hide protein is exposed to the action of a gas that shows varying degrees of affinity for the reactive groups of the protein. If, as was the case in the present work, the sample is contained in an evacuated vessel and a small amount of gas added, the pressure will fall as adsorption of the gas by the protein proceeds. Furthermore, it is to be expected that the initial quantity of gas would approach equilibrium with the protein more rapidly than future additions, by reason of the fact that at the time of the first addition the number of adsorption centers on and within the molecule are at a maximum. The adsorption centers first eliminated from further competition for gas molecules would be those most readily accessible and for which the particular gas in question had the most affinity. If more gas is added it will proceed toward equilibrium with the protein at a slower rate, for any given pressure of gas, than the initial addition. This follows logically from the fact that the reactive groups, for which the diffusing gas molecules have an affinity, are not so abundant and neither are they so accessible. The diminished accessibility of the reactive groups will then require the diffusion of gas molecules through the fiber structure and capillary spaces in order to become fixed through the forces of adsorption. When any particular adsorption center is satisfied it will become increasingly more difficult for the remaining molecules of gas, under a given pressure, to become fixed, as it will require still further and more laborious diffusion for the gas molecules to reach still more inaccessible adsorption centers.

TABLE 1

Change of pressure with time for successive additions of hydrogen chloride to hide protein

5 g. of hide powder used

FIRST ADDITION, 9.6 cc.		SECOND ADDITION, 20.3 cc.		THIRD ADDITION, 30.9 cc.		FOURTH ADDITION, 15.9 cc.		FIFTH ADDITION, 21.8 cc.	
Pressure in mm. of Hg	Elapsed time	Pressure in mm. of Hg	Elapsed time	Pressure in mm. of Hg	Elapsed time	Pressure in mm. of Hg	Elapsed time	Pressure in mm. of Hg	Elapsed time
0.042	20 min.	0.99	1.5 hrs.	2.32	3 hrs.	3.86	30 min.	2.30	5 hrs.
0.011	8.5 hrs.	0.19	4.5 hrs.	1.03	8 hrs.	1.62	3 hrs.	0.60	8 days
0.011	17.5 hrs.	0.07	18 hrs.	0.41	22 hrs.	1.05	8 hrs.	0.54	9 days
0.011	2.5 days	0.04	2 days	0.31	1.3 days	0.62	22 hrs.	0.46	11 days
		0.04	3.7 days	0.23	2 days	0.40	2 days	0.42	12 days
		0.04	4.7 days	0.20	2.3 days	0.31	3 days	0.39	13 days
				0.13	5 days	0.26	4 days	0.37	14 days
				0.11	7.3 days	0.23	5 days	0.36	15 days
				0.10	8.3 days	0.19	7 days		
				0.10	9 days	0.18	8 days		
						0.17	9 days		
						0.16	10 days		
						0.15	12 days		
						0.15	13 days		

Following the same line of reasoning, each successive addition of gas would approach equilibrium less rapidly, for any given pressure, than the preceding one. If the pressure of the gas in the reaction vessel is measured at known intervals of time after an addition, until equilibrium is attained, and the pressures plotted against the corresponding time intervals, one obtains for successive additions of gas a series of curves showing the time taken to reach equilibrium. Furthermore, the curves show that for each addition of gas, longer periods of time are required to reach equilibrium than for the preceding addition. For points of equal pressure on each curve the rate of change of pressure, dP/dT, should be less for each successive addition of gas.

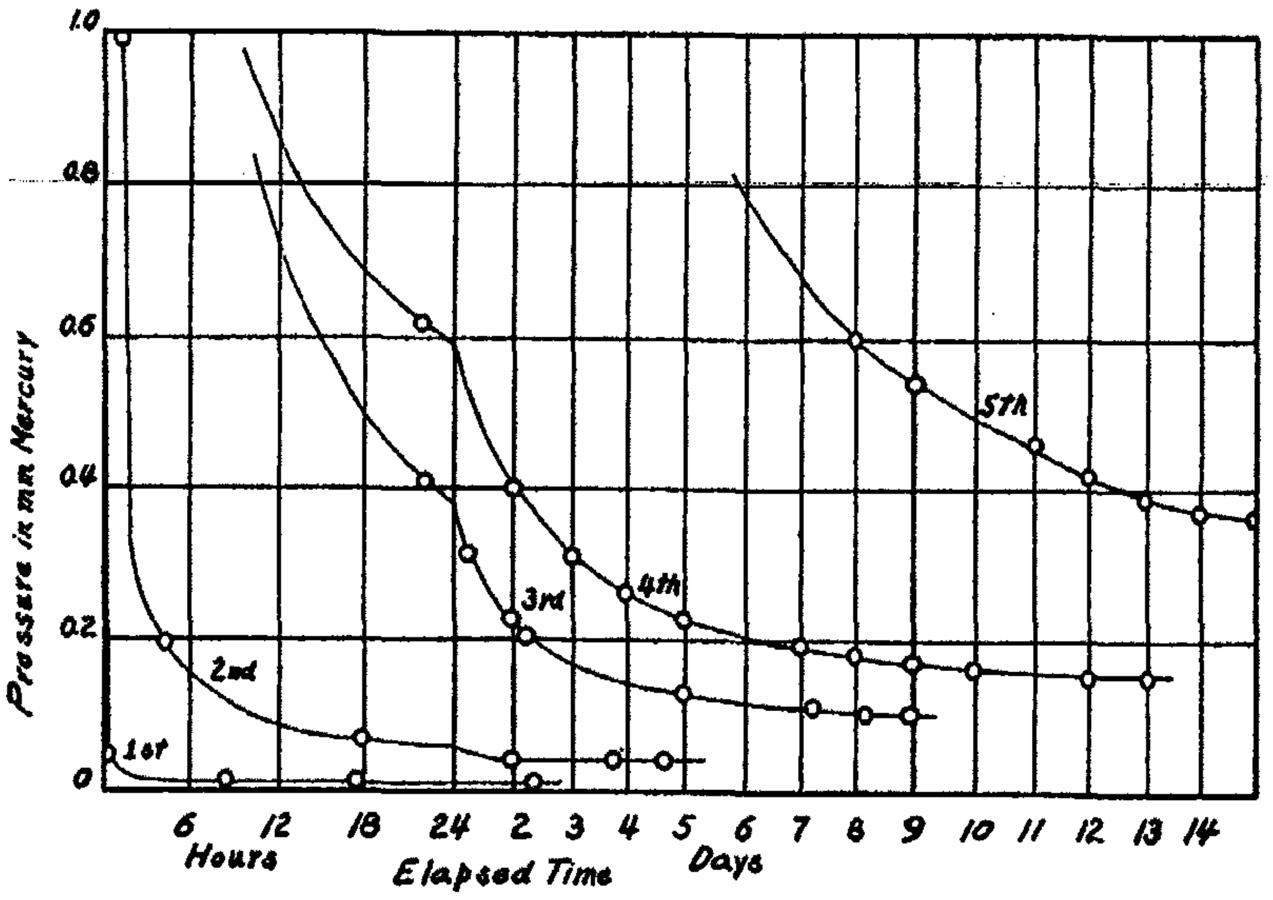


FIG. 1. Change of pressure with time for successive additions of hydrogen chloride

Data supporting this proposed mechanism for the adsorption of hydrogen chloride by hide substance are contained in table 1 and are shown graphically in figure 1.

SUMMARY

1. A mechanism for the adsorption of hydrogen chloride by hide substance has been presented to account for the formation of an adsorption complex.

2. Equilibrium data for the system hydrogen chloride-hide protein are presented in support of the proposed mechanism.

3. The proposed mechanism of adsorption for the system hydrogen

chloride-hide protein can be extended to account for the equilibrium attained in other two-component systems such as that of ammonia and hide substance.

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REACTION MECHANISM OF THE ENZYMES CATALASE AND PEROXIDASE IN THE LIGHT OF THE THEORY OF CHAIN REACTIONS

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About six years ago Haber and Willstätter (6) discussed the action of catalase and peroxidase from the point of view of chain reactions in solution. Soon after the publication of their paper, objections were raised (7) that the theory did not account for the specific behavior of these enzymes and for the kinetics of the enzyme reaction.

During recent years the mechanism of the reactions of hydrogen peroxide —particularly the catalytic decomposition—in homogeneous and heterogeneous systems has been studied in great detail (4, 5, 15). These reactions, studied in simple systems, can serve in some cases as excellent models for the action of the enzymes. In the present paper it is attempted to show that on the basis of such experiments a satisfactory understanding of the enzyme reactions may be obtained.

THE ACTION OF CATALASE

Model reactions

The study of the catalytic decomposition of hydrogen peroxide under various conditions has led to the conclusion that in all cases the hydrogen peroxide molecule is primarily attacked monovalently, yielding the radicals OH or HO_2 (i.e., O_2^-, which is connected with the HO_2 through the electrolytic dissociation equilibrium: $O_2^- + H^+ \rightleftarrows HO_2$, dissociation constant K_{HO_2}). These radicals may give rise to the reactions:

$$OH + H_2O_2 = H_2O + HO_2 \tag{1}$$

$$O_2^- + H_2O_2 = OH^- + OH + O_2 \tag{2}$$

with the formation of molecular oxygen. Reactions 1 and 2 are identical with the "chain reactions" originally proposed (1), except that O_2^- had to be substituted for HO_2 on account of some new experimental facts.

It has been shown that the primary formation of the radicals with the subsequent initiation of the chain reactions 1 and 2 can be accomplished in many different ways, e.g., by the transformation of a metal ion into the one of next higher valency, as in the case of ferrous ions, according to equation 3 (4, 5),

$$Fe^{++} + H_2O_2 = Fe^{+++} + OH^- + OH \qquad (3)$$

or by reduction of a higher valent state, as in the case of the ferric ion catalysis:

$$Fe^{+++} + HO_2^- = Fe^{++} + HO_2 \qquad (4)$$

Hydrogen peroxide can also be split by the action of an ultra-violet light quantum ($h\nu$) (12, 5, 8)

$$H_2O_2 + h\nu = 2OH \qquad (5)$$

In heterogeneous systems, e.g., in the catalytic decomposition of hydrogen peroxide on metal surfaces, the action of the metal atoms on the surface is regarded as being similar to reaction 3, the formation of the radical OH being the result of a simple electron transfer process. The electrons of the metal "electron gas" are, under suitable conditions, able to split a hydrogen peroxide molecule present at the interface metal-solution (5)

$$H_2O_2 + \text{electron}_{(\text{metal})} = OH^- + OH \qquad (6)$$

with the subsequent formation of molecular oxygen through reactions 1 and 2.

Whereas reaction 6 expresses the oxidizing action of the hydrogen peroxide molecule, the reducing properties of hydrogen peroxide must always be attributed to its anion (HO_2^-), according to the following equation (5):

$$HO_2^- = HO_2 + \text{electron} \qquad (7)$$

They are both related through the well-known dissociation equilibrium:

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \text{ (dissociation constant } K_{H_2O_2})$$

It is obvious from the above discussion that there is no fundamental difference between the homogeneous and heterogeneous reactions as far as the elementary processes are concerned (13). This is of interest in the discussion of the action of the enzymes.

Enzyme reaction

According to the investigations of Zeile and Hellström (19) and others, the enzyme catalase consists of an active hematin group—the iron being stabilized in the trivalent state—which is attached to a colloidal carrier.[1]

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[1] K. G. Stern (Nature 136, 302 (1935)), who investigated the prosthetic group of catalase, found that it possesses a porphin ring with the same structure as protohematin IX.

The catalytic decomposition of hydrogen peroxide by catalase is undoubtedly a heterogeneous reaction. It has already been emphasized by Bredig (2) that the best inorganic model for the catalase is to be found in colloidal platinum. The more recent investigations of the heterogeneous catalytic decomposition of hydrogen peroxide by colloidal platinum have strengthened this view.

Colloidal platinum, though a powerful catalyst for the decomposition of hydrogen peroxide, does not act as "peroxidase" in the oxidation of acceptor substances such as iodide ion and pyrogallol. The great sensitivity of colloidal platinum towards various substances such as iodine, hydrogen cyanide, and oxyphenols, which "poison" the surface, is well known from Bredig's experiments. Catalase is also easily poisoned by hydrogen cyanide, iodine, and pyrogallol (1, 18). Accordingly, we have good reason to believe that in both cases the active surfaces are poisoned by the acceptor itself or by the products of its oxidation, and it is not at all surprising therefore that catalase, as well as colloidal platinum, does not exhibit "peroxidase" properties.

In analogy to the action of colloidal platinum, the catalytic decomposition by catalase is to be regarded as a surface reaction involving the radicals OH and HO_2.[2]

In simple heterogeneous systems the chain length for the catalytic decomposition was found to be very small, of the order of about 5 (15). It is probable therefore that also in the enzymatic catalytic decomposition the chain reaction practically degenerates to a simple radical reaction. It should be emphasized that the presence of the radicals OH and HO_2, which also occur in the peroxidase mechanism, introduces no difficulty for the understanding of the specific action of the enzyme. On account of the very short chains, these radicals are present only in such a small concentration that their oxidizing action on acceptors (such as iodide ion or oxyphenols) is not detectable by ordinary analytical methods. On the other hand, as has been discussed above, these acceptors (or their oxidation product) will poison the catalase surface sufficiently quickly and suppress any appreciable oxidation reaction.

[2] G. M. Schwab, B. Rosenfeld, and L. Rudolph (Ber. 66, 661 (1933)), who compared the inhibiting action of various substances on the catalase reaction and on the photochemical decomposition, found that these substances were, with few exceptions, acting in the same way in both reactions. This, however, is not a conclusive proof of the "chain mechanism" of the catalase action. In the heterogeneous enzyme reaction the inhibition can take place not only through chain-breaking processes of the type

$$\text{inhibitor} + \text{radical} \rightarrow$$

as in the homogeneous (photochemical) reaction, but also through poisoning of the catalase surface itself; e.g., the strong inhibiting action of resorcinol for the catalase reaction lends strong support to this view.

It can also be shown that, on the assumption of short chains, the proportionality between reaction velocity and enzyme concentration and hydrogen peroxide concentration is retained. At very low radical concentration the bimolecular interaction of two radicals becomes less important compared with monomolecular reactions of the radicals, and therefore no square root of the enzyme concentration, as suggested by Haldane (7), will appear in the kinetics. The active part of the hematin group of the enzyme is the iron ion (denoted by $C_{Fe^{+++}}$ and $C_{Fe^{++}}$), which is alternatively reduced and oxidized by the hydrogen peroxide during the course of the reaction. The rôle of the iron ions in the porphin ring—such as in the respiration ferments and catalase—is to make possible a very quick electron transfer, i.e., the reversible change between the divalent and trivalent state.[3]

In analogy to the action of colloidal platinum (15) we may represent the action of the catalase by the following processes:

$$C_{Fe}{}^{+++} + HO_2^- \rightleftarrows C_{Fe}{}^{++} + HO_2 \tag{8}$$

$$C_{Fe}{}^{++} + H_2O_2 = C_{Fe}{}^{+++} + OH^- + OH \tag{9}$$

$$C_{Fe}{}^{++} + OH = C_{Fe}{}^{+++} + OH^- \tag{10}$$

whilst reactions 1 and 2 yield molecular oxygen.

In the stationary equilibrium resulting from the above system of reactions, the $C_{Fe^{+++}}$ state is predominant, as shown by experiment.

On the assumption that the rate of the enzyme reaction is not governed by diffusion phenomena on the interface (enzyme/solution) one can derive from the above reactions for the stationary state the following kinetic law (5): (H_2O_2) = total (analytical) hydrogen peroxide concentration:

$$-\frac{d(H_2O_2)}{dt} = 4kg[C_{Fe}{}^{++}](H_2O_2)\frac{[H^+]^2}{([H^+] + {}^aK_{H_2O_2})([H^+] - {}^aK_{HO_2})} \tag{I}$$

In this mechanism reaction 9 is the time-determining reaction and therefore proportionality between the rate of decomposition and the enzyme concentration and hydrogen peroxide concentration is obtained, in agreement with the experimental facts. From equation I it also follows that there is an optimum hydrogen-ion concentration for the rate of decom-

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[3] This is probably because the change of valency of the iron in the porphin ring system is taking place without appreciable movement of heavy particles and not as it could be in the case of ferrous and ferric ions, when the water dipoles in the hydration shell undergo a rearrangement when the charge of the central ion is changed. On the other hand, the system of conjugated double bonds around the iron in the hematin group permits—through their loosely bound *n*-electrons—a rapid "conduction" of the inner electron.

position by the enzyme, in agreement with experiment. This $[H^+]_{opt.}$ can be easily derived (5) from equation I by equating the first differential coefficient with respect to $[H^+]$ to zero, and is given by the expression:

$$[H^+]_{opt.} = \frac{2\,{}^aK_{H_2O_2}\,{}^aK_{HO_2}}{{}^aK_{H_2O_2} - {}^aK_{HO_2}} \qquad \text{(II)}$$

which depends only on the value of the electrolytic dissociation constants of $H_2O_2({}^aK_{H_2O_2})$ and $HO_2({}^aK_{HO_2})$ in the adsorbed phase on the surface of the enzyme, where the decomposition takes place. From this fact it is also conceivable that $[H^+]_{opt.}$ may be different for different colloidal carriers. The form of equation II is due to the fact that not only H_2O_2 and HO_2, but also their corresponding anions, play an important part in the reaction mechanism.[4]

THE ACTION OF PEROXIDASE

Model reactions

It will be shown in the following that the system hydrogen peroxide–iron salt–acceptor, under suitable conditions, represents all essential features of the peroxidase enzyme reaction. There are two types of reactions in this system, as considered in cases a and b.

Case a. The acceptor is only oxidized by the system hydrogen peroxide–ferrous salt and the oxidation of the acceptor practically stops when the ferrous salt is transformed into the ferric form. This is the case with acceptors such as formic acid, phosphoric acid, and arsenic acid. We are dealing here with short reaction chains which are initiated by the OH radicals formed in the ferrous-ferric transfer according to reaction 3. With HCOOH as acceptor the primary formation of the OH is probably followed by short chains of the type:

$$HCOOH + OH = COOH + H_2O$$

$$H_2O_2 + COOH = H_2O + CO_2 + OH$$

and by the chain-breaking

$$COOH + OH = H_2O + CO_2$$

From the above system of equations it may be easily shown that the mean consumption ratio, i.e., the number of moles of formic acid oxidized per mole of ferrous salt used up (which can be regarded as a direct measure of the mean chain length) is a function of the mean ratio of the concentra-

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[4] Secondary processes such as the destruction of the enzyme will not be dealt with here, as they have no particular bearing on our problem (see reference 18). It seems likely, however, that the radicals will exhibit a particularly strong destructive action on the protein part of the enzyme.

tions of the formic acid and ferrous salt. This is in agreement with the experiments of Wieland and Francke (17). It is obvious, however, that this sort of initiated oxidation has not much bearing on the reaction mechanism of the peroxidase action.

Case b. The acceptor is readily oxidized by ferric salt alone (but not by hydrogen peroxide alone). The action of the hydrogen peroxide may consist chiefly in the repeated (rapid) reoxidation of the ferrous salt to the ferric state. This is the case with acceptors such as hydroquinone and iodide ion in acid solution. These are the type of reactions which represent the peroxidase model. In particular we will deal here with the system hydrogen peroxide–iron salt–iodide ion, which has proved to be particularly illuminating.

TABLE 1

Reaction between hydrogen peroxide, ferrous sulfate, and potassium iodide in neutral solution

NO. OF EXPT.	CONCENTRATION $[H_2O_2] \times 10^3$	CONCENTRATION $[I^-] \times 10^3$	CONCENTRATION $[Fe^{++}] \times 10^3$	MEAN CONSUMPTION RATIO $r_M = \frac{\Delta I_2}{\Delta Fe^{++}}$
	moles per liter	*moles per liter*	*moles per liter*	
1	0.655	3.28	1.87	0.15
2	1.83	2.25	2.04	0.11
3	1.79	8.82	2.05	0.23
4	2.54	3.25	1.43	0.20
5	8.70	2.08	1.10	0.33
6	6.10	3.13	1.15	0.34
7	8.48	2.22	0.119	0.38
8	77.8	2.43	1.19	0.49
9	1.74	76.7	1.08	0.72
10	0.731	18.2	0.349	0.86
11	1.74	76.7	0.235	0.81
12	1.05	8.98	0.358	0.90
13	85.2	2.44	0.586	0.92
14	0.74	9.30	0.224	1.05
15	1.03	9.23	0.045	1.10
16	1.04	8.98	0.086	1.15

Similar to the catalytic decomposition of hydrogen peroxide by iron salts, we are dealing here with a rather rapid reaction. In order to obtain reproducible results precautions have to be taken to ensure rapid mixing of the reacting solutions so that the rate of mixing is large compared with the actual reaction velocity. The experiments described below have been carried out in the streaming apparatus originally proposed by Haber and Weiss (5). Into a turbulent stream of a mixture of hydrogen peroxide and potassium iodide a ferrous sulfate solution was injected through a narrow concentric jet, and the united solutions were collected in a suitable receiver and analyzed. In table 1 some of the experiments are summarized.

In all experiments the mean consumption ratio

$$r_m = \frac{\Delta I_2}{\Delta \mathrm{Fe}^{++}}$$

i.e., the number of moles of iodine liberated per mole of ferrous salt oxidized, has been measured. Manchot and coworkers (10, 11) have maintained that the value of r_m is 0.5 in neutral solution, and have proposed a theory based on a stoichiometric equation. The theory has already been criticized by Wieland and Francke (16) and particularly by Haber and Weiss (4).

From the experiments represented in table 1, it will be seen that a constant consumption ratio of 0.5, as postulated by Manchot, is not in agreement with experiment and that it would be impossible to explain the reaction by a stoichiometric equation.

TABLE 2

Reaction between hydrogen peroxide, ferrous sulfate, and potassium iodide in acid solution

NO. OF EXPT.	CONCENTRATION $[H_2O_2] \times 10^2$	CONCENTRATION $[I^-]$	CONCENTRATION $[Fe^{++}] \times 10^3$	CONCENTRATION $[H^+] \times 10^2$	MEAN CONSUMPTION RATIO $r_m = \frac{\Delta I_2}{\Delta Fe^{++}}$
	moles per liter	*moles per liter*	*moles per liter*	*moles per liter*	
1	2.25	1.00	4.00	2.4	6
2	2.40	2.00	4.00	2.0	6.8
3	4.00	1.00	4.00	4.4	9

The experimental results are very well represented by the following mechanism. The ferrous ions first react with hydrogen peroxide according to reaction 3, with the formation of OH radicals. These OH radicals will either oxidize the iodide ion present according to

$$I^- + OH = I + OH^- \qquad (11)$$

and the iodine atoms will then eventually recombine to give iodine molecules

$$2I = I_2 \qquad (12)$$

or the OH radicals will oxidize ferrous ions, according to

$$Fe^{++} + OH = Fe^{+++} + OH^- \qquad (13)$$

For mean consumption ratios up to 0.5, it would seem sufficient to consider only reactions 3, 11, 12, 13, because at sufficiently high iodide-ion concentration practically every OH radical formed will oxidize one I^-, and $\frac{1}{2}I_2$ will be produced for one Fe^{++} used up in the reaction.

The above considerations only hold in neutral solution, where the ferric salt formed during the reaction is precipitated by hydrolysis. In acid solutions, when the ferric ions remain in solution, they will be able to oxidize the iodide ions according to the (reversible) reaction:

$$Fe^{+++} + I^- \rightleftarrows Fe^{++} + I \tag{14}$$

No precipitation of the ferric salt will take place as long as there is enough acid present to neutralize the OH^- which is formed simultaneously with the oxidation of the ferrous ions and the iodide ions. Even for slightly acid solutions, therefore, considerably higher mean consumption ratios are obtained, as may be seen from table 2.

With an excess of acid and a sufficient amount of iodide ions, we obtain "complete catalysis", i.e., the reaction then goes on until the whole of the hydrogen peroxide has disappeared in the oxidation of the iodide ion. (The ferric ions being constantly reduced by the iodide ion, are reoxidized as long as hydrogen peroxide is still present.) There is then in principle no difference whether the reaction is started with the ferrous salt or with the ferric salt (3).

ENZYME REACTION

According to the investigations of Kuhn, Hand, and Florkin (9) the enzyme peroxidase, similar to catalase, consists of an active hematin group and a colloidal carrier.

If we consider the typical action of peroxidase in the oxidation of iodide ion in the presence of hydrogen peroxide, it follows from the above that the system iron salt-hydrogen peroxide-iodide ion in acid solution offers a complete analogy to the peroxidase system even to the extent of explaining the specific action of the enzyme. A ferric salt, being a very good catalyst for the oxidation of iodide ion by hydrogen peroxide, is a very poor catalyst for the catalytic decomposition of hydrogen peroxide into molecular oxygen.[5] From the above discussions this difference can be easily explained. In the "catalase activity," the ferric ions are primarily reduced by the anions of the hydrogen peroxide (HO_2^-), whereas in the peroxidase reaction they are reduced by the acceptor substances (iodide ion, oxyphenols). In the first case the reduction is very slow, but in the second the reaction may often be very fast. We then have the

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[5] This has also been emphasized by A. Wassermann (J. Chem. Soc. **1935**, 826).

following picture for the action of the enzyme peroxidase (denoted by $P_{Fe^{+++}}$ and $P_{Fe^{++}}$).

$$P_{Fe^{+++}} + \text{acceptor} \rightarrow P_{Fe^{++}} + \text{oxidized acceptor} \qquad (15)$$

$$P_{Fe^{++}} + H_2O_2 \rightarrow P_{Fe^{+++}} + OH^- + \dot{O}H \qquad (16)$$

The OH radicals formed in process 16 may either oxidize the acceptor in a manner similar to reaction 11, or they may help in the reoxidation. Generally the acceptor is oxidized by the ferric form of the enzyme, which itself is then rapidly reoxidized by hydrogen peroxide or the radicals.

Peroxidase, like catalase, is capable of a rapid reversible change (electron transfer) between the ferrous and ferric state. The essential difference from catalase is that the ferric form of catalase is relatively rapidly reduced by the hydrogen peroxide anion, HO_2^-, whereas peroxidase needs the stronger reducing acceptor substances for the same purpose.

The reason that peroxidase does not exhibit catalase properties is explained therefore by the difference between the starting process of peroxidase (reaction 5) and that of catalase (reaction 8). The objection may still be made that the peroxidase mechanism suggested here involves the radicals OH and HO_2 which, according to reactions 1 and 2, could give rise to the catalytic decomposition with the liberation of oxygen. A closer discussion, however, shows that the presence of the acceptor substance might very well prevent the radicals from producing molecular oxygen. The catalytic decomposition of hydrogen peroxide would only be expected if the reaction:

$$H_2O_2 + \text{radical} \rightarrow \qquad (17)$$

is faster than the reaction:

$$\text{Acceptor} + \text{radical} \rightarrow \qquad (18)$$

under the conditions in question. Even if the velocity of these two reactions were of the same order, no appreciable decomposition is to be expected, because in the peroxidase reaction the ratio of the concentration $[H_2O_2]/[\text{acceptor}]$ must be kept rather small[6] to allow the peroxidase to act (16.) Reaction 18 will practically always be predominant compared with process 17, and the peroxidase will not be able to exhibit any catalase properties.

The different specific actions of peroxidase and catalase can be easily understood, therefore, on the basis of a radical mechanism involving short chains.

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[6] This ratio of the concentration $[H_2O_2]/[\text{acceptor}]$ might even be shifted to more extreme values on the surface of the enzyme (where the reaction is actually taking place), on account of the difference in the adsorbability of the two substances.

SUMMARY

1. It has been shown that some of the reactions of hydrogen peroxide, in simple systems, can serve as excellent models for the action of the enzymes catalase and peroxidase.

2. The action of colloidal platinum in the catalytic decomposition, which was studied previously, has been discussed with respect to the action of catalase.

3. The system iron salt-hydrogen peroxide-acceptor (the acceptor being particularly iodide ion) has been studied in detail and discussed with respect to the action of peroxidase.

4. The specific action of the enzymes as well as the kinetics of the enzyme reactions can be easily understood on the basis of a mechanism involving short chains with the radicals OH and HO_2.

I wish to express my sincerest thanks to Professor F. G. Donnan, F.R.S., for his interest in this work.

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ON THE THEORETICAL CALCULATION OF THE NORMAL POTENTIAL OF THE NON-METAL

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In the previous paper (1) the normal potential of the metal was calculated by means of thermodynamical cycles. That of the non-metal can be treated in an analogous way.

THE NORMAL POTENTIAL (E_0) OF HALOGEN (X)

The sum of the work done in the following reversible thermodynamical cycle is zero.

(1) One mole of ionic vapor (pressure p^-) is taken out from an equilibrium box containing the platinum electrode and the gaseous phase.

$$\text{Work done} = +RT$$

(2) The pressure of X^- is altered from p^- to c'/k^-, where c' is the concentration of X^- in the solution and k^- is the Henry constant of X^- for this solvent.

$$\text{Work done} = RT \ln \frac{p^-}{c'/k^-}$$

(3) The ionic vapor is dissolved in the solution.

$$\text{Work done} = -RT - F\phi_f$$

$F\phi_f$ = the electrical work needed when one mole of X^- passes through the surface of the solution.

(4) 1/2 mole of X_2 is liberated electrolytically from the solution.

$$\text{Work done} = -E_0F + RT \ln c'$$

(5) One mole of electron is evaporated from the platinum electrode at the expense of the electrical work of $F\phi_e$, and is combined with 1/2 mole of X_2 to form X^- in the equilibrium box.

$$\text{Work done} = -F\phi_e$$

$$\therefore\ +RT + RT \ln \frac{p^-}{c'/k^-} - RT - F\phi_f - E_0F + RT \ln c' - F\phi_e = 0$$

$$\therefore\ E_0 = -(\phi_f + \phi_e) + \frac{RT}{F}(\ln p^- + \ln k^-) \tag{1}$$

As for the equilibrium:

$$1/2X_2 + \text{e (electron)} \rightleftharpoons X^-$$

(the pressure being p_2 p_e p^-)

$$\ln p^- = \tfrac{1}{2} \ln p_2 + \ln p_e + \frac{q_0}{RT} - \int_0^T \frac{\int_0^T c_{2g}\,dT}{2RT^2}\,dT + i^- - \frac{i_2}{2} - i_e$$

The vapor pressure of the electron from platinum is expressed by

$$\ln p_e = -\frac{F\phi_e}{RT} + \frac{5}{2}\ln T + i_e$$

if the independence of ϕ_e on temperature is assumed, where q_0 = the heat of formation of X^- from gaseous halogen at 0°K., c_{2g} = the molecular heat of gaseous X_2 under constant pressure, and i_2, i_e = (the chemical constant of X_2 and electron respectively) × ln 10.

If we calculate as in the previous paper for a difficultly soluble, strong electrolyte MX_x, we have:

$$\ln k^- = \ln x + \frac{1+x}{x}\ln C + \frac{Q}{xRT} + \int_0^T \frac{c_c\,dT}{xRT} - \frac{\int_0^T c_{2g}\,dT}{2RT} - \frac{\int_0^T c_M\,dT}{xRT}$$
$$- \frac{q_0}{RT} - \frac{5}{2}\cdot\frac{(1+x)}{x}\ln T - \frac{i^+ + xi^-}{x} + \frac{(S_0 + \Sigma I_0)}{xRT} - \frac{1}{x}\ln k^+$$

where Q = the heat of formation of MX_x from the metal and the gaseous halogen at $T°$, C = the solubility of MX_x, c_c = the molecular heat of MX_x, and $S_0 + \Sigma I_0$ = the heat of formation of gaseous metallic ion at 0°K. Introducing these relations in equation 1, we have:

$$\begin{aligned} E_0 = -(2\phi_e + \phi_f) &+ \frac{RT}{xF}\left\{x \ln x + (1+x)\ln C + \frac{Q}{RT} + \int_0^T \frac{c_c}{RT}\,dT\right\} \\ &+ \frac{RT}{2F}\left\{\ln p_2 - i_2 - \int_0^T \frac{c_{2g}}{RT}\,dT\right\} \\ &+ \frac{RT}{xF}\left\{\frac{S_0 + \Sigma I_0}{RT} - \frac{\int_0^T c_M\,dT}{RT} - \ln k^+ - \frac{5}{2}\ln T - i^+\right\} \end{aligned} \tag{2}$$

As ϕ_f is equal to that of the pure solvent in the case of a dilute enough solution, and ϕ_e is a constant of platinum,

$$E_0 = \frac{RT}{xF}\left\{x \ln x + (1 + x) \ln C + \frac{Q}{RT} + \int_0^T \frac{c_e}{RT}\, dT\right\} + \frac{RT}{2F}(\ln p_2 - i_2)$$

$$- \frac{RT}{2F}\int_0^T \frac{c_{2g}}{RT}\, dT + (\text{constant depending on cation and solvent}) \qquad (3)$$

or, written in a simpler form:

$$E_0 = B + h - \frac{RT}{2F}\int_0^T \frac{c_{2g}}{RT}\, dT + \text{constant} \qquad (3')$$

THE NORMAL POTENTIAL OF ELECTRODE $1/2\, O_2 + H_2O \mid 2OH^-$

In a similar way as in the case of halogen, the following expression is obtained:

$$E_0 = -(\phi_f + \phi_e) + \frac{RT}{F}(\ln p^- + \ln k^-)$$

p^-, k^- being the values for OH^-. p^- is calculated from the equilibrium,

$$1/2\, O_2 + H_2O + 2e \rightleftharpoons 2OH^-$$

and k^- is calculated by means of the cycle for $M(OH)_x$: hence

$$E_0 = \frac{RT}{xF}\left\{x \ln x + (1 + x) \ln C + \frac{Q}{RT} + \int_0^T \frac{c_c}{RT}\, dT\right\}$$

$$+ \frac{RT}{4F}\left\{\ln p_2 - i_2 - \int_0^T \frac{c_{2g}}{RT}\, dT\right\} + \frac{RT}{2F}\left\{\ln p_{H_2O} - i_{H_2O}\int_0^T \frac{c_{H_2O\cdot g}}{RT}\, dT\right\}$$

$$+ (\text{constant depending on cation and solvent}) \qquad (4)$$

or, written in a simpler form:

$$E_0 = B + h - \frac{RT}{4F}\left\{\int_c^T \frac{c_{2g}}{RT}\, dT + 2\int_0^T \frac{c_{H_2O\cdot g}}{RT}\, dT\right\} + (\text{constant}) \qquad (4')$$

where c_{2g} = the molecular heat of O_2 under constant pressure, $c_{H_2O\cdot g}$ = that of water vapor, and Q = the heat of formation of $M(OH)_x$ from the metal, O_2, and water vapor.

CALCULATED VALUES AT 25°C.

Q was calculated by putting the heat of evaporation of bromine equal to 7.3 kg-cal., the heat of sublimation of iodine equal to 15.8 kg-cal. (according to Eucken), and the heat of evaporation of water equal to 10.4 kg-cal.

	$\int_0^{298} \frac{c_e}{RT}\,\mathrm{d}T$	c_e	B
		cal. per degree	*volts*
PbF_2	(15)*	17.7	3.36
$PbCl_2$	17.1	18.3	1.97
$PbBr_2$	(21)	19.6	1.75
PbI_2	21.1	19.7	1.29
AgCl	11.5	12.5	1.05
AgBr	(14)	13.9	0.82
AgI	13.4	13.0	0.37
CaF_2	8.2		6.05
$Ca(OH)_2$	9.5		3.69

* Values in brackets are assumed comparing the values of c_e.

	p_2	CHEMICAL CONSTANT	h	
	mm.		*volts*	
F_2	760 − 24	+0.29	−0.01	
Cl_2	760 − 24	+1.45	−0.04	
Br_2	213	+2.49	−0.09	
I_2	0.32	+2.992	−0.19	
O_2	760 − 24	+0.531	−0.01	sum = 0.00
H_2O	24	−1.937	+0.01	

The value of $\int_0^T \frac{c_{2g}}{RT}\,\mathrm{d}T$ is unknown. The molecular heats of gases under constant pressure are as follows:

	F_2	Cl_2	Br_2	I_2	$1/2\,O_2 + H_2O$
		8.80	8.86	8.62	3.58 + 8.37
Temperature		13° ~ 202°	83° ~ 228°	206° ~ 377°	100° ~ 200°

If $c_{2g} = 7/2\,R$, $\frac{RT}{2F}\int_0^T \frac{c_{2g}}{RT}\,\mathrm{d}T = 0.26$ volt at 25°C.

The relative value of E_0 was calculated by the formula

$$E_0 = B + h + \text{constant}$$

neglecting the difference between the specific heat terms.

The relative values of the normal potential are as follows:

	F – Cl	Br – Cl	I – Cl	F – O
Pb	1.42	–0.27	–0.83	
Ag		–0.28	–0.83	
Ca				2.35

If it is assumed that E_0 of Cl = + 1.36 volts, we obtain the following values for E_0:

	F	Cl	Br	I	O
E_0 calculated	+2.78	+1.36	+1.08 ∼ 9	+0.53	+0.43
Landolt tables	2.85	1.36	1.07	0.58	0.41
International Critical Tables		1.358_3	1.064_8	0.534_5	
Other literature	2.8		1.08		

A term depending on platinum ($-2\phi_e$) is seen in the formula expressing E_0. But we measure E_0 by constructing a cell one electrode of which is platinum with hydrogen bubbling through it, and it is easily shown that the term ($-2\phi_e$) appears in the E_0 formula of the hydrogen electrode nearly in the same way as in the halogen electrode, and accordingly this term vanishes in the end.

SUMMARY

The relative values of the normal potentials of non-metals are calculated by means of the thermodynamical cycle between non-metals and their ionic solutions.

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THE COMPLEX FORMATION OF FERRIC IONS WITH CHLORIDE IONS

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I. INTRODUCTION

The redox potential ferric-ferrous ion has been investigated by Peters (7), Fredenhagen (2), Maitland (5), Noyes and Brann (6), and Popoff and Kunz (8). In nitrate solutions Maitland (5) has found the value 0.464 volt for the standard potential measured against the 1 N potassium chloride-calomel electrode. By adding 0.2831 volt (Bjerrum and Unmack (1)) the potential against the one-normal activity hydrogen electrode is obtained. Maitland's value of the standard potential thus is E_0 = 0.7471 volt. For the same quantity Noyes and Brann have found the value E_0 = 0.7467 volt, while Popoff and Kunz have found E_0 = 0.7477, a value which they consider correct within 1 millivolt.

The values obtained by these authors are thus in fair agreement, and the following investigation has been made not in order to reëstimate the standard potential, but to analyze the complex formation of ferric ions with chloride ions, a problem which was of considerable interest in connection with other work.

II. THE REDOX POTENTIAL FERRIC-FERROUS ION IN SOLUTIONS CONTAINING HYDROCHLORIC ACID AND VARIOUS QUANTITIES OF POTASSIUM CHLORIDE

The concentration of the ferric chloride solution applied in these experiments has been estimated by reduction to ferrous salt and titration with permanganate in the presence of manganous sulfate and phosphoric acid. Hydrogen sulfide was used as the reducing agent and the excess of this was boiled out in a current of carbon dioxide.

The solutions of ferrous chloride used in the experiments were made by reduction in the same manner from the ferric chloride solution immediately before the experiment and added to a solution of ferric chloride, hydrochloric acid, and a weighed quantity of potassium chloride in a measuring flask placed on the bottom of a deep basin filled with carbon dioxide from a tank. The mixed solution was then transferred to the carbon dioxide-filled electrode vessel (of the ordinary Ostwald type) by means of carbon dioxide gas pressure.

The electrodes of bright platinum were measured against the 3.500 *N* potassium chloride–calomel electrode with a liquid junction of 3.500 *N* potassium chloride.

The calomel electrode vessels were of the Lewis, Brighton, and Sebastian type (4). The voltage of the 3.500 *N* potassium chloride–calomel electrode was measured at 25°C. against the hydrogen electrode in a solution containing 0.01 *N* hydrochloric acid and 0.09 *N* potassium chloride. A consistent value of 0.3725 volt has been obtained with different chemicals and electrodes. When corrected for the liquid junction potential (−0.0011 volt), as calculated by means of the Henderson formula (Bjerrum and Unmack (1)), this gives a corrected voltage of 0.3714 volt.

From this the voltage of the 3.500 *N* potassium chloride–calomel electrode against the one-normal activity hydrogen electrode may be calculated as 0.2496 volt at 25°C. This value is 0.5 millivolt lower than the value adopted by Bjerrum and Unmack (1), but, as it has been found consistently, it will be used in the following.

The results of measuring the cell:

Pt	Fe^{+++} x molar Fe^{++} x molar KCl y normal HCl z normal	3.500 *N* KCl	3.500 *N* KCl HgCl	Hg

at 25°C. are given in tables 1 and 2.

The measured value of the voltage p_m is the average of four or more electrodes measured at different times against three calomel electrodes. The deviation of the individual values from the average never exceeded 0.3 millivolt.

In the tables l is the liquid junction potential calculated by means of the Henderson formula (1), p is the potential corrected for the liquid junction potential, and E is the potential of the ferric–ferrous ion electrode against the one-normal activity hydrogen electrode, obtained by adding 0.2496 volt to the value of p.

In the calculation of the liquid junction potential the ionic mobilities at 18°C. as given by Kohlrausch (3) have been applied.

The values of E in tables 1 and 2 have been plotted against the chloride-ion concentration and by a graphic extrapolation the values of E at zero chloride-ion concentration (as given in the tables) have been obtained. From these values of E in solutions with a total iron salt concentration of 0.004 molar and 0.002 molar, respectively, the standard potential E_0 = 0.747(5) volt (i.e., the potential when the iron salt concentration is infinitely small) has been obtained by a linear extrapolation. Although the method applied for the estimation is not as accurate as the method of Popoff and Kunz, this value is in agreement with the one found by these authors. The reason why the redox potential in a solution containing ferric and ferrous salts decreases with increasing concentration of chloride ions (HCl + KCl) may be due partly to the fact that the activity of the trivalent ferric ion decreases more than the activity of the divalent ferrous ion and partly to a complex formation of ferric ions with chloride ions. It is a well-known fact that a solution of ferric nitrate acidified with nitric acid is almost colorless, while a solution of ferric chloride acidified with hydrochloric acid is intensely yellow. The ferric nitrate solution probably contains the ion $[Fe(H_2O)_6]^{+++}$, while the chloride solution may contain the ion $[Fe(H_2O)_5Cl]^{++}$, or the ion $[Fe(H_2O)\ Cl_2]^{+}$, or both. If it is the

TABLE 1

Results of cell measurements

2.000 millimoles $FeCl_3$ + 2.000 millimoles $FeCl_2$ + 0.1027 mole HCl per liter.
$t = 25°C$.

TOTAL Cl^- CONCENTRATION IN MOLES PER LITER	p_m	l	p	E
0.000				0.7455 (extrapolated)
0.1127	0.4811	0.0055	0.4866	0.7362
0.2127	0.4743	0.0049	0.4792	0.7288
0.3127	0.4697	0.0045	0.4742	0.7238
0.4127	0.4668	0.0042	0.4710	0.7206
0.6127	0.4619	0.0037	0.4656	0.7152
1.1127	0.4549	0.0030	0.4579	0.7075
3.0127	0.4407	0.0012	0.4419	0.6915

TABLE 2

Results of cell measurements

1.000 millimole $FeCl_3$ + 1.000 millimole $FeCl_2$ + 0.1013 mole HCl per liter.
$t = 25°C$.

TOTAL Cl^- CONCENTRATION IN MOLES PER LITER	p_m	l	p	E
0.000				0.7465 (extrapolated)
0.1063	0.4816	0.0055	0.4871	0.7367
0.2063	0.4748	0.0049	0.4797	0.7293
0.3063	0.4700	0.0045	0.4745	0.7241
0.4063	0.4670	0.0042	0.4712	0.7208
0.6063	0.4620	0.0037	0.4657	0.7153
1.1063	0.4550	0.0030	0.4580	0.7076
3.0063	0.4407	0.0012	0.4419	0.6915

first one of these ions which is formed from ferric ions and chloride ions the equilibrium constant is given by the equation:

$$\frac{[[Fe(H_2O)_5Cl]^{++}]\cdot f_i}{[Cl^-]\cdot f_c\cdot [[Fe(H_2O)_6]^{+++}]\cdot f_i} = C \qquad (1)$$

where the f's are the activity coefficients of the ions in question. To be able to calculate the value of C it is necessary to know the ionic concentrations and the activity coefficients.

From the equation

$$E = E_0 + \frac{RT}{F}\ln\frac{[[Fe(H_2O)_6]^{+++}]\cdot f_i}{[Fe^{++}]\cdot f_0} \qquad (2)$$

it is possible to calculate the concentration of the ion $[Fe(H_2O)_6]^{+++}$ when the activity coefficients (f_i and f_0) are known and when it is assumed that the concentration of the ferrous ion is not changed by the addition of chloride ions, i.e., that ferrous ions do not form complex ions with chloride ions.

From freezing-point data available in the literature Randall and Frandsen (9) have calculated the activity coefficient in solutions of ferrous chloride. When the values of $-\log f_0$ are plotted against the square root of the ionic strength it is possible to interpolate to the values of $-\log f_0$ of the ferrous ion for such solutions as have the same ionic strength as the solutions in tables 1 and 2. The results of these interpolations are given in table 3, where μ is the ionic strength. The values are correct only at 0°C., but may be applied at 25°C. without any serious error. The apparent activity coefficient of ferric chloride has been calculated from freezing-point data (see, for instance, Landolt-Börnstein's Physikalisch-Chemische Tabellen). These data, however, have not been corrected for autocomplex formation or hydrolysis, and it is better to apply, therefore, as an approximation, the activity coefficient of other tri-univalent electrolytes.

From Landolt-Börnstein's tables the average values of the activity coefficients of aluminum chlorate and lanthanum nitrate have been calculated. The values of $-\log f_i$, where f_i is the activity coefficient, have been plotted against the square root of the ionic strength and by interpolation the values in table 3 have been obtained.

Taylor (10) has given the average values of the activity coefficient of potassium chloride. From these values in the same manner as above the values of $-\log f_c$ in table 3 have been obtained.

The concentration of the $[Fe(H_2O)_6]^{+++}$ ion in the solutions may now be calculated by applying equation 2. When the concentration of this ion is subtracted from the total ferric salt concentration the concentration of the ion $[Fe(H_2O)_5Cl]^{++}$ may be obtained. These values are given in tables 4 and 5.

TABLE 3

The activity coefficient of ferrous chloride, f_0, of a tri-univalent electrolyte, f_t, and of a uni-univalent electrolyte, f_e

$\sqrt{\mu}$	$-\log f_0$	$-\log f_t$	$-\log f_e$
0.344	0.196	0.337	0.125
0.470	0.224	0.403	0.152
0.566	0.238	0.440	0.169
0.647	0.246	0.470	0.183
0.788	0.252	0.513	0.201
1.059	0.246	0.565	0.229
1.738	0.272	0.583	0.244

TABLE 4

2.000 millimoles $FeCl_3$ + 2.000 millimoles $FeCl_2$ + 0.1027 mole HCl per liter. Various concentrations of KCl

TOTAL Cl^- CONCENTRATION	$Fe(H_2O)_6^{+++}$	$Fe(H_2O)_5Cl^{++}$	C
0.1127	0.00178	0.00022	(2.01)
0.2127	0.00146	0.00054	3.74
0.3127	0.00126	0.00074	4.38
0.4127	0.00118	0.00082	4.37
0.6127	0.00104	0.00096	4.40
1.1127	0.00088	0.00112	4.05
3.0127	0.00058	0.00142	(3.68)
Mean			4.2

TABLE 5

1.000 millimole $FeCl_3$ + 1.000 millimole $FeCl_2$ + 0.1013 mole HCl per liter. Various concentrations of KCl

TOTAL Cl^- CONCENTRATION	$Fe(H_2O)_6^{+++}$	$Fe(H_2O)_5Cl^{++}$	C
0.1063	0.0009097	0.000090	(1.72)
0.2063	0.000743	0.000257	3.58
0.3063	0.000640	0.000360	4.32
0.4063	0.000599	0.000401	4.21
0.6063	0.000520	0.000480	4.41
1.1063	0.000440	0.000560	4.06
3.0063	0.000291	0.000709	(3.67)
Mean			4.0
General mean			4.1

All the quantities necessary for the calculation of C are now known with the exception of f_i', the activity coefficient of the divalent complex ion $[Fe(H_2O)_5Cl]^{++}$. We have no means, however, to estimate this, but it may be replaced, without any serious error, by the activity coefficient of the divalent ferrous ion f_0, as given in table 3.

The values of C in tables 4 and 5 have been calculated, therefore, from the equation:

$$\frac{[[Fe(H_2O)_5Cl]^{++}]\cdot f_0}{[Cl^-]\cdot f_o\cdot[[Fe(H_2O)_6]^{+++}]\cdot f_t} = C$$

The values of C, as may be observed from tables 4 and 5, are fairly constant when such solutions are excepted as have a low and a high chloride-ion concentration. In the first case, when the chloride-ion concentration is low (the solutions contain no potassium chloride, but hydrochloric acid only), the complex formation is small and a slight error in the estimation of the potential may affect the value of C considerably. In the other case, when the solutions have a high ionic concentration, the individual properties of the ions are so pronounced that it is not permissible to apply the average value of the activity coefficient of a trivalent ion to the ferric ion, or the value of the activity coefficient of the ferrous ion to the ferric monochloride complex ion. Leaving out these problematic values, the general mean of the complex constant is $C = 4.1$, and the affinity in the complex formation is $A = RT \ln C = 834$ cal.

SUMMARY

The standard potential $Fe^{+++} + e \rightleftarrows Fe^{++}$ has been estimated and a value of 0.747(5) volt at 25°C. has been obtained. This value is in agreement with the measurements of Maitland and of Popoff and Kunz.

The complex formation of ferric ions with chloride ions has been investigated and the value of the complex constant

$$C = \frac{[(Fe(H_2O)_5Cl)^{++}]}{[(Fe(H_2O)_6)^{+++}]\cdot[Cl^-]} = 4.1$$

(here the square brackets indicate activities) has been estimated.

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THE VISCOSITIES OF SOLUTIONS OF CHLORIDES IN CERTAIN SOLVENTS[1]

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Recent theoretical studies have aroused new interest in the study of the viscosity of aqueous solutions. The measurements reported in this paper were made during a study of the physical properties of certain solutions that were, in the main, of non-aqueous character. As concerns viscosity the intention was primarily to test equations developed by Jones and his students (4, 5) by attempting to apply them to the viscosities of non-aqueous solutions.

MATERIALS

Absolute ethyl alcohol was prepared by repeated treatment with finely divided, freshly dehydrated calcium oxide. Aldehydes and other impurities were removed by the usual methods, and the product was thoroughly fractionated. Precautions were taken to exclude air and moisture at all times. The purity of the product was checked by measurements of the refractive index and the density. Only freshly prepared alcohol was used in making up the solutions. Carefully prepared conductivity water was used in making up aqueous solutions or solutions in mixed solvents containing water. Carbon tetrachloride was purified by the method of McClendon (7). Pure, anhydrous acetic acid and ethyl acetate were further treated to remove water and fractionally distilled.

Stannic chloride was prepared by distillation from a mixture of the hydrate and concentrated sulfuric acid, and precautions were taken to prevent the decomposition of the acid. The anhydrous, liquid stannic chloride was collected in small tubes, which were sealed without allowing the contents to be exposed to the atmosphere. The purity of the product was checked by density measurements. Ferric chloride was prepared by treating thoroughly cleaned and dried pure iron with chlorine. All other salts

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[1] This paper has been prepared from a portion of a thesis submitted by Frank E. Dolian to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. To save space in printing, representative graphical relationships, rather than complete plots of all data, have frequently been given.

were prepared by thoroughly purifying and carefully dehydrating the purest products obtainable.

METHOD

The viscosities of the solutions were measured in a modified form of the Ostwald type of viscometer. Precautions were taken to prevent changes in concentration by evaporation of volatile solvents and contamination with moisture from the air. The measurements were made at 25°C. ± 0.05°, and were checked by several determinations for each solution. The viscometers were cleaned and dried with absolute alcohol and pure dry air. They were standardized with pure water. The time of flow was measured with a stop watch, which was accurate in readings to 0.1 sec. The density measurements were made in pycnometers of approximately 25-ml. capacity in a constant temperature bath at 25°C. and calculated with reference to pure, carbon dioxide-free water at 4°C. Table 1 serves to give information concerning the viscometers, including total time of passage of liquid, volumes of liquids used, etc.

TABLE 1

Standardization of viscometers

VISCOMETER NO.	VOLUME OF LIQUID	TIME OF PASSAGE (WATER)	ρT (DENSITY × TIME)
	ml.	*seconds*	
1	6	91.95	91.6782
2	8	85.14	84.8883
3	6	73.48	73.2682
4	6	76.46	76.2340

In view of likely percentages of error in the measurements and in temperature control, the viscosity values have been rounded off to four figures.

RESULTS AND DISCUSSION

The densities and relative viscosities (with reference to the viscosity of water as 0.00894 poise at 25°C.) of solutions of nickel chloride, cobalt chloride, cupric chloride, ferric chloride, cadmium chloride, aluminum chloride, stannic chloride, and mercuric chloride in ethyl alcohol as the solvent are shown in table 2. The viscosities of six of these solutions are plotted against the weight fractions of the solutes in figure 1. The results show that these salts increase the viscosity of ethyl alcohol in the following order: $NiCl_2 > AlCl_3 > CoCl_2 > CuCl_2 > FeCl_3 > CdCl_2 > SnCl_4 > HgCl_2$. The results for solutions of aluminum chloride, nickel chloride, cupric chloride, and cadmium chloride in water are shown in table 3. The salts increase the viscosity of water in the following order: $AlCl_3 > NiCl_2 > CuCl_2 > CdCl_2$. Except for the anomalous behavior of aluminum chloride, the order in which the salts affect the viscosity of each solvent is the same as the order of their molecular weights. The relative effect of aluminum chloride upon the viscosity of ethyl alcohol is greater than one might predict from a consideration of molecular weights alone, and in water the effect is still further pronounced. This behavior may be the result of the reaction of aluminum chloride with the solvents to form large numbers of ions in the solutions. This explanation would be in keeping with McLeod's (8) principle that the formation of ions leads to a decrease in the free space and to an increase in the viscosity. That the effect is

TABLE 2

Viscosities of solutions of salts in ethyl alcohol

$HgCl_2$			$AlCl_3$			$FeCl_3$		
Weight fraction	Density 25°/4°C.	η	Weight fraction	Density 25°/4°C.	η	Weight fraction	Density 25°/4°C.	η
0.00000	0.78530	0.0107	0.00000	0.78530	0.0108	0.00000	0.78545	0.0107
0.01008	0.79281		0.00389	0.78860	0.0112	0.00424	0.78795	0.0108
0.01996	0.80056	0.0110	0.00757	0.79161	0.0114	0.00845	0.79083	0.0111
0.04164	0.81524	0.0111	0.01501	0.79798	0.0126	0.01679	0.79583	0.0115
0.08035	0.84515		0.02955	0.81075	0.0144	0.03313	0.80648	0.0121
0.15020	0.90406	0.0122	0.05734	0.83563	0.0193	0.06454	0.82808	0.0137

$SnCl_4$			$CoCl_2$			$NiCl_2$		
Weight fraction	Density 25°/4°C.	η	Weight fraction	Density 25°/4°C.	η	Weight fraction	Density 25°/4°C.	η
0.00000	0.78545	0.0107	0.00000	0.78523	0.0108	0.00000	0.78533	0.0110
0.00550	0.78913	0.0109	0.00515	0.78888	0.0111	0.00192	0.78849	0.0112
0.01095	0.79243	0.0110	0.01024	0.79276	0.0113	0.00382	0.79145	0.0114
0.02172	0.79890	0.0113	0.02030	0.79994	0.0119	0.00757	0.79811	0.0120
0.04266	0.81356	0.0119	0.03986	0.81462	0.0132	0.01492	0.81012	0.0134
0.08242	0.84217	0.0132	0.07719	0.84139	0.0162			

$CdCl_2$			$CuCl_2$		
Weight fraction	Density 25°/4°C.	η	Weight fraction	Density 25°/4°C.	η
0.00000	0.78641	0.0109	0.00000	0.78572	0.0108
0.00393	0.78920	0.0111	0.00526	0.78935	
0.00784	0.79173	0.0111	0.01050	0.79173	0.0112
0.01557	0.79739	0.0115	0.02028	0.80058	0.0117
0.03072	0.80832	0.0119	0.04134	0.81375	
			0.07957	0.84549	0.0144

caused by ions appears to be substantiated, at least in part, by a comparison of the results in alcoholic and aqueous solutions. If the change in viscosity, or the viscosity increment, $\Delta\eta$, is plotted against the weight fraction of the same solute in different solvents, the curves are found to rise more steeply in every case for the solutions in ethyl alcohol than they do for the aqueous solutions. This might be predicted from the interionic attraction theory. The "tightening" effect and consequent increase in viscosity should probably be less in water than in alcohol, because of the great difference in the dielectric constants of the two liquids. The viscosity increment-weight fraction curves for solutions of several salts in methyl alcohol were found (in work not reported here) to lie in all cases between the curves for ethyl alcohol and water.

TABLE 3

Viscosities of aqueous solutions of certain salts

$AlCl_3$			$CdCl_2$		
Weight fraction	Density 25°/4°C.	η	Weight fraction	Density 25°/4°C.	η
0.00000	0.99704	0.0089	0.00000	0.99704	0.0089
0.00230	0.99949	0.0091	0.00190	0.99879	0.0090
0.00470	1.00157	0.0092	0.00378	1.00047	0.0090
0.00930	1.00585	0.0095	0.00760	1.00284	0.0091
0.01840	1.01536	0.0101	0.01500	1.01055	0.0092
0.03610	1.03297	0.0113	0.02960	1.02306	0.0095

$CuCl_2$			$NiCl_2$		
Weight fraction	Density 25°/4°C.	η	Weight fraction	Density 25°/4°C.	η
0.00000	0.99704	0.0089	0.00000	0.99704	0.0089
0.00420	1.00097	0.0091	0.00290	0.99991	0.0091
0.00830	1.00479	0.0092	0.00570	1.00270	0.0092
0.01650	1.01161	0.0094	0.01140	1.00748	0.0093
0.03250	1.02726	0.0098	0.02250	1.01848	0.0097
0.06350	1.05645	0.0108	0.04410	1.03974	0.0103

The effect of a solute upon the viscosity of a solvent has also been explained frequently as the result of the action of particles of the dissolved substance upon the association of solvent molecules. In an effort to determine the effect of a change of solvent upon the viscosity of a solution of aluminum chloride, the viscosities of solutions in different mixtures of ethyl alcohol and water were investigated. These two solvents were selected because the viscosity-mole fraction curve for these two liquids shows a very decided maximum. This maximum has long been recognized and is generally attributed to "further association and eventually complex formation" by the two liquids. This is in accordance with the theory of Dunstan and Thole (2), although it is sometimes stated that such maxima are caused by dissociation of "associated complexes" or of molecules. The viscosities of solutions of aluminum chloride in different mixtures of ethyl alcohol and water are given in table 4 and shown graphically in figure 2. If the theory of Dunstan and Thole is correct, it appears that the addition of aluminum chloride to a mixture of ethyl alcohol and water leads to an increase in the association of the two liquids, since the solute increases the viscosity of the mixture corresponding to the maximum more than it does any other mixture of the two solvents. It is difficult to explain these results purely upon the basis of ionic effects.

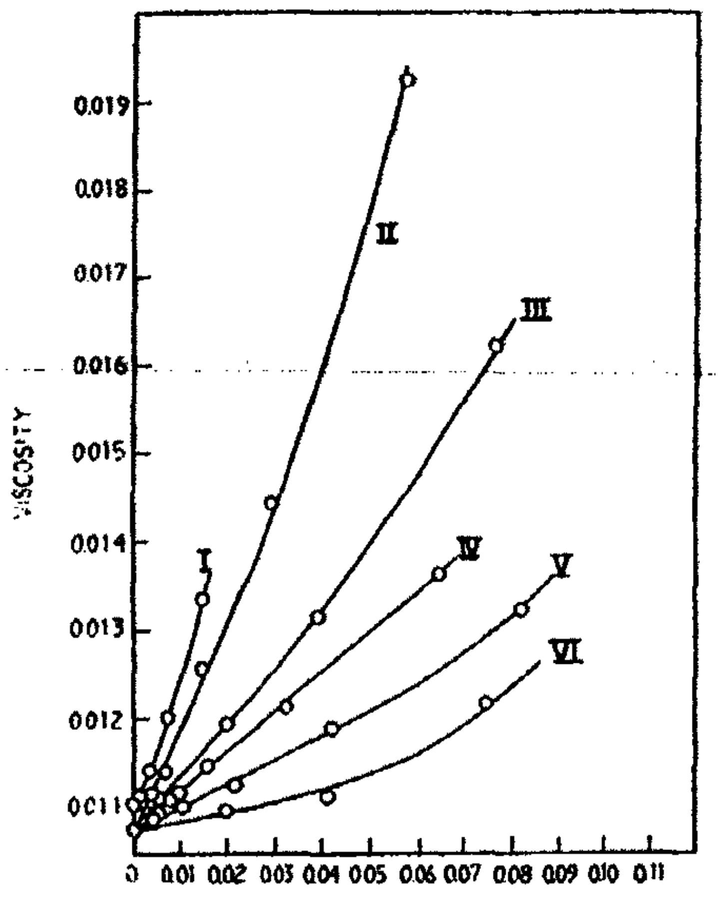

FIG. 1

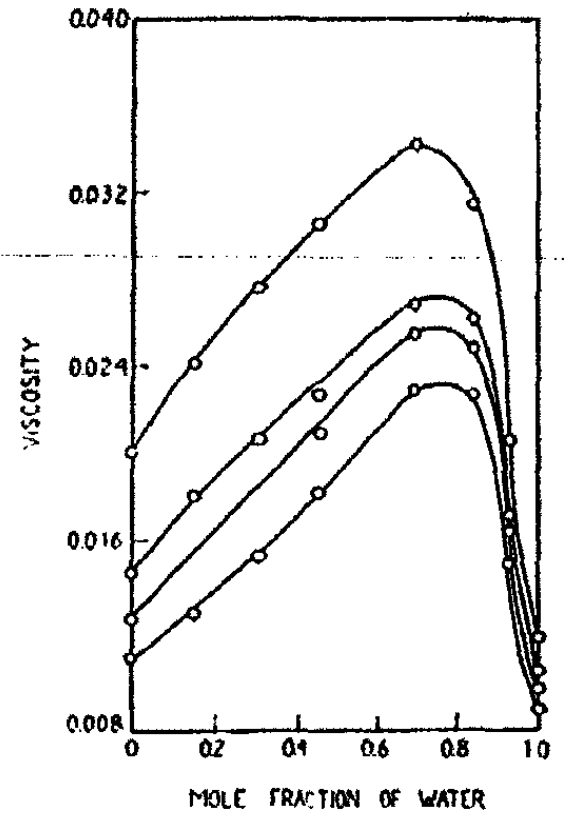

FIG. 2

FIG. 1. The viscosities of solution of salts in ethyl alcohol. I, $NiCl_2$; II, $AlCl_3$; III, $CoCl_2$; IV, $FeCl_3$; V, $SnCl_4$; VI, $HgCl_2$.

FIG. 2. Viscosities of solutions of aluminum chloride in mixtures of ethyl alcohol and water. The concentrations of aluminum chloride are (in moles per liter) 0.0000, 0.0937, 0.1874, and 0.3748, reading from the bottom curve to the one at the top.

Minima in viscosity-concentration curves (1, 9) have been explained by assuming that one substance causes the dissociation of associated molecules of the other. Results of this character are shown by our data for mixtures of ethyl alcohol and carbon tetrachloride (table 5 and figure 3). The position of the minimum in the region of dilute solutions of ethyl alcohol carries out the idea that dissociation is more complete at high dilution.

TABLE 4

Solutions of aluminum chloride in ethyl alcohol and water

SOLVENT COMPOSITION (MOLE FRACTION OF H_2O)	$AlCl_3$ CONCENTRATION IN MOLES PER LITER	VISCOSITY
0.147	0.0000	0.0129
	0.1874	0.0180
	0.3748	0.0242
0.302	0.0000	0.0153
	0.1874	0.0206
	0.3748	0.0276
0.449	0.0000	0.0182
	0.0937	0.0209
	0.1874	0.0226
	0.3748	0.0306
0.685	0.0000	0.0228
	0.0937	0.0255
	0.1874	0.0269
	0.3748	0.0342
0.830	0.0000	0.0227
	0.0937	0.0249
	0.1874	0.0262
	0.3748	0.0315
0.929	0.0000	0.0150
	0.0937	0.0165
	0.1874	0.0172
	0.3748	0.0205

TABLE 5

Viscosities of ethyl alcohol-carbon tetrachloride solutions

CONCENTRATION (MOLE FRACTION OF CCl_4)	VISCOSITY
0.000 (C_2H_5OH)	0.0107
0.063	0.0107
0.131	0.0107
0.205	0.0105
0.330	0.0102
0.473	0.0098
0.642	0.0094
0.843	0.0089
0.917	0.0089
1.000 (CCl_4)	0.0092

Jones and Talley and Jones and Dole (4, 5) have proposed an equation,

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} \pm Bc$$

to express the relation between the relative viscosity and the concentration, c, in moles per liter. This equation can be transformed into

$$\frac{\frac{\eta}{\eta_0} \quad 1}{\sqrt{c}} = A \pm B\sqrt{c}\,.$$

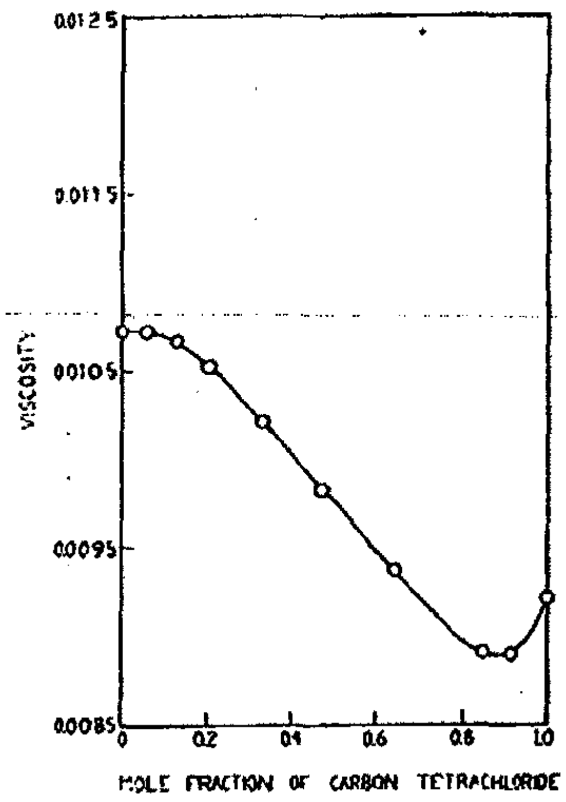

FIG. 3

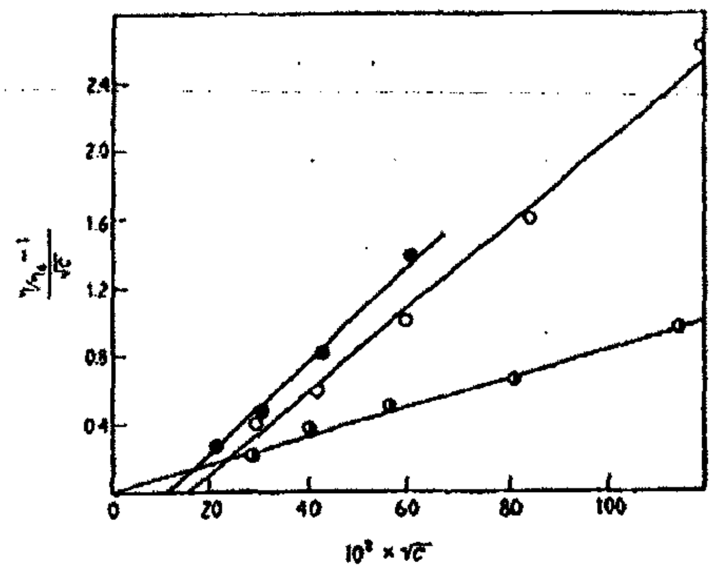

FIG. 4

FIG. 3. The viscosities of mixtures of ethyl alcohol and carbon tetrachloride

FIG. 4. The Falkenhagen equation. ●, $NiCl_2$; ○, $AlCl_3$; ◐, $FeCl_3$

When $\frac{\frac{\eta}{\eta_0} - 1}{\sqrt{c}}$ is plotted against $\sqrt{c}$, the result is a straight line, whose intercept on the vertical axis is A and whose slope is B.

The values of $\frac{\frac{\eta}{\eta_0} - 1}{\sqrt{c}}$ and $\sqrt{c}$ for different solutions of salts in ethyl alcohol are given in table 6. The results for three of these solutions are shown in figure 4. All the curves are similar to one or the other of the two types shown in this figure, and, in order to save space, those given have been selected as typical cases. Straight lines passing through, or approximately through, the zero point on the vertical axis were obtained for solutions of cobalt chloride, ferric chloride, stannic chloride, cupric chloride, mercuric chloride, and cadmium chloride in ethyl alcohol. For these curves the value of the constant A is approximately zero, and the relation

TABLE 6

Viscosities of solutions of certain salts in ethyl alcohol

C IN MOLES PER LITER	η	$\frac{\frac{\eta}{\eta_0}-1}{\sqrt{c}}$	$10^3 \times \sqrt{c}$	C IN MOLES PER LITER	η	$\frac{\frac{\eta}{\eta_0}-1}{\sqrt{c}}$	$10^3 \times \sqrt{c}$
$NiCl_2$ in C_2H_5OH ($\eta_0 = 0.0110$)				$HgCl_2$ in C_2H_5OH ($\eta_0 = 0.0107$)			
0.0000	0.0110	indet.	00.00	0.0000	0.0107	indet.	00.00
0.0117	0.0112	0.134	10.82	0.0313			
0.0233	0.0114	0.231	15.26	0.0625	0.0110	0.086	25.00
0.0466	0.0120	0.411	21.60	0.1250	0.0111	0.098	35.36
0.0932	0.0134	0.695	30.53	0.2500			
				0.5000	0.0122	0.188	70.71
$FeCl_3$ in C_2H_5OH ($\eta_0 = 0.0107$)				$SnCl_4$ in C_2H_5OH ($\eta_0 = 0.0107$)			
0.00000	0.0107	indet.	00.00	0.00000		indet.	00.00
0.02059	0.0109	0.111	14.35	0.01665	0.0109	0.171	12.9
0.04118	0.0111	0.190	20.19	0.03330	0.0110	0.132	18.2
0.08235	0.0115	0.258	28.70	0.06660	0.0113	0.202	25.8
0.1647	0.0121	0.335	40.58	0.13319	0.0119	0.307	36.5
0.3294	0.0137	0.486	57.40	0.26638	0.0132	0.463	51.6
$CdCl_2$ in C_2H_5OH ($\eta_0 = 0.0110$)				$SnCl_4$ in C_2H_5OH ($\eta_0 = 0.00439$)			
0.0000	0.0109	indet.	00.00	0.0000	0.0044	indet.	00.00
0.0169	0.0111	0.098	13.00	0.0394	0.0045	0.139	19.87
0.0339	0.0111	0.089	18.41	0.0789	0.0047	0.224	28.09
0.0677	0.0115	0.186	26.02	0.1577	0.0050	0.349	39.71
0.1354	0.0119	0.251	36.80	0.3154	0.0055	0.438	56.16
				0.6308	0.0072	0.811	79.42
$CuCl_2$ in C_2H_5OH ($\eta_0 = 0.0108$)							
0.0000	0.0108	indet.	00.00				
0.0625	0.0112	0.148	25.00				
0.1250	0.0117	0.231	35.36				
0.5000	0.0144	0.478	70.71				

between viscosity and concentration is expressed for these solutions by the equation

$$\frac{\eta}{\eta_0} = 1 + Bc$$

The positive value of B indicates the positive slopes of the curves.

The curves for aluminum chloride and nickel chloride in ethyl alcohol differ from those of the other salts in that the straight lines connecting the points pass below the zero of the vertical axis. This means that for these solutions the value of the constant A is negative.

The meaning of the constants A and B has been considered by Falkenhagen and Vernon (3), Jones and Dole (4), and Jones and Talley (5). Falkenhagen and Vernon compute A for aqueous solutions of a uni-univalent salt by means of the following equation:

$$A = \frac{1.45}{\eta_0\sqrt{2D_0T}}\left[\frac{l_1 + l_2}{4l_1l_2} - \frac{(l_1 - l_2)^2}{(3 - \sqrt{2})\, l_1l_2(l_1 + l_2)}\right]$$

in which η_0 and D_0 are the absolute viscosity and dielectric constant of water at temperature T, and l_1 and l_2 represent the equivalent conductances of the two ions at zero concentrations. This equation shows that the value of A is determined largely by the different factors involved in the Debye–Hückel theory. For a given salt in a given solvent, A depends upon the valence type of the salt, upon the dielectric constant of the solvent, and upon the mobilities of the ions of the salt. Of the factors that determine B, very little is known at the present time, but results obtained (2) with aqueous solutions of sucrose and urea indicate that the value of this constant depends upon factors that involve relationships between molecules of solute and solvent, rather than ions.

TABLE 7

Viscosities of solutions of $HgCl_2$ *in acetic acid*

WEIGHT FRACTION	DENSITY 25°/4°C.	η
0.00000	1.04465	0.0117
0.00550	1.04929	0.0117
0.01100	1.05429	0.0118
0.02200	1.06344	0.0120

Viscosities of solutions of $SnCl_4$ *in ethyl acetate*

WEIGHT FRACTION	DENSITY 25°/4°C.	η
0.00000	0.89374	0.0044
0.01110	0.90208	0.0045
0.02220	0.90997	0.0047
0.04440	0.92565	0.0050
0.08570	0.95853	0.0055
0.16090	1.02197	0.0072

The results obtained in this investigation for a majority of the salts in ethyl alcohol show that the conditions determining A are not of great significance, or possibly that the effects of different factors cancel each other. The negative values of A for solutions of aluminum chloride and nickel chloride in ethyl alcohol must arise, according to the equation of Falkenhagen and Vernon, from very great differences in the mobilities of the ions present in the solution. Such a condition might be expected in solutions containing highly complex solvated metallic ions and simple anions. Although they are somewhat apart from the other results reported in this paper, we have added in table 7 the viscosities of solutions of mercuric chloride in glacial acetic acid and stannic chloride in ethyl acetate. So far as we know the viscosities of these solutions have not been reported previously. The results for stannic chloride in ethyl acetate show a sharp increase in slope at higher concentrations, indicating a probable maximum and complex formation. This solution gives a negative value for A and a positive value for B in the Falkenhagen and Vernon equation.

SUMMARY

The viscosities and densities of solutions of eight metallic chlorides in ethyl alcohol, of solutions of four of the same salts in water, of aluminum chloride in mixtures of ethyl alcohol and water, of mercuric chloride in acetic acid, of stannic chloride in ethyl acetate, and of carbon tetrachloride in ethyl alcohol are reported.

All of the salts studied increased the viscosity of the solvent, and the viscosity increase is greater for alcohol than for water.

Aluminum chloride increases the viscosity of the solution of ethyl alcohol and water having the maximum viscosity to a greater extent than it does the viscosity of any other mixture of these two liquids. The viscosity-concentration curve for mixtures of ethyl alcohol and carbon tetrachloride has been shown to give a minimum.

Results for the solutions in ethyl alcohol have been discussed in the light of different theories, especially the Jones and Dole equation involving the viscosity of solutions of electrolytes.

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THE SPREADING OF INSOLUBLE FILMS PRODUCED BY A SOLUBLE SUBSTANCE

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I. INTRODUCTION

The formation of surface films by spontaneous spreading from solids has been observed by various workers (4, 5, 1). Cary and Rideal (2), specifically, have made very interesting studies of the spreading along the surface of long-chain, solid substances. They showed, among other things, that the rate of spreading is proportional to the perimeter of the solid in contact with liquid surface, and to the difference, $F_e - F$, between the spreading pressure and the pressure of the film. The equation

$$\frac{dF}{dt} = K(F_e - F) \tag{1}$$

was quite accurately obeyed. They have shown also that the spreading pressure F_e varied in an interesting way with temperature.

The spreading of nigrosine[1] (water-soluble) along the surface of water has been studied by the present writer from somewhat different angles. The previous workers studied the change with time of the rate of spreading under conditions in which the entire surface of the liquid was covered by the film, while the present writer has studied the rate of spreading of the film with the final area only a fraction of the free surface. This latter method gives rise to the spreading of solids under almost constant pressure of the film, while the former gives rise to spreading under continuously changing film pressure.

II. THE FORMATION OF THE FILM

If the free surface of distilled water has a radius smaller than about 15 cm., the spreading from nigrosine, after the whole surface is filled with the film, obeys equation 1. As the pressure of the film is increased by the continued spreading from nigrosine, the film becomes quite unstable and will begin to dissolve into the liquid. If the surface of the water is larger

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[1] This was a product of the National Aniline and Chemical Company. Its chemical formula is not known. For its probable composition see the British Color Index.

than the above-mentioned area, the continued spreading from nigrosine will not appreciably increase the radius of the circular film. The film thickens near the circumference, giving rise to a certain limit to the area of the spread film. The film thus made, however, is quite stable on the surface unless the nigrosine particle happens to be quite large (about 1.5 mg. or more).

The liquid film of nigrosine spread on tap water is stable on the surface, and is partially insoluble in water. An interesting feature of the liquid film is that there arises a dark circular ring around the spreading nigrosine particle, as is shown in figure 1. The film seems to be compressed greatly near the particle, as indicated by the blackness of the ring. This agrees with the result of Cary and Rideal (2), who definitely observed a slightly higher film pressure near the spreading particle than further away. These facts support strongly the suggestion of Rideal (4) that the spreading is not a "pulled out" effect due to the surface tension of water, but a "pushing out" effect from solids. It appears almost impossible to account for the existence of the dark ring by other than "pushing out" hypotheses. If the dark ring mentioned above had not been produced under controlled experimental conditions, the significance would have been reduced a great deal. However, it is possible to reproduce the condition of tap water which gives rise to the ring by introducing into distilled water a small amount of either calcium nitrate or aluminum potassium sulfate and a dilute solution of gelatin. The former are the only substances among many tried (calcium carbonate, calcium chloride, potassium nitrate, potassium chloride, aluminum sulfate, etc.) which make the film of nigrosine more and more insoluble as the concentration is increased, while the gelatin seems to give rise to a necessary amount of pressure to the film during the process of spreading. Details of the effects of these substances on spreading will be discussed later. Thus it appears that a certain impurity in tap water makes the film of nigrosine partially insoluble, while various colloidal particles in water give a pressure necessary for the expansion of the film as a liquid film. The fact that a considerable film pressure is necessary for obtaining the ring can be shown by spreading the nigrosine on a dilute aluminum potassium sulfate solution whose free surface is sufficiently small to obtain increased pressure after a certain period of time. Then as the pressure of the film increases, the ring begins to appear more and more clearly.

If the concentration of calcium nitrate or aluminum potassium sulfate in distilled water increases, the spreading changes gradually from gaseous film to liquid film and then to solid film. Figure 2 shows the nigrosine particle spreading as a solid film. As the concentration is increased, the white spot in figure 2 surrounding the particle will disappear, and the solid film will spread immediately from the solid. If the concentration is still further increased, the spreading will cease, and the nigrosine will sink into the liquid as an insoluble particle. These facts indicate that apparently some chemical action takes place between nigrosine and calcium nitrate or aluminum potassium sulfate, and that a new compound which is insoluble in water is formed. It is impossible, however, to speculate on this point further, since the composition of nigrosine is yet uncertain. An interesting feature of the solid film is the fact that it is so fragile that a gentle flow of air on the film breaks the film into pieces, which fly away in all directions on the surface. It appears that as the film becomes more solid, the cohesive forces between its molecules become smaller. The fact that the gaseous film is stable seems to indicate that the solubility of nigrosine is different for different orientations on water. Thus the molecules of nigrosine in the gaseous film have a greater opportunity to assume orientation on water in which they are readily soluble, while mutual attractions among nigrosine molecules in the liquid film keep the molecules from falling into an orientation in which they are readily soluble. A very fragile solid film of nigrosine produced on aluminum potassium sulfate solution loses its fragility if the film stands in air for a long time (about six hours or more), and the film becomes very viscous and sticky. This may be taking place very slowly. These complicated phenomena require further elucidation and research.

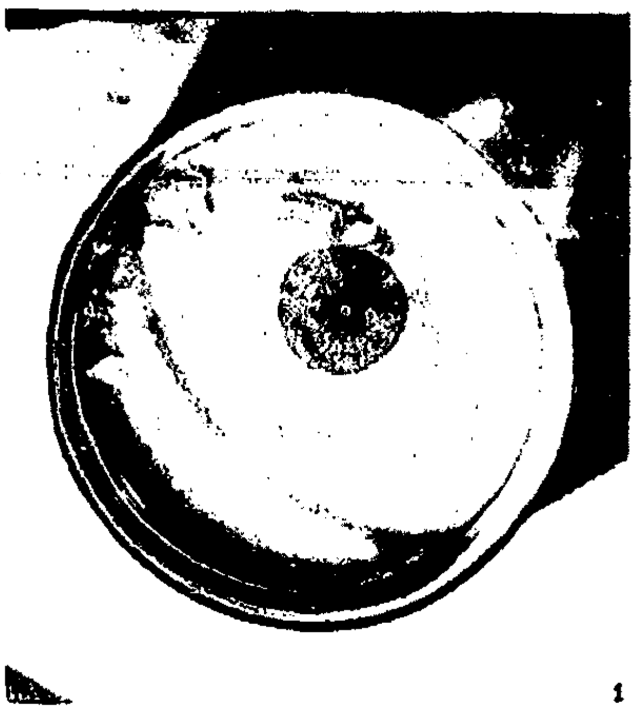

FIG. 1

FIG. 2

FIG. 1. Liquid film of nigrosine spread on tap water
FIG. 2. Nigrosine particle spreading as a solid film

III. RATE OF SPREADING

The spreading of nigrosine as a liquid film on tap water is sufficiently slow for an accurate measurement to be easily obtained. Taking the instant of dropping a small nigrosine particle (estimated to be about 0.002 mg.) as zero time, we can measure with time the diameter of the circular film as it expands; we then obtain results represented by straight lines on log-log graph paper, as is indicated by figure 3. The main characteristic of these straight lines is that they all have points at which the slopes of the lines undergo sudden changes. The curve A is obtained when the temperature of the tap water is at 16.8°C., while curves B are obtained when the temperature of the water is lowered to 7.8°C. It is very clearly indicated in the figure that the initial slope of the straight line depends on the temperature of the water, but as long as the temperature and the condition of the water are the same, the initial slope remains almost the same for particles of various sizes and shapes. The curves B are obtained for particles of the order of mass of 0.001 mg., the particles being spread on cylindrical dishes of diameter 7.5 cm. and 11.2 cm. In order to make sure that the initial slope of the curves under given conditions of temperature remains constant for very much larger particles, experiments on particles whose mass was about 0.6 mg. were carried out. One example for such particles is given in figure 4. We see by this figure that the initial slope remains constant within the experimental error when the mass of the particles is varied by a factor of 40. The dish used for spreading these particles had a surface of 30 x 37 cm.^{2} to allow sufficient area for spreading.

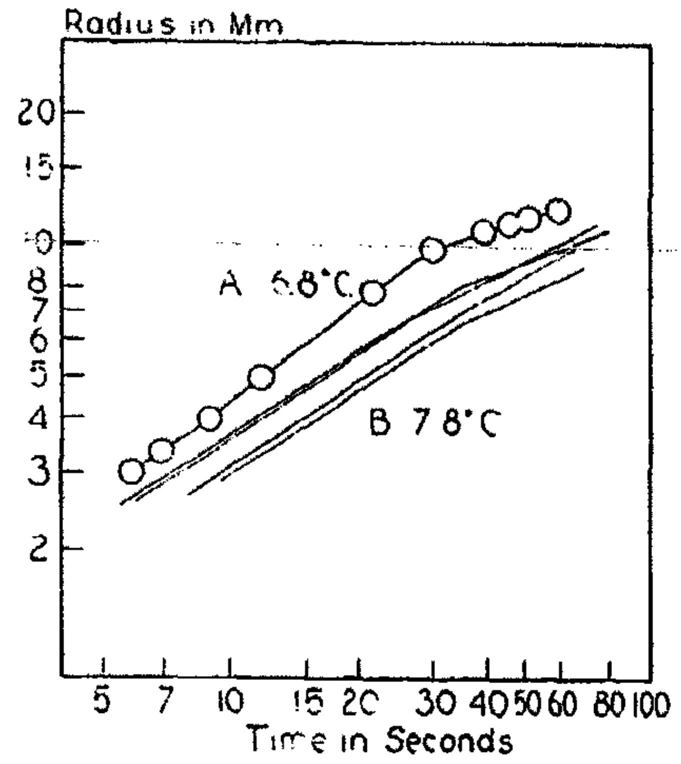

FIG. 3

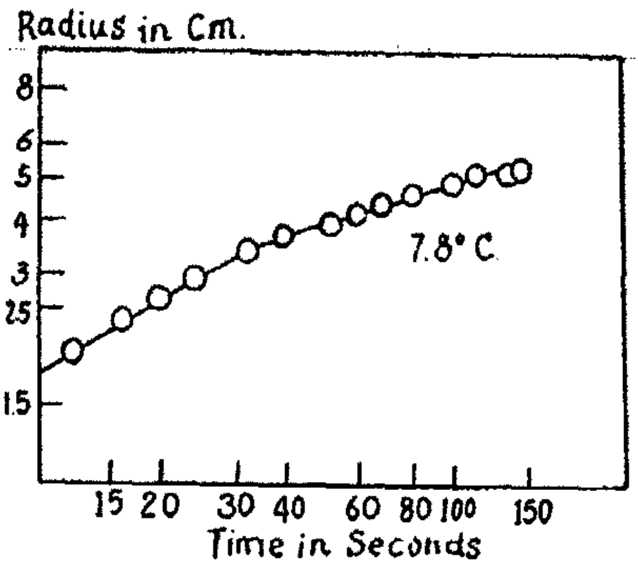

FIG. 4

FIG. 3. The curves show the relation between the radius of the circular film and the time as the film expands.

FIG. 4. The curve shows the relation between the radius of the circular film and time as the film expands for a large particle.

It appears from comparison of a large number of curves thus obtained that the magnitude of the change of slope depends on the shape of the particle as well as on the shape and surface area of the vessel in which the spreading takes place. No definite relationship was obtained, however, among these variables.

The equation of these straight lines is given by

$$t = CR^k \tag{2}$$

where t is the time, R is the radius, and k and C are constants. In particular, for curve A, k is 1.39 and 3.28 for initial and final slopes, respectively. For curves B the initial slope is 1.54.

Differentiating equation 2, we obtain

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{1}{Ck} R^{1-k} \tag{3}$$

If we use area $A = \pi R^2$ instead, we get

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{2\pi^{\frac{k}{2}}}{CK} A^{1-\frac{k}{2}} \tag{4}$$

If we take into consideration the fact that the film is sufficiently uniform so that the mass per unit area of the film, m, may be taken as constant, equation 4 becomes

$$\frac{\mathrm{d}m}{\mathrm{d}t} = Bm^{1-\frac{k}{2}} \tag{5}$$

where B is a constant.

Thus the rate (at a given time) at which nigrosine spreads on the surface of water is proportional to a constant power of the mass of nigrosine that has already spread from the solid, and this power is almost the same for all shapes and masses of solids, as long as the conditions of the experiment remain sufficiently constant. An exact theoretical explanation for this simple relationship seems to be a matter of great difficulty. Qualitatively, however, it may be considered in the following way: The number of nigrosine molecules which come into contact with water molecules as the nigrosine particle is placed on the water surface increases with time until the decrease of the mass of the particle begins appreciably to affect the rate of increase of the number of contact molecules. One might consider that a certain percentage of such contact nigrosine molecules are in favorable orientation with respect to the water molecules, so that between these nigrosine molecules and the water molecules there is created a large enough cohesive force to cause the molecules of nigrosine to be carried away from the solid when the water molecules attain sufficient kinetic energy of thermal vibration along the surface. As these molecules spread out and collide with others, the favorable orientation between nigrosine and water may be upset, thus making it more difficult for the molecules, once they have spread out, to return to the solid (3). The above-considered process may be of such a statistical nature as to produce a rate of spreading which is somewhat independent of shapes and sizes of particles.

When the time required for complete spreading of the particle, T, is plotted against the final radius of the circular film, we obtain the results indicated in figure 5. Experimental points have a tendency to cluster along certain straight lines, and the straight lines show different slopes with different temperatures. The effect of the size of the vessel is also apparent in curves A and B. A was obtained for a cylindrical vessel of diameter 11.2 cm.; B was obtained for a conical vessel, the diameter of the circular surface being 7.5 cm. The masses of particles used for this experiment were of the order of 0.001 mg.

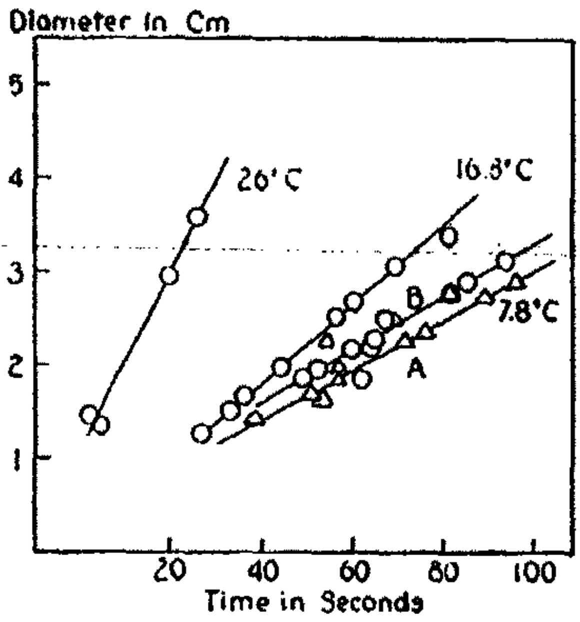

FIG. 5

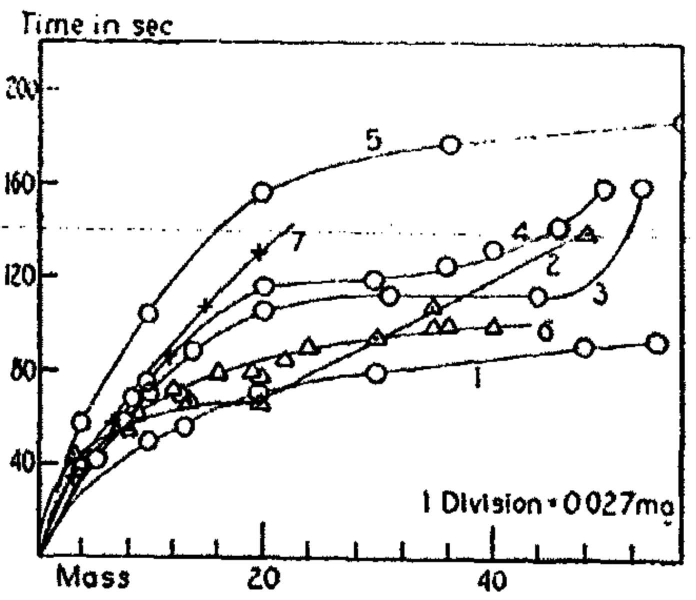

FIG. 6

FIG. 5. The curves show the relation between the time required for the complete spreading of nigrosine (water-soluble) and the final diameter of the film.

FIG. 6. The curves show the relation between the time required for the complete spreading of the particle and the mass of the particle. 1, gelatin solution (1 g. per 1600 cc.); 2, gelatin solution (1 g. per 800 cc.); 3, distilled water; 4, calcium nitrate solution (1/160 mole per liter); 5, calcium nitrate solution (1/80 mole per liter); 6, aluminum potassium sulfate (1/400 mole per liter); 7, aluminum potassium sulfate (1/400 mole per liter).

In general, as the temperature is increased the spreading is accelerated, so that above 30°C. the tap water behaves similarly to the distilled water of about room temperature. This is due, perhaps, to the increase in the kinetic energy of thermal motion of water molecules.

In order to see whether or not this sort of straight-line relationship is obtained when distilled water with the afore-mentioned solutions is used, the following experiment was carried out: Using a large vessel of surface area of 30 x 37 cm.^{2}, cleaned thoroughly with cleaning solution, we measured the total time, *T*, required for complete spreading of a nigrosine particle of weight, *W*, measured by a microbalance. If we plot the relation between *T* and *W* thus measured, we get the curves shown in figure 6, corresponding to various solutions on whose surface nigrosine is spread. For distilled water very distinct "saturation time" is obtained, and for other solutions there are definite indications that the curves tend to reach a saturation time as the mass of the particle is increased. An unexpected result is obtained in the case of the gelatin solution, which seems to accelerate the spreading for solutions of sufficiently small concentrations. The sudden rise in time for the curve of distilled water when the mass of the nigrosine particle becomes as great as 1.3 mg. may be due to the increased pressure of the film from its constant value by virtue of the existence, as mentioned earlier, of the limit to the area of spreading. As the pressure is increased in the film the rate of spreading will be reduced exponentially, as is apparent from equation 1, given by Rideal.

The existence of the "saturation curve" for spreading may be explained qualitatively by considering the change of area of nigrosine in contact with the liquid, although quantitative manipulation of the theory of this phenomenon seems almost prohibitive at this stage of the research. It may be considered that, as the mass of the particle is increased, more time is necessary for complete spreading, and that the rate of increase in total time *T* will diminish because of the fact that the contact area from which spreading occurs also increases as the mass increases. There will be, as a result, a point at which the two effects might compensate each other, so that further increase in mass increases the time, *T*, very little. What sort of rôle chemical action plays in the mechanism of spreading is a matter of importance and also a matter of further elucidation.

IV. THICKNESS OF THE FILM

The thickness of a mono-layer of the solid film of nigrosine made by spreading on a solution of aluminum potassium sulfate may be measured by using a Michelson interferometer after the film is caught on a thin mica film of uniform thickness. The refractive index of the solid film of nigrosine is measured by the usual method employed in determining the refractive indices of metals (6). The thickness thus obtained is 687×10^{-8} cm. ± 10 per cent, the index of refraction, n, $= 1.75$, and the absorption index, μ, $= 0.0175$.

By measuring the total area of the solid film produced from a known mass of nigrosine, the mass per square centimeter for the solid film of nigrosine was calculated to be 0.019 mg. ± 10 per cent. Thus if we know the molecular weight of nigrosine, it is easy to calculate the size of one molecule.

SUMMARY

The method of spreading nigrosine (water-soluble) on water as gaseous, liquid, and solid films, under almost constant film pressure, is described. The rate of spreading is found to obey a very simple mathematical relationship irrespective of the size and mass of the nigrosine particles. The relationship between masses of nigrosine and the time required for complete spreading is also measured for various solutions. A method of measuring the thickness of the solid film is described, and the thickness of the film is given as 687 × 10^{-8} cm. ± 10 per cent. The index of refraction, n, of the film is found to be 1.75, and the absorption index, μ, is 0.0175. The mass per square centimeter of solid film is 0.019 mg. ± 10 per cent.

The author wishes to express his thanks to Dr. H. A. Erikson for the great interest he has shown throughout the work and for his helpful suggestions, and also to Dr. F. H. MacDougall and Dr. J. Valasek for their helpful suggestions.

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NEW BOOKS

Laboratory Manual of Colloid and Surface Chemistry. By FLOYD E. BARTELL, Professor of Chemistry, University of Michigan. 187 pp.; 42 fig. Edwards Brothers, Inc., Ann Arbor, Michigan.

This laboratory manual consists of one hundred and twenty-six experiments grouped under the following headings: optical properties; particle size and sedimentation; filtration and ultrafiltration; dialysis and electrodialysis; electrokinetic phenomena; surface energy, surface tension, interfacial tension, and pore diameter of capillaries; contact angles, adhesion tension, and degree of wetting; adsorption and catalytic action; flocculation and protective action; viscosity; plasticity and liquid absorption; emulsions and foams; gels; osmotic effects; synthetic resins and plastic molding.

The author has included a remarkable list of experiments selected to illustrate the theory and applications of colloidal behavior. The user of the volume will be glad to know that the experiments will work, since all of them have been performed in connection with the regular laboratory course in colloid and surface chemistry at the University of Michigan. In so far as practicable, the experiments are of a quantitative character and the attempt has been made to present the directions so that the work may be done with little assistance from the instructor. At the end of each chapter, a number of selected references are given for the use of the student who wishes to inform himself more fully concerning the experimental procedures and applications. This is as it should be, since students of colloid chemistry are usually advanced undergraduates or graduates who should be teaching themselves the experimental methods of the science with a minimum of assistance from manuals.

The author is to be congratulated on preparing a manual of colloid chemistry which, in the reviewer's opinion, is the most useful to student and instructor alike that has yet appeared. The science has gone well beyond the qualitative stage, and teachers who wish to emphasize quantitative experimental methods in their laboratory course will find this volume invaluable.

HARRY B. WEISER.

Origins of Clerk Maxwell's Electric Ideas. Edited by Sir Joseph Larmor. 56 pp. Cambridge University Press. New York: The MacMillan Company, 1937. Price: $1.00.

We quote from the introduction by the Editor: "James Clerk Maxwell, in his days of early development, made a practice of communicating his progress in ideas by informal letters to his scientific friends, G. G. Stokes and W. Thomson, who were in the habit of preserving their correspondence. . . . The letters which are here printed have emerged among Lord Kelvin's manuscript remains. . . . The letters now published present a sharp and crisp account of the genesis and rapid progress of Clerk Maxwell's ideas as he groped toward a structural theory of the electric and magnetic field, here informally expounded by him in his close relationship to his friend Thomson—in fact it is an informal study in the natural mentality of a man of proved genius."

F. H. MACDOUGALL.

Electricity and Magnetism for Degree Students. 6th Edition. By S. G. Starling. 22 x 14 cm.; v and 630 pp. London: Longmans, Green and Co., 1937. Price: 12s. 6d.

The virtues of Starling's standard work on electricity and magnetism are too well known to require commendation, and the fact that during the twenty-five years of its existence there have appeared no less than six editions and seven new impressions, affords some indication of its popularity.

In the present edition the book appears in a rather more elaborate guise with bolder type and a modified title; but the major improvement lies in the omission of matter that has become of less importance and the substitution of additional material concerned with what, for lack of a better term, is usually described as "modern physics." While in the first three quarters of the book, which is devoted to classical electricity and magnetism, there is much evidence of careful treatment and logical proof, the remaining three chapters have in one or two places left the impression that thoroughness of treatment has been sacrificed to the exigencies of space.

Students of chemistry offering physics as a subsidiary subject will find in this edition an up-to-date account of electricity which amply covers their present requirements and will subsequently prove of value for reference.

E. J. Irons.

Man in a Chemical World. By A. Cressy Morrison. 23 x 16.5 cm.; xiv + 292 pp. New York: Charles Scribner's Sons, 1937. Price: $3.00.

This book is intended "to impress the man in the street with the fact that the chemical industries of the United States render a service that touches practically every activity in which he engages," p. ix.

"Chlorine has for many years provided a germ-free water; but, until the advent of activated carbon, many waters—although quite safe for drinking purposes—were at times unpalatable as compared with clear spring water," p. 38.

"In addition to the preventive vaccine which has practically wiped out smallpox among the plagues of mankind, similar treatments have been developed, and are produced in quantity, which act with the utmost certainty in preventing tetanus, hydrophobia, diphtheria, and, in livestock, canine distemper, rabies, and hog cholera. There are numerous other diseases—scarlet fever, the common cold, and spinal meningitis—for which similar treatments are partially successful," p. 49.

"Cocaine has bad qualities as well as good, among which is the property of making addicts of those who use it. . . . The result of combined research of chemistry and medicine was materialized finally by the chemical industry into a substance known as procaine or novocaine, whose sole characteristic is the deadening of certain sensory nerves to pain," p. 63.

"Despite the centuries of experience of the race in the treatment of human diseases, there are now known but a mere handful of specific curative medicines. The first of these (and the one on which our whole theory of specific curatives is based) was the cure of malarial fever by the administration of quinine. . . . Ehrlich found that a certain type of organic compound of arsenic was effective in destroying the parasite of syphilis. . . . Insulin, adrenalin, pituitrin, and thyroxin are typical of the glandular principles used extensively in modern therapy for the cure of diseases caused by their deficiency. In a very similar way it has lately been shown that pernicious anaemia may be cured [?] by introducing into the system the extract of fresh calves' livers," p. 65.

"Careful study of insect life reveals that one of their most vulnerable points is the peculiarity of their breathing apparatus. Indeed, the fact that nature failed to provide them with lungs, but rather distributed their breathing apparatus over the whole surface of their bodies, has been shown to be the limiting factor in the growth of insects. As their bulk increases, the surface of their bodies shrinks in relation to their volume and the largest species are weak because of their inability to breathe enough air," p. 89.

"Our annual losses of grains through the depredation of insects in stored grain and flour have been greater than $300,000,000. The cost of the fumigants supplied by the chemical industry for the purpose [of killing these insects] has amounted to only a fraction of one per cent of this amount," p. 93.

The average tire mileage in the United States is estimated at 4,000 in 1906 and 15,000 in 1934 (p. 113). The first figure seems high.

"One of the most recent contributions of chemistry to the efficiency of submarine cables has been the perfection of a nickel-iron alloy (permalloy) which, when built into the sheathing of the cable, reduces materially the loss of current from induction between the wire and the surrounding sea water," p. 145.

"The better light at less cost made possible by the universal use of argon in our electric light bulbs is a gift to the people of millions of dollars a year. Neon, which gives a brilliant red light in the now common electric tube signs of modern advertising, is found to the extent of only one part in fifty-five thousand of air," p. 226.

"Regardless of either the effectiveness or the disastrous consequence of using 'poison gases,' they will continue to be employed whenever a nation at war feels that its interests will be served by such a use. This is a situation which has become an acknowledged fact and can never be controlled by international agreement," p. 235.

WILDER D. BANCROFT.

Atomic Structures of Minerals. By W. L. BRAGG. 6 x 9 in.; 295 pp.; 144 fig. Ithaca, N. Y.: Cornell University Press, 1937. Price: $3.75.

This book on structures of minerals was begun by Professor Bragg while he was Baker Non-Resident Professor at Cornell University in 1934. It includes, however, references to research as late as the end of 1936. There are sixteen chapters in the volume. Three short ones treat of the geometry of crystal lattices and of x-ray analysis proper. Since the text is intended to be a description of the known structures of minerals, these 40 introductory pages are entirely adequate for the student who is not interested in x-ray analysis as such. The structures themselves are described in 230 pages. It is to the great credit of the author that he was able to present in such a small space so much information clearly and precisely without omitting any of the essential features. The illustrations are masterfully chosen and executed and contribute largely to the understanding of an otherwise very difficult subject.

Five chapters explain the structures of the elements, halides, sulfides, oxides, and oxygen salts. The remaining eight are devoted to the silicates, and constitute easily the most complete treatise of them published so far.

Each mineral description is headed by the formula, space group symbols, number of molecules in the unit cell, and the dimensions and angles of the unit cell. Commonly the axial ratios are given too. Owing to this arrangement the book becomes a fine reference work, especially since the footnotes provide a nearly complete index to the literature of the structures investigated. Besides footnotes, an index of authors and, of course, an alphabetical index of subjects are found at the end of the volume. An appendix contains the four different sets of symbols used today in designating space groups.

There are remarkably few typographical errors in the text. On page 200 a statement that amphibole asbestos fibers are more silky and longer than chrysotile fibers might be misleading. The greatest compliment the reviewer can pay Professor Bragg is that the book is so interestingly written and stimulating to further thought that one does not think of it as a reference work but as an entertaining story of the progress of the physical sciences. The printing, paper, and binding are very good.

JOHN W. GRUNER.

Chemical Kinetics and Chain Reactions. By N. SEMENOFF. 480 pp. Oxford: Clarendon Press, 1935. Price: $10.50.

One of the most important developments of chemical kinetics since the discovery of chain mechanism by Bodenstein in 1912 has been the introduction by Semenoff of the theory of chain branching and chain breaking. He has shown how the combination of these two competing processes, the one increasing, the other diminishing the number of reaction chains, completely controls the kinetics of many types of reaction, especially those of ignition, flame propagation, and explosion.

The author has expressed the view that chemical kinetics requires complete reconstruction from the standpoint of chain mechanism. The results of this undertaking he presents in a masterly way in the present work.

After developing the general theory and equations he treats the experimental material in three parts of several chapters each, one on reactions involving the halogens, one on oxidation, and one on decomposition and polymerization. The upper and lower limits of pressure in gaseous explosions are discussed in about a dozen systems each, the induction period and time lag, the effect of wall, of the addition of nitrogen peroxide, of water vapor, and of inhibitors and inducers are thoroughly discussed.

The work is thoroughly modern and represents tremendous progress in the very difficult and complicated field of chemical kinetics.

S. C. LIND.

Modern Alchemy. By DOROTHY FISK. 165 pp. New York: D. Appleton-Century Co., 1936. Price: $1.75.

A popular account of radioactivity, transmutation, and artificial radioactivity is attractively presented. The book is recommended for those who are interested in a non-technical description of the new accomplishments in the field of nuclear chemistry and physics.

S. C. LIND.

L'Action Chimique des Rayons Alpha en Phase Gazeuse. By W. MUND. 47 pp. Paris: Hermann et Cie, 1935.

This is the fourth general review of the work and theories in this field which Professor Mund has published since 1924. No one is better qualified for such an undertaking, since many of the most important advances, both experimental and theoretical, have been made by Professor Mund and his collaborators.

Some of the newer discoveries indicate that gas reactions under the influence of alpha rays have a more complicated system of kinetics than appeared from the earlier studies. The yield per ion of air in the combination of hydrogen with bromine or iodine, for example, is highly dependent on the relative proportion of the reactants, on the intensity of radiation, on the temperature, and to a lesser extent on the pressure.

Evidently the complete kinetic solution of such complex reactions will require much more experimentation and theorizing.

Professor Mund's discussions of the present status of the kinetics of chemical reactions induced by alpha rays are very useful, not only as milestones of progress, but also as direction guides for future researches.

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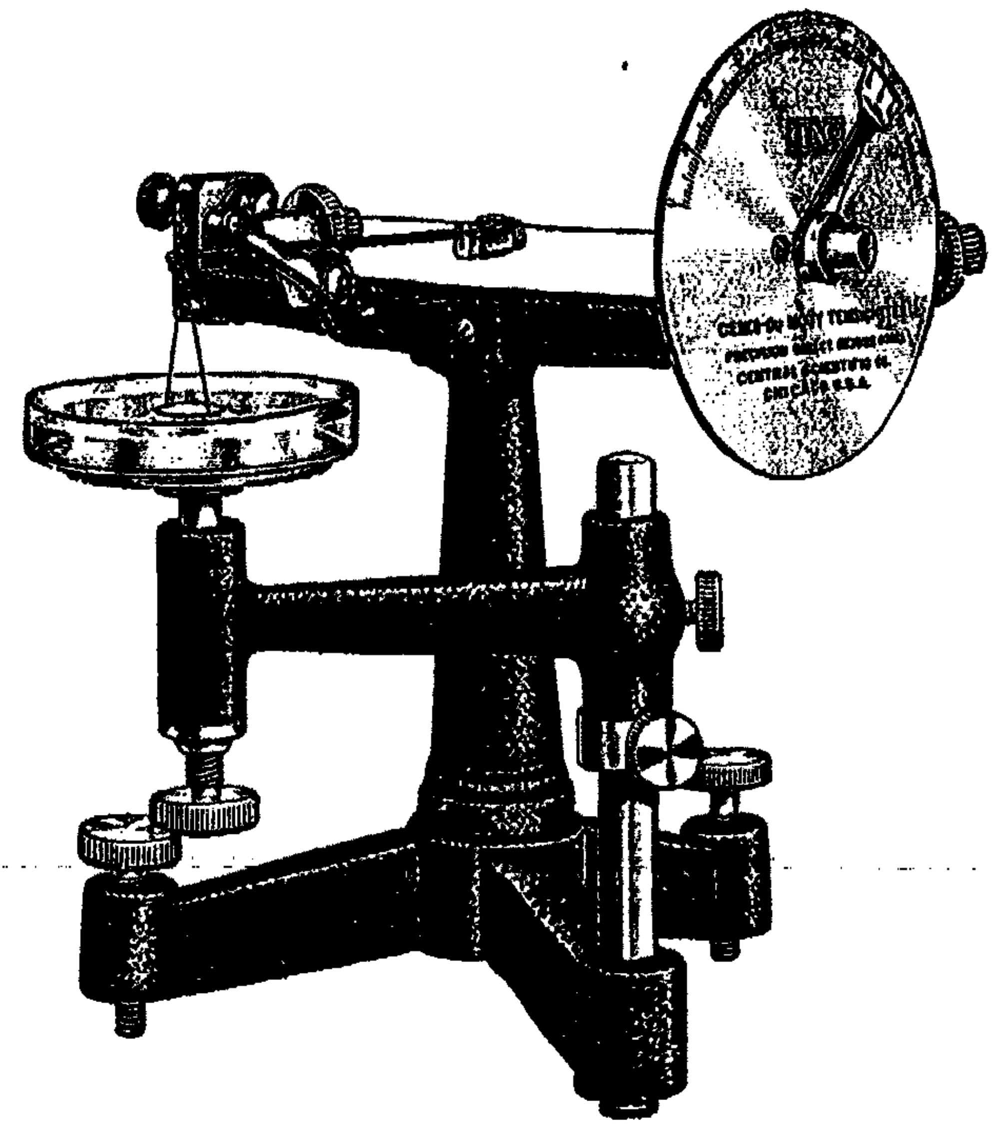

COLLOIDAL STRUCTURES IN BIOLOGY[1]

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University College, London, England

Received August 1, 1937

It is perhaps not going too far to say that in living organisms a majority of chemical reactions are bound to a special structure, and conversely, though not quite to the same extent, that all structures are bound to chemical reactions. In the development of an egg or in growth, the formation of new interfaces and the extension and stretching of old ones always parallel chemical changes. It is evident that in muscle contraction mechanical processes are closely correlated to chemical ones. When nerves act, one is dealing with the propagation of a chemical reaction in space, because one end of the nerve behaves differently from the other, allowing special substances (acetylcholine, adrenaline) to exude (36). On the other hand A. V. Hill (28) showed that the normal structure and irritability of a muscle or a nerve fiber are kept up only if oxidation is going on. Runnström (48) proved the same for the normal structure of eggs. I doubt whether in a living system we are ever dealing with a homogeneous reaction in a one-phase system. All processes appear to be either chemical reactions which are propagated in space in specially favored directions, the existing structure changing either reversibly or irreversibly, i.e., growing, or they are surface reactions, etc.

Thus morphology means much more than mere description, and we are right in being interested in the subtleties of structures in organisms, down to the structural elements of colloidal size. I intend to discuss a few types of structures found in colloidal systems which probably are also important in biological processes.

Structures made of rod-shaped particles are frequent. I am not thinking only of the integuments like those containing cellulose, chitin, etc., which are not "living" in the strict sense of the word. It was one of the most interesting results of x-ray studies—connected with the names of Scherrer, R. O. Herzog, Sponsler and Dore, Mark and K. H. Meyer and others—that the old conception of Nägeli and Ambronn was proved to be correct: these substances have a microcrystalline structure, they contain a high percentage of colloidal crystallites, having a long axis lying chiefly

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

in one direction, and these crystallites consist of macromolecules standing parallel to each other. Rod-shaped particles are also found in body liquids, in protoplasm, etc. The fibrin of the blood is one of the oldest examples known (53). The myosin in muscles gave particularly interesting results (8, 39). Its colloidal solutions behave very similarly to those of vanadium pentoxide, the latter having the properties of sols containing rod-shaped particles in a most pronounced degree. Myosin solutions are, for instance, strongly stream double refracting, i.e., they become double refracting when streaming without turbulence. The rod-shaped, anisotropic particles of myosin are orientated practically parallel to the lines of flow. Thus a layer of flowing liquid behaves optically similarly to a sheet of a uniaxial crystal cut parallel to its optical axis. If the myosin sol is rotated in a cylinder, the particles orient themselves more or less in concentric circles and hence a cross of isocline appears, no light passing through, between crossed nicols, where the particles lie with their long axis in one of the planes of polarization.

In concentrated sols containing rod-shaped particles the latter may orient themselves spontaneously (58, 60). If a layer of a concentrated vanadium pentoxide sol is kept between objective and cover-glass under a polarization microscope, the nicols being crossed, it first looks fairly homogeneous and dark, but in the course of time double refracting, spindle-shaped spots appear (figure 1). In these regions the rod-shaped particles are lying practically parallel to each other. This can be proved by investigating the same layer of sol in an ultramicroscope using one-sided illumination; a slit ultramicroscope is suitable or a cardioid ultramicroscope with a so-called azimuth diaphragm. Then only those particles become distinctly visible which are lying with their long axes normal to the direction of the incident light. It is found that, depending upon the direction of the incident light, actually the same spots are seen under the ultramicroscope as are seen as double refracting in the polarization microscope. These structures are called tactoids; the rest of the sol, not showing spontaneous orientation but capable of becoming double refracting on streaming, is termed atactosol. In very concentrated sols of this kind the tactoids may unite to a coherent double refracting phase, in which non-double refracting, black spots of the atactosol are left free.

Tactoids or structures very similar to them have been observed in biological systems. The most interesting research of Stanley (52) has shown the virus of the tobacco mosaic disease to be (or to be bound to) a protein-like substance whose particles are crystalline and distinctly rod-shaped. Its solutions are stream double refracting and, if they are concentrated by ultracentrifuging, tactoids are found in the concentrated sol, visible in the polarization microscope (figure 2) and looking exactly like those of vanadium pentoxide. These experiments were done by Bernal and his collaborators (3, 4).

The spindles formed in mitosis not only look like tactoids, but several other facts make it probable that they consist of fibers of rod-shaped particles (10). A direct mechanical evidence was given by Bělăr (2), experimenting under the microscope. The fibers may be sufficiently regular and optically anisotropic and their refractive index may differ sufficiently from that of the surrounding medium to make the spindle double refracting. Runnström (47) observed indications of double refraction in spindles, and W. J. Schmidt (50) has published photographs of eggs in mitosis under the polarization microscope, which give quite the impression of tactoid structures (figure 3). Chloroplasts are double refracting and probably also dichroic (34, 38, 49, 55). The experimental facts are perhaps not yet sufficiently conclusive to enable one to say whether their structure is that of tactoids. According to J. Weiss (56),

FIG. 1. A concentrated vanadium pentoxide sol as seen between crossed nicols under a polarization microscope.

FIG. 2. Tactoids in a concentrated sol of the virus of the tobacco mosaic disease

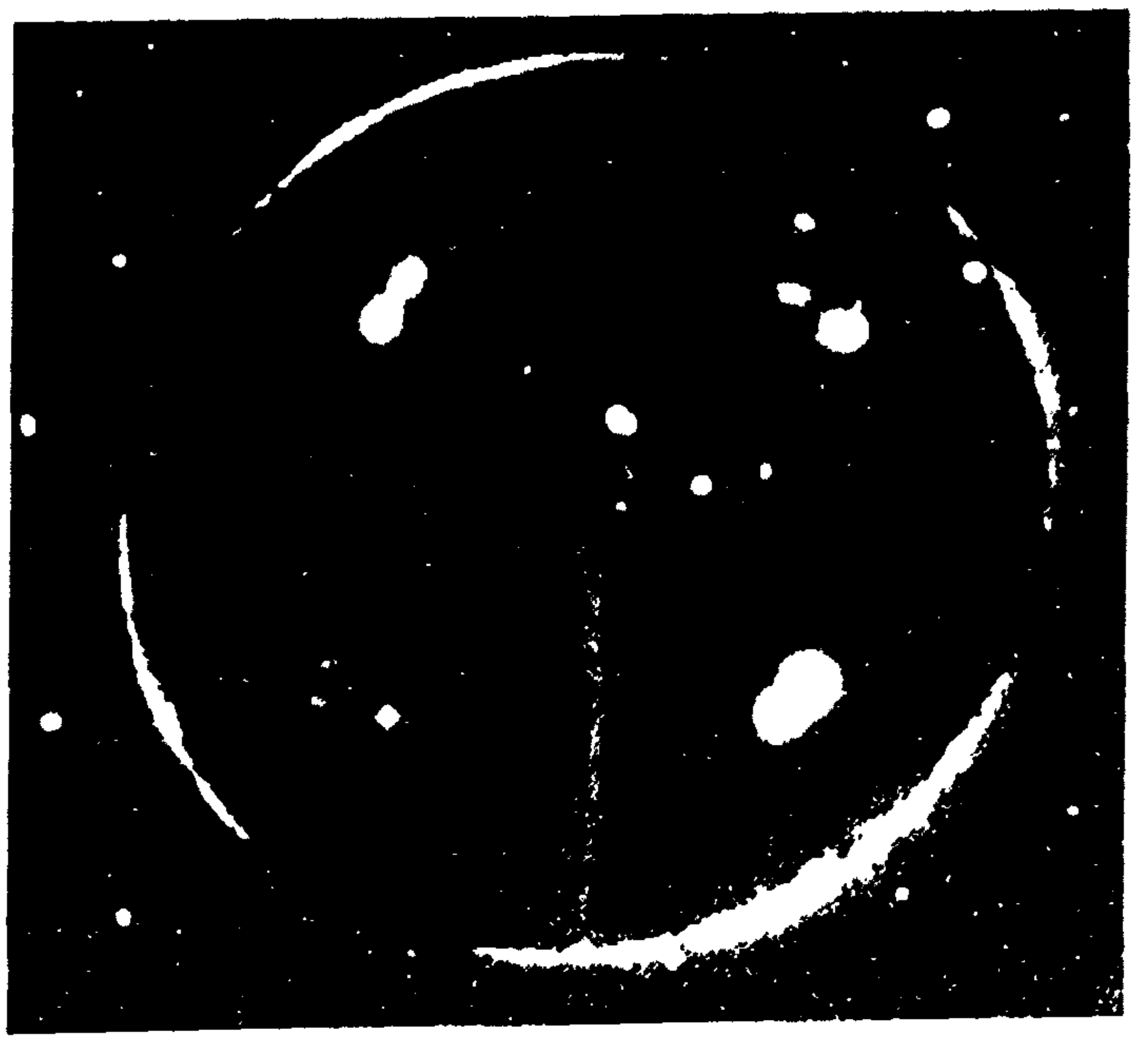

FIG. 3. Eggs in mitosis under the polarization microscope

the anisotropy of chloroplasts may be an important feature in the mechanism of assimilation.

In vanadium pentoxide sols the tactoids are formed in fairly pure, homodisperse, colloidal solution. The same holds for the tactoids observed in concentrated dyestuff solutions, for instance, those of benzopurpurin (58). The biological experiments mostly refer to more complicated systems containing all sorts of other substances in true and colloidal solution. This might be considered to be a substantial difference. Hence it is worth adding that tactoids of vanadium pentoxide and of benzopurpurin, respectively, are formed in mixed solutions of these two colloids (23). The two kinds of tactoids may be distinguished, because those of vanadium pentoxide are positively double refracting, while those of benzopurpurin are negatively double refracting. The presence of foreign substances obviously does not interfere with the formation of tactoids of one kind of particles.

On the other hand, the possibility must not be excluded that the formation of colloidal particles of a new phase is favored by the presence of other substances or that colloidal particles of two different substances unite to form a new phase. In other words, we may have in protoplasm and in the formation of tactoids all the possibilities discussed by Bungenberg de Jong (5) in his investigations on coacervation. Sometimes tactoids are simply called liquid crystals. Both structures are certainly closely related: in a double refracting layer of a liquid crystal anisotropic molecules are orientated parallel to each other; in tactoids the same holds for macromolecules or colloidal particles. I, nevertheless, believe that an identification of liquid crystals and tactoids masks a rather important fact: in tactoids the particles may be so far apart that a rotatory Brownian movement of the single particles is observed under the ultramicroscope. We have to realize again the existence of far-reaching forces acting between colloidal particles as in many other colloidal phenomena. Perhaps the modern conception of van der Waals' forces, as developed by London, accounts for such an effect (25, 31). In normal liquid crystals it is not surprising that ordinary van der Waals' forces between closely packed, anisotropic molecules cause them to become oriented.

These far-reaching forces are a connecting link to the second group of phenomena I should like to discuss briefly. The latter are concerned not with any special structure, as the tactoids are, but with the more general question of the liquid and solid state. In a survey of the older physiological literature it becomes obvious that the difficulties concerning the liquid or solid state of protoplasm were perceived very soon; it seemed to react sometimes as a liquid, sometimes as a solid. It was recognized only some years ago, however, that such an equivocal behavior is frequently found in concentrated colloidal systems, not rarely in rather dilute ones.

Occasional experiments performed quite a long time ago had proved, it is true, that sol-gel transformation may be reversible and isothermal and be influenced strongly by shaking, etc. But it was realized only lately that this is a very general and distinct property of many sols and gels (13, 54). Instead of the cumbrous term "isothermal, reversible sol-gel transformation" the term "thixotropy" has been introduced (40). A gel is thixotropic if it is liquefied to a sol by shaking and sets again to a gel in course of time when left to itself. A (mostly concentrated) sol may also be thixotropic, if its "viscosity" or other mechanical properties decrease on shaking, etc., and return to the original value in course of time if the sol is left to itself.

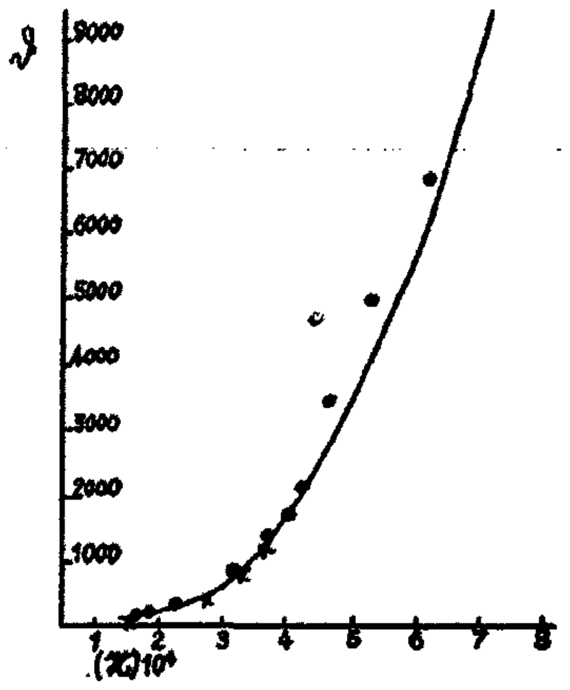

Fig. 4

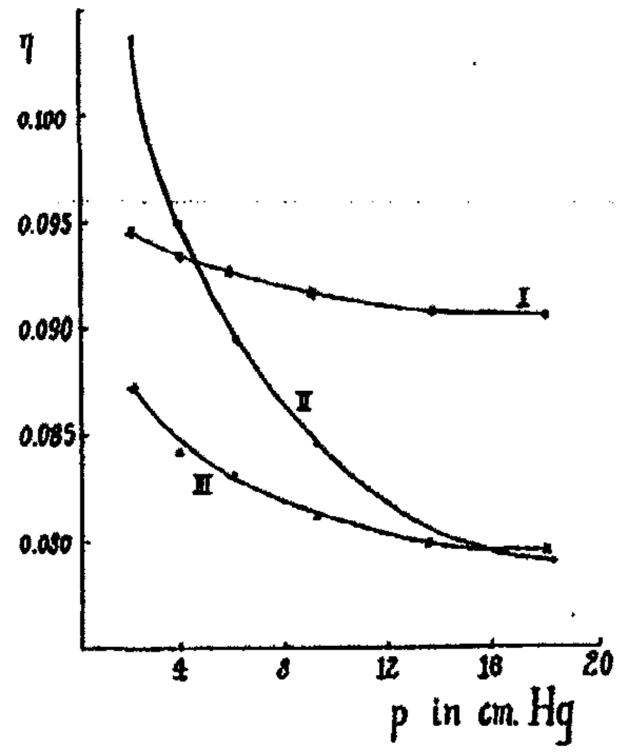

Fig. 5

Fig. 4. Effect of pH on time of setting of ferric oxide sols
Fig. 5. Viscosity of a methylcellulose sol

A concentrated ferric oxide sol containing a suitable amount of electrolyte, e.g., sodium chloride, is a good example of a thixotropic system (54); further, many other inorganic sols (of aluminum oxide, vanadium pentoxide, etc.). Suitably concentrated aqueous gelatin solutions change their "viscosity" reversibly on mechanical agitation (14). Thixotropy is also found in non-aqueous systems, for instance, with colloidal barium malonate in a medium of methanol plus glycerol (59). The particles need not be of strictly colloidal size; suspensions of bentonite (7, 19, 20, 26) and clays (20) in water and aqueous solutions, pastes of powdered Solnhofen slate (15), etc., in water and aqueous solutions and of mercaptobenzothiazole (45) in many organic liquids are also thixotropic.

These thixotropic transformations are frequently very sensitive towards small changes in the composition of the medium (21). In the ferric oxide sols mentioned the time of setting increases strongly with decreasing pH, as is shown in figure 4 where ϑ, the ordinate, is the time of solidification, and the hydrogen-ion concentration is the abscissa. This influence is so strong that the minute change in pH caused by a noble metal like silver becomes conspicuous: the time of setting decreases from 33 min. to 72 sec., if the sol has been in touch for 18 hr. with a sheet of silver (4.5 qcm. per cubic centimeter of sol); the corresponding change in pH was from 3.37 to 3.79. Other substances, for instance amino acids, cause an increase of ϑ, although they also increase the pH. The points marked by crosses in figure 4 refer to experiments where the difference in hydrogen-ion concentration was caused by the solution of different amounts of silver.

It is readily understood that changes in the chemical composition of the sol or gel caused by an electric current are accompanied by solidification or liquefaction. Karrer (32) found that a thixotropic paste of clay between two electrodes immediately flows down as soon as a current passes through it.

The anisotropic protein in the muscles, myosin, forms strongly thixotropic sols (39). According to Péterfi (41, 42) and Fauré-Fremiet (9) protoplasm may frequently be thixotropic. That of amoebae, for instance, may exist in an active mobile state and in a passive viscous state; it is transformed from the latter to the former by mechanical treatment (9). In living systems it is difficult to distinguish between a thixotropic state, as such, and one of, so to speak, potential thixotropy (12), i.e., the mechanical treatment may first cause some chemical changes and the production of some substance which is then instrumental in making the protoplasm thixotropic. In amoebae ultra-violet light also causes a transformation of the passive state into the mobile one. Potential thixotropy might be compared to the state of a ferric oxide gel having a pH too high to be liquefied, but becoming thixotropic if a small amount of acid were formed in the medium of dispersion of the gel. As far back as 1891 Pfeffer (43) observed that the protoplasm of myxomycetes may readily change from the solid to the liquid state and *vice versa*, a phenomenon he called "Kohäsionswechsel." And still older is an observation by Kühne (33) in 1863: he saw a nematode moving in the protoplasm of a still living muscle (musculus iliococcygeus of a frog); the regular orientation of the stripes was disturbed by the movements of the little animal, but they returned to their original arrangement as soon as the nematode had passed.

Thixotropic gels may be liquefied also by ultrasonic waves of sufficiently high energy (11, 18, 22, 31). This destructive action of ultrasonics, like many other destructive processes caused by them in cells, etc., is due to the collapse of cavities which are formed when the liquid is unduly stretched during the expansion phase of the sound waves. That strong mechanical effects may be produced by this process was shown by Rayleigh.

It is the same effect when the structural and anomalous viscosity of a colloidal solution, which may be reduced by mechanical treatment, is also decreased by a short treatment with ultrasonics. A striking example is an aqueous colloidal solution of methylcellulose (27). This sol undergoes inverse gelation; it becomes a gel with increasing temperature, for instance, at 55°C. When cooled, the gel is liquefied, but the viscosity of the sol is strongly anomalous, as is shown by curve II in figure 5. The viscosity was measured with an Ostwald viscosimeter. In figure 5 the abscissa is the pressure and the ordinate is the viscosity coefficient

$$\eta = \frac{\pi r^4 pt}{8lv}$$

which ought to be constant if the viscosity is normal, i.e., the curve ought to be a straight line parallel to the abscissa. Obviously the viscosity of this sol is markedly anomalous, η decreasing with rising pressure. If the sol is treated for a short time with ultrasonics, the behavior of its viscosity coefficient is given by curve III (figure 5); the viscosity is smaller and less anomalous. Curve III differs from curve I, because the particles of methylcellulose are dehydrated at higher temperature and are rehydrated but slowly; in course of time, favored by lowering the temperature, rehydration takes place and the behavior of the system then agrees again with curve I. A sensitivity towards ultrasonics like this is found only in structural viscosity. A truly viscous liquid, like an aqueous solution of glycerol, does not change its viscosity when treated in the same way with ultrasonic waves (46).

The rather enigmatical viscosity of protoplasm is probably, if not certainly, due to an anomalous viscosity caused by the colloids present (12, 24). Hence the viscosity found depends strongly on the method used. If the latter is such that the structure is practically destroyed, the "viscosity" measured, which may be compared with the true viscosity of a normal liquid such as water, glycerol, etc., is fairly small, not very different from that of water. It is much larger if the method does not cause the structure to be destroyed. If it were possible to treat the protoplasm of cells with ultrasonics in such a way that only the structure is destroyed without any other fundamental changes, measurements with a method of the second kind would also result in smaller values of viscosity.

Structural viscosity does not influence the electrical conductivity markedly (1, 35). That is why very likely values of the conductivity of protoplasm are found, assuming a value of viscosity about that of water, whereas the values become quite improbable, taking the structural viscosity to be the true one (24).

Ultrasonics not only have these destructive effects upon disperse systems. If their energy is not too high, they also may cause coagulation (51), provided that the particles in the system are large enough to scatter the sound energy sufficiently. The effect is marked with particles having a diameter above 0.5 μ; it was not observed with truly colloidal particles, i.e., with particles whose diameter was smaller than some tenths of a micron. Coagulation is due to the phenomenon known as "Kundt's dust figures," an accumulation of the particles in the nodes or antinodes of stationary waves which may readily lead to the formation of particle clusters. In concentrated thixotropic suspensions a similar action of ultrasonics involves a more rapid solidification than would take place spontaneously (6, 30). Thus ultrasonics may have both a dispersing, liquefying effect when sufficiently strong, and a coagulating, solidifying one when suitably weak, but not too weak. This acceleration of thixotropic setting owing to gentle movement has been termed rheopexy (16, 30). A gentle movement, like tapping a test tube containing a suitable thixotropic suspension or rolling it between the palms of the hands, acts similarly to not too strong ultrasonic waves.

Finally, ultrasonics may influence disperse systems in a third way. Non-spherical particles in suspension can be orientated by weak ultrasonics so that their longest axis lies normal to the flux of energy (6).

It might be interesting to replace by ultrasonics any mechanical action such as shaking in experiments where such mechanical action markedly influences biological processes: the creeping out of the butterfly is strongly retarded if pupae of *Pieris napi* are shaken for several hours (51); in *Papilio dardanus* the formation of anomalously colored females takes place if, during the sensitive period of pupation, the caterpillars are exposed to mechanical shocks (44). The advantages of ultrasonics would probably consist in the possibility of locating the point of attack of the effect and of deciding whether an orientation of non-spherical particles (perhaps of spindles ?), or a coagulation (and solidification), or a destructive, liquefying effect is essential.

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HOW TO DETERMINE STRUCTURAL FORMULAS FOR PROTEINS[1,2]

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Received August 1, 1937

The biochemists are agreed that the determination of the structural formulas of proteins is a very important problem. They are also agreed that they do not see any promising method of attacking the problem. The matter does not seem to us to be quite so serious as that, for we think that we know how it should be attacked. With proteins having apparent molecular weights of 15,000 and upwards, the ordinary methods of fractional hydrolysis, isolation, and purification are futile. An entirely new technique must be devised. Fortunately, that new technique is available. The equivalent weight of gelatin with reference to the stoichiometric addition of hydrogen chloride gas is about 300 (2, 4). We may therefore consider gelatin as made up of statistical groups or units, with an average equivalent weight of 300 with reference to the stoichiometric addition of hydrogen chloride to nitrogen, or with reference to stoichiometric nitrogen, as we shall call it. These units are only statistically of the same size and will necessarily vary in composition, because it is not possible to put radicals of all the amino acids to be obtained from gelatin into one unit and keep the equivalent weight as obtained down to 300. The problem is therefore to devise as many ways as possible of breaking up the protein molecule, so as to throw as much light as possible on the composition of the actual units. It is not likely that the protein molecules are absolutely unsymmetrical, and the action of enzymes shows a tendency to break into groups which are not identical for the different enzymes.

For the moment it is necessary to make an exhaustive study of the types of nitrogen in any given protein and of the way in which these relative amounts vary with progressive decomposition and rearrangement of the protein. In any protein or any mixture of hydrolyzates or other decomposition products of that protein, it is possible to determine total nitrogen

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

[2] This work is part of the program carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

(Kjeldahl), so-called amino nitrogen (Van Slyke), so-called stoichiometric nitrogen (Bancroft (1)), and free ammonia. It is possible also to determine how much formaldehyde can be added and, within limits, how it will affect the types of nitrogen already specified. Levy (8) reports that "only the amino groups of arginine, histidine, and lysine are considered as reacting with formaldehyde, each of them reacting with one or two molecules of formaldehyde successively." It is probable that other characterizations of nitrogen will be found when people concentrate on this point (5).

Gurin and Clarke (6) report that "the position of the free amino groups in polypeptides and proteins can be determined by benzenesulphonylation, followed by hydrolysis under conditions in which the peptide linkages are opened without appreciable attack on the sulphonamino grouping.... Treatment of gelatine with benzenesulfochloride blocks the free amino groups completely with no apparent degradation of the protein.... At least fifty per cent of the free amino groups in gelatine may therefore be ascribed to the ϵ-amino group of lysine. Not more than five-tenths per cent of the free amino nitrogen in gelatin can be allocated to monoamino acids."

We advise doing fractional hydrolysis of a protein, say gelatin, with water, acid, alkali, pepsin, trypsin, and erepsin; also fractional photochemical decomposition, taking the word "photochemical" in its broadest sense, to include cathode rays, canal rays, emanations and other bombardments. At the end of the short run, the system should be separated into two (or more) portions varying in composition, by filtering off any insoluble portion, by fractional solution, by fractional precipitation with alcohol, acetone, or any other suitable agent, by electrodialysis, etc. The two (or more) portions are to be evaporated to dryness in the cold and examined without purification for the different types of nitrogen. Other runs can be made with the original substance for longer times and any fraction may be treated further. It is worth noting that the proteoses are soluble in benzaldehyde (3), while the amino acids and the proteins are not, egg albumin being something of an exception.

In general, isolation and purification of individual compounds will be carried out only at such stages as seem desirable, thereby saving enormous amounts of time. Some of this time will be lost, owing to the slowness of the present method of determining stoichiometric nitrogen, but it is probable that methods of speeding up these determinations will be found. Czarnetzky claims to have made some improvement, but he gives no figures and his data for ammonia are known to be wrong. The value given in his thesis for the dissociation pressure of hydrated sodium sulfate is badly in error, and the value in the journal article is even more incorrect. It does not appear definitely whether his experiments were done at constant partial pressure and varying total quantity of water or at constant total quantity and varying partial pressure of water, presumably the first. Both ways are wrong unless suitable corrections are made. As these corrections were not mentioned, they were probably omitted. Czarnetsky has also overlooked the fact that a flat in a concentration–pressure curve indicates only the appearance of a new phase of approximately constant composition and does not necessarily mean the formation of an ammonium salt. It is quite possible, however, that ammonia might combine stoichiometrically with some of the hydrolysis products of casein, in which case such experiments might be helpful in our problem.

When a mass of data has been obtained under suitably controlled conditions, it will undoubtedly be a terrible job to fit the jig-saw puzzle together, but at least we shall have the pieces, whereas now we face the admittedly impossible problem of constructing the puzzle from non-existent pieces. We feel certain that the differences between the enzyme hydrolyses and the pH hydrolyses will be marked and will prove very helpful.

Our own experiments were cut short by the illness of Mr. Browning in 1932 and will probably not be carried to a definite conclusion because of the retirement of the senior author. In 1932 we had not realized the importance of doing fractional precipitation on the soluble hydrolyzates, and consequently the only definite results are that the water-insoluble or non-peptizable portion acts in some respects like unchanged casein, and that the soluble or peptizable hydrolysis products change in composition while there is still what behaves in some respects like unchanged casein. This means that some of the more hydrolyzed products of casein are hydrolyzed somewhat more rapidly than some of the less hydrolyzed products and makes it not impossible that some catalyst would cut out pretty completely one of the intermediate products, just as nitrite can be made to occur only in small amounts in the reduction of nitrate.

After experiments with both concentrated and dilute hydrochloric and sulfuric acids, dilute sulfuric acid (4.44 per cent) was decided to be the best for several reasons: (*a*) The use of hydrochloric acid involves the determination of chlorides, which is complicated by the presence of so much organic matter. (*b*) Hydrolysis with hydrochloric acid gives a small, presumably variable, amount of black humin substance (10), while sulfuric acid gives only a trace of it. (*c*) The soluble portion from the hydrolysis with both concentrated (20 per cent) and dilute (6 per cent) hydrochloric acid is extremely hygroscopic after being dried and powdered, so that it is difficult to weigh out samples, while the product obtained after hydrolysis with sulfuric acid is much less hygroscopic. (*d*) Concentrated acids produce such rapid hydrolysis that the first stages cannot be observed, while this is not the case with the more dilute acid. (*e*)

Besides not producing so much black "humin" substance, sulfuric acid can be neutralized by an equivalent weight of barium hydroxide, and the resulting precipitate of barium sulfate can be removed by filtration.

The Kjeldahl method for the determination of total nitrogen (7) and the method of Van Slyke (11) for the determination of amino nitrogen were used throughout. For the determination of the amino nitrogen in the insoluble portions of the short-time hydrolyzates, a very fine suspension in water of the weighed sample was made up in a volumetric flask and an aliquot portion of this suspension was used. The Van Slyke apparatus was shaken by motor for five minutes for all determinations.

For the work with 4.44 per cent sulfuric acid, exactly 100 cc. of the acid was added to 10 g. of the casein.[3]

When it was desired to stop the hydrolysis, the flame was removed and the mixture was filtered immediately with suction on two thicknesses of filter paper. The residue on the paper was washed with several portions of hot water, and the washings were combined with the first filtrate. There was an insoluble portion after the 1-hour hydrolysis and after the 2-hour hydrolysis; but not after the 4-hour hydrolysis. The insoluble portion was dried in a desiccator over sulfuric acid. The total and amino nitrogens and the curve with hydrogen chloride were determined on the dried material after it had been powdered finely.

The soluble portion from the hydrolysis was treated by heating the first filtrate quickly to boiling, adding an amount of powdered barium hydroxide equivalent in weight to the sulfuric acid used, and mixing this thoroughly with the solution by shaking. The mixture was again heated quickly to boiling and the barium sulfate was filtered off with suction on two thicknesses of filter paper and washed twice with hot water. The washings were combined with the filtrate, which was then evaporated nearly to dryness in an oven held at 65–75°C. When the product had dried to a very viscous mass, the dish was placed in a vacuum desiccator which was then exhausted. After standing several days the product could be powdered easily.

The original casein contained 14.8 per cent nitrogen and 1 g. of it combined stoichiometrically with about 90 mg. of hydrogen chloride. This means that 23.3 per cent of the total nitrogen is what we call stoichiometric nitrogen. The statistical group or unit is therefore about 416, as against about 300 for gelatin. During the hydrolysis with 4.44 per cent sulfuric acid, ammonia was set free, practically all of it in the first hour of hydrol-

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[3] Casein, refined, prepared by Schering-Kahlbaum, Berlin. Since the casein had an ash content of only 1.2 per cent, we considered it unnecessary to purify it further for the preliminary orienting work to be described in this paper. Bancroft and Barnett (J. Phys. Chem. 34, 479 (1930)) have shown that a small amount of impurity does not change the curve for stoichiometric nitrogen much.

ysis. The apparent losses in grams of ammonia per 100 grams of casein were: 1 hour, 3.84 g.; 2 hours, 3.83 g.; 16 hours, 3.83 g.; 32 hours, 3.80 g. The data are shown graphically in figure 1. The average of 3.85 g. of ammonia corresponds to 3.15 g. of nitrogen or 21.3 per cent of the total nitrogen. This value is adopted in table 1. These results do not agree quantitatively with those of Pittom (9) obtained over twenty years ago. He found that the rate of liberation of ammonia was very rapid in the first stages of the hydrolysis and that, after that, the ammonia comes off at a steady, slow rate for a time. The great discrepancy is that Pittom obtained only about 1.5 per cent of the total nitrogen in the form of ammonia, whereas we get about 3.15 per cent, or practically twice as much. Pittom's conditions of hydrolysis were quite different from those in our experiment, and that may possibly account for the difference in the results. The matter should be looked into, because it would be very interesting and probably helpful, if the liberation of ammonia could be varied considerably by varying the conditions of hydrolysis.

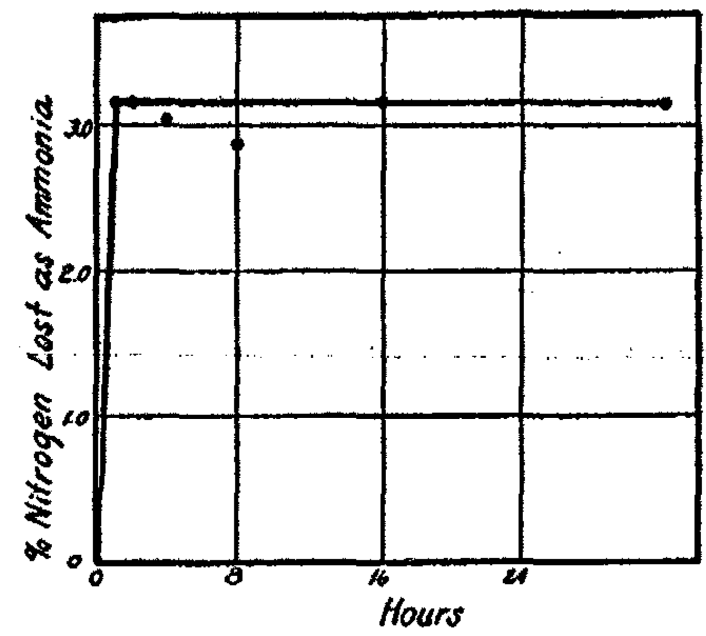

FIG. 1. Loss of nitrogen as ammonia

TABLE 1

Hydrolysis of casein with 4.44 per cent sulfuric acid

Variation of the soluble portion

MATERIAL AND TREATMENT	STOICHIOMETRIC NITROGEN	NON-STOICHIOMETRIC NITROGEN	APPROXIMATE LOSS OF NITROGEN AS AMMONIA
	per cent	*per cent*	*per cent*
Original casein	23.3	76.7	0
1-hr. hydrolysis	34.5	44.2	21.3
2-hr. hydrolysis	37.5	41.2	21.3
4-hr. hydrolysis	44.1	34.3	21.3
32-hr. hydrolysis	53.1	25.6	21.3

The insoluble portion of the casein, left after 1 and 2 hours' hydrolysis with 4.44 per cent sulfuric acid, showed the same percentage of stoichiometric nitrogen as the original casein within the limits of the experimental error and was, therefore, probably unchanged casein. The data for the stoichiometric addition of hydrogen chloride are presented graphically in figure 2. Curves A and B are for unchanged casein; curve C is for casein after 1-hour hydrolysis; and curve D is for casein after 2-hour hydrolysis. In order to differentiate these curves it was necessary to enlarge the scale of abscissas. This makes the actual break very blurred. Figure 3 shows what can be done by a judicious choice of scale.

Dr. R. A. Gortner does not believe that any casein could survive 2 hours' boiling with dilute sulfuric acid and he therefore considers the insoluble product as a decomposition product. It is true that only one kind of test was applied, and it is possible that casein may decompose in such a way as to keep the percentage of stoichiometric and of total nitrogen constant, but it does not seem probable. One point, which supports Gortner's view, is that the 3-hour hydrolysis did not give appreciably more ammonia than the 1-hour hydrolysis and one would have expected an additional amount, coming from the casein assumed not to have been decomposed in the first hour. This difficulty would be met if it were shown that the presence of hydrolysis products of casein interfered with the setting-free of ammonia. This has not yet been shown, but is an additional reason why someone should study carefully the conditions under which ammonia is split off.

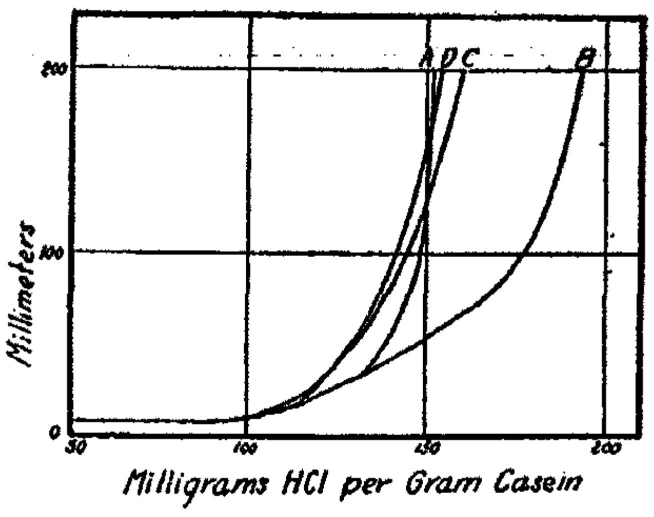

FIG. 2

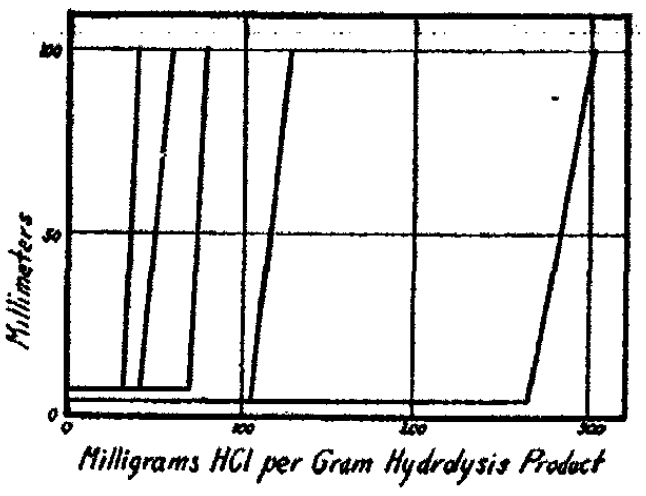

FIG. 3

FIG. 2. Data for stoichiometric addition of hydrogen chloride. Curves A and B, unchanged casein; curve C, 1-hour hydrolysis; curve D, 2-hour hydrolysis.

FIG. 3. Curves represent 1-hour, 2-hour, 3-hour, 16-hour, and 32-hour hydrolysis.

Some of the results that were obtained with the hydrolyzed portions are summarized in table 1.

The stoichiometric nitrogen, as found, increases from 23.3 per cent of the total nitrogen to 53.1 per cent in the product which has been hydrolyzed for 32 hours. If we include the ammonia nitrogen as stoichiometric nitrogen—which of course should be done—the change is from 23.3 per cent to 74.4 per cent and gives some indication of the probable helpfulness of studying stoichiometric nitrogen. At the end of 32 hours' hydrolysis the amount of hydrogen chloride combining stoichiometrically with 1 g. of hydrolyzed casein (exclusive of ammonia) had risen from about 90 mg. to about 265 mg. The data are shown graphically in figure 3.

If one is going to undertake seriously the determination of the constitution of any protein, he must be willing to accept facts as they are, and that is not the case at present. Since the living organism can hydrolyze proteins more or less completely to amino acids and can synthesize the needed proteins from amino acids, and since the hydrolytic decomposition can also be done in the test-tube, it has seemed self-evident to everybody that the peptide linkage —C(:O)NH— must predominate in the proteins. We even speak of certain decomposition products of proteins as polypeptides, without having as yet any proof that these substances are polypeptides. It has been shown by Bancroft and Barnett that the nitrogen in a peptide linkage is normally stoichiometric nitrogen. In casein not over 20 per cent of the nitrogen linkages can possibly be normal peptide linkages and the number may be considerably less than that. Zein contains apparently no stoichiometric nitrogen and therefore no normal peptide linkages. That conclusion must be either accepted or explained away.

CONCLUSIONS

1. Sulfuric acid is better than hydrochloric acid for hydrolyzing casein and is probably better for hydrolyzing all proteins.
2. When casein is hydrolyzed for a short time, there is apparently some unchanged casein left. Dr. R. A. Gortner does not accept this conclusion, and we are not in a position to prove that he is wrong. The soluble hydrolysis products vary in composition while there is still present what we call unchanged casein.
3. Under the conditions prevailing in our experiments practically all the ammonia is split off during the first hour of hydrolysis. The percentage of total nitrogen split off as ammonia is about 21.3.
4. The stoichiometric nitrogen increases from 23.3 per cent of the total nitrogen in the original casein to 53.1 per cent in 32 hours' hydrolysis if one does not include the ammonia nitrogen, and to 74.4 per cent if one does.
5. One gram of the original casein combines stoichiometrically with about 90 mg. of hydrogen chloride. This makes the equivalent weight with respect to stoichiometric nitrogen about 415. After 32 hours' hydrolysis the value (exclusive of ammonia) has dropped to about 140.
6. It is claimed that great progress in the determination of constitu-

tional formulas of proteins will be made if we discard temporarily the idea that only pure substances should be analyzed.

7. It is believed that it will be helpful to study the amounts of various types of nitrogen in suitably prepared, fractional hydrolyzates of the proteins.

8. The importance of stoichiometric nitrogen must be recognized, and also the corollary that the normal peptide linkage is not so prevalent as organic chemists have assumed.

9. The important problem is to devise methods for cleaving the protein molecule into relatively large, natural fractions rather than to nibble off small fragments from the circumference of the molecule. That is why the enzyme attack will probably be most helpful.

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DIELECTRIC CONSTANT AND PARTICLE SIZE

STUDIES WITH CHLORINATED RUBBER SOLUTIONS[1]

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Quantitative studies of high molecular weight polymeric compounds are of great theoretical and technical interest. An important object of such work is to assist in the discovery of the structural plan of these molecules. It is possible that there may be found some comparatively simple method of classification. For example, we may be enabled eventually to distinguish (*1*) association polymers in which smaller molecular units or residues are held together to form the aggregates through secondary valence forces, and (*2*) macromolecules in which the fundamental groups are chains or fibrils of such residues which are held together by primary valence forces.

Recent theoretical developments make it possible to estimate the size of spherical or ellipsoidal polar molecules, provided the latter are dissolved in non-polar media and provided the physical or molecular kinetic unit and the electrical molecule are identical. From dielectric constant–frequency data obtained with dilute solutions, the average time constants and molecular weights of zein, gliadin, and lignin have been determined. In these cases the molecular weight values so obtained agree with figures which have resulted from the application of the classical diffusion, sedimentation, and osmotic pressure methods; in other words, the electrical and kinetic units are identical. Data obtained in other laboratories appear to indicate that egg albumin, hemoglobin, and serum albumin molecules show similar characteristics when allowance is made for their shapes.

On the other hand, the results of unpublished measurements made in this laboratory with relatively dilute solutions (1 to 3 per cent) of certain other polymers (ω–hydroxydecanoic acids, methyl methacrylate, rubber hydrochloride, neoprene) do not give a dispersion of ordinary dielectric constant which can be detected with our present apparatus over the wavelength range now accessible (λ = 10 m to λ = 10,000 m), although the

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

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experimental data show a definite orientation contribution of the solute molecules to the dielectric constant of the solution.[3]

Dilute solutions of chlorinated rubber also were found not to give a dispersion of the dielectric constant over the available wave-length interval, although an effect of this kind would be expected if electrical and kinetic units are equivalent. Inasmuch as the dipole theory is restricted in exact application to dielectric constant and density data obtained with dilute solutions, the significance of results obtained at moderate concentrations may be somewhat questionable, but it was decided to experiment with solutions containing the somewhat larger amounts of chlorinated rubber as solute. Measurable dielectric constant dispersions were observed with solutions containing 3 to 7 per cent of this substance and the calculated times of relaxation appear to be independent of concentration.

The Debye modification of the Clausius-Mosotti formula (2), which shows frequency as well as temperature variation of dielectric constant, has the form

$$\frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{M}{d} = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT}\cdot\frac{1}{1 + i\omega\tau}\right) \qquad (1)$$

In this equation, M is the molecular weight, d is the density, N is the Avogadro number, α_0 is the optical polarization, μ is the electric moment, ω ($=2\pi\nu$) is the frequency, τ is the time of relaxation or time constant, T is the absolute temperature, k is the Boltzmann constant, and $\epsilon = \epsilon' - i\epsilon''$. The dielectric constants ϵ' and ϵ'' are the real part and imaginary part, respectively. The dielectric constant observed in a capacity measurement is ϵ'.

It varies with frequency according to the expression,

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\right)^2 \omega^2\tau^2} \qquad (2)$$

in which ϵ_0 is the static dielectric constant, ϵ_∞ is the corresponding optical quantity, and

$$\tau = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\cdot\frac{1}{2\pi\nu_c}$$

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[3] Mr. Wilbur Bridgman of this laboratory has made a detailed study of the dielectric behavior of several of the polymeric ω-hydroxydecanoic acids in dilute benzene solution. In order to account for the data it seems necessary to assume contributions to the polarization resulting from orientations in the electric field of recurring units which make up the several solute molecules. A report of this work will be available in the near future.

The frequency ν_c is that frequency for which

$$\epsilon = \frac{\epsilon_\infty + \epsilon_0}{2}$$

If we wish to express the time constant in terms of the frequency ν_f at which the dielectric constant-frequency or dispersion curve passes through its point of inflection we have

$$\tau = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \cdot \frac{1}{2\pi\nu_f} \cdot \frac{1}{\sqrt{3}}$$

For the calculations to be made in connection with this report, we shall use the frequency at which the dielectric constant assumes its mean value.

By remembering that it is necessary to exert a torque to rotate a spherical molecule against the inner friction of a medium in which it is suspended, the time of relaxation of such a molecule may be expressed in terms of its radius, r, to give the important result,

$$\tau_0 = \frac{4\pi\eta r^3}{kT} \qquad (3)$$

The symbol τ_0 will be used to designate the time of relaxation of a spherical molecule. In deriving this equation the assumption has been made that the inner friction of the medium can be expressed in terms of η, its ordinary or macroscopic coefficient of viscosity. Thus, for the molecular weight, M, of a spherical solute, we have

$$M = \frac{1}{3}\tau_0 \frac{RT}{\eta V} \qquad (4)$$

where V is the partial specific volume of the molecule in solution.

If the molecule has the shape of an ellipsoid of revolution with long axis a and short axis b ($b/a = \rho$), and the rotation is about the long axis in a medium of viscosity η, the relaxation time becomes (4)

$$\tau = \frac{4\pi a b^2 \eta}{kT} \cdot \frac{4}{3} \frac{(1 - \rho^4)}{1 + (1 - 2\rho^2)\,\rho^2/\sqrt{1 - \rho^2}\, \ln\left(\frac{1 + \sqrt{1 - \rho^2}}{\rho}\right)} \qquad (5)$$

Further,

$$\frac{4\pi a b^2}{3} = \frac{MV}{N}$$

It is the present purpose to attempt to demonstrate the use of the dipole theory in particle size determinations by calculations made by using the observations of frequency variations of dielectric constant of solutions of chlorinated rubber in non-polar solvents. Studies were made with solutions of five samples of chlorinated rubber prepared by us and three samples of commercial chlorinated rubber (Tornesit).[4] The chlorine contents of the specimens varied between those corresponding to the trichloro and to the tetrachloro derivatives.

PREPARATION AND PURIFICATION OF MATERIALS

In the experimental work benzene and carbon tetrachloride were used as solvents. Each was subjected to careful and rigorous purification by following procedures given by Weissberger and Proskauer (5). As a test of the purity of the liquids used the boiling points, refractive indices, and densities were determined and compared with data of the International Critical Tables.

The chlorinated rubber was prepared by direct chlorination of acetone-extracted pale crepe rubber.[5] Purified chlorine gas was passed into a warm solution of the pale crepe rubber in carbon tetrachloride. This solution of chlorinated rubber was then poured into hot water which had been made slightly alkaline by the addition of sodium carbonate, and the chlorinated rubber was precipitated out in white sheets. The product was then redissolved in carbon tetrachloride and reprecipitated from hot neutral water. It was dried in air between filter papers and over calcium chloride in a desiccator, rinsed with alcohol, and dried *in vacuo.*

EXPERIMENTAL

In the majority of cases the dielectric constants were obtained by determining the capacity of a calibrated fixed cell or the capacity difference between rotor positions of a variable cell by means of either of two assemblies of apparatus for the heterodyne beat method of measurement. The first one, used with but slight modification, has been described in the literature (3). The cell is calibrated by finding its capacity in air and in benzene, the standard liquid, and from this calibration the dielectric constant of the solution is obtained from a single condenser reading. The second apparatus consisted of three distinct circuits, an electron coupled standard oscillator, a detector, and a variable oscillator containing standard precision condenser and dielectric cell connected in parallel. Similar arrangements for dielectric constant measurements are described in a recent laboratory manual (1). Again purified benzene was used as liquid of known dielectric constant for the calibration.

[4] On two occasions samples of Tornesit were presented to us by the Hercules Powder Company of Wilmington, Delaware.

[5] This material was supplied with the compliments of the B. F. Goodrich Company through Dr. W. F. Busse of the Physical Research Laboratory.

Additional dielectric constant measurements were made at wave lengths $\lambda = 10$ m to $\lambda = 100$ m by using a resonance apparatus and at $\lambda = 1000$ m to $\lambda = 8500$ m with a special radio frequency bridge. The resonance point was established by means of a voltmeter circuit containing a duplex diode triode tube. The position of balance in the bridge was observed with the aid of an oscillating detector and a two-stage amplifier of conventional design. These additional data were always consistent with the values obtained with the heterodyne beat method at the intermediate wave

TABLE 1

Physical and analytical data for chlorinated rubber solutions

EXPT. NO.	SUBSTANCE INVESTIGATED	SOLVENT	CONCENTRATION (GRAMS PER 100 CC. OF SOLVENT)	n_D^2	DENSITY	PER CENT Cl IN SOLUTE
1	Benzene			2.236	0.8737	
2	Carbon tetrachloride			2.122	1.5830	
5	Chlorinated rubber I	CCl_4	3.9012	2.132	1.5843	61.28
6	Chlorinated rubber I	CCl_4	2.5341	2.128	1.5842	61.28
7	Chlorinated rubber I	C_6H_6	5.3635	2.247	0.8972	61.28
8	Chlorinated rubber II	CCl_4	4.9101	2.134	1.5846	66.13
9	Chlorinated rubber II	CCl_4	1.2865			66.13
10	Chlorinated rubber II	C_6H_6	3.8456	2.247	0.8906	66.13
11	Chlorinated rubber II	C_6H_6	4.1265	2.253	0.8919	66.13
12	Chlorinated rubber III	C_6H_6	5.5594	2.250	0.8980	60.32
13	Chlorinated rubber IV	C_6H_6	4.1668	2.247	0.8923	59.56
14	Chlorinated rubber V	C_6H_6	2.9298	2.243		58.98

TABLE 1a

Dielectric constant data for chlorinated rubber solutions

EXPT. NO.*	600 m	350 m	156.2 m	78.1 m	39.1 m	26 m	17.4 m
1	2.273	2.273	2.273	2.273	2.273	2.273	2.273
2	2.236	2.236	2.237	2.236	2.238	2.234	2.236
5		2.303	2.302	2.300	2.292	2.284	2.271
6		2.272	2.271	2.268	2.266	2.263	2.259
7		2.336	2.336	2.331	2.330	2.326	2.323
8			2.307	2.303	2.298	2.281	2.265
9			2.261	2.262	2.259	2.257	2.262
10		2.328	2.325	2.324	2.322	2.316	2.313
11	2.335	2.334	2.334	2.332	2.329	2.325	2.321
12		2.360	2.357	2.351	2.346	2.341	2.337
13			2.343	2.340	2.334	2.328	2.324
14	2.322	2.322	2.321	2.319	2.318	2.314	2.311

* The experiment numbers refer to corresponding numbers of table 1.

TABLE 2

Physical and analytical data for Tornesit solutions

EXPT. NO.	SUBSTANCE INVESTIGATED	SOLVENT	CONCENTRATION	n_D^t	DENSITY	PER CENT Cl IN SOLUTE
15	Imported Tornesit	CCl_4	5.4613	2.138	1.5854	65.75
16	Imported Tornesit	CCl_4	3.6081	2.135	1.5848	65.75
17	Imported Tornesit	CCl_4	3.0212	2.133	1.5845	65.75
18	Imported Tornesit	C_6H_6	1.6037	2.241	0.8809	65.75
19	Imported Tornesit	C_6H_6	1.5509	2.240	0.8806	65.75
20	Domestic Tornesit I	CCl_4	2.5147	2.131	1.5844	64.53
21	Domestic Tornesit I	CCl_4	2.6078	2.132		64.53
22	Domestic Tornesit I	CCl_4	3.3699	2.135	1.5849	64.53
23	Domestic Tornesit I	C_6H_6	1.9581	2.243	0.8826	64.53
24	Domestic Tornesit I	C_6H_6	2.7113	2.245	0.8858	64.53
25	Domestic Tornesit I	C_6H_6	3.9101	2.247		64.53
26	Domestic Tornesit I	C_6H_6	4.9368	2.250	0.8957	64.53
27	Domestic Tornesit I	C_6H_6	5.2753	2.250	0.8968	64.53
28	Domestic Tornesit I	C_6H_6	7.6379	2.257	0.9069	64.53
29	Domestic Tornesit II	CCl_4	2.5030	2.133	1.5846	64.14
30	Domestic Tornesit II	C_6H_6	2.9223	2.247		64.14
31	Domestic Tornesit II	C_6H_6	3.4682	2.248	0.8906	64.14
32	Domestic Tornesit II	C_6H_6	4.4027	2.250	0.8952	64.14

TABLE 2a

Dielectric constant data for Tornesit solutions

EXPT. NO.	600 m	350 m	156.2 m	78.1 m	26 m	17.4 m
15		2.297	2.297	2.294	2.283	2.277
16			2.278	2.275	2.264	2.262
17	2.272	2.271	2.271	2.269	2.264	2.258
18	2.316	2.314	2.314	2.315	2.315	2.312
19			2.297	2.294	2.294	2.294
20		2.270	2.268	2.264	2.258	2.256
21	2.277	2.276	2.272	2.269	2.260	2.256
22	2.287	2.286	2.284	2.279	2.272	2.266
23	2.302	2.300	2.300	2.299	2.298	2.298
24		2.316	2.316	2.315	2.309	2.305
25		2.330	2.328	2.327	2.319	2.314
26	2.342	2.341	2.339	2.336	2.329	2.323
27	2.351	2.351	2.348	2.345	2.337	2.330
28		2.380	2.378	2.373	2.357	2.350
29		2.267	2.266	2.265	2.258	2.255
30	2.316	2.316	2.315	2.313	2.308	2.306
31	2.325	2.325	2.323	2.321	2.316	2.314
32	2.344	2.344	2.341	2.339	2.332	2.327

lengths, and they serve as an excellent check upon the results to be presented in the tables which follow.

The partial specific volume of the chlorinated rubber was observed pycnometrically at 25°C., the calculation being made according to the formula,

$$V = \frac{[w - (l - h)]}{d_0 h}$$

where V is the partial specific volume, w is the weight of the solvent in the pycnometer, l is the weight of the solution, h is the weight of the chlorinated rubber, and d_0 is the density of the solvent. The concentration of the solution was determined by evaporating known volumes of the solution in an oven at 90°C. and weighing the residues.

The refractive indices were measured with a Pulfrich refractometer. Relative viscosities were determined by viscometers of the Ostwald type. All such measurements were made in a thermostat regulated to 25°C. ± 0.01°.

The results of the experimental work, physicochemical and analytical, are presented in tables 1 and 2. The dielectric constant data are accurate to about ± 0.1 per cent. Such a degree of accuracy is required in view of the small actual change in the dielectric constant of the chlorinated rubber solutions which is to be expected.

CALCULATIONS

In any monodisperse system the dielectric constant may be expressed as a function of the frequency by equation 2. Since in many of the experiments harmonics of a fundamental frequency are used, the frequency ν or $\frac{\omega}{2\pi}$ may be replaced by $n\nu_0$, where n is an integer and ν_0 is the fundamental frequency. Thus equation 2 may be written in the form,

$$\epsilon' = a\epsilon_\infty x^2 - a\epsilon' x^2 + \epsilon_0 \tag{2a}$$

in which

$$a = \left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \cdot 2\pi\nu_0 \cdot \tau\right)^2$$

Equation 2a has three constants to be evaluated, a, ϵ_0, and ϵ_∞. Ordinarily this is accomplished by the method of least squares, but here the calculations can be simplified because there are independent means by which the quantities ϵ_0 and ϵ_∞ may be approximated. The dielectric constant at infinite frequency ϵ_∞ is obtained in the following manner. For the non-polar solvents the square of the refractive index is equal to the dielectric constant at infinite frequency, except for the small difference due to infra-red absorption. For carbon tetrachloride, $n_D^2 = 2.122$, and the difference between this value and the observed dielectric constant for the liquid ($\epsilon = 2.236$) is 0.114. Since the solutions investigated were reasonably dilute, it is assumed that the effects due to infra-red absorption are unchanged, so that for the carbon tetrachloride solutions ϵ_∞ is taken as the sum of 0.114 and the square of the refractive index. The constant ϵ_0 has been assigned the value of ϵ' at $\lambda = 1000$ m. With these fixed values of ϵ_∞ and ϵ_0, the constant a and the time of relaxation τ were ob-

TABLE 3

Time of relaxation data for chlorinated rubber and Tornesit

SOLUTE	EXPT. NO.	$\frac{\epsilon_0 - \epsilon}{\text{CONCENTRATION}}$	$\tau \cdot 10^9$
Chlorinated rubber I			
In CCl_4	5	1.44	9.3
	6	1.18	9.1
In C_6H_6	7	0.97	6.5
Chlorinated rubber II			
In CCl_4	8	1.20	11.4
In C_6H_6	10	1.12	7.5
	11	1.09	7.4
Chlorinated rubber III			
In C_6H_6	12	1.26	7.3
Chlorinated rubber IV			
In C_6H_6	13	1.41	7.6
Chlorinated rubber V			
In C_6H_6	14	1.43	6.7
Imported Tornesit			
In CCl_4	15	0.82	10.4
	16	0.81	11.3
	17	0.80	10.8
Domestic Tornesit I			
In CCl_4	20	0.91	11.5
	21	1.00	11.6
	22	1.10	11.3
In C_6H_6	24	1.25	7.0
	25	1.15	7.4
	26	1.05	7.1
	27	1.20	7.0
	28	1.09	7.6
Domestic Tornesit II			
In CCl_4	29	0.80	11.6
In C_6H_6	30	1.09	7.2
	31	1.12	6.4
	32	1.25	6.4

tained from the experimental measurement of the dielectric constant. The results of the calculations for the times of relaxation of the five laboratory and the three commercial preparations of chlorinated rubber are presented in table 3.

Chlorinated rubber in solution displays a diffusion and viscosity behavior which suggests that the macromolecules exist in solution as highly elongated units. In order to calculate the apparent molecular weights from the time of relaxation data, use is made of the formula

$$M = \frac{1}{4}\tau \frac{RT}{\eta V}$$

which has been obtained by combining equations 4 and 5. We assume that the observed times of relaxation are characteristic of a rotation about the long axis of the molecule and the magnitude of ρ is of the order 0.1 or less. For the coefficient of viscosity, η, of the solvents we have used $\eta_{C_6H_6} = 0.00584$ and $\eta_{CCl_4} = 0.00918$. The partial specific volume of chlorinated rubber in solution is 0.62. As an average result for the apparent molecular weight of chlorinated rubber we calculate 12,000. If the three figures for chlorinated rubber I are excluded from consideration, it is found that the values for M always vary between 11,000 and 12,900. Chlorinated rubber I gives M in the neighborhood of 10,000.

DISCUSSION

In the Debye dipole theory it is assumed that molecules may possess a permanent electric moment and as a result can show an orientation as well as distortion polarization in an applied electrical field. High frequency and high viscosity interfere with the orientation of dipole molecules in an alternating field in a way such that in a liquid system containing these molecules the dielectric constant may decrease with increasing frequency even if the temperature is maintained constant. It is this frequency variation of dielectric constant which enables us to estimate the size of the orienting units, provided the latter have definite shape and are dissolved in a proper medium of known inner friction.

It has been shown by work done in this and other laboratories that in a number of cases molecular weight data obtained by using the dielectric constant method agree well with corresponding figures which have resulted from the application of the more generally recognized molecular kinetic methods. Thus, when allowance is made for the shape of the dissolved units, it has been possible to show the equivalence of the electrical and the kinetic units in the case of zein, gliadin, lignin, and hemoglobin. These molecules are either nearly spherical or they may be considered as ellipsoids of revolution with low eccentricity.

It was thought to be important to investigate the dielectric constant behavior of typical linear or long-chain polymeric molecules in solution, because eventually it will be desirable to find an answer to the question of the influence of the shape of the dissolved unit. Since rubber derivatives and substitutes are soluble in non-polar or slightly polar liquids to give systems of low electrical conductivity, it is not unnatural that the start was made with these materials. In this report we present data for chlorinated rubber, a typical linear macromolecular colloid.

In the case of the linear polymers, the data will be more difficult to interpret because, in addition to the rotations of the molecule as a whole, we can expect restricted rotations or orientations of any polar atomic groups which are joined by single valence bonds within the molecular unit. As noted above, the experimental data for dilute solutions of several of the linear polymeric substances show a definite but constant orientation contribution of the solute to the dielectric constant of the solution over our wave-length interval, and it seems necessary to assume this additional type of orientation to account for the experimental data. Since the time constants characteristic of such group rotations would be low and the ordinary molecular orientation contribution is small, it is not surprising that a dispersion of dielectric constant was not observed with the solutions of low concentration.

At the higher solute concentrations a definite dispersion of dielectric constant has been shown to exist, and it is assumed that the dispersion is due to an orientation in the electrical field of the molecular kinetic unit of the chlorinated rubber about its long axis of revolution. From the time constant of the orientation an apparent molecular weight has been calculated and recorded. It is important to note in the tables that the times of relaxation obtained are independent of the concentration of the solute molecules and directly proportional to the coefficients of viscosity of the solvents, as is required by equation 3. This suggests that the effective resistance to the rotation of the large units will be measured with a reasonable degree of accuracy by the ordinary coefficient of viscosity of the medium. Thus, we can have confidence that the molecular weight result may have some significance; in other words, it appears to be of the proper order of magnitude.

Determinations of dielectric constant of chlorinated rubber solutions at longer wave lengths showed that the maximum or static value is reached at approximately $\lambda = 1000$ m. If we plot dielectric constant at this wave length as a function of concentration in benzene and carbon tetrachloride, straight lines with identical slope are obtained with molar dielectric constant increment $\vartheta \cong 30$. The dipole moment of the chlorinated rubber unit is calculated to be in the neighborhood of 12×10^{-18} E.S.U. Dielectric constant increment and dipole moment are very small when compared with the values for these quantities found for typical proteins. This can be understood when we remember that over the wave-length interval λ = 10 m to λ = 1000 m, a 7 per cent chlorinated rubber solution shows a 2 per cent change in dielectric constant, while a 2 per cent zein solution will give a dielectric constant variation of more than 40 per cent.

Departure from spherical form increases the frictional resistance to the rotation and translation of a particle of given volume in a viscous medium. We have made preliminary studies of the linear diffusion behavior of chlorinated rubber in solution, but of course weight values for the linear molecules calculated from diffusion by the equation for spherical particles must give a result which is anomalously high; furthermore, it will be variable with concentration. Diffusion constant data extrapolated to zero concentration of solute give a molecular weight value for chlorinated rubber which is roughly double that given by the calculation made by using the dispersion of dielectric constant data. In order to decide with certainty whether the electrical and molecular kinetic units of chlorinated rubber are to be identified with each other, it will be necessary to determine the osmotic pressure, or its equivalent, the sedimentation equilibrium value of the molecular weight. It is our intention to proceed at once with the necessary experiments.

SUMMARY

The dielectric behavior of solutions of chlorinated rubber in benzene and carbon tetrachloride has been investigated. At moderate solute concentrations evidence is found for a polarization due to the rotation of the molecular unit as a whole. The molecular weight calculated from dispersion of dielectric constant data for these solutions by assuming rotation about the long axis is believed to be of the correct order of magnitude. At all concentrations studied there is an additional polarization contribution to the dielectric constant (tentatively ascribed to restricted rotations of the recurring groups within the molecule in the electrical field), but a variation of this contribution with wave length (λ = 10 m to λ = 1000 m) is not observed. In dilute solution variation with wave length due to the ordinary molecular rotations in the electrical field can not be detected. Molar dielectric constant increment and molar dipole moment for chlorinated rubber are small.

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EQUILIBRIUM RELATIONS AND FACTORS INFLUENCING THEIR DETERMINATION IN THE SYSTEM K_2SiO_3-SiO_2

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In an earlier paper (2) the equilibrium relations at the liquidus, and to some extent those among the crystal phases occurring in this system, were described. Further work in this Laboratory disclosed that the liquidus relations for the disilicate $K_2Si_2O_5$ required modification for reasons which will be discussed below, and accordingly the opportunity was taken to work over the entire system. The new results are presented particularly from the point of view of emphasizing the factors which influence the attainment of equilibrium.

EXPERIMENTAL METHODS FOR THE LIQUIDUS

The methods of study remained the same as before, the liquidus being determined in all cases by the method of quenching. For details we refer to the earlier paper. All the mixtures studied were freshly prepared, crystallized dry, and the liquidus was determined on the crystallized material at once to avoid the disturbing effects produced by the absorption of moisture. For this reason we also have avoided the use of hydrothermal methods of crystallization used formerly to develop $K_2Si_4O_9$ and quartz crystals in the appropriate region of the system. The tetrasilicate, $K_2Si_4O_9$, was found to crystallize in the dry way with some reluctance at 680°C. to 700°C., the most advantageous procedure being alternate heating and crushing to distribute the nuclei formed throughout the mass of the preparation. Usually three crushings with intermediate heatings of about two hours' duration sufficed to produce an abundance of small $K_2Si_4O_9$ crystals. Quartz crystals, on the other hand, have never been obtained in this system by dry crystallization, and accordingly the silica liquidus at temperatures below 870°C. is determined for tridymite instead of quartz as the primary phase.

Preparations in this system, particularly those richer in K_2O than the disilicate, are very hygroscopic. As will be seen from later discussion, it is important that this factor be taken into special consideration, since moisture in the glasses tends to produce excessive large crystals upon devitrification, and thus to introduce inhomogeneity into the preparations.

TABLE 1

1. Composition and melting-point data

NUMBER	WEIGHT PER CENT OF SiO_2	TIME IN HOURS	t IN °C.	
			c	g
A. Solid phase: cristobalite				
51	95.0	1	1575	1579
52	95.0	½	1575	1579
53	93.0	1	1537	1541
54	92.0	1	1516	1518
55	91.0	1	1496	1499
90	94.0	2	1550	1555
91	93.0	2	1530	1535
92	91.5	3	1500	1505
93	90.0	3	1470	1475
B. Solid phase: tridymite				
56	89.0	1	1455	1460
57	86.0	1	1377	1382
58	82.0	3	1245	1250
59	78.9	12	1124	1129
60	77.0	12	990	994
61	75.5	24	888	892
62	74.4	24	825	828
63	73.4	100	767	769
4	77.5	12	1031	1036
7	74.8	16	829	838
9	73.7	24	778	782
93	90.0	3	1470	1475
94	88.0	2	1430	1435
95	86.0	5	1380	1385
96	84.5	4	1340	1345
97	83.0	5	1280	1285
98	79.3	46	1130	1135
99	77.0	150	1010	1015
100	75.0	150	855	860
101	74.0	150	(785)	785
102	73.5	150	768	
102	73.5	24	770	
102	73.5	75	770	
102	73.5	160		770
C. Solid phase: $K_2Si_4O_9$				
63	73.4	100	766	769
64	73.0	15	766	768

TABLE 1—*Continued*

NUMBER	WEIGHT PER CENT OF SiO_2	TIME IN HOURS	*t* IN °C.	
			c	g
		C. Solid phase: $K_2Si_4O_9$—*Concluded*		
65	72.5	15	767	769
66	71.9	24	769	770
67	71.8	24	769	770
68	71.0	24	767	769
69	69.9	24	766	767
70	68.9	40	758	760
71	68.0	40	746	750
103	72.5	100	770	772
104	71.8	24	770	773
105	71.0	100	770	772
106	70.0	150	768	770
107	69.0	150	760	762
108	68.0	150	749	752
		D. Solid phase: $K_2Si_2O_5$		
72	67.3	20	762	765
73	66.9	24	770	773
74	66.0	5	811	813
75	64.0	5	896	898
76	62.1	2	952	954
77	60.0	2	1008	1010
78	58.0	2	1034	1036
79	56.4	2	1042	1046
80	56.1	2	1045	1046
81	56.0	2	1043	1045
82	54.0	1	1036	1039
83	52.0	1	1011	1014
84	49.9	1	(970)	970
85	48.4	1	918	920
86	46.4	1	824	828
109	67.0	150	775	(775)
110	66.0	3	815	820
111	64.0	2	900	905
112	62.0	2	960	965
113	60.0	2	999	1004
114	58.0	2	1037	1042
115	56.1	1	1043	1045
116	54.0	2	1037	1042
117	52.0	2	1012	1017
118	50.0	2	975	980
119	48.0	2	915	920
120	46.0	2	815	820

TABLE 1—*Continued*

NUMBER	WEIGHT PER CENT OF SiO_2	TIME IN HOURS	t IN °C.	
			c	g
D. Solid phase: $K_2Si_2O_5$—*Concluded*				
121	62.2		952	
122	66.1		815	
22	65.6	2	837	842
23	64.8	4	876	880
24	63.7	5	897	901
E. Solid phase: K_2SiO_3				
87	44.9	2	787	796

2. Eutectic data

NUMBER	t IN °C.	TIME IN HOURS	CONDITION
(a) $K_2Si_4O_9$–Tridymite			
9			Precrystallized sample had both $K_2Si_4O_9$ and tridymite, some glass
	766	10	$K_2Si_4O_9$, tridymite, little glass
	768	14	Tridymite, much glass, eroded fragments of $K_2Si_4O_9$
63			Precrystallized sample had $K_2Si_4O_9$ and tridymite
	765	16	$K_2Si_4O_9$ and tridymite in sharply grown crystals
	767	8	No $K_2Si_4O_9$. Tridymite remnants in glass
	766	100	Both $K_2Si_4O_9$ and tridymite, some glass
	769	100	Glass only
(b) $K_2Si_2O_5$–$K_2Si_4O_9$			
73			Precrystallized sample had both $K_2Si_2O_5$ and $K_2Si_4O_9$
	742	24	Both kinds of crystals, little glass
	746	24	Much glass and $K_2Si_2O_5$; no $K_2Si_4O_9$
(c) K_2SiO_3–$K_2Si_4O_9$			
87	771	2	Completely crystalline
	787	2	Much glass and K_2SiO_3
	796	3	All glass

TABLE 1—*Concluded*

3. Fixed points in system: K_2SiO_3–SiO_2

CRYSTALLINE PHASES	REACTION	PER CENT SiO_2	*t* IN °C.
Cristobalite	Melting	100	1713
Cristobalite-tridymite	Inversion	89.7	1470
Tridymite-quartz	Inversion	74.9	870
Tridymite-$K_2Si_4O_9$	Eutectic	73.6	767
Quartz-$K_2Si_4O_9$	Eutectic	(72.5)	(769)
$K_2Si_4O_9$	Melting	71.84	770
$K_2Si_4O_9$–$K_2Si_2O_5$	Eutectic	67.6	742
$K_2Si_2O_5$	Melting	56.05	1045
$K_2Si_2O_5$–K_2SiO_3	Eutectic	45.5	780
K_2SiO_3	Melting	38.94	976

Compositions are derived from data on synthesis. All preparations were precrystallized for quenching work. Under the heading of temperature c = crystals and glass in quenched sample, g = glass only. Time = approximate time of treatment of quench.

EXPERIMENTAL RESULTS FOR THE LIQUIDUS

Data essential to the defining of the liquidus and eutectic compositions and temperatures are collected in table 1, and are graphically represented in figure 1. To avoid confusion in the diagram points from the earlier publication have not been included in the figure.

Comparison of the earlier data with those now presented discloses a considerable modification in the disilicate liquidus. The differences are beyond the ordinary errors of determination; the analysis of the factors responsible, however, is preferably reserved until after the discussion of the next section of the paper.

THERMAL ANALYSIS OF REACTIONS IN THE CRYSTAL PHASES

1. Apparatus

The arrangement employed is illustrated in figure 2. The essential parts are (*1*) a differential thermoelement assembly using a Pt–90 Pt 10 Rh measuring element, and a 90 Pt 10 Rh–40 Pd 60 Au–90 Pt 10 Rh differential element, and (*2*) an interchangeable container for the sample consisting of a 5-g. platinum crucible provided with a reëntrant nipple which fits snugly over the triple junction of the measuring and differential elements. The neutral body is a platinum capsule. The various wires are suitably insulated by refractory capillary tubing. Connection to a selecting switch and Feussner-type Wolff potentiometer is made in the usual way by means of cold junctions kept in ice. The scale sensitivity was 1 microvolt per division.

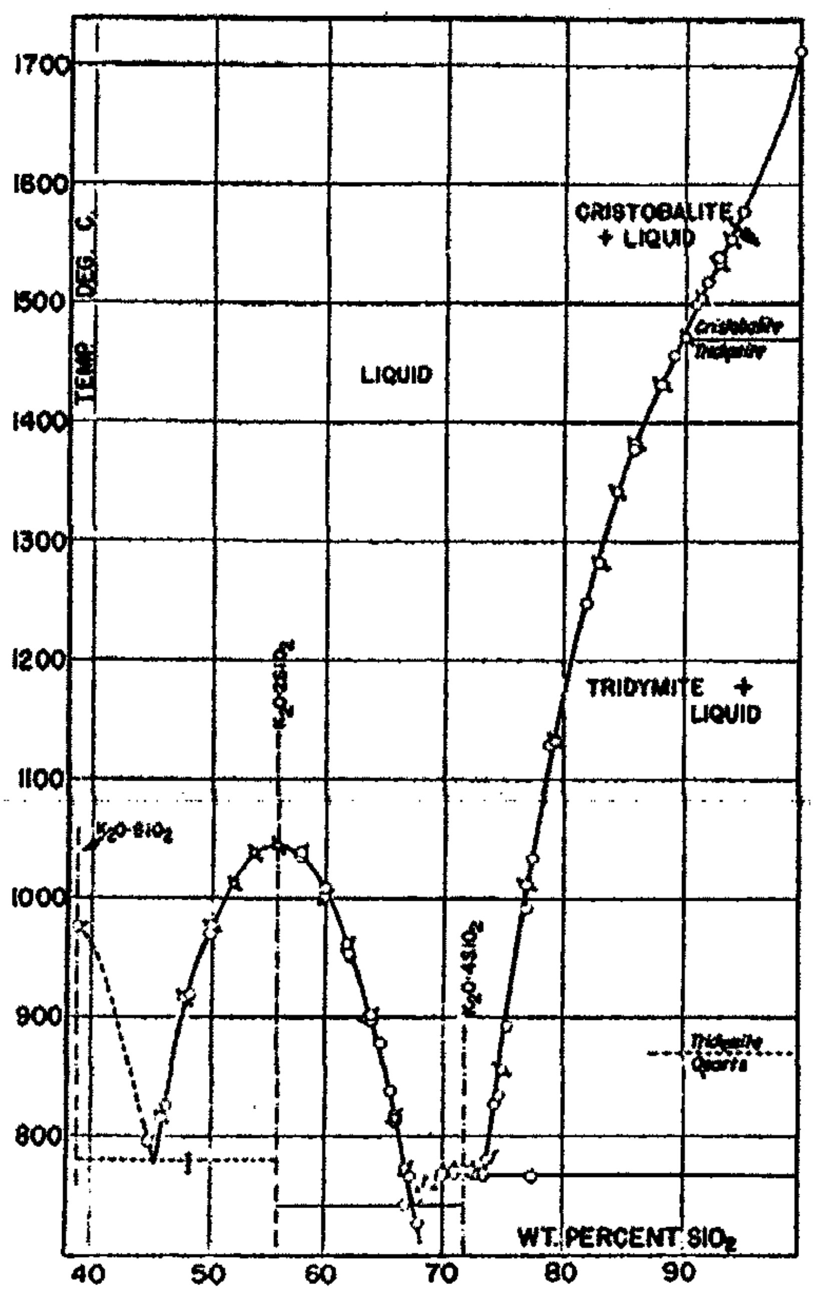

FIG. 1. Liquidus relations in the system, K_2SiO_3–SiO_2. Plain and marked circles refer to different series of preparations in table 1.

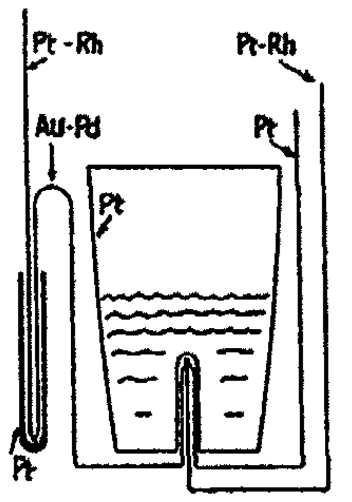

FIG. 2. Diagram of the thermoelement and container assembly for differential thermal analysis of silicate preparations.

2. *Reversible inversions in crystalline* $K_2Si_2O_5$ *and* $K_2Si_4O_9$

In the earlier paper a reversible inversion occurring at 590–596°C. in $K_2Si_2O_5$ was reported. Later, Goranson and Kracek (1) measured, under various pressures, a reversible inversion in $K_2Si_4O_9$, occurring at 592°C. ± 2°

at the pressure of 1 atm. Further measurements were made over an extended range of compositions, with the results summarized in table 2.

From the data presented in table 2 it may be concluded that the equilibrium inversion temperatures are 592°C. ± 2° near $K_2Si_4O_9$, and 594°C. ± 2° near $K_2Si_2O_5$. Typical measurements are illustrated in figure 3.

TABLE 2

Inversions in crystalline $K_2Si_2O_5$ *and* $K_2Si_4O_9$

PER CENT SiO_2 IN PREPARATION	AVERAGE TEMPERATURE OF PEAK OF THE ARREST	
	Heating	Cooling
	°C.	°C.
77.5	593.0 ± 1	590.5 ± 1
71.8*	593.8	590.5
66.9	593.0	590.0
60.0	595.5	592.0
56.1**	595.5	592.0
54.0	595.5	591.5
52.0	595.5	591.5
46.4	596	591
46.1	595	592

* The asterisks mark the compounds $K_2Si_4O_9$ and $K_2Si_2O_5$.

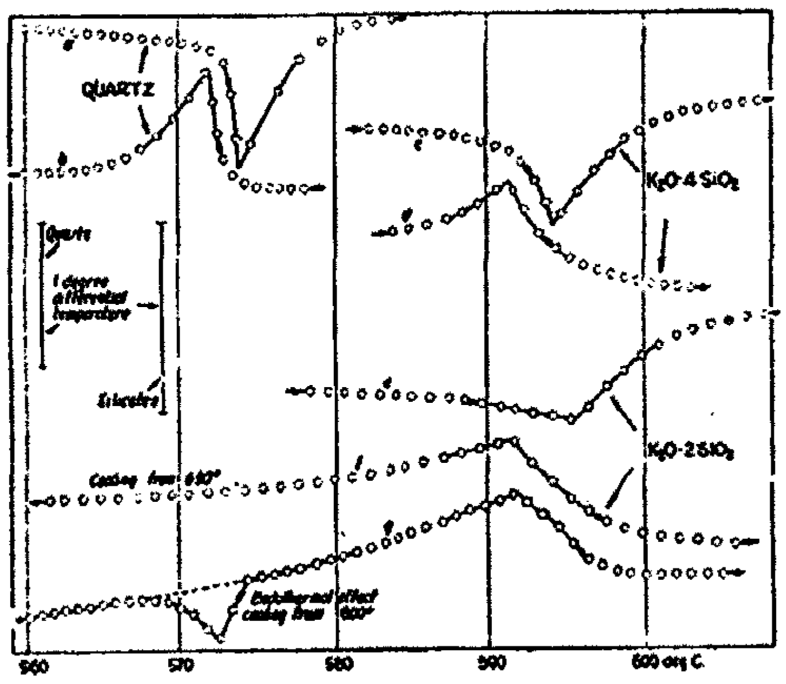

FIG. 3. Typical thermal analysis curves of crystal inversions in quartz, $K_2Si_4O_9$, and $K_2Si_2O_5$. Arrows indicate whether heating or cooling.

The characteristics of these inversions resemble those of the high-low quartz inversion at 573°C. ± 1°. The latent heat of inversion in the tetrasilicate is given by Goranson and Kracek as 2.3 ± 0.3 cal. per gram. Measurements by the same method yield 1.2 ± 0.5 cal. per gram for the latent heat of inversion in the disilicate, and 2.9 ± 0.3 cal. per gram for that in quartz. The value for quartz is in good agreement with the figure usually assumed.[1]

An interesting phenomenon observed in connection with the inversion in $K_2Si_2O_5$ is the occurrence of the small *endothermal* effect on *cooling* from *above* the eutectic temperatures, illustrated by curve g in figure 3. This endothermal effect has not been observed on cooling completely crystalline preparations from temperatures *below* the eutectics. Its location is somewhat variable, occurring always below 585°C. The effect may be due to liberation of a small amount of moisture, absorbed from the air (*vide infra*).

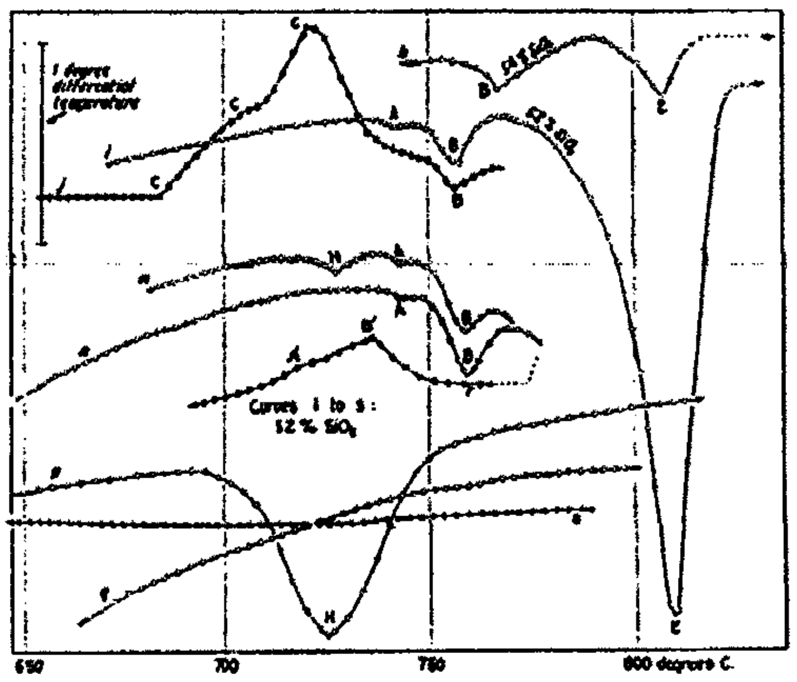

FIG. 4. Typical thermal analysis curves for inversions in K_2SiO_3 (curves h, i, m, n, r), crystallization of K_2SiO_3 in the presence of crystalline $K_2Si_2O_5$ and undercooled melt (CCC on curve j), and the dehydration of a preparation containing crystalline $K_2Si_2O_5$ and undercooled hydrated melt (curve p). For details consult the text.

3. Phase reactions dependent on the presence of crystalline potassium metasilicate, K_2SiO_3

Preparations of 46 to 56 per cent SiO_2, when completely devitrified, contain crystalline K_2SiO_3 and $K_2Si_2O_5$. In this region of compositions we previously reported arrests at 770–775°C., and at 805–815°C. With the present more sensitive experimental arrangement we find in this region: (*a*) the $K_2Si_2O_5$ inversion at 594°C. ± 2°; (*b*) two small reversible inversions, with some tendency towards delayed occurrence, at 740°C. ± 5° and 760°C. ± 10° on heating, 732°C. ± 2° and 717°C. ± 2° on cooling (see A, B, A′, B′ of figure 4); (*c*) eutectic melting of K_2SiO_3 beginning near 780°C. and ending at 805–815°C., depending upon the rate of heating (see E of figure 4).

When such preparations containing crystalline $K_2Si_2O_5$ and melt are

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[1] Sosman (3) gives 2.5 cal. per gram for quartz.

cooled from above the eutectic temperature, there is no arrest until the 594°C. inversion in $K_2Si_2O_5$, which then is always followed by the small endothermal effect below 585°C. K_2SiO_3 exhibits accordingly a considerable reluctance to crystallize; even after crystallization has begun, the rate is low, as shown by CCC in curve j, figure 4. The transitions A,A′, B,B′ occur only when crystalline K_2SiO_3 is present.

4. *Effect of absorbed moisture*

Preparations in the disilicate region, and particularly those of less than 56 per cent SiO_2, when kept in the apparatus at temperatures up to 500°C. absorb water vapor from the atmosphere if the air is even moderately humid. This moisture is slowly evolved with the absorption of heat on heating, beginning at about 700°C.; see H on curves m and p, figure 4. Curve p represents measurements on a 52 per cent SiO_2 preparation kept at about 450°C. for twenty-four hours in a summer atmosphere. The preparation contained crystalline $K_2Si_2O_5$ and glass, K_2SiO_3 having first been destroyed by heating above 850°C. and cooling rapidly. Curves q and s, figure 4, represent corresponding measurements in a dry winter atmosphere.

5. *The thermal arrest*

Search for the thermal arrest previously reported at 980–995°C. was made with a 60 per cent SiO_2 preparation whose liquidus is 1009°C. The curve obtained was similar to that of preparation 28, figure 3 of the previous paper (reference 2, page 1877). Careful repetition of the experiment showed that there is no reproducible arrest at 980–995°C., but that the temperature differential begins to change rapidly here owing to a delayed melting of the bulk of $K_2Si_2O_5$ crystals on approach to the liquidus, which was found to be 1012°C. and 1016°C. in two trials by thermal analysis.

EFFECT OF ABSORBED MOISTURE ON THE DETERMINATION OF THE LIQUIDUS

Vitreous K_2O–SiO_2 preparations are exceedingly hygroscopic; the moisture is not merely adsorbed on the surfaces of grains, as is the case with most ordinary glasses, but penetrates into the interior of the grains in consequence of their high aqueous solubility. These preparations, preserved over potassium hydroxide in desiccators, gradually absorb moisture, which, as has already been shown in the thermal analysis experiments, is driven out only at relatively high temperatures. This moisture may affect the experimental results in at least two important aspects. The first of these is the effect upon the composition of the mixtures; the second is the effect upon crystal growth.

In the former publication we reported compositions of the mixtures based on analysis by evaporation with hydrofluoric acid and sulfuric acid, the preparations having been dried at about 500°C. The results of analysis differed from compositions derived by synthesis by as much as 1 per cent in the cases of compositions from 45 to 56 per cent SiO_2; in the more siliceous mixtures, however, the analytical and synthetic compositions agreed to within a very small error. In view of the information now available, the discrepancy evidently arose from incomplete expulsion of moisture.

The second effect mentioned above, namely, the effect of absorbed moisture upon crystal growth, is of importance for a different reason. Moisture in the preparation facilitates the nucleation and growth of crystals remarkably, as is well known from experience with hydrothermal crystallization. While this is advantageous in certain cases, it also tends to produce exceedingly large crystals, and thus to introduce inhomogeneity if the composition of the crystals is markedly different from the bulk composition of the preparation. If the viscosity of the melt is high, it will then be practically impossible to determine the correct liquidus temperature on such a preparation. The discrepancies between the former and the new results in the region from 60 to 69 per cent SiO_2 of the system are ascribable to this cause. As an example, we quote the results on preparation 21 of the former paper (2). The composition is 66.03 per cent SiO_2 by synthesis, 66.0 by analysis; former liquidus determination (reference 2, page 1866) showed crystals and glass up to 920°C., and glass only at 926°C. Glass from the desiccator was dried at 740°C., powdered, then melted at above 1050°C., powdered, and crystallized at 790°C. Quenches at 813°C. and 816°C. contained uniformly distributed small crystals of $K_2Si_2O_5$ in glass, and at 820°C. only glass. This is in good agreement with results on new preparations 74 and 110 of table 1. Another portion of the glass from the desiccator was crystallized at 740°C. without remelting. The crystals were large; attempts to dissolve them in the melt at 825°C. showed that abundant crystallization persisted even after several days at the temperature of the experiment. Examination of other old preparations in the region of compositions from 60 to 68 per cent SiO_2 led to parallel results. It seems reasonable to draw from such facts the conclusion that absorbed moisture is responsible for the growth of the excessively large crystals and the corresponding introduction of inhomogeneity, which then leads to the determination of a false liquidus temperature. In such hygroscopic systems as this, the only certain remedy is to employ freshly melted preparations for the crystallizations preparatory to liquidus determination.

SUMMARY

Equilibrium relations at the liquidus in the system, K_2SiO_3-SiO_2, have been reinvestigated, and the influence of absorbed moisture upon the

crystallization phenomena has been studied. In addition to these, a study has been made of inversions in the crystalline compounds K_2SiO_3, $K_2Si_2O_5$, and $K_2Si_4O_9$.

A special acknowledgment is due to our colleagues J. F. Schairer, who prepared and studied many of the preparations reported upon in this paper, and Earl Ingerson, for help in some phases of the investigation.

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A SIMPLIFIED TECHNIC FOR THE DETERMINATION OF CONTACT ANGLES AND ITS APPLICATION TO STUDIES ON WETTING[1]

31-12

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During the progress of an investigation on the properties of tooth surfaces it was found desirable to obtain information regarding the relative wetting characteristics of these surfaces. The method used was a relatively crude "horizontal-plate" technic for determining the angle of contact in the system solid–liquid–air. At the start it was felt that only approximate values would be obtained, but subsequent studies indicated that surprising accuracy could be secured. The data reported indicate the accuracy to be expected and illustrate the adaptability of such a method to allied problems.

The horizontal-plate method, as discussed and compared with other common technics by Bartell and Hatch (3), appears to have definite limitations. Its use is limited to the investigation of plane surfaces which in many instances may be difficult to obtain. Much difficulty is introduced where dual contact angles occur. For instance, the observed contact angle of water on galena varied from an "advancing" angle of 90° to a "receding" angle of 0°. The apparatus used for measuring the angle is rather elaborate and may not be readily accessible to many laboratories. Emphasis has been placed on the advisability of the determination being made in an atmosphere saturated with the liquid under observation. The angle formed has usually been calculated from the measured height and radius of the drop or from the measured radius and volume (8). Photographing the drop in contact with a solid and projection or enlargement of the image has made possible the direct measurement of angles by means of a protractor (14).

Our apparatus for direct measurement of contact angle consists of an arc lamp, condensing lens system, adjustable stage, and a small picture frame, and is shown schematically in figure 1. A thin sheet of paper is fastened to the picture frame by means of thumb tacks, so that it lies flat

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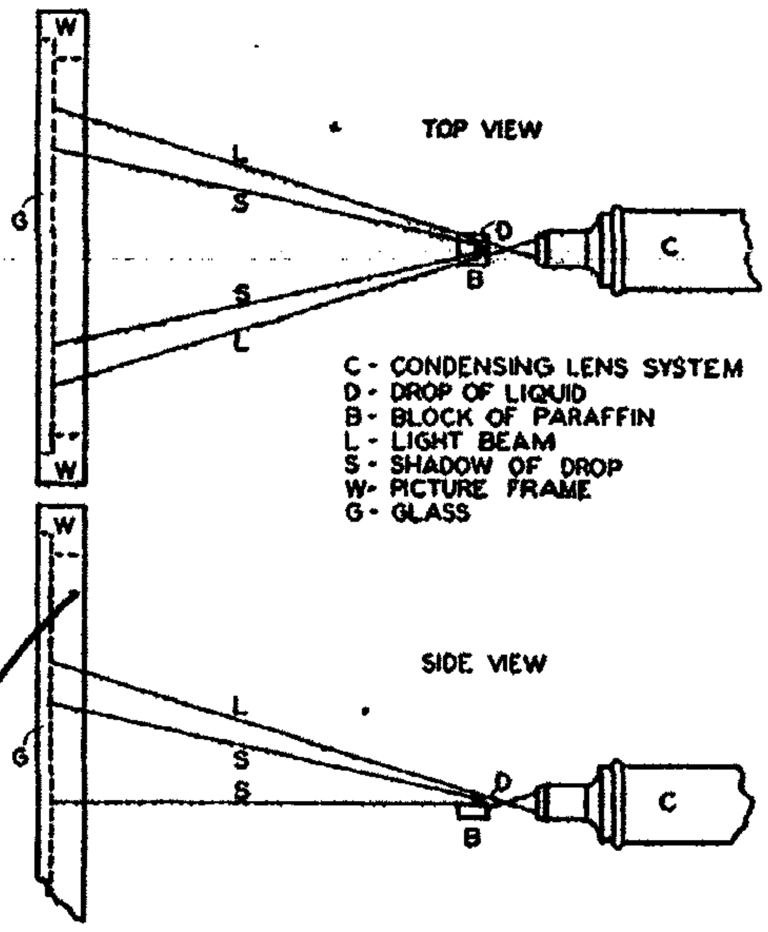
against the glass. The measurements are carried out in a darkened closed room. The beam of light from the arc lamp is passed through the condensing lens across the plane surface to be measured. The plane surface is placed beyond the focus of the lens and a drop of liquid to be tested is placed on the surface in the path of the beam. The image of the drop is projected through the glass and paper where it may be outlined in pencil by hand. The paper may then be removed and the contact angle measured by means of a tangent meter. Depending on the size of the drop and its position between the focus of the lens and the picture frame, the magnification may vary from about 20 to 30 diameters. The condensing lens system and carbon arc lamp from a Zsigmondy ultramicroscope system are admirably adapted to the method. For some work a microscopic stage adjustable in the vertical axis is adequate. Where small objects with only one plane surface are to be used their base may be embedded in a paraffin block mounted on a leveling holder adjustable in the horizontal plane. As recommended by Mack (8), small drops delivered by the capillary point of a small pipet are used in order to insure the observed angle being the advancing angle rather than something in between this and the receding angle. It was found that drops varying in size up to 0.3 cm. in diameter gave satisfactory results. Careful control of humidity or temperature is not essential. The drawing can be completed in less than thirty seconds after the drop has come in contact with the surface.



6.508

Fig. 1. The apparatus

Under such conditions evaporation can be neglected in the case of water and aqueous solutions, in fact, the contact angle shows no appreciable change over a period of two to three minutes.

EXPERIMENTAL

In order to test thoroughly the accuracy of the method a large number of determinations were made with the system paraffin–water–air. Table 1 illustrates the results obtained.

Two kinds of paraffin blocks were used; those termed "melted" were formed by melting paraffin (ordinary Parowax), allowing it to settle, and then pouring it into paper molds of approximately 1 cm.^{3} in volume. After solidification one surface was shaved smooth with a microtome. The blocks termed "natural" were simply cut out of a paraffin block by means of a razor blade, and one surface was smoothed with a microtome. While the individual determinations on each block show variation the means agree closely, and the mean of 105.1° for all ninety determinations on nine blocks agrees with the value of approximately 105°, reported in the literature (2, 17, 1, 4). It is somewhat divergent from the values of 108.0° and 109.8° reported by Mack and Lee (9), and 108° by Nietz (12). Another series was run using microscope slides which were dipped into melted paraffin and allowed to drain and solidify in air. The mean value of thirty-nine determinations of water on this surface was 110.4°. This

TABLE 1

Contact angles of water on paraffin

EXPT. NO.	TREATMENT	NUMBER OF REPLICATES	CONTACT ANGLE		
			Highest value	Lowest value	Mean value
			degrees	*degrees*	*degrees*
1 Block	Melted	9	108.0	103.5	105.5
2 Block	"Natural"	12	108.0	103.5	105.0
3 Block	Melted	16	108.0	102.0	105.6
4 Block	Melted	14	109.0	103.5	106.3
5 Block	"Natural"	14	106.0	100.0	104.3
6 Block	Melted	2	105.5	104.5	105.0
7 Block	Melted	14	106.5	100.5	103.3
8 Block	"Natural"	4	108.0	105.0	106.1
9 Block	Melted	5	109.5	105.0	106.4
10 Slide		7	112.0	107.0	110.4
11 Slide		8	115.0	107.0	110.4
12 Slide		9	112.0	107.0	110.3
13 Slide		7	115.0	108.0	110.9
14 Slide		8	113.0	106.0	110.3

compares favorably with the recent values of Wenzel (18) of 109.5° to 113.2° for paraffin on glass or metal slides. At a later date and with a different sample of paraffin we found an angle of 115° for paraffin on a glass slide.

Table 2 compares our values with those recorded in the literature for several substances in contact with water. It is apparent that the proposed method gives results which compare very favorably with reported values. It is interesting to note that Bartell and Hatch (3) report that it is very difficult to obtain the advancing angle of 90° for water on galena when using the horizontal-plate technic. We found it almost impossible to get any value but 90° even when using somewhat faulted surfaces or relatively large drops.

TABLE 2

Comparison of values found with values reported in the literature for the contact angle of water on various solids

SUBSTANCE	TREATMENT	CONTACT ANGLE		LITERATURE REFERENCE
		Found	Literature	
		degrees	*degrees*	
Galena	Fresh cleavage surface	90.0	90	(3)
Benzoic acid	"Chip"	61.5	65	(12)
Stearic acid	Non-polar	105.0	106	(12)
			100–105	(2)
Palmitic acid	Non-polar	105.0	111	(12)
			100–105	(2)

Evaluation of the wetting capacity of soaps

For these determinations the contact angles between paraffin and the sodium salts of a series of fatty acids were measured. The solutions employed were 0.01 molar throughout. The paraffin surface used was obtained by immersing a glass slide in hot paraffin and then allowing it to drain and solidify. The water-paraffin contact angle was 115°. Figure 2 shows the results obtained. A progressive slight decrease in contact angle is evident with sodium butyrate, sodium caproate, and sodium caprylate. With increasing length of the carbon chain following the eight-carbon atom compound, sodium caprylate, there is a progressive rapid increase in wetting. The fact that this increase approaches a straight-line relationship becomes increasingly significant when it is seen that by extrapolation theoretical complete wetting of paraffin might be postulated with a 0.01 molar solution of sodium palmitate. It is unfortunate that the insolubility and tendency to gel of both 0.01 molar sodium palmitate and 0.01 molar stearate prevent their use by this simplified technic. The first part of the curve corresponds roughly to the observed effect of adding the various sodium salts on lowering the surface tension of water (7). It has been emphasized (13) that in order for a surface to be wet by a liquid, reduction of the "solid-liquid" interfacial tension is of primary consideration in order to arrive at conditions such that the "solid-air" surface tension shall be greater than the sum of the "liquid-air" surface tension and "solid-liquid" interfacial tension. Data of Donnan and Potts (5) illustrate that the presence of the sodium salt of myristic acid in the aqueous phase brings about a pronounced reduction in the interfacial tension "paraffin-oil-water" over that induced by sodium laurate. Figure 2 gives a clear picture of the wetting characteristics of soap solutions.

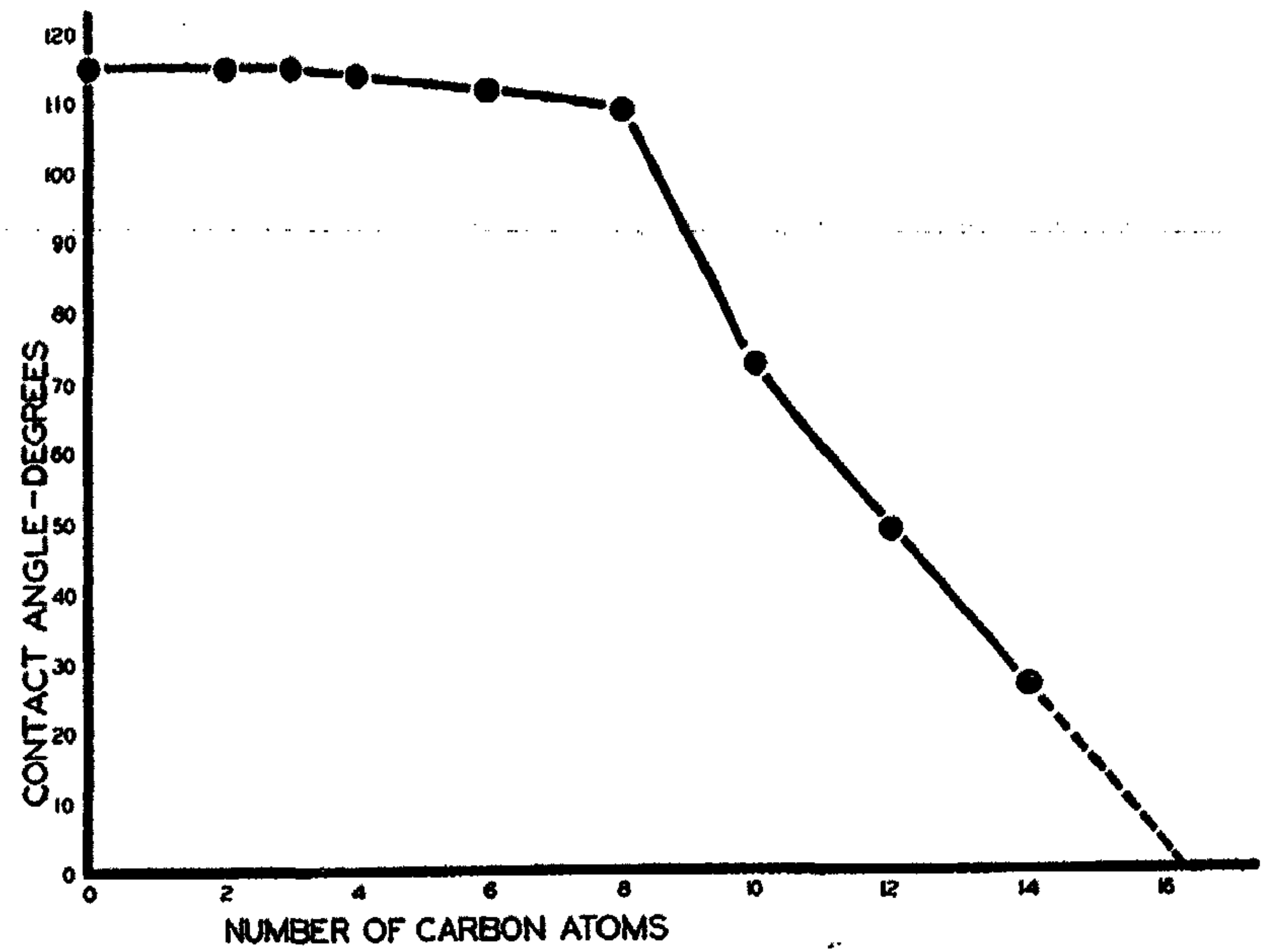


FIG. 2. Contact angles between paraffin and the sodium salts of a series of fatty acids

Evaluation of the degree of polarity of surfaces

Theoretically the angle of contact between water and a solid surface should give a quantitative measurement of the polarity of that surface. Adam and Jessop (2) attempted to produce polar surfaces on solids whose surface is normally not polar in nature, such as paraffin and palmitic and stearic acids, the degree of polarity being measured by the "water-solid" contact angle. Their efforts were not entirely successful. If a polar surface could be produced its presence should be easily demonstrated by means of the contact angle. Stearic and palmitic acids were chosen as substances whose surfaces might be transformed to the polar condition.

Polar surfaces were obtained by the following procedure: Glass slides were very carefully cleaned and dried without contamination. The fatty acid was carefully melted on the glass surface and by tilting allowed to run down to one end. It was then permitted to solidify in this position, giving a lump of material. By loosening one edge with a razor blade the mass may be lifted from the glass, the under side being a smooth plane surface well adapted to the horizontal-plate method. Table 3 illustrates the results obtained. The value for highly polar benzoic acid is inserted for comparison. It is obvious that the surfaces of stearic and palmitic acids which were originally in contact with the glass are both highly polar, the higher value for palmitic acid being probably attributable to traces of impurities present in it. The "non-polar" surfaces are those of the "air-acid" when the melted acid solidifies on a glass slide. While the drop of water did not appreciably wet the polar stearic acid surface on contact it started to spread immediately, the equilibrium angle being reached in about fifteen seconds.

TABLE 3

Contact angles of polar and non-polar surfaces against water

SUBSTANCE	SURFACE	CONTACT ANGLE
		degrees
Stearic acid	Non-polar	105.0
Stearic acid	Polar	64.0
Palmitic acid	Non-polar	105.0
Palmitic acid	Polar	71.3
Benzoic acid	Polar	61.5

Wetting properties of cholesterol towards water

During investigations on the electrophoresis of sterols, Moyer (11) concluded that some of the phenomena observed must be due to changes in wetting of the crystals. We accordingly investigated this phenomenon by contact-angle technic. Two types of cholesterol surfaces were used, one being formed in contact with glass in order to form a "polar" surface. A different surface was formed by allowing melted cholesterol to solidify in the hollow of a "hanging drop" slide. In the latter case a plane surface was secured by shaving the upper surface with a clean sharp razor blade. Readings were made on the "chip" (surface formed in contact with glass) immediately and at the end of a twelve-hour period. The mean angles were 76° and 75.8°, respectively. This surface showed no tendency to wet more during the three minutes of contact permissible before evaporation distorted the angle. In the case of the shaved surface an entirely different behavior was observed. The drop spreads slowly over the surface and may or may not reach equilibrium before the end of three minutes. The mean value of a number of determinations made at the end of a two-minute interval from time of contact was 60°.

Since cholesterol appears to wet more on standing in contact with water, the same shaved surface of cholesterol was immersed in water for twenty-four hours, dried in the air, and re-read at various time intervals. Table 4 shows the results obtained. The whole surface of this cholesterol mass appears to be remarkably uniform in its wetting as measured immediately on contact. However, the speed of wetting varies rather pronouncedly with different surface areas. Of most significance is the rapidity with which the contact angle decreases. While it has been observed that certain surfaces tend to become more wetted on standing in contact with water (15), this phenomenon has been considered to be the result of rather long periods of contact. Obviously with surfaces such as cholesterol time intervals of minutes rather than hours or days are significant.

TABLE 4

The increase in wetting (change in contact angle) of a shaved cholesterol surface while in contact with water

PLACE ON THE SURFACE	INTERVAL BETWEEN CONTACT AND MEASUREMENT OF CONTACT ANGLE				
	0.5 min.	1.0 min.	1.5 min.	2.0 min.	3.0 min.
	degrees	*degrees*	*degrees*	*degrees*	*degrees*
1	81.0	81.0	81.0	81.0	74.0
2	78.0	55.0	52.0	49.0	49.0
3	82.0		46.0	38.0	
4	81.0				76.0
5	85.0				74.0
6	80.0				65.0
7	81.0				64.0

The wetting capacity of leaf surfaces

It has been recognized by various workers (16, 10, 6) that the ability of insecticidal and fungicidal solutions to wet leaf surfaces is of prime importance in considering the effectiveness of sprays. Attempts to apply the contact-angle technic have not been completely satisfactory. With the coöperation of Mr. J. H. Pepper of the Montana Experiment Station a method was developed which has given satisfactory results. Briefly, the technic consists of mounting small sections of leaves on the plane surfaces of small paraffin blocks. The paraffin surface is lightly smeared with a nitrocellulose adhesive and the freshly cut leaf segment placed on this and gently pressed down so as to give a rigid, non-curling surface. Contact angles with the desired solution are run immediately. Since the entire procedure may be performed very rapidly it is believed that such factors as leaf drying or reaction with the cement may be neglected. By this means the behavior of one kind of leaf toward various solutions or the behavior of various kinds of leaves toward the same solution may be easily and quantitatively determined. It is obvious that this technic is limited to relatively smooth surfaces. Cabbage and ivy leaves were used successfully in an investigation of their wettability by water and by certain arsenicals.

The wetting properties of tooth surfaces

For this study extracted human teeth were used. A plane surface was obtained by grinding with paper disks and a dental drill. Just sufficient grinding was done to obtain the smallest usable plane surface, care being taken that a surface of enamel was retained without exposing the dentine. The surfaces were cleaned thoroughly before use with soap and water and repeated rinsings. After drying in air they were inserted into the holder in such a manner that the plane surface was horizontal, and contact angle measurements made according to the usual procedure. Table 5 shows typical results with this type of surface. It would appear that the measurement of contact angles is well adapted to investigations dealing with the ability of solutions to wet tooth surfaces.

TABLE 5

Angles given by various solutions in contact with a tooth surface

SOLUTION	CONCENTRATION	CONTACT ANGLE
		degrees
Water		81.0
Sodium caprylate	0.01 molar	74.0
Sodium oleate	0.01 molar	53.0
Sodium lauryl sulfate	0.01 molar	30.0

SUMMARY

1. A simple, adequate horizontal-plate technic for determining contact angles in the system solid–liquid–air is described and its accuracy demonstrated.
2. Applications of this method are illustrated and discussed with reference to (*a*) the evaluation of the wetting capacity of soaps, (*b*) the evaluation of the degree of polarity of surfaces, (*c*) the wetting properties of cholesterol toward water, (*d*) the wetting capacity of leaf surfaces, and (*e*) the wetting properties of tooth surfaces.

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LIQUID DROPS ON LIQUID SURFACES

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It is a common observation that drops of a liquid may exist for some time on the surface of the same liquid in bulk before coalescence occurs. Such drops are frequently observed during the process of refluxing an organic solvent, the splashing of raindrops in puddles, the drip of water from oars, or the splashing of sea water against a rocky shore. They are sufficiently interesting to have attracted the notice of several men whose observations have appeared from time to time in the scientific periodicals, e.g., Lord Rayleigh (8), Reynolds (9), Kaiser (5), Seth (10), and Mahajan (7).

The drops are formed in two distinct ways. The falling drop may fail to penetrate the surface of the bulk liquid and may rest there, preserving its identity for a matter of many seconds, or it may fall with such force that the surface is penetrated and a splash occurs with the consequent formation of several small drops which may draw their substance from the bulk liquid rather than from the falling drop. Drops of the first kind, known as primary drops, are the ones to which we have directed our attention.

A brief summary of the experimental methods and results will be followed by a discussion of these results in the light of the theories which have been proposed by previous writers and the one which is brought forward in this paper.

EXPERIMENTAL MATERIAL

No difficulty is experienced in forming primary drops by allowing liquid contained in a capillary pipet to drip slowly upon the bulk liquid, the tip of the pipet being a few millimeters from the surface. Only in rare cases is there any doubt as to whether the drops actually form. They last from a couple of seconds up to nearly a minute. Attempts to measure the life of the floating drops proved futile because of exceedingly irregular results, although it is usually easy to tell qualitatively whether the drops are relatively "stable." Such records may be supplemented by tables of the one quantitative measurement available, namely, the "critical height," which is the maximum distance between the tip of the pipet and the surface of the bulk liquid for which the formation of primary drops will occur. Results of this sort were first obtained by Mahajan (7). The critical height is characteristic of the liquid under consideration and is also affected by the size of the capillary used and the temperature. It is reproducible within ±0.2 mm.

TABLE 1

Critical heights

LIQUID	FORMULA	CRITICAL HEIGHT
		mm.
o-Cresyl-*p*-toluenesulfonate	$CH_3C_6H_4SO_3C_6H_4CH_3$	20.3
Octyl ester of *N*-phenyl-*C*-dimethylglycine	$C_6H_5NHC(CH_3)_2COOC_8H_{17}$	20.3
Ethanol	C_2H_5OH	17.9
β-Diethylaminoethyl alcohol	$(C_2H_5)_2NCH_2CH_2OH$	15.4
n-Propyl alcohol	C_3H_7OH	14.5
Benzene	C_6H_6	14.5
Dimethylformamide	$HCON(CH_3)_2$	14.0
Cellosolve	$HOC_2H_4OC_2H_5$	13.9
Methanol	CH_3OH	13.7
Allyl cyclohexyl ether	$CH_2{:}CHCH_2OC_6H_{11}$	13.7
Acetone cyanohydrin	$(CH_3)_2COHCN$	13.6
Acetone	$(CH_3)_2CO$	13.0
o-Xylene	$(CH_3)_2C_6H_4$	10.9
Methylformamide	$HCONHCH_3$	10.3
Diethyl ether	$(C_2H_5)_2O$	10.0
Carbon tetrachloride	CCl_4	8.0
Perchloroethylene	$Cl_2C{:}CCl_2$ (?)	7
Triethylene glycol	$HOC_2H_4OC_2H_4OC_2H_4OH$	6.3
Formal glycerol	 $\underbrace{OCH_2CHOHCH_2O}_{CH_2}$	4.3
Water	H_2O	0.0
Formic acid	$HCOOH$	0.0
Ethylene glycol	$C_2H_4(OH)_2$	0.0
Glycerol	$C_3H_5(OH)_3$	0.0
Methylene chloride	CH_2Cl_2	0.0
Diallyl ether	$(CH_2{:}CHCH_2)_2O$	0.0
Methanol dropping on ethanol		10.9
Ethanol dropping on methanol		9.0

Table 1 shows the values of the critical height for various liquids which we tried. A value of zero indicates that such liquids do not form primary drops at all.

The original contribution of the present paper lies in the results obtained by dropping one liquid upon the surface of another. This has apparently never been tried before. The findings point to the necessity of revising previous theories of the existence of the drops and indicate an important correlation between the critical height and the molecular structure of the liquid.

The somewhat paradoxical result was found that *the more nearly alike the drop and bulk liquids are, the less likely they are to merge instantly.* In fact, unless the liquids show pronounced similarities, drops will not form at all. The three isomeric xylenes will form drops on one another, although not with equal facility. Table 2 shows the results obtained with a series of aliphatic alcohols. Methanol forms unstable drops on propanol, but propanol forms no drops on methanol. On the other hand, the pair ethanol-benzene shows no drop formation at all. At the extreme of dissimilarity, water, while it does not mix with kerosene, fails to form floating drops. Instead, the drops sink instantly to a level at which they are all but submerged and are then more slowly covered with a film of kerosene, after which they fall to the bottom. Similarly, kerosene drops do not maintain their spherical shape and float on water but flatten into a lens, thus, in a manner of speaking, doing their best to merge instantly.

TABLE 2

Drop formation of aliphatic alcohols

ALCOHOL DROPPED	ALCOHOL USED IN BULK					
	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isoamyl
Methyl	A[*]	AA	C	C	C	C
Ethyl	AA	A	D	D	D	D
Propyl			A		B	B
Isopropyl				A		D
Butyl			B		A	B
Isoamyl			B		B	A

[*] The letters express ease of formation of primary drops, A being normal.

In an effort to find how nearly alike the drop and bulk must be in order to permit floating drop formation, mixtures of benzene and ethanol were prepared and drops of ethanol and of benzene were allowed to fall upon them. Of course the drops altered the original concentration, but only to an entirely negligible extent. It was found that benzene would not form drops on the mixtures at all unless they were more than 90 per cent benzene, and an even higher percentage was necessary to permit formation of drops as stable as those of benzene upon benzene. Mixtures of 20, 40, 50, 60, and 80 per cent ethanol in benzene were tried on themselves and on each other. They formed drops on themselves as readily as a pure liquid upon itself, but they showed no drop formation on each other.

Evidently a chemically pure liquid is not essential for the formation of floating drops.

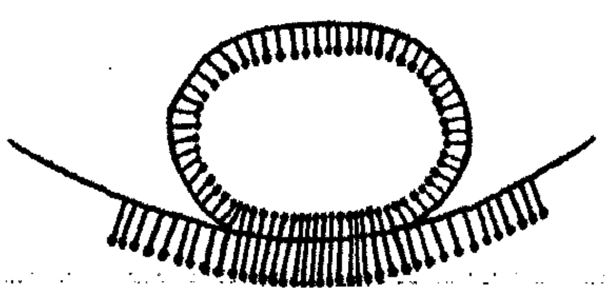
A most remarkable pair is methanol and ethanol. As might have been expected from their similarity, they form drops upon one another but, in contrast to the results previously presented, they actually work better on one another than on themselves. Thus drops of ethanol on ethanol last about five seconds. Drops of methanol on methanol last about the same length of time. Drops of methanol on ethanol last on the average fifty seconds, and drops of ethanol on methanol last about twenty-five seconds. The critical heights for these liquids upon themselves and upon each other, as shown in table 1, do not parallel this order of stability.

DISCUSSION

Previous theories advanced to account for floating drops have been based upon two hypotheses: electrical charges upon the drop and bulk resulting in a mutual repulsion, and the presence of a cushioning film of air or vapor which prevents the surfaces of drop and bulk from coming into intimate contact. While the plausibility of these two notions may be admitted as long as attention is directed to drops upon the bulk of the same liquid, it is not at all clear how the electrical charge or the cushioning film can exercise discretion and prevent the coalescence of a drop of benzene with benzene, while graciously permitting and even enforcing the coalescence of a drop of benzene with toluene. It is perhaps wrong to dispose of these hypotheses so cavalierly, since it can be demonstrated quite clearly that electrical effects strongly influence the existence of secondary drops, but the weight of evidence here presented shows unquestionably that some other factor is the dominating one.

In particular, the air or vapor film theory may be dismissed, because direct evidence shows that the drop and liquid are in actual contact and can exchange liquid even while the drop is floating. The drops of methanol upon ethanol are so long-lived that detailed observation is possible, and it is easy to distinguish the streams of denser methanol sinking through the mass of ethanol. A further evidence, drawn from the same pair of liquids, is as follows: Drops of methanol on ethanol are quiescent, such motion as they may have being too small to be noticed by simple visual observation. On the other hand, drops of ethanol upon methanol are in constant motion, just as a bit of camphor on water would be. The presumption is that the methanol, being denser and of higher surface tension than the ethanol, sinks away from the surface and does not tend to spread over it. Hence methanol, passing from its drop to the bulk of ethanol, would not contaminate the surface. The less dense ethanol spreads over the surface of the methanol and lowers its surface tension, just as camphor spreads over water, the resulting unbalanced tensions producing violent motion.

Such observations are obviously impossible with drops of a liquid upon itself, because of the lack of differences in surface tension, density, or refractive index, but it seems highly likely that a similar exchange of material can occur between the like surfaces. A less direct bit of evidence tending to the same conclusion is that some floating drops, instead of being absorbed instantaneously as usual, are absorbed stepwise, becoming successively smaller and smaller with quiescent stages in between. As many as three stages have been observed with drops of benzene on benzene. Occasionally the smaller drop remains in the position previously occupied by the larger one, but frequently the small drop is projected with some violence along the surface of the liquid and comes to a new resting place. This indicates that the barrier between the two surfaces has been broken locally and that much liquid has flowed from the drop through the gap, but, in spite of the fact that a channel of communication has been established, complete absorption does not take place. The surface forces of the diminishing drop are able to work upon it causing it to regain a spherical shape, and, unless the "break" was symmetrically located, making the new droplet shoot off laterally (see figure 1c). Similar phenomena have been observed to occur, although more rarely, with the ethanol-methanol pair, so that there can be little doubt that the cases are really analogous and that there is no film of air or vapor intervening between the adjacent surfaces.



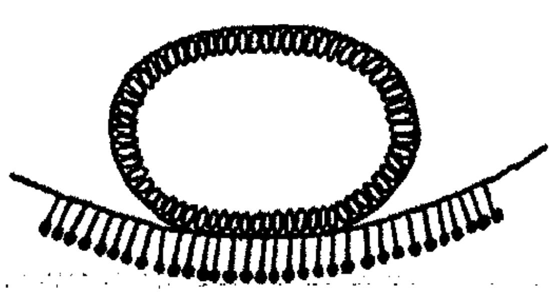


FIG. 1a. Illustrating a drop of an aliphatic acid resting on the surface of the acid in bulk, showing the "fit" of the two oriented films in contact. The drop is stable.

FIG. 1b. Illustrating a drop of benzene on the surface of a liquid aliphatic acid, showing the lack of "fit" across the interface. The drop is not stable.

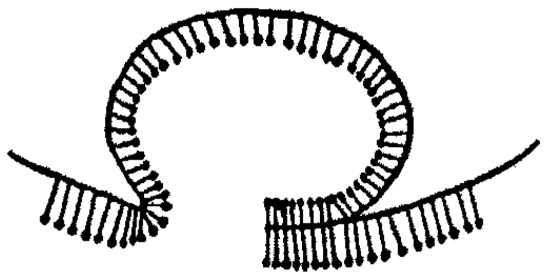


FIG. 1c. Illustrating a "break" in the interface, unsymmetrically located. The residual drop, if any, will shoot off violently to one side.

On the other hand, *some* barrier must exist, because the drop does not "wet" the bulk liquid in the ordinary sense of the word, that is, it fails to spread. The area of actual contact is very small, being limited to the surface just around the lowest point of the drop. Electrical forces might conceivably prevent the surfaces from coming into intimate contact, but that contact once established, no further difference of potential could exist and the drop would be absorbed instantly. The only barrier that can exist is a strongly oriented and relatively rigid film of molecules in the two surfaces concerned. This hypothesis is capable of explaining the results already obtained and of predicting qualitatively the behavior of liquids and pairs of liquids as yet untried.

It is appropriate to adduce other evidence indicating the existence of some such film in liquid surfaces. Among the more recent papers upon the subject may be mentioned the work of Alty and Mackay (1) on the evaporation and accommodation coefficients of water. Their results indicated that less than 4 per cent of water molecules impinging upon the surface of a water drop actually condenses upon it, and they explain this by assuming the liquid surface to be quasi-solid. Berdennikov (3) found that electron diffraction patterns of the surface of liquid mercury indicated the presence of numerous crystallites of hexagonal symmetry with the axis normal to the surface. The cybotactic phenomena described by Stewart (11) are also relevant. We may cite also the work of Langmuir (6) and Harkins (4).

Generalizing from these and similar experimental results, it is assumed that the surface of any liquid is quasi-solid, being composed of crystallites similar in a general way to the actual crystalline state of the substance in question. The surface must thus possess a certain rigidity combined with a flexibility permitting it to bend appreciably over distances large compared with the molecular units of which it is composed. It is analogous roughly to a skin of ice on the surface of a pond, permitting flat objects of considerable weight to be "skittered" over the surface, although it breaks readily if the weight falls from above a critical height or if the object has sharp points which cause intense localized forces.

The forces (apart from gravity) acting across the boundary between drop and bulk are molecular forces of the same nature as those acting between layers of molecules in a molecular lattice. Consider the crystal structure of an aliphatic acid such as stearic acid. Using the conventionalized representation of such a molecule with a round "polar" head for the carboxyl group and a long "non-polar" hydrocarbon tail, the structure is as follows: The molecules pair off by putting their heads together. The pairs arrange themselves side by side, thus presumably best satisfying the residual force emanating from the polar heads and the much weaker forces from the long tails. The *layers* of double molecules thus formed are then packed one on top of the other, and it is well known that these layers readily *slip* past one another, indicating a relatively very weak force across the boundary from layer to layer. Just such forces probably are exerted across the boundary between a drop of molten stearic acid and the surface of the bulk. In order for such an interface to "break," some disturbing unsymmetrical localized force must cause puckering of one or the other of the layers. But if the drop is identical in nature with the main bulk, the layers are identical in structure, and their fields of force are identical and will *fit* one another just as they might do in the crystal. Thus a certain stability is indicated, and the drop will float until some accident leads to a definite rupture of the surface film.

If the drop and bulk are not identical, then, even though the forces across the boundary are weak, the two fields of force will not *fit* and many local strains will be set up which readily disturb the surface film. This is represented (very diagrammatically) in figure 1, in which is shown the molecular structure of the surface films first for a drop of, say, stearic acid on itself, and second, for a drop of benzene upon stearic acid. The second case is inevitably one of great instability, and no accidental external force is necessary to break the film. Generalizing the idea, it might be predicted that two liquids which can form mixed crystals should also form drops upon one another. The converse would not necessarily be true, because our hypothesis demands only that the *force fields between layers* in the crystal be identical, whereas the condition for the formation of mixed crystals is that individual molecules of the one substance may be substituted for those of the other.

The phenomena of solution observed in connection with drops of methanol on ethanol and presumably operative in all cases are thought to be caused by the passage of material through the interstices between the crystallites forming the surface. In this way there is a gradual draining of the liquid from the drop. Such interstices are potential channels for rapid absorption if they grow too large, and in fact most drops vanish with great suddenness. Many, however, drain regularly and gradually, indicating the presence of a channel of moderate size *which does not get larger*. Mahajan has noted that floating drops are usually more long-lived the more rapidly they move. The motion would prevent cracks in the surface of the drops and cracks in the surface of the bulk from being in line more than momentarily. This would inhibit the growth of channels. Mahajan's observations are thus in accord with the present hypothesis.

Since any cause for localized intense forces would work for the puckering and breakdown of the film, it is to be expected that the presence of solid particles of dust or the like, or perhaps even colloidally dispersed liquid droplets, would be a hindrance to the formation of floating drops. Rayleigh (8) and Mahajan (7) both note this, and the results of the former show that this effect is operative even in the case of secondary drops.

There are some molecules so constructed that they are unable to orient themselves in such a way as to present only non-polar groups to the surrounding universe. Among these may be mentioned molten electrolytes, water, formic acid, formaldehyde, and ethylene glycol. These molecules are forced to have a polar oxygen or hydroxyl group exposed, or else a still more highly polar ion. They are also short molecules and very roughly spherical, certainly not rod-like. They are surrounded by strong fields of force and are highly associated, not only to dimers, but probably to high polymers. Although they would form relatively rigid films, the forces across the boundary between two such films would be so strong and so similar to the field in the interior of the liquid that it would scarcely be expected that the two surfaces would preserve their individuality when brought into close contact. The range of force about a dipole is much greater than that around a highly symmetrical methyl group ending a hydrocarbon chain. The short, roughly spherical molecules, with a low moment of inertia (compared to a long hydrocarbon chain), would have a very short period of rotation and be less strongly oriented. Reference to table 1 shows that in fact water, formic acid, ethylene glycol, glycerol, diallyl ether, and methylene chloride fail to form floating primary drops. Apparently the ethylene linkage possesses enough polarity to make the formation of drops difficult, as evidenced by diallyl ether and by the fact that perchloroethylene forms drops only with some difficulty. While no molten electrolytes have been tried, it may be confidently predicted that they will form no primary drops.

What factors determine the rigidity of a film? They are of two types: those which determine the lateral adhesion of two molecules, and those which determine its resistance to end-over-end rotation. The lateral adhesion of the molecules may be regarded as the resistance which would prevent two adjacent molecules from being pulled apart by a force acting in the plane of the surface. For simple hydrocarbon chains it would be proportional to the length of the chains, since every CH_2 group is the seat of attractive forces. If the molecules contain polar groups, this lateral force will be proportional to the number of such groups and to the strength of their dipoles in addition to the weaker forces due to the hydrocarbon chain itself. It is obvious that the stronger the lateral adhesion, the less the chance for a break in the film due to separation along a vertical plane.

On the other hand, the symmetry and so the rigidity of the film may be fundamentally disturbed by rotation of the molecules end-over-end, which would inevitably expose any polar groups it might contain and also would drag other molecules from their equilibrium positions and produce new and unsymmetrical forces. Such rotation is opposed by the same type of forces which gives rise to lateral adhesion and also by the viscosity of the medium (in particular, of the film itself) and the shape of the molecule. The viscosity of the quasi-solid film is probably much higher than that of the bulk liquid. The experiments of Bastow and Bowden (2), showing that the viscosity of films of the order of 10^{-5} mm. is the same as that of the bulk, do not contradict this, since the quasi-solid film is not thicker than the length of two molecules. Also, for a given viscosity, the end-over-end rotation is vastly more difficult for a rod-shaped than for an ellipsoidal or spherical molecule. Also, the natural period of rotation depends upon the moment of inertia, and this is greater for rods than for spheres of the same total mass. All these considerations show that long rod-shaped molecules, preferably with a few polar groups located conveniently far away from the ends, should be among the best liquids for forming floating drops. This is amply confirmed by experiment. Note that the greatest critical heights recorded are for liquids of this type. Casual observation of molten fats, paraffin, and drying oils indicates that they are excellent drop formers. Mahajan notes that the largest drops he could procure were those of molten paraffin (on itself).

It may be well to prevent two misapprehensions. The critical heights alone are not absolute measures of the rigidity of the films, for the force with which the drops strike the surface is determined, not only by the height from which the drop falls, but also by the mass of the drop. This in turn is fixed by the size of the capillary, the surface tension of the liquid, and the density of the liquid. Secondly, it should be pointed out that surface tension and rigidity of surface are not the same thing. Measurements of surface tension involve essentially bringing interior molecules into the surface layer. Measurements of rigidity should be made by forcing molecules from the exterior through the surface layer, and it is by no means obvious that these two measurements should yield the same result. Undoubtedly, however, there is a certain parallelism between them, and it has been found that, as regards pairs of liquids, drops of the liquid of low surface tension upon a liquid of higher surface tension form more easily than the reverse arrangement. A case in point is the pair carbon tetrachloride-chloroform.

SUMMARY

Drops of certain liquids, falling from a limited height onto a liquid surface, do not merge with the body of the liquid immediately, but may roll or remain at rest upon the surface for a short time. Previous reports on "rolling drops" have considered only drops of the same liquid, and the explanations advanced have involved either (*a*) electrical charges or (*b*) films of adsorbed air or vapor.

Our experiments include the formation of drops upon the same and upon different liquids and show that:

1. Most pure liquids will form drops upon themselves. Exceptions are water, formic acid, ethylene glycol, and glycerol.
2. One liquid will not form drops upon another unless the two liquids are closely related, e.g., the xylenes.
3. Drop formation is not reciprocal for some liquid pairs.
4. A solution of, for example, ethyl alcohol and benzene will form drops upon the same solution, but neither of the pure components will form drops upon this solution.

The results of these experiments indicate that current explanations of this phenomenon are inadequate, and suggest that the character and stability of the oriented surface film is the determining factor. Long-chain molecules with polar groups located near the center are the "best" drop formers. A table of critical heights for a variety of liquids is presented.

In conclusion, the authors wish to thank Dr. Elmer O. Kraemer, of the DuPont Experiment Station, Wilmington, Delaware, for supplying samples of certain of the less common liquids upon which experiments were made.

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THE SOLUBILITIES OF GASES AND SURFACE TENSION[1]

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The lack of adequate theory and of sufficiently exact experimental data has in the past discouraged attempts to correlate gas solubility data. Hildebrand (3) emphasized the lack of consistent data and Tammann (11) pointed out that certain deviations from calculated relations, using an integrated thermodynamic expression for the solubility, could be ascribed to experimental error. Tammann proposed the following expression derived from the Clausius-Clapeyron equation:

$$\frac{\mathrm{d}\ln\gamma}{\mathrm{d}T} = \frac{-\ln\gamma}{T} - \frac{q}{RT^2} \tag{1}$$

where γ is the Ostwald coefficient of solubility or the ratio of concentration of gas in the solvent to the concentration of gas in equilibrium with the solvent, q/RT^2 is a heat of solution correction term over and above a work term $\ln\gamma/T$, and R and T have the usual meaning. In cases in which q could be neglected it was shown that the average value of $\frac{1}{\ln\gamma}\cdot\frac{\mathrm{d}\ln\gamma}{\mathrm{d}T}$ for several gases in a variety of solvents was given by the reciprocal of the absolute temperature T. Horiuti (4) showed that, reasoning from thermodynamics, one obtains the equation:

$$\frac{\mathrm{d}\ln\gamma}{\mathrm{d}T} = \frac{-L_s}{RT^2} - \frac{\mathrm{d}\ln V_1}{\mathrm{d}T}$$

where V_1 is the molal volume of solute and L_s is the so-called internal heat of solution equal to $\Delta H - RT$. The internal heat of solution is in this instance equal, therefore, to $-\Delta U$, the change in energy of the system.

Sisskind and Kasarnowsky (9), treating the solubility of argon in various solvents, showed similarly to Tammann that the energy of solution could be divided into two terms. The first is a work term proportional to $4\pi r^2\sigma$, where r is the radius of the solute molecule and σ is the surface tension of the solvent. The second is a molecular solvent-solute interac-

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tion term. Despite the proximity of solvent and solute molecules, the authors attempted to evaluate this term using London's expression for the attractive force between two non-polar molecules.

In the present paper an expression for the solubility is derived starting with premises differing from those of either Tammann or Horiuti but similar to those of Sisskind and Kasarnowsky, which can be reduced to the thermodynamic equation. The derived equation expresses the solubility of a gas as a function of its molecular radius and the surface tension of the solvent. It is employed successfully in correlating the data for the solubilities of several gases reported in the literature, and in addition sheds light on the physical processes which accompany the solution of one substance by another.

DERIVATION OF AN EXPRESSION FOR THE SOLUBILITY OF A GAS

If we assume a spherical gas molecule of radius r to enter the solvent, a spherical cavity is produced in the solvent of essentially the same radius. A certain amount of work is done in producing this cavity, since any increase in surface of a liquid is associated with a definite energy change. This energy change is, in its simplest terms, given by the increase in area of the cavity multiplied by the surface tension of the solvent, or $4\pi r^2\sigma$, where σ is the surface tension in ergs per square centimeter.

In calculating this effect in this simple manner we are using a macroscopic concept, namely, surface tension at molecular dimensions, which introduces, of course, an approximation. In a comparison with experiment, however, it is shown later that deviations arising from this effect alone are apparently not large even in the cases of gases of smallest dimensions.

In addition to the surface tension term there are energy terms which arise because of interaction of solvent and solute molecules and which account for repulsive or attractive forces at the intermolecular distances characteristic of molecular separation in liquids. The nature and magnitude of the latter forces depend on the specific properties of the solute and solvent molecules which, in general, present a complex picture too difficult to resolve using the present-day theories of molecular interaction. A qualitative picture is possible, however; for example, interaction would be expected to be large and positive between a gas and solvent molecule constituted of many dipole groups, with or without a resultant moment, and relatively small or of opposite sign for an elementary gas dissolved in a non-polar solvent. If we group all energies of the latter category under the designation "interaction energies" and call these E, then Δu, the change in energy of the system in transferring a molecule from the solvent phase to a low pressure gas phase, is given by:

$$\Delta u = 4\pi r^2\sigma - E \tag{2}$$

In the above expression the energies attending interaction between solute molecules and gas-phase solvent molecules are neglected, since at any but appreciably high solvent vapor pressures these are small. Using the Maxwell-Boltzmann distribution theorem, it is well known that the equilibrium concentrations of solute molecules in the two phases can be calculated as follows:

$$\frac{c'}{c} = e^{\frac{-\Delta u}{kT}} \tag{3}$$

where c' is the concentration of gas molecules in the solvent, c is the concentration of gas molecules in the gas phase, Δu is the energy difference in transferring a molecule from the solvent to the gas phase, k is Boltzmann's constant, and T is the absolute temperature. But

$$\frac{c'}{c} = \gamma \tag{4}$$

by definition, where γ is the Ostwald coefficient of solubility. The quantity γ in the region where Henry's law is obeyed is independent of the pressure. It is possible, therefore, to extend calculated values of γ at limiting low pressures to practical pressures for which experimental data exist. In expression 2, Δu is actually the free energy, not the total energy, change. In substituting a free energy change for Δu in the Maxwell-Boltzmann equation this equation then becomes analogous to the thermodynamic equation expressing the free energy change of transfer of a perfect solute from one concentration to another concentration (6). Substituting expression 2 for Δu and γ for c'/c we can express equation 3 as

$$\ln \gamma = \frac{-4\pi r^2 \sigma + E}{kT} \tag{5}$$

Expression 5 indicates that if the interaction energy E remains constant, then the greater the radius of the solute molecule and the surface tension of the solvent, the smaller will be the solubility γ. If there are gases which interact but little with the surrounding solvent molecules and do not tend to become solvated, we should expect that E for these gases would be small. We should also expect that variations in the solvent-solute interaction in going from one solvent to another would be inappreciable and hence the major portion of the solubility would depend on the magnitude of the term $4\pi r^2\sigma$. It is readily seen, therefore, that for gases of this kind, if $\log \gamma$, the logarithm of the solubility, is plotted with σ, the surface tension of the solvent for which values of γ correspond, a straight line should result whose slope would be proportional to the square of the gas molecular radius and whose intercept would be a measure of *E*. Gases normally expected to fit into this category would be the elementary gases hydrogen, oxygen, nitrogen, and the inert gases, although evidence is presented later that interaction characterized by repulsive forces is appreciable for hydrogen, helium, and neon. J. Horiuti (5) a few years ago published accurate solubilities of the first three gases in carbon tetrachloride, acetone, benzene, ethyl ether, chlorobenzene, and methyl acetate. His data at 20°C., plotted with surface tension data taken from the International Critical Tables at the same temperature, are shown in figure 1. A straight line can be drawn through the data for each gas. From the slope we can calculate the molecular radii of the solutes. The values obtained are 1.43×10^{-8} cm. for nitrogen, 1.36×10^{-8} cm. for oxygen, and 1.38×10^{-8} cm. for hydrogen, which are in good agreement with the values 1.57, 1.45, and 1.38×10^{-8} cm., respectively, calculated from van der Waals' gas constants as given in Landolt-Börnstein's tables. Recently Maxted and Moon (8) published data on the solubility of hydrogen in ethyl alcohol, ethyl acetate, benzene, chloroform, and acetic acid at various temperatures. Their data, when treated as Horiuti's data, give a molecular radius for H_2 of 1.29 A.U. as compared with 1.38 A.U.

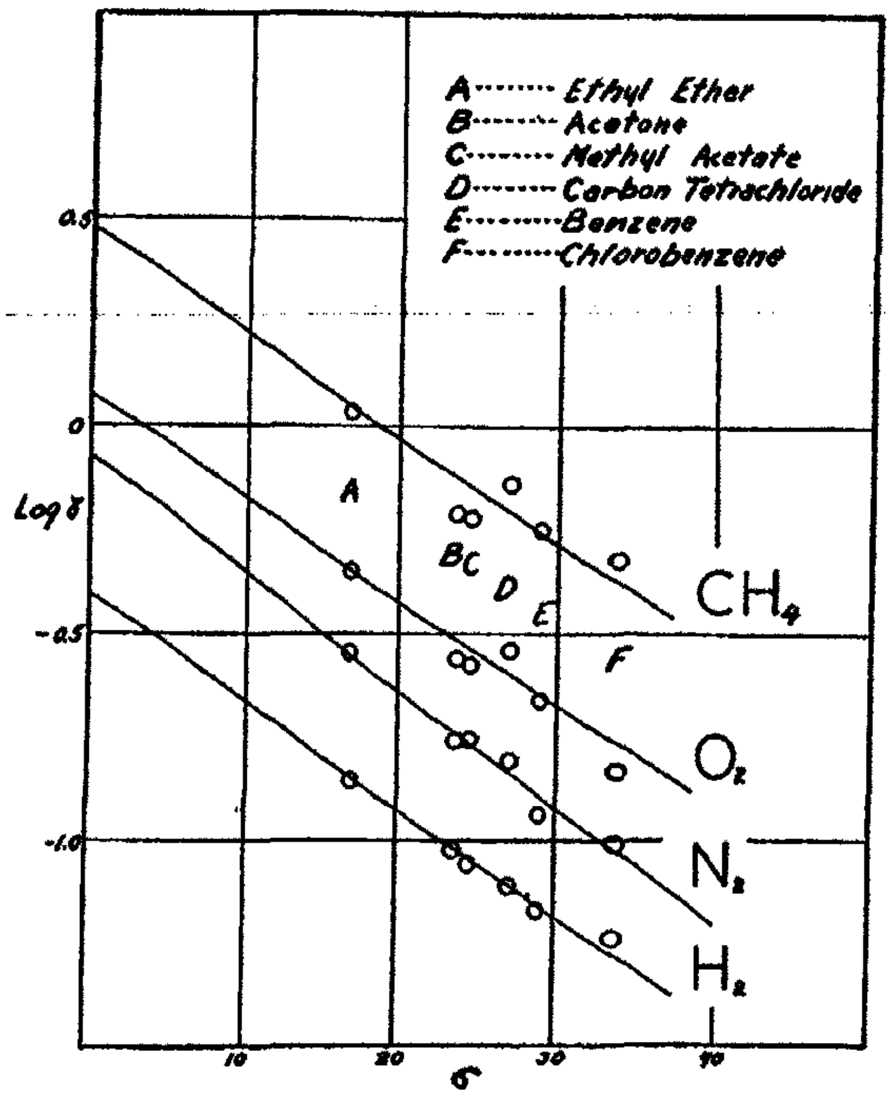

FIG. 1. Relation between the logarithm of gas solubility and surface tension of solvent

The intercept for Horiuti's data for nitrogen is very nearly zero, for oxygen slightly positive, but for hydrogen is definitely negative. This negative intercept can be interpreted as an absorption of energy by the system when hydrogen dissolves, which serves to diminish the solubility of the gas as compared with other gases and accounts in part, according to the rule of Le Chatelier, for the increase in solubility of hydrogen with increase in temperature. This negative energy E for hydrogen can also be associated with repulsive forces at close range acting between hydrogen and the solvent molecules which increase the effective radii of the cavities surrounding the hydrogen molecules. It will be noticed that the radius of hydrogen calculated from the slope is larger than the value usually assigned to H in the crystal lattice. For oxygen the energy E is positive, the forces attractive, and the radius of O_2 more nearly corresponds to the radius given by crystal lattice dimensions of O. It is interesting to observe for the three gases that relatively small deviations from linearity, recalling experimental difficulties of the measurements, show that interaction with large organic solvent molecules is approximately the same in each instance. It is also interesting to observe that the smaller the surface tension of the solvent, the greater is the capacity to dissolve gases. The qualitative relation between surface tension and gas solubility was observed in the early part of this century by Skirrow (10) and by Christoff (1). Their qualitative observations become definitive in equation 5, according to which the reciprocal relation between surface tension and solubility holds for those solvents and solutes for which E is either small or only slightly variable in going from one solvent to another.

The success which attended the plot of the data for oxygen, nitrogen, and hydrogen prompted similar treatment for other gases. In figure 1 Horiuti's data for methane are plotted; in figure 2 data for carbon monoxide and ethylene. Methane and carbon monoxide show a regular linear arrangement with positive intercepts. Despite a small permanent moment for carbon monoxide, interaction with solvents is small, as shown by the small value of E. The larger positive intercept for methane can be interpreted as appreciable interaction or solvation, which may also account for more pronounced scattering of the data. When the interaction term E becomes appreciable, it is reasonable to suppose that specific interaction effects with one solvent, as compared with another, will then become noticeable. In the case of ethylene, for example, the regularity of the data plotted as in figure 2 is not as good as for the gases previously considered. Interaction with the solvent is distinctly more pronounced, solubility is larger, and specific effects are apparent. To assist in determining the slope, the solubility of ethylene in water obtained from Landolt-Börnstein's tables was used. From the slope a radius for ethylene of 1.51×10^{-8} cm. and an intercept of 1.4 are calculated. The large positive intercept indicates attractive forces between solute and solvent, and the calculated value of the radius should approximate crystal lattice dimensions. This is found to be the case. Horiuti's data for acetylene and ethane behave much as those for ethylene, the acetylene data showing the largest scattering.

The water solubility data for the gases mentioned above found in Landolt-Börnstein's tables do not in every case fall on the line which best fits Horiuti's data. Good agreement exists for oxygen and methane, but not for carbon monoxide, nitrogen, and hydrogen. No explanation is apparent.

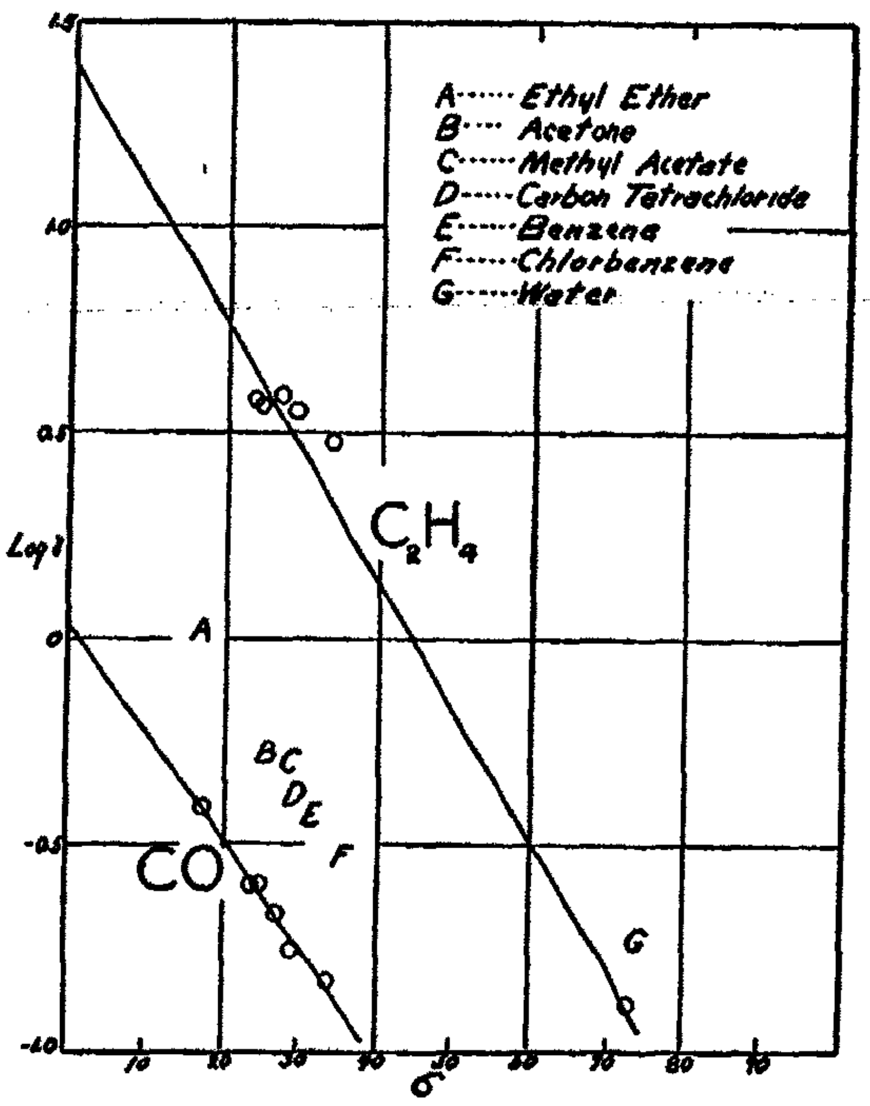

FIG. 2. Relation between the logarithm of gas solubility and surface tension of solvent

In table 1 values are given for the slopes $\frac{d \log \gamma}{d\sigma}$ and intercepts $\frac{E}{2.303kT}$ of the data plotted in figures 1 and 2, the radii of the gas molecules calculated from the slopes, and comparative radii obtained from other sources such as from compressibility data (van der Waals) or viscosity data taken from Landolt-Börnstein's tables or crystal lattice dimensions. Constants derived for helium, neon, and argon are also included, the gas solubility data being taken from Lannung's (7) measurements in methyl alcohol, ethyl alcohol, acetone, benzene, and water. Lannung's data for organic solvents alone are not sufficiently regular to define a singular slope, but by including his values for water, the surface tension of which is approximately three times that of the organic solvents, the slopes are readily determined. All the derived constants are taken from measurements at 20°C.

Considering the simplicity of the theory, the radii calculated from the solubility measurements are in good agreement with radii calculated from other types of physical measurements. The gases with smallest solubility show the lowest values for the intercept and *vice versa.* It is interesting to observe that the intercepts are fairly linear with the boiling points of the solutes.

From equation 5 certain deductions can be made with regard to the temperature coefficient of the solubility of gases. It will be observed that if $4\pi r^2\sigma > E$, the solubility of a gas will increase in temperature, while if $4\pi r^2\sigma < E$, the solubility will decrease in temperature. Tammann (11) generalized similarly on the sign of the temperature coefficient of solubility in which he stated that if $\gamma > 1$ the temperature coefficient will be positive, and that if $\gamma < 1$, it will be negative. This rule seems to hold fairly generally except for water.

TABLE 1

Radii of gas solutes from solubility

GAS	$\frac{d \log \gamma}{d\sigma}$	$\frac{E}{2.303\, kT}$	$r \times 10^8$ cm.	
			Calculated	Observed
N_2	0.0294	−0.065	1.43	1.57 (van der Waals)
H_2	0.0259	−0.40	1.38	1.38 (van der Waals)
O_2	0.0252	0.08	1.36	1.45 (van der Waals)
CO	0.0263	0.037	1.40	1.15 (band spectra)
CH_4	0.0254	0.48	1.37	1.4 (atomic radii)
He	0.0114	−1.20	0.92	1.00 (viscosity)
Ne	0.0122	−1.07	0.95	1.17 (viscosity)
A	0.0183	−0.12	1.16	1.43 (viscosity)
C_2H_4	0.0313	1.40	1.51	1.5 (atomic radii)

With a knowledge of values of E through plots of $\log \gamma$ with σ it is possible to compute the temperature coefficient of solubility. This has been done and calculated values have been compared with the observed coefficients recorded by Horiuti and Lannung. Instead of computing the coefficients $\frac{d \log \gamma}{d\, 1/T}$ which, referring to equation 5, is equivalent to

$$\frac{-4\pi r^2\sigma + E}{2.303\, k}$$

values of the free energy of solution, $-4\pi r^2\sigma + E$, have been computed in calories per mole. To arrive at values for $-4\pi r^2\sigma + E$, from surface tension and temperature dependence of solubilities, the following relations were employed:

$$-4\pi r^2\sigma + E = 2.303\,kT\left(\sigma\,\frac{\mathrm{d}\log\gamma}{\mathrm{d}\sigma} + I\right)$$

$$= 2.303\,k\,\frac{\mathrm{d}\log\gamma}{\mathrm{d}\,1/T}$$

where I is the intercept in the plotted data of $\log\gamma$ with σ and $\frac{\mathrm{d}\log\gamma}{\mathrm{d}\sigma}$ is the slope. The quantity $\frac{\mathrm{d}\log\gamma}{\mathrm{d}\,1/T}$ is taken from the observations of Horiuti (4); Lannung's (7) published values of this quantity from his own data are used for helium, neon, and argon. The values are given in table 2 for the solvents benzene and acetone. These solvents were chosen at random,—any of the other organic solvents show similar correspondence.

By and large, agreement in the values for the free energy of solution $-4\pi r^2\sigma + E$ calculated from surface tension and temperature dependence of solubility is as good as the simplified theory warrants. For many of the gases listed in table 2, the calculated values are well within the experimental error. Mention has already been made of the difficult technique and large experimental error in measuring gas solubilities. Methane values show the largest deviation between observed and calculated values, owing probably to the specific interaction with solvent which was assumed to be the cause of the somewhat scattered data for methane in figure 1. In this connection, although the calculated values are not recorded in table 2, water appears to be an anomalous solvent.

From Horiuti's data, extending over a considerable temperature range, it is possible to calculate the temperature dependence of the solute radius r and the solvent-solute interaction E. Surface tension data were obtained by making use of a compilation of surface tension data by A. Ferguson and S. Kennedy (2) and by reference to the International Critical Tables. Slopes and intercepts of the logarithms of the solubility plotted with corresponding surface tension data for the solvents were obtained by the method of least squares. In table 3 values are listed for r and E for nitrogen and carbon monoxide at three temperatures. The solute radius r is constant for nitrogen and very nearly so for carbon monoxide over a temperature range of 40°C. The interaction energy E, shown previously to be approximately the same for all solutes at the same temperature, is shown to decrease with increase in temperature. Values of E actually represent the differences in energy of interaction of solute-solvent molecules in the liquid phase as compared with the gas phase of the solvent. As the temperature increases near the critical temperature of the solvent, the distinguishing differences between gas and liquid tend to disappear, until at the critical temperature or above one phase is possible and differences no longer exist. It appears reasonable therefore that values of E go through a minimum with increasing temperature and that at the critical temperature their values become zero. This is illustrated in figure 3.

TABLE 2

Molal free energy of solutions from surface tension data

Calories per mole at 20°C.

GAS	$4\pi r^2\sigma$	E	$-4\pi r^2\sigma + E$	
			Calculated	Observed
Solvent: benzene				
N_2	−1135	−53.7	−1189	−1390
CO	−1030	67.1	−963	−990
CH_4	−984	645	−339	−92
H_2	−1002	−537	−1539	−1840
He	−442	−1610	−2052	−2850
Ne	−472	−1439	−1911	−2700
A	−708	−161	−869	−1000
O_2	−998	110	−889	−810
Solvent: acetone				
N_2	−935	−53.7	−989	−980
CO	−847	67.1	−807	−640
CH_4	−808	654	−154	91.5
H_2	−825	−537	−1362	−1640
He	−362	−1610	−1972	−3300
Ne	−388	−1439	−1827	−2000
A	−582	−161	−743	−800
O_2	−819	110	−709	−646

TABLE 3

Effect of temperature on gas radius and "E"

T IN °C.	$r \times 10^8$ cm.		E IN CALORIES PER MOLE	
	N_2	CO	N_2	CO
0	1.43	1.36	−10.3	127
20	1.45	1.39	−89	51
40	1.43	1.41	−210	−23

Values of E in calories per mole for nitrogen and methane in chlorobenzene are plotted with the absolute temperature. The dotted line represents an extrapolation of the experimental data in accordance with the expected trend. At the critical temperature of chlorobenzene (359°C.), the values of E for both gases are shown to be zero.

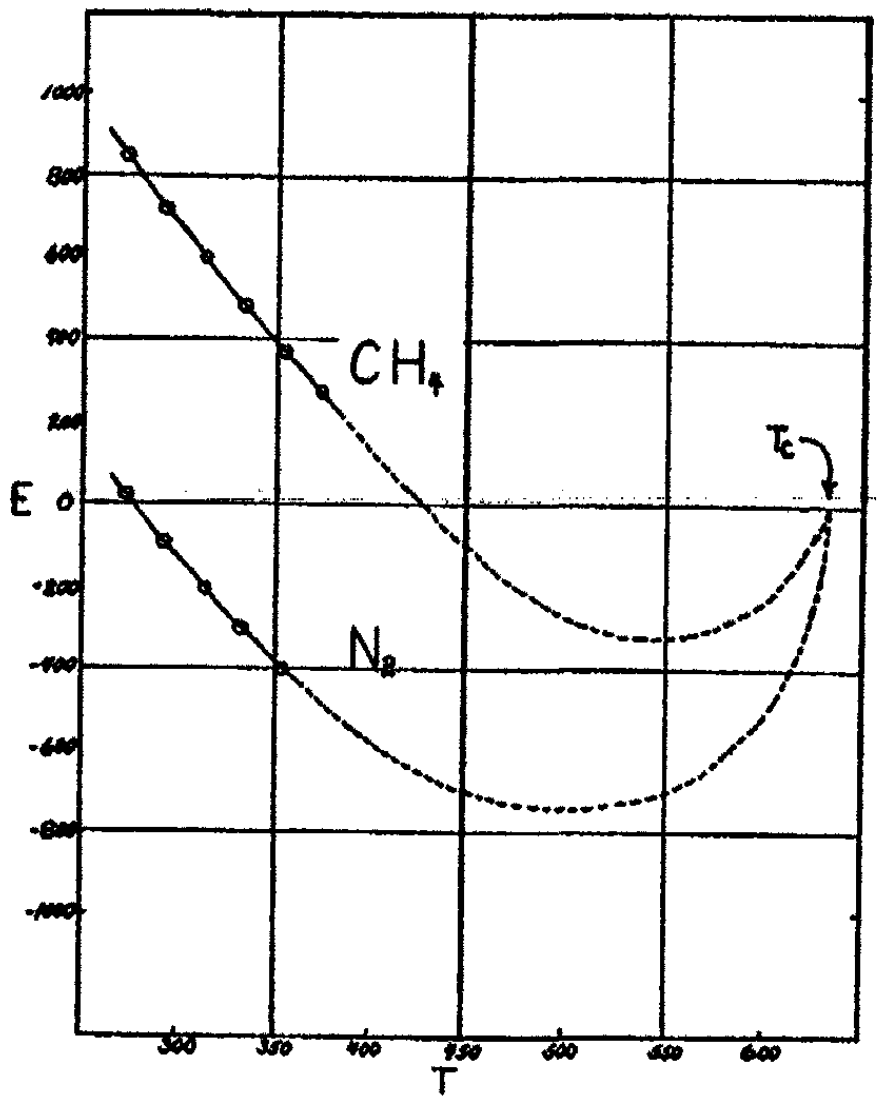

FIG. 3. Relation between solvent-solute interaction energy and absolute temperature

SUMMARY

Considering the energy change in transferring a solute molecule of radius r to a solvent of surface tension σ, an expression as follows, making use of the Maxwell-Boltzmann distribution theorem, is derived for the solubility of a gas:

$$\ln \gamma = \frac{-4\pi r^2\sigma + E}{kT}$$

E is called the interaction energy of solute and solvent, and γ is the ratio of concentration of solute in the solvent to that in the gas phase. For several gases, including oxygen, hydrogen, nitrogen, carbon monoxide, and methane, E is found to be approximately constant for any one gas in a

variety of solvents. From a plot of log γ with surface tension of the solvents (for any gas), a straight line is obtained from the slope of which can be calculated the solute molecular radius. The radii calculated in this manner are in good agreement with radii calculated from physical measurements of other types. Values of E, the interaction energy, are determined from the intercept. In general, if the solubility of a gas is small, E is negative; if large, positive. From values of E so determined, the free energies of solution of gases can be calculated. These calculated values compare favorably with values obtained from the temperature dependence of gas solubility for most solvents, the notable exception being water.

Least square treatment of Horiuti's data for nitrogen and carbon monoxide data over a 40°C. range of temperature show that the solute molecular radii determined from the surface tension plots tend to be constant. The interaction energies decrease with increase in temperature. Because the interaction term E is the difference in the solute-solvent interaction of gas and liquid phases, its value at the critical temperature must be zero. It is shown that E passes through a minimum at some temperature lower than the critical temperature of the solvent.

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NEW BOOKS

Disperse Systems in Gases; Dust, Smoke, and Fog. A general discussion held by the Faraday Society, April, 1936. 25 x 16 cm.; pp. 1041–1300. London and Edinburgh: Gurney and Jackson, 1936. Price: 12s. 6d.

This book is a report of the meeting held by the Faraday Society in Leeds in 1936, at which the many aspects of disperse systems in gases were discussed from various points of view. The report includes all the papers contributed to the meeting, together with the discussion thereon, and in it much detailed information is assembled in such a form that the reader can obtain from this one source a thorough knowledge of recent developments in this field of investigation.

The subject is considered under two main heads, viz., the general properties and behavior of disperse systems, and the industrial aspect of such systems. Subdivision of the first part is made into disperse systems composed of solid and liquid non-volatile particles (smoke, dust, oil, fogs, etc.) and those consisting of aqueous and other volatile particles (mist, cloud, hygroscopic nuclei, town and country fogs). The first of these subsections includes such matters as methods for determining the number of particles in smokes and size distribution in smokes and mineral dusts, the dust-free space surrounding hot bodies, and cohesion between smoke particles. The effects of such influences as pressure temperature gradients, sonic and supersonic vibrations, and ionic currents are also discussed. The second subsection deals, amongst other matters, with the nature of dispersoids in country and town air, the determination of the mass and size of atmospheric condensation nuclei, hygroscopic nuclei in the formation of fog, sorption of fog by liquids, sulfuric acid mist, and with the removal of mist by centrifugal methods. The industrial section contains papers on the inflammation of dust clouds, the spread of smoke and gases from chimneys, the dissipation of fog, the physical basis of electrical gas purification, and the physical and chemical problems involved in the design of a plant for removal of smoke and oxides of sulfur from flue gas. This section also includes an interesting paper on twenty-five years' progress in smoke abatement, which deals with air pollution records of some twenty-three centers in Great Britain.

It is very pleasing to have available in one volume such a comprehensive treatment of this extremely varied subject, and in a form in which there is so much of interest both to the pure scientist and to those who seek to apply in industry the physicochemical principles involved.

H. W. Cremer.

Die Chemie der natürlichen und künstlichen organischen Farbstoffe. By G. Schiemann. 20.5 x 13 cm.; viii + 136 pp. Leipzig: Leopold Voss, 1936. Price: 7.20 RM.

The author of this introductory survey of the theory and practice of color chemistry is to be congratulated on the selection and arrangement of the material. This admirable book at reasonable cost is eminently suitable for chemists to obtain an outline of the chemistry of coloring matters or to avoid pitfalls when they use dyes in their researches.

The subject is treated as a whole by including natural and synthetic coloring matters together in the appropriate chapters which are arranged according to the common chromophore or the chemical class of the compounds under discussion. A brief introduction on the relation between color, constitution, and dyeing properties is amplified in the light of modern theories in subsequent chapters. The preparation of sufficient examples of each class of dyes is outlined, the main uses and properties of the dyes are stated, and the whole is well illustrated by formulas. Some errors have escaped correction in the proofs.

F. M. Rowe.

Review of Ebulliometry. By Wojciech Swietoslawski. First edition. 196 pp. Jagellonian University Press, 1936.

The author of this monograph is responsible for the development of a refined and highly specialized technique of boiling-point determination. Although he has retained the Cottrell principle of using a vapor lift to spray the boiling liquid upon the thermometer bulb, the apparatus which he and his coworkers have designed has been mechanically simplified, refined, and modified to serve a variety of purposes. The construction of the apparatus and the technique of its use are adequately described with the aid of a number of line drawings. The book includes very few references to methods which were not developed in the author's laboratory at Warsaw; for example, Menzies' differential thermometer is not mentioned. In the reviewer's opinion, the value of the book as a comprehensive monograph would be increased if a critical discussion of other common methods were included, even when these methods are inferior to those proposed by the author.

In addition to the description of experimental methods, the book contains a brief discussion of the general principles of distillation. The chapters on azeotropy and azeotropic methods of purifying liquids are especially interesting.

Second Edition, 204 pp. Chemical Publishing Co., 1937. Price $3.00.

The second edition of this monograph differs from the first in only two particulars; a six-page supplement, descriptive of some recent researches, has been added, and the printing and binding are noticeably inferior.

Robert Livingston.

Structure and Molecular Forces in (a) Liquids and (b) Pure Solutions. A General Discussion. 25 x 16 cm.; 282 pp. London: Gurney and Jackson, 1937. Price: 12s. 6d. net.

The study of liquids, particularly from the point of view of structure and statistical theory, is receiving considerable attention at the present time, and the recent Discussions of the Faraday Society were opportune in bringing certain important aspects to the fore. Seventeen papers were contributed to the first part of the discussions, and fifteen to the second; perhaps one may be forgiven for concentrating on one or two particular aspects for review.

The structure of liquids has been studied a great deal of recent years by the x-ray method (as one of the least indirect); this work was in fact started by Debye in 1916. Since that time ideas of structure and groups of molecules in liquids have gradually developed, and were expressed most effectively for organic materials by Stewart. Many liquids have also been studied rather more quantitatively by utilizing Fourier analysis of the scattering curves, and this in particular has led to a greater understanding of the small groups of atoms or molecules coördinated for small periods of time. Such results have been of great value, and a notable example of what can be done in this way is the work of Bernal and Fowler on water. But no outstanding contribution to statistical theory, capable of deriving the physical properties of liquids, had until recently appeared. The recent work of Eyring, Altar, and others suggests that a good start has now been made in this direction; it is unfortunate that Eyring's contribution to the Discussion was not of a more general and less mathematical nature. Eyring's idea is that a liquid contains a considerable number of holes. The total number of degrees of freedom in a liquid may be divided into a number of smaller groups, and each of the small groups is supposed to maintain a small spherical cavity in the liquid, the liquid surrounding the hole as if it were an incompressible fluid, so that the laws of hydrodynamics may be applied. The state of motion of a liquid on this basis depends on the total surface, composed of all the internal boundary surfaces. Whilst such ideas may be physically a little crude, they are at the present time allowing partition functions to be expressed, which is a considerable advance in the statistical theory of liquids.

Bernal in his paper extends the ideas and possibilities of the distribution function of x-ray analysis, and, whilst rigor is disclaimed, his paper is extremely suggestive and valuable on the structural side. The valuable papers of London and Simon should also be mentioned. Raman spectra of liquids are discussed by Magat, and the reduced temperature scale is used with effect by Bauer, Magat, and Surdin in a general discussion of properties.

The general quality of the papers in this volume is very high, and perhaps enough has been written to indicate that both the quality and the interest of the work contributed are also very high.

J. T. Randall.

Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikatforschung in Berlin-Dahlem. 30 x 21 cm.; pp. i + 188. Braunschweig: Fr. Vieweg und Sohn, 1937.

The practice of issuing the collected papers pertaining to research on silicates from Dr. Eitel's laboratory continues, and the present volume contains the published work of 1936. Such a practice must always lead to volumes and parts of volumes of unequal merit.

Eighteen papers are collected together, and mention of a few of the more interesting only will be made: Bussem and Weyl discuss the structure of glass in a useful survey paper covering physicochemical work, as well as the more recent x-ray work. T. v. Takats discusses the reaction of silicates with sulfur dioxide; W. Eitel writes on the sillimanite-mullite problem; Bussem discusses the water content of various hydrated calcium sulfates; and Haegermann and Schweite have investigated certain cements used for street buildings. W. Eitel and Oberlies write on the properties of glass fibers.

J. T. Randall.

Atomic Structure and Atomic Spectra. By G. Herzberg. English translation by J. W. Spinks with the coöperation of the author. 257 pp.; 80 fig. New York: Prentice-Hall, Inc., 1937.

The topic covered in this volume is clearly indicated in the title. The treatment is most concise and matter of fact. To this end the author has not included in the text any complicated mathematical developments, but he has stated the needed propositions simply and without proof. For example, the famous expression of the hydrogen series is given on p. 11 without any detailed and cumbersome derivation. This form of treatment makes the book very readable to the informed individual, for it furnishes a compact summary of the field under discussion. However, the beginning student will have to supplement his study of the subject by further reading of other work where the topics are treated on a more analytical basis. The modern views of atomic structure are introduced at once in the first chapter by a brief formulation of the important concepts of wave mechanics. These results are used throughout the volume wherever needed. The six chapters cover the usual material: hydrogen spectra; Bohr theory of the atom; energy diagrams; wave mechanics; alkali, helium, and alkaline-earth spectra; multiplet structure of line spectra and electron spin; Zeeman and Stark effects; Pauli principle and periodic system of the elements; intensities of spectrum lines; types of coupling; hyperfine structure; isotope effect and nuclear spin; magnetic susceptibility and chemical considerations. The book is a valuable addition to the existing literature on the subject.

Geo. Glockler.

Absorption Spectroscopy in the Ultra-violet. By F. Ellinger. Reprint from *Tabulae Biologicae*, Vol. XII. 52 pp.; 188 fig. Den Haag: Verlag Dr. W. Junk, 1937.

This pamphlet consists of a collection of absorption curves of biologically important substances: proteins, carbohydrates, fats and related compounds. Biochemists should find it useful in their work.

Geo. Glockler.

La Fluorescence en Biochimie. By Ch. Dhéré. 25 x 16 cm.; xii + 318 pp.; 27 plates. Paris: Les Presses Universitaires de France, 1937. Price: 80 francs.

The author of this volume is well known as an authority both on the study of fluorescence phenomena and on certain branches of biochemistry, and in producing this exhaustive compilation he has performed a notable service to both branches of knowledge. His firm belief in the spectroscopic method of approach is reflected in the book, which is concerned mainly with this point of view to the exclusion of the more familiar visual technique commonly referred to as fluorescence analysis. It also explains certain omissions (for example, of that most valuable aid to the study of fluorescence in biochemistry, the fluorescence microscope), and as a consequence, makes the title a little misleading.

The book deals firstly with experimental methods, and then systematically and thoroughly with the results obtained with various classes of substances of biochemical interest (including sugars, fats, proteins, alkaloids, plant substances, porphyrins, vitamins, hormones, enzymes, organisms and biochemical fluids such as sera, blood, etc.). It concludes with an appendix of fifty-six typical spectrograms.

The book is to be recommended strongly to physical chemists in general, as well as to the specialists in biochemistry for whom, doubtless, it is principally intended.

Julius Grant.

Kolloidchemische Grundlagen der Textilveredlung. By Dr. Emmerich Valkó. 701 pp.; 346 fig. Berlin: Julius Springer, 1937. Price: unbound, 57 RM; bound, 60 RM.

During the years which have elapsed since the World War, the attention given to textile materials and processes by research workers throughout the world has resulted in the accumulation of sufficient knowledge for textile technology to take its place as a branch of applied science. Hitherto, such knowledge was to be found only in original papers in the scientific and technical journals, and Dr. Valkó's book, which provides an admirable summary of the striking advances which have been made, will therefore be especially welcome. Although its price is unduly high, the book will undoubtedly come to be regarded as the standard reference book for students and research workers in textile technology, color chemistry, and dyeing.

Commencing with an account of the chemical constitution, morphology, histology, and crystal structure of the various textile fibers, the author then discusses water adsorption in great detail, paying particular attention to cotton and wool. Thereafter, in various chapters, cotton receives detailed consideration as regards surface potential phenomena, the recognition and measurement of damage, and mercerization. No less exhaustive is the treatment given to the animal fibers: after discussing the behavior of wool and silk as amphoteric colloids, separate chapters are devoted to an examination of the influence of disulfide bond reactivity on the properties and processing of wool and to the scientific aspects of felting and milling. With the preceding information as basis, the colloid chemistry of dyes and dyeing processes and the behavior of dyes on the fiber are discussed in three excellent chapters, in which the author makes use of his specialized knowledge. Finally, there are three chapters devoted to the colloid chemistry of soaps, detergents, wetting agents, and sizing materials.

The book is beautifully produced, is well illustrated, and has an excellent bibliography at the end of each chapter. Dr. Valkó is to be congratulated on this important contribution to the advancement of the science of textile materials and processes.

J. B. Speakman.

Principles of Chemical Engineering. By W. H. Walker, W. K. Lewis, W. H. McAdams, and E. R. Gilliland. 23.3 x 16 cm.; ix + 749 pp. 3rd edition. New York: McGraw-Hill Book Company, Inc., 1937. Price: $5.50.

The third edition of this book has been considerably revised and much of it rewritten. Many changes have been made in the chapters on flow of fluids, flow of heat, and those having to do with diffusional processes, including the newer theoretical developments and data and fundamental constants. All of the material is treated from the quantitative or mathematical standpoint, as was done in the previous editions. Though the presentation of material is usually clear, the treatment may cause some difficulties for students beginning the subject of the chemical engineering unit operations. It is to be noted that a fourth author has been added to the group writing earlier editions. This is one of the excellent standard texts on chemical engineering principles.

Charles A. Mann.

Numerical Data on Radioactivity. Nuclear Physics. Transmutations. Neutrons. Positrons. By I. Joliot-Curie, B. Grinberg, R. J. Walen. Excerpt from Annual Tables of Constants. 57 pp. Paris: Gauthier-Villars, 1931–36.

This represents the data in the field of radioactivity and nuclear physics published during the period 1931 to 1936. Naturally most of the space is devoted to the new nuclear transmutations and to artificial radioactivity. Of the elements Nos. 1 to 30, only helium has not been transmuted, and only hydrogen, helium, beryllium, and chromium have not been shown to have artificial radioactive isotopes, though those for nickel and cobalt have not been positively identified. From No. 31 to No. 92 only nine elements of the non-radioactive elements have not been transmuted or made radioactive. In addition, new artificially radioactive isotopes have been produced from thorium and uranium.

S. C. Lind.

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