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ELECTROKINETICS. XIV

A Critical Comparison of Electrophoresis, Streaming Potential, and Electrosmosis[1]

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Received June 14, 1934

There have been various attempts to check the different methods of measuring electrokinetic potentials against one another. Thus Saxén (18) working with clay plates found good agreement between streaming potential and electrosmosis. Kanamaru (16), on the other hand, was unable to find agreement between electrosmosis and streaming potential for diaphragms made of cellulose. Briggs (5) attempted to check with streaming potential technique the values obtained by Abramson (1), using quartz particles coated with egg albumin. Excellent agreement was found. Since, however, both of these workers used relatively impure samples of egg albumin from completely different sources and also different buffer systems, the agreement appears to be fortuitous. This conclusion is borne out by subsequent observations by Abramson and Grossman (3). Abramson (2) has found good correspondence between electrosmosis and electrophoresis, using protein-covered surfaces.

It appeared worth while to the author to reëxamine the whole question and compare systems as nearly alike and under as similar conditions as possible.

EXPERIMENTAL

The streaming potential apparatus used was the same as that reported in a previous communication by the author (7) and was arranged in the same fashion, except that two capillaries were used in series in order to increase the streaming potential.

The electrophoretic cell was a radical modification of the one reported by Buzágh (12), and a further modification of the one used by Bull and Söllner (11) and also by Bull, Ellefson, and Taylor (8). No complete description

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of this apparatus has been published. It therefore seems worth while to describe the cell, since it combines the virtues of being inexpensive, simple in operation and construction, and easily cleaned. It consisted simply of a strip of plate glass into which a groove 1 mm. deep and 1.5 cm. wide had been cut, ground and polished lengthwise on its face. Small holes were ground through the strip of glass about 2 cm. from each end. These holes had glass tubes sealed into them and served as inlet and outlet for the cell. The electrodes consisted of copper wire imbedded in plaster of Paris made with half-saturated potassium chloride and inserted in the ends of the groove. The plaster was smoothed off, a thin cover glass obtained from an old photographic plate was laid over the groove, and the joint between the cover glass and the plate glass was sealed with melted paraffin wax. Melted wax was also poured behind the electrodes. The wax was allowed to solidify and the cell was ready for calibration. (The complete cell is shown in figure 1.) The fitting together of the cell requires only a few minutes so that the cell may be taken apart, cleaned, and put together again with no great trouble. The cell was placed upon the stage of a microscope equipped with a 12.5 × ocular and an 8 mm. objective which combined working distance with sufficient magnification. The thickness of the chamber when filled with water was measured by means of the screw micrometer of the microscope. The copper electrodes were connected to the D.C. source of current. The potential gradient was obtained by measuring the distance between the electrodes, and dividing this into the total potential drop as determined by an accurately calibrated voltmeter. The potential across the cell was usually around 200 volts.

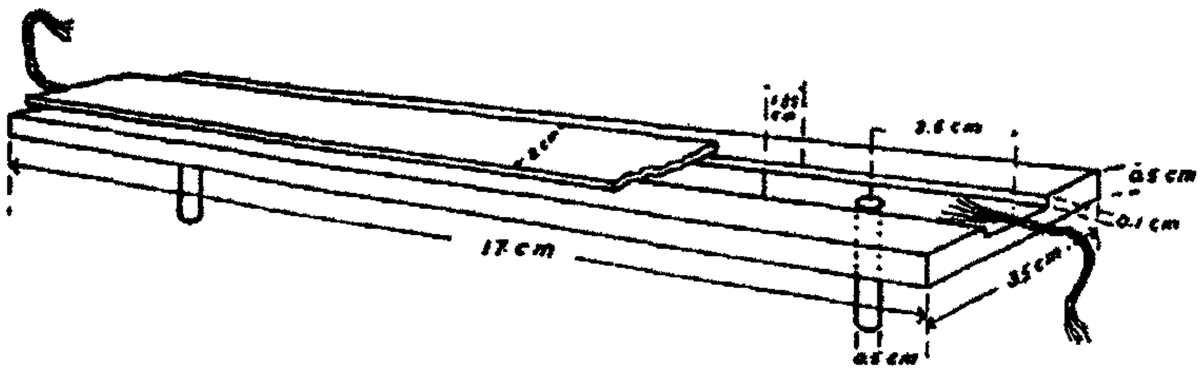

Fig. 1. The Modified Buzágh Electrophoresis Apparatus

In accordance with the formulation by Smoluchowski (21), measurements were made at the stationary levels. These stationary levels lie at 0.21 and 0.79 of the total depth of the cell. A series of four readings was made in one direction and a like number in the opposite, until at least sixteen measurements had been obtained at each level. Velocity was measured with a stop watch by determining the time required for a particle in sharp focus to travel between two lines of the ocular micrometer. The electrosmotic velocity was determined by making use of the technique employed by Abramson (2). Sixteen determinations of mobility were made at the half depth of the cell. The electrophoretic mobility was subtracted from these and multiplied by 2. The result is the electrosmotic velocity of the solution. Both the electrophoretic and electrosmotic mobilities are expressed in μ per second per volt per centimeter.

Conductivity was determined with an A.C. galvanometer. This instrument had been previously checked against a 1000-cycle vibrator and earphones. The usual bridge arrangement was used. The 1000-cycle frequency was used to determine the cell constant. The method and values of Parker and Parker (17) were used for the calibration with $N/10$ potassium chloride.

The particles used in the electrophoretic measurements were Pyrex glass particles of about 1 μ in diameter. Pyrex glass was selected instead of quartz to insure the same surface as that of the capillaries which were used in the streaming potential measurements.

Two proteins were used to coat the particles and capillary walls. They were electrodialyzed Bacto gelatin prepared by Sinclair and Gortner with an ash content of 0.05 per cent, and egg albumin made from fresh eggs and crystallized three times from ammonium sulfate, according to Sörensen (19). The egg albumin was subsequently electrodialyzed.

The protein solutions were made up the day before the experiment was to be conducted. This was to allow the solution to come completely to equilibrium. The electrophoretic and streaming potential measurements were always made on the same day and usually within two hours of each other. The temperature was 25° ± 1°C.

Hydrochloric acid was used to bring the protein solutions to the desired hydrogen-ion concentration. The use of the ordinary buffer systems was avoided, owing to the desire to keep the conductivity as low as possible and thus obtain a higher streaming potential. The hydrogen-ion concentrations were determined with a quinhydrone-platinum electrode, using Clark's values for the electrodes.

The streaming potential measurements were conducted first. The entire protein solutions were streamed through the capillaries several times before readings were taken. In all cases at least twenty-one readings were made at different pressures and in reverse directions. Upon the completion of the streaming potential measurements the protein solution was removed to a flask, a portion poured out, and powdered Pyrex glass added. This was allowed to stand fifteen minutes, and the electrophoretic velocities determined.

The ratio between the zeta potential as determined by streaming potential and electrophoresis was obtained by use of the following formulas:

$$\zeta_s = \frac{4\pi\kappa H\eta}{DP} \text{ (streaming potential)} \qquad (1)$$

TABLE 1

EXPT. NO.	SYSTEM	pH	$\kappa \times 10^6$	H/P	$\kappa H/P \times 10^6$	V_e*	V_o†	$\frac{\zeta_s‡}{\zeta_e§}$	$\frac{\zeta_o¶}{\zeta_e}$	$\frac{\zeta_s}{\zeta_o}$
			ohms^{-1}	*mv. per cm. of* Hg		*μ/sec./volt/cm.*	*μ/sec./volt/cm.*			
1	0.0672 per cent egg albumin in 3 × 10^{-4} *N* HCl	4.00	6.87	4.33	29.70	2.06		1.09		
2	0.0672 per cent egg albumin in 3 × 10^{-4} *N* HCl	4.03	6.65	4.095	27.20	2.348		0.88		
3	0.134 per cent egg albumin in 3 × 10^{-4} *N* HCl	4.49	5.35	4.353	23.30	2.087		0.85		
4	0.168 per cent egg albumin in 4 × 10^{-4} *N* HCl	4.40	6.58	3.882	25.60	2.123		0.91		
5	0.168 per cent egg albumin in 5 × 10^{-4} *N* HCl	4.26	8.35	3.25	27.20	2.596		0.79		
6	0.202 per cent egg albumin in 3.5 × 10^{-4} *N* HCl	4.17	10.85	2.38	25.80	2.000	1.882	0.98	0.94	1.04
7	0.158 per cent gelatin in 4 × 10^{-4} *N* HCl	4.24				1.553	1.72		1.11	
8	0.174 per cent gelatin in 5 × 10^{-4} *N* HCl	4.12	12.85	1.82	23.40	1.632	1.682	1.08	1.03	1.05
9	0.166 per cent gelatin in 6.3 × 10^{-4} *N* HCl	4.01	15.22	1.779	27.10	1.852	1.624	1.11	0.88	1.26
10	0.166 per cent gelatin in 7.0 × 10^{-4} *N* HCl	3.77	16.30	1.238	20.20	1.876	1.794	0.81	0.96	0.84
11	0.180 per cent gelatin in 7.5 × 10^{-4} *N* HCl	3.68	17.70	1.031	18.25	2.03	2.00	0.68	0.99	0.69
12	0.175 per cent gelatin in 7.5 × 10^{-4} *N* HCl	3.62	18.50	1.965	36.40	2.06	2.26	1.34	1.10	1.22
13	0.226 per cent gelatin in 8.0 × 10^{-4} *N* HCl	3.72	18.00	1.339	24.10	1.87	1.98	0.98	1.06	0.93
14	0.207 per cent gelatin in 6.5 × 10^{-4} *N* HCl	3.82	14.48	1.547	22.40	1.86	1.92	0.91	1.03	0.88
15	0.219 per cent gelatin in 5.0 × 10^{-4} *N* HCl	4.01	12.30	1.784	22.0	1.72	1.72	0.97	1.00	0.97
Average for protein-covered surfaces								0.97	1.01	0.99
Quartz in 2 × 10^{-4} *N* NaCl					84.97	4.317		1.48		
Quartz in 2 × 10^{-4} *N* NaCl					84.97	4.40		1.47		
Cellulose in 2 × 10^{-4} *N* NaCl					13.75	3.71		0.28		

* V_e = electrophoretic mobility. † V_o = electrosmotic mobility. ‡ ζ_s = potential from stream potential. § ζ_e = potential from electrophoresis. ¶ ζ_o = potential from electrosmosis.

$$\zeta_e = \frac{4\pi\eta V}{DX} \text{ (electrophoresis)} \tag{2}$$

where κ is the conductivity in reciprocal ohms, H the streaming potential, η the coefficient of viscosity, P the pressure forcing the liquid through the capillaries, X the potential gradient across the electrophoretic cell, D the dielectric constant, and V the velocity of the particle.

Dividing equation 1 by equation 2

$$\frac{\zeta_s}{\zeta_e} = \frac{\kappa H}{P}\frac{X}{V} \tag{3}$$

and introducing the proper constants to convert the ordinary units into electrostatic units we have

$$\frac{\zeta_s}{\zeta_e} = 7.57 \times 10^3 \frac{H\kappa}{P}\frac{X}{V} \tag{4}$$

This equation was used to calculate the values given in table 1.

It was thought that it might also be interesting to compare the two methods using surfaces which were not covered with protein. Accordingly, some of the same quartz used by Bull and Gortner (10) in their study on particle size was suspended in $2 \times 10^{-4}M$ sodium chloride and its electrophoretic velocity determined. The true streaming potential was assumed to be given by the quartz where the potential no longer varied with the particle size, that is, at the largest size of particle. No decided trend in speed was noted between the various particle sizes. The electrophoretic speed of cellulose fibers was also measured. The cellulose was the same as that used by Bull and Gortner (9), and the streaming potential data was taken from their paper.

DISCUSSION

Although there are only fifteen ratios reported for the relation between streaming potential and electrophoresis for protein surfaces, actually these represent a great many measurements. There have been 480 electrophoretic measurements and 294 streaming potential determinations, so the whole takes on the color of a statistical analysis. The ratio comes out to be 0.97, which within experimental error may be considered equal to 1. The ratio of the electrophoretic potential to the electrosmotic potential is very close to 1, which is in good agreement with the results of Abramson (2). There is also satisfactory agreement between the electrophoretic potential and the electrosmotic potential. Thus it is seen that with protein-coated surfaces there is good correspondence between the three methods of determining the electrokinetic potentials. This lends support to the customary theoretical treatment of these phenomena, and would seem to support the factor of 4 in the equation for electrophoresis as derived by von Smoluchowski (20) and Henry (14).[9]

The values for quartz and cellulose are quite disturbing. There is indeed very little resemblance between the electrophoretic values and the streaming potential results. It is not certain that the surface potential on the larger quartz particles is the same as that for the very small ones used in the electrophoretic study, though there was no evidence of any very decided trend in the potential as determined with electrophoresis. The results obtained from these measurements seem to bear out the factor of 6π, instead of 4π as proposed by Debye and Hückel (13, 15). The values obtained for cellulose by the streaming potential method are much too low. If the results of Kanamaru (16) be accepted for the streaming potential ~~on cellulose, the agreement between the streaming potential and~~ electrophoresis becomes much better; however the electrosmotic results then fall out of line. It may be that the small values for the streaming potential with cellulose are due to the diminished pore size in the diaphragm packed tightly with cellulose. This is in keeping with the experimental results of White, Urban, and Van Atta (22) and also of Bull and Gortner (10) and with the theoretical considerations of Bull (6) and also of Bikerman (4). More investigation of surfaces which derive their charge by adsorption rather than by dissociation, as with proteins, is badly needed.

SUMMARY

1. A new electrophoretic cell has been described.
2. The electrophoretic, electrosmotic, and streaming potential methods

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[9] Henry proposes the equation

$$U = \frac{3\mu}{2\mu + \mu'} \frac{\zeta DX}{6\pi\eta}$$

for the electrophoretic mobility, where μ is the specific conductivity of the dispersions medium, μ' is the specific conductivity of the particle, and the other letters have the same significance as previously noted. It can be seen that when dealing with nonconducting particles the factor for the equation becomes 4π. With highly conducting particles the mobility should approach zero. This has not been generally observed. Henry explains this by assuming that the particles become polarized and are in this fashion rendered non-conducting. Bull and Söllner (11) have published mobility data obtained with mercury particles in a mercurous nitrate solution. These particles should be non-polarizable. Substituting approximate values in the Henry equation for the specific conductivities of the mercury and a 0.001 *M* mercurous chloride solution, we find that the equation becomes approximately

$$U = 50 \times 10^{-6} \frac{\zeta DX}{6\pi\eta}$$

This indicates that the mobility should be in the order of 1/100,000th of that observed. This represents a large discrepancy between the theoretical and experimental results.

of measuring the electrokinetic potentials have been compared, using the same solution and surface.

3. Good agreement was found when dealing with protein-coated surfaces.
4. Poor correspondence was found between electrophoresis and streaming potential for quartz and cellulose surfaces.

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A COMPARISON OF THE ELECTROPHORETIC, ELECTROSMOTIC AND STREAM POTENTIAL ISOELECTRIC POINTS AT GLASS AND GELATIN SURFACES[1]

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According to modern conceptions the ionic double layer responsible for electrokinetic phenomena consists of a sheet of ions containing an excess of either positive or negative charges rigidly attached to the solid wall, and a second layer of ions in the adjacent liquid containing an equal excess of charges of the opposite sign. The wall (inner Helmholtz) layer does not move under the influence either of an applied hydrostatic pressure or of an imposed E.M.F. The outer layer, according to Stern (13), may be further divided into a diffuse (Gouy) component which is moved by an applied hydrostatic pressure, and a second (outer Helmholtz) component immediately adjacent to the wall layer, which cannot be moved by hydrostatic forces. The potential drop across the diffuse, movable component is the electrokinetic or zeta potential.

Urban, White, and Strassner (14) suggest that although the outer Helmholtz layer is not displaced by hydrostatic forces, it may nevertheless move in an electric field. They point out that, on this assumption, only the outermost or diffuse component contributes to stream potential, whereas both the diffuse and the outer Helmholtz layers contribute to electrosmotic velocity. If u_m is the electrosmotic velocity in the center of a capillary, and u_0 and u_h the velocity of the diffuse and Helmholtz layers, respectively, then:—

$$u_m = u_0 + u_h = \frac{ED\zeta}{4\pi\eta} + \frac{ED(\psi - \zeta)}{4\pi\eta} = \frac{ED\psi}{4\pi\eta}$$

where E = applied E.M.F. per unit length of capillary,
D = dielectric constant,
η = viscosity,
ζ = potential drop across the diffuse layer, and
ψ = potential drop across the entire double layer.

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

This leads to the conclusion that when ζ (as measured by the stream potential method) becomes zero, electrosmosis may persist, provided that ψ is not also zero. Further, if ζ and ψ are of opposite sign, stream potential may reverse while electrosmosis continues in the original direction. The symbol ψ here designates the potential difference across the entire double layer and does not refer to the potential measured by the glass electrode, the latter apparently depending, within the range of concentrations studied by us, only on the hydrogen-ion concentration.

These deductions may be tested experimentally by determining the direction and velocity of electrosmosis when ζ, as measured by stream potential, is zero. This paper is concerned only with a comparison of isoelectric concentrations for stream potential, electrophoresis and electrosmosis, respectively; a discussion of the absolute magnitude of the electrokinetic potentials at other concentrations will be deferred.

The literature contains only one record of a direct comparison of the stream potential isoelectric point with electrosmotic or electrophoretic isoelectric points on the same material. Abramson and Grossman (3) found that the hydrogen-ion activity required to stop electrosmosis and electrophoresis in an albumin-covered electrophoresis cell with albumin-covered particles was practically the same as that previously found by Briggs (4) to be isoelectric for stream potential through a diaphragm covered with the same protein.

Isolated observations on isoelectric points of surfaces other than protein, however, do not show the same agreement with the two methods. Elissafoff (7) found a concentration of 1.9×10^{-6} M thorium nitrate to be isoelectric for electrosmosis in a quartz capillary and about 7×10^{-6} M thorium nitrate for a Jena glass capillary; whereas Freundlich and Ettisch (8) and Kruyt and van der Willigen (9) both found that stream potential in a glass capillary was already reversed at concentrations of 3 to 4×10^{-7} M thorium nitrate. The possibility remained, of course, that differences in the kind of glass used might have been responsible for this wide discrepancy.

Powis (11) found that a concentration of 3×10^{-5} M thorium chloride was required to reverse the electrophoretic movement of droplets of "cylinder oil," while Bull and Gortner (5) report that 1.2×10^{-6} M thorium chloride is isoelectric for stream potential on Nujol. Here again, a difference in the kind of oil used might account for the results.

EXPERIMENTAL

In the present paper, stream potential, electrosmotic, and electrophoretic isoelectric concentrations are obtained of (1) hydrogen ion with gelatin, and (2) thorium chloride, ferric chloride, and aluminum chloride with Pyrex glass.

Electrosmotic and electrophoretic isoelectric concentrations were determined by observing the movement of Pyrex glass particles in a closed Pyrex electrophoresis cell of the flat Northrop-Kunitz type. Abramson (1) discusses the use of such cells for electrosmosis and electrophoresis. The observed velocity of the particles at any given depth in the cell is the algebraic sum of the true electrophoretic velocity plus the electrosmotic velocity at that depth. The true electrophoretic velocity, V_p, is the observed velocity of the particles at 0.211 of the distance from the top or bottom of the cell. The true electrosmotic velocity, V_w, may then be obtained either according to the formula $V_w = 2(V_{\frac{1}{2}} - V_p)$, where $V_{\frac{1}{2}}$ is the observed velocity in the middle of the cell, or according to the formula $V_w = V_0 - V_p$, where V_0 is the observed velocity at the wall of the cell. It was found in preliminary experiments that when the particle velocity was plotted against cell depth a symmetrical parabola was obtained; also that values of V_w as calculated from the two formulas given above showed good agreement. In subsequent experiments, therefore, observations were made only at the bottom of the cell and at 0.211 of the distance from the bottom, and the electrosmotic velocity calculated from the second formula.

In the case of thorium chloride with Pyrex, the electrosmotic isoelectric point was also determined directly by applying an E.M.F. across a Pyrex capillary of 600μ diameter containing varying concentrations of thorium chloride and observing the rise or fall of liquid in the recording arm of the apparatus due to electrosmotic transport across the capillary (Quincke (12)). The two methods gave the same results.

Stream potential determinations were carried out on a Pyrex capillary of 300μ diameter by the method described by White, Urban, and Van Atta (15).

For all isoelectric point determinations on gelatin, solutions which were 4×10^{-4} N with respect to potassium chloride plus hydrogen chloride and which contained 0.01 g. gelatin per liter were used. The pH was varied by changing the proportion of hydrogen chloride to potassium chloride. Measurements of pH were performed by the glass electrode method. Both particles and cell were allowed to stand in contact with the gelatin solution for one hour before measurements were begun, in order to allow the glass surfaces to become coated with the protein. It has been shown repeatedly (Abramson (2); Dummett and Bowden (6)) that many substances, including glass, adsorb a complete coating of gelatin from dilute solutions of this protein, and that such protein-covered surfaces no longer behave like glass surfaces, but rather show the properties of the adsorbed protein. That is, by treating the glass surfaces as described they have in effect been converted into gelatin surfaces, so that it is now possible to study the effect of ions (in this case hydrogen ions) on electrokinetic phenomena at a gelatin surface. To obtain reproducible results with such poorly buffered solutions it was found necessary to increase the length of the side arms on the electrophoresis cell to about 20 cm. on each side in order to prevent diffusion of acid from the electrodes into the flat part of the cell during a series of readings.

Stream potential measurements were made on gelatin-coated glass capillaries, using the same solutions that were used for electrosmosis and electrophoresis. In order to secure complete coating of the capillary in a short time, a more concentrated gelatin solution (0.1 g. gelatin per liter) was run through for a few minutes before the determinations began. At hydrogen-ion activities close to the isoelectric point the stream potential generally required several hours to reach a constant value.

The isoelectric point data are summarized in table 1.

A few words concerning the accuracy and reproducibility of these results may be inserted here. It should be pointed out that the figures listed are not the result of isolated observations near the isoelectric point, but are taken from smooth curves representing electrokinetic potential over a wide range of concentrations. A typical set of curves is reproduced in figure 1. The absolute magnitudes of the electrokinetic potentials obtained by the three methods are not of quantitative significance; we were interested here only in the isoelectric points, and conditions essential to a quantitative measurement of electrokinetic potential were not adequately controlled. The isoelectric concentrations are given only to the nearest whole number, since the curves are not reproducible with greater accuracy than this. For example, on six experiments on the electrophoresis cell, the isoelectric concentration varied between 2 and 4 × 10^{-6} *M* thorium chloride. In two experiments with the Quincke set-up the curve crossed the zero potential line between 2.5 and 3 × 10^{-6} *M* thorium chloride. However, experimental variations in the isoelectric point (due probably to slight contamination of the surfaces or to differences in the time allowed for equilibrium, etc.) do not go beyond these limits; at a concentration of 1 × 10^{-6} *M* thorium chloride, electrophoresis and electrosmosis always

TABLE 1

Isoelectric pH for gelatin and isoelectric ion concentrations with Pyrex glass

	ISOELECTRIC pH FOR GELATIN	ISOELECTRIC CONCENTRATIONS OF $ThCl_4$ WITH PYREX	ISOELECTRIC CONCENTRATIONS OF $AlCl_3$ WITH PYREX	ISOELECTRIC CONCENTRATIONS OF $FeCl_3$ WITH PYREX
		M	*M*	*M*
Stream potential	4.75	4 × 10^{-7}	1 × 10^{-6}	1 × 10^{-6}
Electrosmosis	4.75	3 × 10^{-6}	3 × 10^{-6}	3 × 10^{-6}
Electrophoresis	4.75	3 × 10^{-6}	3 × 10^{-6}	3 × 10^{-6}

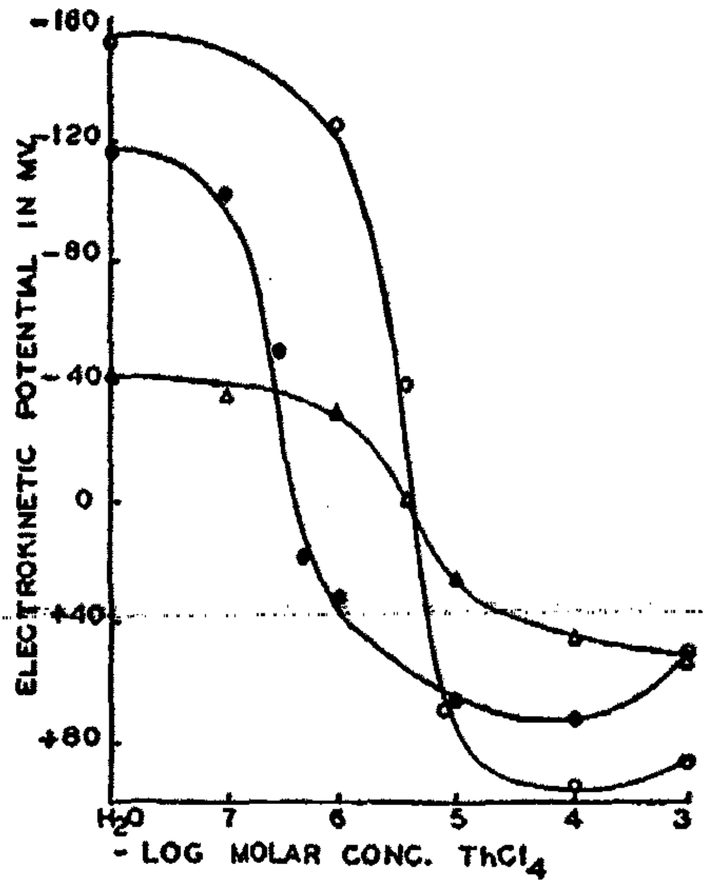

FIG. 1. ELECTROKINETIC POTENTIAL AS A FUNCTION OF $ThCl_4$ CONCENTRATION
○, electrosmosis; ●, stream potential; △, electrophoresis

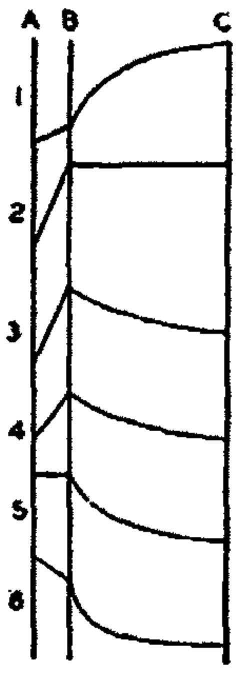

FIG. 2. SCHEMATIC REPRESENTATION OF THE COURSE OF THE POTENTIAL CURVES IN VARYING CONCENTRATIONS OF $ThCl_4$

A represents the solid wall, B the outer Helmholtz layer, C the outer boundary of the diffuse layer. The potential difference between A and C = ψ; that between B and C = ζ. Curve 1 represents the condition in water, where ψ and ζ have the same sign; curve 2, 4×10^{-7} *M* thorium chloride, stream potential isoelectric; curve 3, 8×10^{-7} *M* thorium chloride, stream potential reversed; curve 4, 3×10^{-6} *M* thorium chloride, stream potential reversed, electrosmosis isoelectric; curve 5, 1×10^{-5} *M* thorium chloride, stream potential and electrosmosis the same, both reversed; curve 6, 1×10^{-4} *M* thorium chloride, both reversed, electrosmosis greater than stream potential.

have the same sign as in water, while at a concentration of 5×10^{-7} *M* thorium chloride, stream potential is always reversed. With trivalent aluminum and iron the difference in the isoelectric concentrations for stream potential on the one hand and electrophoresis and electrosmosis on the other hand is not so great as with thorium chloride, but no less definite. On the gelatin surfaces all curves crossed the zero potential line at a pH between 4.7 and 4.8.

DISCUSSION

From the experimental data on thorium–glass it is evident that even when the glass surfaces are the same[3] (Pyrex) and the solutions identical, a great difference exists in the isoelectric concentrations of thorium chloride for stream potential on the one hand and for electrosmosis and electrophoresis on the other hand. At concentrations such that stream potential is reversed (between 4×10^{-7} *M* and 3×10^{-6} *M* thorium chloride, electrosmosis and electrophoresis continue in the original direction. This is interpreted to mean that a potential drop may exist across the outer Helmholtz layer when the ζ-potential is zero, and further that the potential of the outer Helmholtz layer may be of opposite sign from that of the diffuse layer. In dilute solutions of thorium chloride, for example, if some of the hydrogen-ions in the outer Helmholtz layer are replaced by tetravalent thorium ions, with their attendant anions in the diffuse layer, then there may actually be an excess of anions in the diffuse component, with a resultant reversal of stream potential. At the same time, if the boundary between mobile and immobile components of the electrical layer, which might here be designated as a triple layer, lies closer to the wall for electrosmosis and electrophoresis than for stream potential, the sign of the former remains unchanged. This sign will be reversed only when the adsorption process has proceeded to the point (with increasing thorium concentration) where the potential at the outer boundary of the diffuse layer is less than that at the wall, which apparently does not take place until the thorium concentration has been increased at least sevenfold above that required for isoelectric stream potential. Figure 2 illustrates schematically this concept of variations in the course of the potential–distance curves as the thorium concentration is increased. Similar considerations hold for the aluminum–glass and iron–glass systems. It is recognized that some colloidal thorium, aluminum, or iron is almost certainly present, but this has no bearing on the reality of a difference in the isoelectric concentration of stream potential on the one hand and of electrosmosis and electrophoresis on the other.

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[3] The surfaces for electrosmosis and stream potential are certainly the same, i.e., fused smooth surfaces. We have also shown (10) that the electrophoretic behavior of broken (particle) and fused (sphere) glass surfaces is the same.

On the other hand, the isoelectric hydrogen-ion concentration for gelatin is the same for electrosmosis, electrophoresis, and stream potential. In this case, when ζ becomes zero, ψ is also zero, and the two are never of opposite sign. Without entering into an adequate discussion of the mechanisms involved in the two cases, it should be pointed out that the layers are probably quite different on the two types of surfaces under consideration. In the case of gelatin the double layer is produced by an ionization process which gives rise only to varying ratios of univalent anions and cations in the solution, the total concentration remaining the same. It is difficult to see how such a process could produce a difference in sign of the outer Helmholtz as compared with the diffuse layer.

SUMMARY

The isoelectric concentration for electrosmosis and electrophoresis on Pyrex glass is found to be for thorium about seven and for aluminum and iron about three times as great as the isoelectric concentration for stream potential on the same kind of glass. The hydrogen-ion isoelectric concentration for gelatin, on the other hand, is the same for electrosmosis, electrophoresis, and stream potential. The results are explained on the assumption that only the diffuse component of the double layer is moved by hydrostatic forces, while both the diffuse and the outer Helmholtz layers move in an electric field.

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IONIC EXCHANGE IN RELATION TO THE STABILITY OF COLLOIDAL SYSTEMS

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INTRODUCTION

Numerous investigators (5, 7) have demonstrated a close relation between the elektrokinetic potential (zeta potential) of colloidal particles and the amount of electrolyte necessary to flocculate the system. A number of years ago Wiegner (10) called attention to the rôle of ionic exchange in modifying the stability of a suspensoid, and it appeared that the significance of the interchange phenomenon had been greatly underestimated by many students of coagulation processes. The present study attempts to clarify the relation among ionic exchange, zeta potential, and flocculation value for colloidal clay systems and to furnish quantitative correlations among these three magnitudes.

EXPERIMENTAL TECHNIQUE

Ionic exchange

The technique of ionic exchange experiments has been fully reported previously (3). In principle, natural Putnam clays were electrodialyzed and the resulting H-clays converted into basic clays (Na-clay, Ca-clay, etc.) by addition of known amounts of hydroxides, except in the case of La- and Th-clays and methylene blue clay, which were obtained by leaching of NH_4-clay with lanthanum nitrate, thorium chloride, and methylene blue chloride. To these basic clays electrolytes were added at various concentrations, and the exchange adsorption determined by analysis of the supernatant liquid. The amount of electrolyte added to the clay sols is expressed in terms of symmetry concentrations, that is, in multiples of the number of milliequivalents of adsorbed ions in the system. In particular, the magnitude of exchange expressed in percentage for the symmetry concentration equal to one ($S = 1$) is called symmetry value. All exchange data used in the present publication are symmetry values and have been reported previously (4).

Zeta potentials

All measurements of migration velocities were made with an ultramicroscope and an open cataphoresis cell as described by Tuorila (8). The cell was improved by introducing removable electrodes to permit thorough cleaning, which reduced the mean error of measurement to 2 per cent. The cell constructed obeyed Smoluchowski's equation strictly. Table 1 contains only a single observed migration velocity for each type of clay, but the average value of the zeta potentials calculated according to the equation

TABLE 1

Data on zeta potentials, adsorption, and flocculation

TYPE OF COLLOIDAL CLAY	MIGRATION VELOCITY* (ALL NEGATIVE)	TEMPERATURE °C.	AVERAGE ZETA POTENTIAL IN MILLIVOLTS (NEGATIVE)	PER CENT RELEASE OF ADSORBED ION (SYMMETRY VALUES)	FLOCCULATION VALUE FOR KCl (IN TERMS OF S CONCENTRATIONS)	FLOCCULATION VALUE FOR COMMON CATION AS CHLORIDE (S-CONCENTRATION
Li-clay	3.45	30.3	58.8	68.0	21.6	26
Na-clay	3.31	28.9	57.6	66.5	11.2	14.8
K-clay			56.4†	48.7	7.8	7.8
NH_4-clay	3.48	33.2	56.0	50	5.4	4.9
Rb-clay	3.25	30.3	54.9	37.4		
Cs-clay	3.02	30.3	51.2	31.2	5.6	4.2
H-clay	2.84	30.3	48.4	14.5	1.5	0.36
Mg-clay	3.18	30.3	53.9	31.32	2.9	0.69
Ca-clay	3.27	32.8	52.6	28.80	3.0	0.55
Sr-clay	3.06	30.3	51.8	25.76	2.6	
Ba-clay	3.01	30.3	50.8	26.75	2.3	
La-clay	2.74	21.2	45.5	13.96	0.86	
Th-clay	3.11	32.2	50.4 47.1	1.85	0.60	
M.B.-clay	2.57	33.7	40.5		0.0	

* Microns per second per volt per centimeter.

† Interpolated from a corresponding monovalent series (Li, Na, K) of Putnam clay.

$$\zeta = \frac{6\eta\pi\mu}{HD}(300)^2 \tag{1}$$

where ζ = zeta potential,

η = viscosity of the solution (H_2O) in poises,

μ = migration velocity of particle in cm. sec.$^{-1}$, measured at a depth of 0.2113 times the thickness of the cell.

D = dielectric constant (80),
H = potential gradient in volts $cm.^{-1}$, and
300 = ratio of electrostatic unit to practical electromagnetic unit of potential.

Although equation 1 is subject to criticism, we prefer to report the results as zeta potentials rather than migration velocities.

The migration velocity was found to be directly proportional to the potential difference between the electrodes, and appeared to be independent of the size of the particles. As the concentration of the sol increased the velocity decreased, as shown in figure 2. All data reported were measured at a sol concentration of 0.001 per cent on the basis of the weight of H-clay. The sols were kept in stock solutions of 0.5 per cent and 1.0 per cent, and it was observed that after dilution to 0.001 per cent the zeta potentials varied with the age of the diluted sol (figure 1). Final measurements were taken four to six days after dilution. All clays were negative, even the Th- and La-clays, in spite of the fact that addition of thorium chloride or lanthanum nitrate to a K-clay yields positive particles. Evidently during the process of removal of the excess electrolyte by leaching with distilled water the stabilizing chloride ions were replaced by OH^- and HCO_3^- and a negative clay resulted. Somewhat similar observations have been reported by Lottermoser (6). The zeta potential of the Th-clay appears to be too high, as will be demonstrated later.

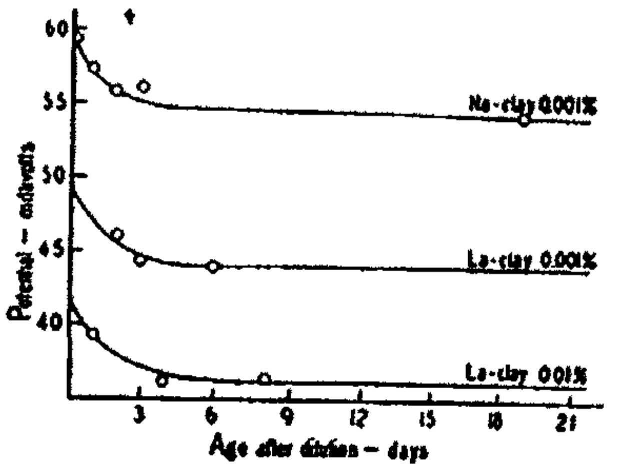

FIG. 1

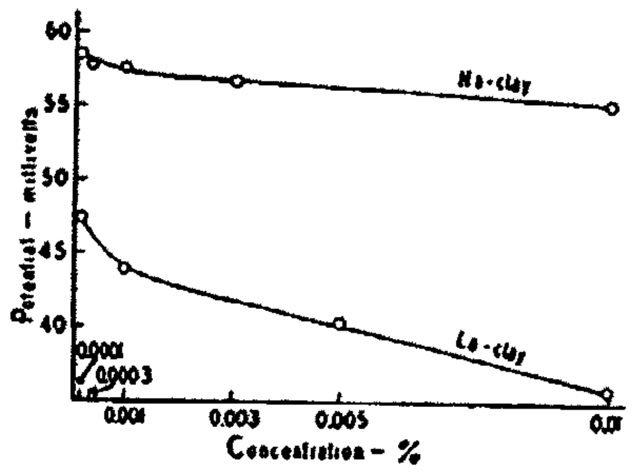

FIG. 2

FIG. 1. EFFECT OF DILUTION AGE ON THE POTENTIAL OF CLAY PARTICLES

FIG. 2. EFFECT OF CLAY CONCENTRATION ON THE ZETA POTENTIAL OF CLAY PARTICLES

Flocculation values

It is difficult to reproduce satisfactorily flocculation values for clay sols because of the great influence of such factors as method of shaking, age of sol, mode of diluting, etc. The following procedure was adhered to rigidly. Into a 75-cc. test tube were placed 5 cc. of 2.66 per cent clay sol (on the basis of H-clay), x cc. of redistilled water, and y cc. of electrolyte solution.

The final volume (5 + x + y) was always 35 cc. For fifteen minutes the tube was gently shaken with a mechanical device and care was taken that no air bubbles formed. Ten cc. of the mixture was then transferred into another 75-cc. tube which contained 25 cc. of water, and both tubes were shaken fifty times. This procedure permitted the determination of flocculation values at two different clay concentrations. In this paper only the values for the second (dilute) system are given. The tubes were put into a thermostat (30°C.), and after six hours the presence or absence of sedimentation was recorded. The flocculation values are expressed in terms of symmetry concentrations, which notation furnishes more instructive figures than does the customary designation as millimoles per liter.

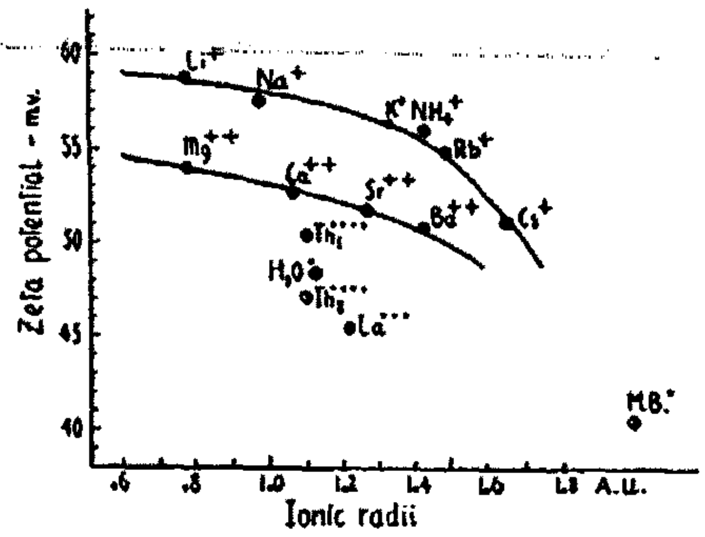

FIG. 3. EFFECT OF CHARGE AND SIZE OF ADSORBED CATIONS UPON THE POTENTIAL OF COLLOIDAL CLAY PARTICLES (Li-CLAY, Ca-CLAY, ETC.)

ZETA POTENTIALS AS INFLUENCED BY CHARGE AND SIZE OF THE ADSORBED CATIONS

In view of the fact that all clays prepared carry the same number of adsorbed cations, namely 60 milliequivalents per 100 g. of clay, the zeta potentials can be directly related to the nature of the ion in the outer swarm of the electric double layer. According to the data in table 1 and the curves in figure 3, certain regular trends are evident, and in particular an ionic charge and size effect come into prominence. *For rare gas type ions of equal size the zeta potentials of the clays tend to be lower as the electric charge of the adsorbed ion is higher.* The restriction of the comparison to ions of equal size is essential because certain mono-clays (e.g., Cs-clay) have lower potentials than some of the di-clays (Mg-clay, etc.). Evidently the statement often found in literature that clays with adsorbed divalent cations have lower potentials than mono-clays is too general, and applies only to ions with equal crystal lattice radii (Goldschmidt's values). The rôle of ionic size can be formulated as follows: *For rare gas type ions of equal valency the zeta potential is the higher the smaller the adsorbed cation.* This observation is in agreement with Wiegner's idea (10), according to which the most hydrated ion (small ions are very strongly hydrated) brings about the highest zeta potential.

On the basis of Helmholtz's classical picture of the electric double layer, the potential is higher as the number of electric charges (e) and the average distance (δ) of the double layer are greater. For ionic crystals such as clay particles, dissociation can be considered as complete (heteropolar linkage) and consequently the magnitude of the zeta potential becomes solely a function of δ. On account of the water shell, the centers of hydrated cations cannot approach the negative wall of the particle as closely as those of the smaller non-hydrated ions. Consequently ions with small crystal lattice radii but great effective sizes (hydrodynamic radii) widen the distance of the double layer and cause high potentials as demonstrated in figure 3.

ZETA POTENTIAL AND IONIC EXCHANGE

The mechanism of ionic exchange can be visualized as follows: Colloidal clay particles are plate-shaped crystals which hold on their surface adsorbed cations. Owing to heat motion and Brownian movement the adsorbed ions are not at rest but oscillate, and at times are at a considerable distance from the wall. If it so happens that on account of Brownian movement a cation of an added electrolyte slips between the negative wall and the positive oscillating ion, the electrolyte cation will become "adsorbed" while the surface ion remains in the solution as an exchanged ion. The more loosely an ion is held the greater is the average distance of oscillation and the greater is the possibility of replacement or, vice versa, the more tenaciously an ion sticks to the surface the less readily it will be released by the cations of an electrolyte added to the colloidal system. The average distance of oscillation corresponds directly to the average thickness of the electric double layer, and on the basis of the picture outlined one would conclude at once *that clays with high zeta potentials contain easily exchangeable ions.*

To test the validity of this conclusion it becomes necessary to learn the ease of replacement of the ions adsorbed on the clays listed in table 1. For this purpose data previously published were used which refer to the very same clay systems used in the present study. The release of the polyvalent cations was accomplished by addition of potassium chloride, while that of the monovalent cations was calculated from the exchange values with NH_4-clay. Since potassium ions and ammonium ions are equally well adsorbed and released, the data permit quantitative comparison.

According to figure 4 it is evident that ions which are easily released are also responsible for high zeta potentials. Lithium and sodium ions are loosely held, and about 70 per cent of them are exchanged by addition of an equal number of ammonium ions (symmetry concentration), while the clays with low potentials (La-clay, Th-clay) have exchange values below 20 per cent. The divalent cations occupy an intermediate position.

Neglecting the wave-like shape of the curves, the general trend of the exchange–zeta potential relation is of parabolic nature as seen in figure 5. The relationship can be satisfactorily described by the equation

$$E = 3.55 \cdot 10^{-10} \zeta^{6.43} \tag{2}$$

where E represents the percentage release of the adsorbed ion at 1 S concentration, and ζ the zeta potential in millivolts. The curve rises in a very pronounced fashion, approximately as the sixth power of the potential.

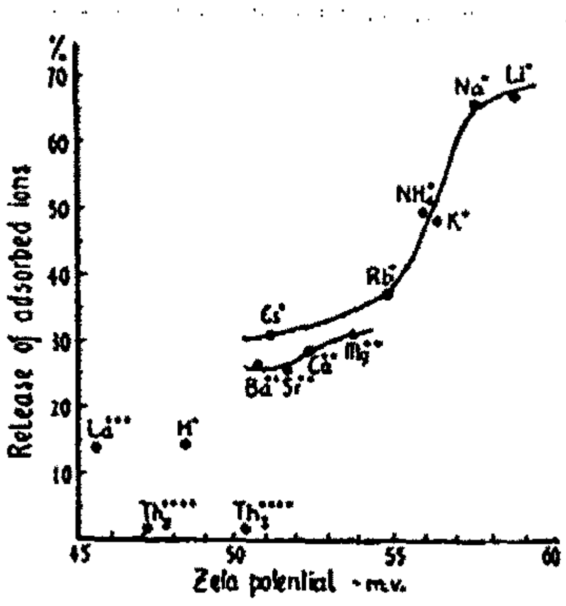

FIG. 4

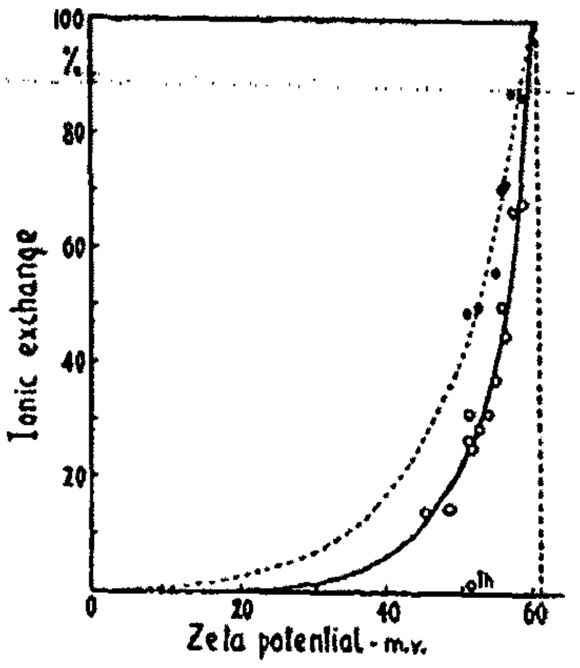

FIG. 5

FIG. 4. RELEASE OF ADSORBED CATIONS IN RELATION TO ZETA POTENTIAL

For example, release of lithium from Li-clay or barium from Ba-clay. Exchange expressed as symmetry values.

FIG. 5. THE INTENSITY OF IONIC EXCHANGE INCREASES APPROXIMATELY AS THE SIXTH POWER OF THE ZETA POTENTIAL

Note the indication of a maximum potential. Black points refer to release by calcium; the white points to exchange with potassium and ammonium.

According to the strong adsorption of thorium the value of the zeta potential of the Th-clay appears to be questionable.

The curves in figure 5 further indicate that the ionic exchange is zero if the zeta potential is zero, in other words, the adsorbed ions are so tightly held that they become an integral part of the particle with a corresponding annihilation of the double layer. Inspection of the upper part of the curve is equally instructive. Since ionic exchange cannot exceed 100 per cent, the trend of the curve strongly suggests that the clay systems investigated possess a definite maximum potential which is slightly above 60 millivolts. These data can be taken as a confirmation of Hevesy's concept (2) and also of Freundlich's statement (1) that the potential of colloidal particles tends to stay below 100 millivolts.

ZETA POTENTIALS IN RELATION TO FLOCCULATION[1] VALUES

The contention of colloid chemists that the zeta potential bears a close relationship to the stability of a colloidal system is well illustrated by figure 6. A series of clays carrying equal amounts but different kinds of cations were flocculated with potassium chloride according to the method mentioned on pages 595–6. It takes much more electrolyte to flocculate a clay with a high potential than one with a low potential. The relation between the flocculation value and the zeta potential also is of parabolic form, showing that the stability increases many-fold with a slight rise in the zeta potential. To flocculate a clay with maximum potential, extrapolation would give a value of about 50 *S*, which corresponds to an electrolyte concentration of 0.0326 *N* potassium chloride for the systems in question.

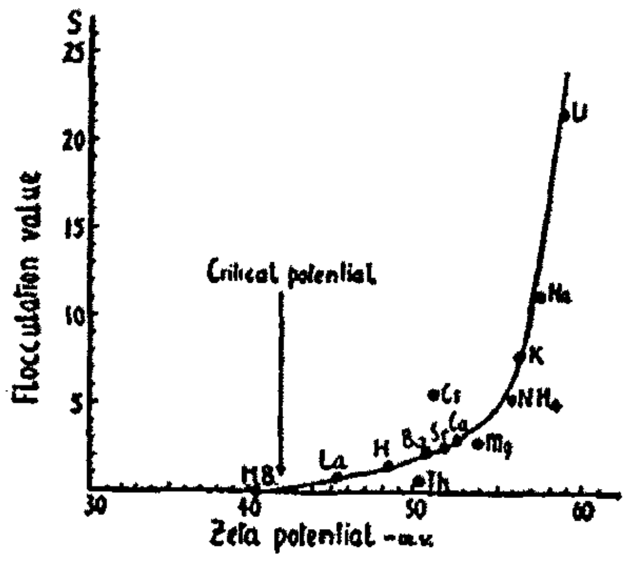

Fig. 6

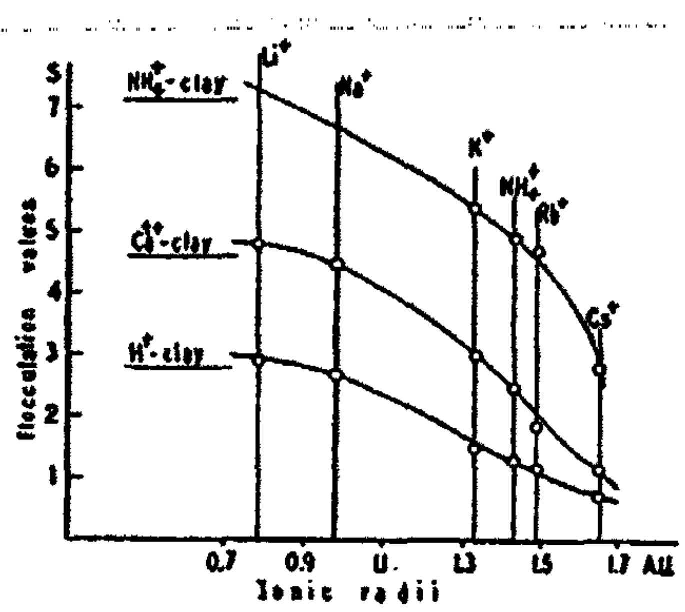

Fig. 7

Fig. 6. Flocculation of Mono- and Poly-clays by Potassium Chloride

The higher the initial potential of the colloidal particle the greater the flocculation value. The critical potential has a value of about 42 millivolts.

Fig. 7. Flocculation Values of Various Cations in Relation to their Crystal Lattice Radii

The curve in figure 6 tends to cut the X-axis at a potential which is far above zero, and therefore is in accord with the concept of the critical potential, advanced by Powis (7). This value appears to correspond to about 42 millivolts for the type of experimental procedure applied. In confirmation of this magnitude, the methylene blue clay with a potential of 40.5 millivolts sediments completely without the addition of electrolyte.

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[1] "Flocculation" and "coagulation" are used synonymously in this paper.

FLOCCULATION VALUES AS AFFECTED BY CHARGE AND SIZE OF THE FLOCCULATING IONS

Charge of ion

The well-known flocculation rule of Schulze-Hardy, as formulated by Wetham (9), states that the reciprocal flocculation values expressed in moles follow the proportion

$$1_{I} : x_{II} : x_{III}^{2} : x_{IV}^{3} \qquad (3)$$

where the Roman subscript denotes the valency of the flocculating ion. This rule is grossly violated in the case of clay systems (table 2). For NH_4-clay and Ca-clay the average flocculation values for the mono- and poly-valent cations yield quotients of the form

$$1_{I} : x_{II} : 2.03x_{III} : 3.21x_{IV} \text{ (NH}_4\text{-clay)} \qquad (4)$$

$$1_{I} : x_{II} : 1.76x_{III} : 3.14x_{IV} \text{ (Ca-clay)} \qquad (5)$$

In other words, the polyvalent cations are much less effective coagulators than is indicated by the valency rule. For the two clay systems given, the order of magnitude of effectiveness is much better expressed by a proportion of the type

$$1_{I} : x_{II} : 2x_{III} : 3x_{IV} \qquad (6)$$

where the exponents of Wetham's equation have become mere factors.

Size of ion

In figure 7 the flocculation values have been plotted against the crystal lattice radii of the corresponding ions, and it is clearly seen that for a given type of clay the flocculation value is higher as the size of the ion is smaller. The more highly hydrated a cation, the smaller is its efficiency as a coagulator.

FLOCCULATION VALUES AND EXCHANGE ADSORPTION

In the flocculation of ultramicrons, two important cases must be separated. First, the cation of the electrolyte and the colloidal particles possess common ions only (e.g., K-clay + potassium chloride); secondly, the coagulation agent contains only foreign ions with respect to the particle. In the former case flocculation results from repression of the double layer (diminishing of δ). In the second case it constitutes a combination of ionic exchange and the repression phenomenon.

In regard to the common ion effect the data in table 1 vary considerably for different clay systems. Since the osmotic pressures of dilute strong electrolytes of equal normalities vary but little, the great difference in the flocculation values must be attributed to the magnitude of the original zeta potential rather than to the repression efficiency of the various salts. Indeed, the figures for the common ion effect are of the same order of magnitude as the potassium chloride-set values (table 1).

Whenever the flocculating electrolyte contains a foreign cation, exchange adsorption is bound to occur. A comparison between the flocculation

TABLE 2

Relation between flocculation values and exchange adsorption

ELECTROLYTE	NH_4-CLAY		Ca-CLAY		H-CLAY	
	Flocculation value (*S*)	Adsorption (*S*)	Flocculation value (*S*)	Adsorption (*S*)	Flocculation value (*S*)	Adsorption (*S*)
LiCl	8.0	32.0	4.8	13.08	2.9	6.6
NaCl	8.0	33.5	4.5	12.74	2.7	6.2
KCl	5.4	51.33	3.0	28.80	1.5	14.5
NH_4Cl	4.9	50	2.5	29.35	1.3	
RbCl	4.7	62.56	1.87	43.85	1.17	28.20
CsCl	2.8	68.78	1.17	50.83	0.73	39.73
HCl	0.98	84.89	0.55	77.80	0.36	50
$MgCl_2$	1.22	65.44	0.59	47.53	0.47	15.78
$CaCl_2$	1.27	63.56	0.55	50	0.47	26.89
$BaCl_2$	1.16	71.67	0.55	52.96	0.35	23.78
$La(NO_3)_3$	0.90		0.47		0.18	
$ThCl_4$	0.75	80.89	0.36	80.24	0.16	

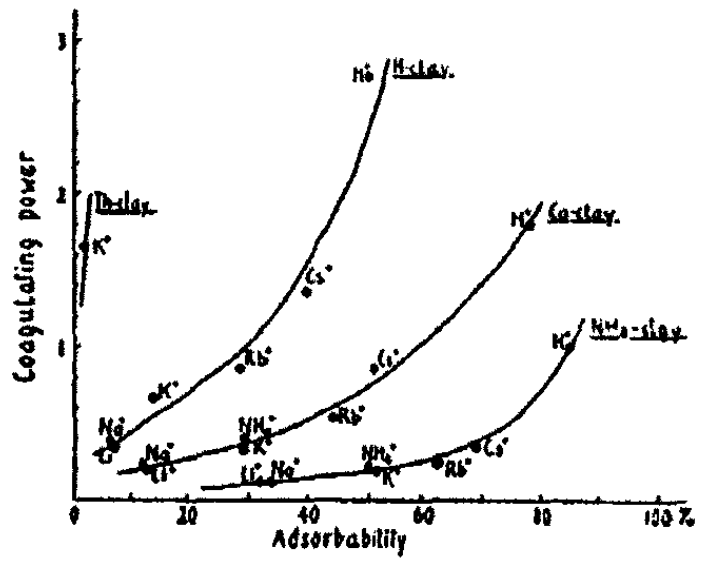

FIG. 8. RELATION BETWEEN ADSORBABILITY OF A MONOVALENT ION AND ITS COAGULATING POWER

values and the ionic exchange data (table 2) points toward an intimate association of the two phenomena. For any specific clay system (NH_4-clay, Ca-clay, etc.) those ions which are poorly adsorbed yield high flocculation values, while cations easily taken in by the colloidal particle coagulate the system at relatively low electrolyte concentrations. The two sets of values suggest a direct correlation which is of negative exponential type, and the experimental points satisfy the empirical equations

$$F_v = 7.16e^{-0.0332E} \text{ (for Ca-clay)} \tag{7}$$

$$F_v = 3.52e^{-0.0431E} \text{ (for H-clay)} \tag{8}$$

where F_v represents flocculation value and E the intensity of electrolyte adsorption expressed in terms of symmetry values. The reciprocal of the flocculation value can be taken as an index of the flocculation power of a cation, and the relation of the latter to the adsorbability of the ion is graphically represented in figure 8. The functions are of the form

$$F_p = 0.140e^{0.0332E} \text{ (for Ca-clay)} \tag{9}$$

$$F_p = 0.284e^{0.0431E} \text{ (for H-clay)} \tag{10}$$

where F_p represents the flocculating power and E the adsorbability (exchange). For the sols tested, the coagulating effect of an ion increases exponentially with its adsorbability. The position of the various curves stresses the fact that for a specific ion its flocculative effect depends largely on the nature of the ion initially adsorbed.

FLOCCULATION BY X-RAYS

The sols listed in table 1 were subjected to x-ray treatment. Th-, La-, and H-clay flocculated after a dosage of 10,503 r units, while the di-clays required about double the amount. None of the mono-clays (except H-clay) showed any signs of sedimentation, even after a dosage of 20,503 r units. Zeta potentials of treated and untreated samples of Th-, Mg-, H-, and K-clays were measured, and it was observed that in every case the zeta potential was reduced in magnitudes varying from 3.2 to 7.8 per cent. Conductivity measurements failed to reveal the presence of significant amounts of coagulating electrolytes. It must be concluded that the efficiency of x-rays in destroying the stability of the clay systems depends—among other things—on the nature of the adsorbed cation. It appears that the x-rays directly modify the composition of the electric double layer.

MECHANISM OF FLOCCULATION WITH SPECIAL REFERENCE TO THE RÔLE PLAYED BY IONIC EXCHANGE

The data secured in this investigation enables one to draw a rather detailed picture of the significance of ionic exchange in the problem of colloid stability. Hitherto, too much emphasis has been attributed to the behavior of the flocculating electrolyte alone, while the results reported in this paper indicate that the nature of the cations initially adsorbed on the colloid is equally important.

Every electrolyte coagulation is associated with an ionic exchange reaction. Two specific cases of flocculation will be discussed. First, that of a clay system which contains adsorbed monovalent cations of a highly hydrated nature, and secondly, the behavior of particles carrying either non-hydrated monovalent cations or polyvalent ions.

In the first case, which deals with clays containing highly hydrated monovalent ions (e.g., Na-clay), the zeta potential is high because the ions are but loosely held and oscillate over considerable distances. The effective width of the double layer is great (or, the degree of dissociation is high). Although the addition of sufficient amounts of any electrolyte will cause the system to settle out, the magnitude of the flocculation value is a function of the properties of the coagulating cation. If it is also monovalent and strongly hydrated (e.g., Li^+) the extent of ionic exchange will be moderate, in the neighborhood of 50 per cent. The zeta potential becomes but little altered and flocculation has to be brought about by the repression of the double layer (or, decrease in dissociation), which requires large amounts of electrolytes of the order of 15 to 20 *S*.

An entirely different mechanism prevails if the cation of the added electrolyte is monovalent but not hydrated, as Cs^+, or polyvalent as La^{+++}. Under such conditions, ionic exchange assumes a dominating influence. At symmetry concentration, from 75 to 95 per cent of the cations change places. The colloidal particle acquires an entirely new coat consisting of ions which are strongly attracted by the inner layer, and as a result, the zeta potential drops sharply. Very little electrolyte is necessary to repress the new outer swarm of ions to the critical distance which is characteristic of the critical potential. The flocculation values are small, and of the order of 1 *S*.

In regard to the second case, which embraces clays carrying non-hydrated monovalent ions (Cs^+-clay) or polyvalent cations (La^{+++}-clay), the zeta potentials are low to begin with, because the oxygen and hydroxyl ions of the crystal lattice act as powerful adsorbents, and the average oscillation distance of the adsorbed ion is relatively small. Addition of electrolytes possessing hydrated monovalent cations (lithium chloride) will produce a modest exchange only (less than 25 per cent) which, nevertheless, tends to raise the average distance of the double layer and consequently the zeta potential. The stability of the system is definitely augmented, but the repression effect of the electrolyte finally counterbalances the peptization due to ionic exchange and precipitation takes place. The flocculation values are of medium magnitude (2 to 10 *S*), but higher than the common ion values.

If the coagulating cation is of similar nature to the one initially adsorbed (non-hydrated, or polyvalent), ionic exchange assumes again greater dimensions (about 50 per cent) without, however, greatly modifying the zeta potential. Flocculation is accomplished mainly through repression (or decrease of ionization), which is effective at very low electrolyte concentration, often less than 1 *S*.

SUMMARY

1. Zeta potentials of Putnam clay particles depend on the charge and size of the adsorbed ion. For rare gas type ions of equal size, the potential tends to be lower as the valency of the ion is higher. If the charge of the ion is kept constant, the potential is higher as the adsorbed cation (crystal lattice radii) is smaller.

2. Colloidal particles with high potentials carry adsorbed ions which are easily exchangeable. The ease of replacement increases as the sixth power of the zeta potential. Data indicate the existence of a maximum potential which amounts to about 62 millivolts.

3. The flocculation value of a given electrolyte increases potentially with the zeta potential. The critical potential was found to be 42 millivolts.

4. The valency rule of Schulze-Hardy is grossly violated in the case of clay systems. For monovalent cations the flocculation value is the higher the smaller the size of the ion.

5. The flocculating power of a cation is a positive exponential function of its ionic exchange ability.

6. A detailed picture of the mechanism of flocculation in relation to ionic exchange is presented.

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A.C. AND D.C. SURFACE CONDUCTIVITY MEASUREMENTS IN PYREX SLITS[1]

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In a previous communication (5), White, Urban, and Van Atta reported a value of 2.24×10^{-9} mhos for the specific surface conductivity of fused Pyrex glass, in a 5×10^{-4} *M* potassium chloride solution. This value represented an average obtained from D.C. resistance measurements in a number of capillaries of known dimensions. Since the resistances of these capillaries were quite high, i.e., between 10^{10} and 10^{11} ohms, determination of the resistance by means of A.C. was not considered feasible.

In the present paper, surface conductivity measurements in Pyrex slits, carried out both with D.C. and A.C., are described. The slits were obtained by the simple expedient of cracking Pyrex flasks; the width of these slits varied between 0.6 and 16 μ, in different flasks.

DETERMINATION OF LENGTH AND THICKNESS OF THE SLITS

The slit length was determined by means of a pantograph, the magnification being between 8 and 10. The thickness of the glass was measured with micrometer calipers, along the entire length of the slit. An average of these measurements was used for the thickness of the slit.

After the resistance measurements had been completed, potassium ferrocyanide solution was sucked into the slit, which was then immersed in ferric chloride solution. Two parallel blue lines are seen where the slit is open; these indicate the top and bottom of the slit. In the very narrow slits, this method did not give satisfactory results, and the deposit of Prussian blue had to be formed by electrolysis.

APPARATUS

The resistance measurements were carried out in a water bath at 25.00 ±0.01°C. The Wheatstone bridge was a 5-dial Gray instrument, with coils accurate to 0.025 per cent. The A.C. current was supplied by a 1000-cycle motor generator. The d'Arsonval galvanometer (D.C. measurements) had a sensitivity of 10^{-10} ampere.

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A.C. MEASUREMENTS

Platinized platinum electrodes (one made of platinum gauze, the other one a perforated platinum disk) were equilibrated with the solution, and then placed one below and one above the slit.

The absence of a Parker effect (2) is demonstrated by the constancy, within experimental error, of the cell constants. The behavior of slit No. 1 is representative. The cell constants were 269.8 in 0.1 *M* potassium chloride; 272.1 in 0.2 *M* potassium chloride; 270.2 in 0.5 *M* potassium chloride; 271.3 in 1.0 *M* potassium chloride; average, 270.8.

TABLE 1

Specific surface conductivity in 5 × 10^{-4} M potassium chloride

SLIT NO.	CELL CONSTANT	LENGTH	AVERAGE THICKNESS	A.C. RESISTANCE	A.C. SPECIFIC SURFACE CONDUCTIVITY
		cm.	*cm.*	Ω	*mhos*
10	3.344	30.1	0.078	39,000	4.1 × 10^{-9}
11	11.94	22.6	0.067	108,800	4.3 × 10^{-9}
8*	71.00	10.6	0.125	600,000	3.6 × 10^{-9}
7	347.1	8.0	0.180	1,680,000	4.27 × 10^{-9}

* The low value for the specific surface conductivity in slit No. 8 is believed to be due to insufficient washing with hot water. Six flasks not treated with hot water gave a value of 3.6 × 10^{-9} mho with A.C. in 5 × 10^{-4} *M* potassium chloride.

TABLE 2

Specific surface conductivities at concentrations other than 5 × 10^{-4} M potassium chloride

CONCENTRATION OF KCl	SPECIFIC SURFACE CONDUCTIVITY	
	Slit No. 10	Slit No. 11
M		
1.25 × 10^{-4}	0.52	0.51
2.5 × 10^{-4}	0.60	0.53
5.0 × 10^{-4}	1.00	1.00
1.0 × 10^{-3}	1.90	1.94
3.0 × 10^{-3}	4.72	4.97
1.0 × 10^{-2}	8.80*	

* This value was obtained with slit No. 13.

Hot distilled water was sucked through the slits for several hours before using; they were then equilibrated with solution, by sucking the latter through them for some time. Then the resistance measurements were carried out.

The series was started with 1.25 × 10^{-4} *M* potassium chloride and ended with 0.1 *M* potassium chloride, unless the Parker effect was being investigated. The slit was then treated with hot distilled water, again equilibrated with 1.25×10^{-4} M potassium chloride, and the series repeated. Good agreement was obtained.

As a result of these measurements, we calculate a specific surface conductivity in 5×10^{-4} M potassium chloride, of 4.3×10^{-9} mhos. This is a weighted average, based on measurements in four slits. The data are summarized in table 1.

The fraction of the total conductivity contributed by the surface was as follows: slit No. 10, 12.3 per cent; No. 11, 31.6 per cent; No. 8, 37.3 per cent; No. 7, 63.8 per cent. The width of the slits, calculated from cell constants, length, and thickness, is: slit No. 8, 16 μ; No. 10, 8 μ; No. 11, 3 μ; No. 7, 0.6 μ. The fact that specific surface conductivity is independent of the width of the slit (table 1) is noteworthy. This indicates absence of membrane potentials.[3]

TABLE 3

Apparent specific surface conductivities

SLIT NO.	APPARENT D.C. RESISTANCE CORRECTED FOR LEADS	CELL CONSTANT	APPARENT D.C. SPECIFIC SURFACE CONDUCTIVITY
	ohms		*mhos*
10	41,500	3.344	2.2×10^{-9}
11	128,000	11.935	2.3×10^{-9}
8*	726,000	71.00	1.9×10^{-9}
7	3,000,000	347.1	1.3×10^{-9}

* See footnote to table 1.

The A.C. specific surface conductivities at concentrations other than 5×10^{-4} M potassium chloride, are given in table 2, for two slits. The specific surface conductivity in 5×10^{-4} M potassium chloride has been selected as reference and assigned the value of unity.

D.C. MEASUREMENTS

The D.C. surface conductivities, calculated from D.C. resistance measurements, may be expected to be lower than the A.C. surface conductivities. This is due to the existence of a counter E.M.F., the membrane potential, which simulates a greater resistance than actually exists.[2]

The polarization to be expected at platinum electrodes was avoided by the use of calomel electrodes of large surface. The E.M.F. used was that of the calomel cell potential difference, or about 3 millivolts. The cells were prepared with 5×10^{-4} M potassium chloride.

The slit was placed between the calomel cells, and the deflection of the galvanometer in series was noted. Next the slit was removed, and a

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[3] The membrane potential is defined as a counter E.M.F. which occurs when an electrosmotic current flows through a slit or capillary (1).

known resistance of such magnitude placed in the circuit that the galvanometer deflection was exactly the same as before. The value of this known resistance is the apparent resistance of the slit. These readings could be duplicated several times in succession. The apparent specific surface conductivities were calculated from the apparent resistances, A.C. cell constants being used. The apparent specific surface conductivities are summarized in table 3.

The average of the first three values is 2.13×10^{-9} mhos, and agrees well, within experimental error, with the value of 2.24×10^{-9} mhos found by White, Urban, and van Atta (5) with capillaries having a surface/volume ratio of the same order, i.e., 8000. The low value for the apparent specific surface conductivity in slit No. 7 is due to the extreme narrowness (0.6 μ). The surface volume ratio of this slit is 33,000. The smallest capillary of White, Urban, and van Atta (4) had a surface/volume ratio of about 22,000, and its specific surface conductivity was found to be 1.55×10^{-9} mhos.

TABLE 4

"True" D.C. resistances and specific surface conductivities calculated therefrom
(5×10^{-4} M potassium chloride)

SLIT NO.	A "TRUE" D.C. RESISTANCE	B A.C. RESISTANCE	C APPARENT D.C. RESISTANCE	SPECIFIC SURFACE CONDUCTIVITY FROM		
				A	B	C
10	38,700	39,000	41,500	4.4×10^{-9}	4.1×10^{-9}	2.2×10^{-9}
11	108,000	108,800	128,000	4.6	4.3	2.3
8*	597,000	600,000	726,000	3.7	3.6	1.9

SLIT NO.	i_1	i_2	E_1	R_1	R_2	LEAD RESISTANCE
	scale divisions	*scale divisions*	*volts*	*ohms*	*ohms*	*ohms*
10	7.45	9.90	0.0015	80,000	50,000	2,500
11	4.1	5.4	0.0015	100,000	50,000	
8*	5.3	5.65	0.0075	50,000	10,000	

* See footnote to table 1.

This falling-off in apparent specific surface conductivity finds its natural explanation in the statement made by Bikerman (1) that the counter E.M.F. (membrane potential) increases with the surface/volume ratio.

DETERMINATION OF "TRUE" D.C. RESISTANCE OF SLITS

The "true" D.C. resistance of the slits was determined by means of an approximate method.

If a small E.M.F. is applied to the slit, through a known resistance, it follows that

$$i_1R_s + i_1R_1 = E - E_{m_1} - E_{p_1} \qquad (1)$$

where i = current, R_s = resistance of slit, R_1 = known resistance, E = applied E.M.F., E_{m_1} = membrane potential, and E_{p_1} = electrode (polarization) potential. Changing the known resistance to the value R_2:

$$i_2R_s + i_2R_2 = E - E_{m_2} - E_{p_2} \tag{2}$$

Making the assumption that $E_{m_1} + E_{p_1} \cong E_{m_2} + E_{p_2}$ when the change in i is small, it follows that

$$i_1R_s + i_1R_1 = i_2R_s + i_2R_2 \tag{3}$$

from which R_s can be calculated when i_1 and i_2 are determined. These quantities are simply proportional to the galvanometer deflections.

The "true" D.C. resistances obtained by this approximation method, and specific surface conductivities calculated therefrom, are given in table 4. For comparison, the A.C. and apparent D.C. values are also included.

DISCUSSION

The agreement between apparent surface conductivities in slits and capillaries, of the same order of surface/volume ratio, indicates that there is no difference in the surface conductivity of fused and fractured glass surfaces, respectively. This conclusion finds further support in the findings of White, Monaghan, and Urban (4) on the influence of electrolyte concentration on the ratio of electrosmotic and electrophoretic mobilities, and of Monaghan and White (3) that ζ-potential is the same at fused and unfused glass surfaces.

Not too much weight should be attached to the "true" D.C. surface conductivity, as the closeness of the approximation is not known. If the "true" surface conductivity can be confirmed by a different method, then the inference would be justified that electrosmose is almost as pronounced with 1000-cycle A.C., as it is with D.C.

SUMMARY

1. Specific surface conductivities of Pyrex slits were determined with 1000-cycle A.C. (1.25×10^{-4} to 1×10^{-2} M potassium chloride) and with D.C. (5×10^{-4} M potassium chloride).
2. The apparent D.C. specific surface conductivity is lower than A.C. surface conductivity. This is due to membrane potentials.
3. The apparent D.C. specific surface conductivity of fractured glass agrees with that obtained previously in smooth capillaries.

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THE INFLUENCE OF ELECTROLYTE CONCENTRATION ON THE RATIO OF ELECTROSMOTIC TO ELECTROPHORETIC MOBILITIES

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Within the past few years it has become evident that the theoretical treatment of electrophoresis and electrosmosis of Helmholtz, Perrin, and von Smoluchowski must be considerably amplified. The expression developed by these authors is as follows:

$$V = \frac{XD\zeta}{4\pi\eta}$$

where V represents either electrophoretic or electrosmotic velocity, X is the applied field, D the dielectric constant, ζ the electrokinetic potential, and η the viscosity of the medium. According to this formulation, the electrophoretic migration velocity of a particle through a given liquid should equal the velocity of flow of the liquid past a fixed surface of the same material as the particle, irrespective of the size or shape of the particle or the nature of the liquid, provided ζ remains constant.

In 1924 Debye and Hückel (10, 16) published a new formula for electrophoretic mobility,

$$V = \frac{XD\zeta}{K\pi\eta}$$

in which K varies as the shape of the particle, having a numerical value of 6 for spherical particles. However, Mooney (19) and Henry (15) pointed out that Debye and Hückel neglected to allow for the distortion of the electric field caused by the particle, a factor which is negligible only when the diameter of the particle $\leqq$ the thickness of the double layer. The von Smoluchowski formula is valid when the ratio of particle diameter to double layer thickness $\geqq$ 600. (Müller (20) misquotes Henry on this point.) For particles of about 1μ diameter the Debye and Hückel formula, according to Henry, should apply in pure water; in solutions more concentrated than $M/100$ the von Smoluchowski formula applies, and in intermediate concentrations the factor K should vary between the limits set by the two formulas, i.e., between 6 and 4 for spherical particles. It will be shown later that under the influence of this effect the factor 6 is approached but never attained.

A second consideration, the distortion of the charge distribution in the double layer caused by the imposed field, may also affect electrophoretic velocity. Müller (20) points out that if the double layer is very thin, the disturbing effect of an applied field of the order of a few volts per centimeter is negligible, since the electric field of the double layer itself is over 1000 volts per centimeter. However, if the double layer is very thick, the outermost ions are in a weak field and hence may be influenced by the external E.M.F. Müller, assuming that this effect is analogous to the retardation of moving ions due to the asymmetrical surrounding field discussed by Debye and Hückel (9), concludes that electrophoretic velocity may be considerably diminished in dilute solutions because of this factor. However, no quantitative expression for this effect on the retardation of electrophoretic velocity is yet available, and indeed Mooney (18) speaks of polarization increasing the velocity of the particle, although this enhancing effect now seems improbable.

Aside from these suggested amplifications of the Helmholtz-Perrin-von Smoluchowski formula, there is the further possibility that the ζ-potential of a small particle may differ from that of a flat surface. This may occur either by a change of charge density or of double layer thickness or of both.

$$\zeta = \frac{4\pi\sigma\lambda}{D}$$

where σ is charge density and λ is the effective thickness of the double layer. Following Müller's treatment in Abramson's paper (4)

$$\lambda = \frac{1}{\kappa}\,\frac{\kappa r}{1 + \kappa r}$$

where κ is a function of ionic concentration and r is the radius of the particle. According to this treatment the double layer thickness will vary significantly with r when $\kappa r \leqq 5$. This predicts a decrease of double layer thickness, of ζ, and of electrophoretic mobility with decreasing radius of particle. It also predicts that with increasing electrolyte concentration "the size effect is shifted to smaller radii or disappears."

The dependence of the adsorbed charge density on the radius of the particle is discussed by Abramson (4). According to his treatment the negative logarithm of the particle velocity should be inversely proportional to the particle radius. It may be pointed out that, unlike the influence of particle radius on double layer thickness, the influence of radius on charge density should operate in all concentrations up to that in which charge density reaches its saturation value, which has been found by Abramson and Müller (7) to be for most materials at about $M/100$ for ions not reversing sign of charge. Since, however, the vapor pressure is increased by only 1 per cent above normal with droplets of 2μ diameter and by only 10 per cent with droplets of $20m\mu$ diameter, this effect will be negligible with particles in the microscopic range, if the analogy between vapor pressure and solution pressure holds.

From the foregoing considerations it may be predicted (1) that in solutions more concentrated than $M/100$ electrophoretic velocity should be independent of the size and shape of the particle, except for extremely small particles, and should be numerically the same as electrosmotic velocity over a flat surface, and (2) that in solutions less concentrated than $M/100$, electrophoretic velocity may become less than electrosmotic velocity. For a given solution the ratio, R, of electrosmotic velocity to electrophoretic velocity should increase as the radius of the particle decreases; for a given particle size, R should increase as the concentration of the solution decreases. The absolute magnitude of R for a given particle size in a given solution cannot be predicted, but one should be able to demonstrate qualitatively that changes in R take place under the conditions indicated.

Mooney (18) made the first experimental attempt to compare electrophoretic with electrosmotic velocity on the same substance. He found that the mobility of oil droplets in distilled water increased with diameter. The diameter above which no further increase in mobility occurred was established in a later paper (19) as about 100μ. The influence of droplet size on mobility was reduced or abolished by the addition of electrolyte. He compared electrosmotic with electrophoretic velocity in distilled water and in $4 \times 10^{-4}\ M$ copper sulfate. In water the velocity of the small droplets was less than that of electrosmosis; that of the larger (about 40μ) was the same as or greater than electrosmosis. The finding of electrophoretic > electrosmotic velocity is, even for the larger particles, probably in error. In the copper sulfate solution the velocities of all droplets were equal and almost as great as that of electrosmosis. Mooney (19) added further data and compared the experimental findings with the limiting slope of his theoretical mobility–diameter curve. In general, he found the expected correlation between mobility and droplet size in the less concentrated solutions, while in the more concentrated solutions droplets of all sizes moved at approximately the same velocity, as predicted. However, a rather wide scattering of the experimental points and the anomalous effects mentioned by Mooney indicated the desirability of similar experiments on a more stable system.

Aside from the work of Mooney there appears to be no direct experimental evidence in support of the theoretical predictions mentioned above. On the contrary, Abramson (4), after reviewing the experimental work of himself and others, concludes that, when the surfaces compared are chemically identical, (1) electrophoretic mobility is independent of particle size, and (2) electrophoretic and electrosmotic velocities are identical. However, a further investigation of the data reviewed by Abramson brings out the fact that in practically every case experimental conditions were such that no size effect would be expected, i.e., either the solutions used were too concentrated or the range in particle size investigated was not sufficiently wide. For example, Abramson (2) found that protein-coated particles of microscopic size have the same migration velocity as the ultra-microscopic protein micelles investigated by Svedberg and Tiselius (23), and Abramson (3, 5) and Dummett and Bowden (11) demonstrated that the migration velocity of protein-covered particles is the same as electrosmotic velocity on a protein-covered surface of zero or small curvature. Since, however, all of these observations were carried out in concentrated solutions (usually $M/50$ buffers) it is evident that no differences in velocity would be expected. The same objection applies to the experiments of Hardy (14) on protein sols in $N/50$ acetic acid, of Abramson (1) on blood platelets and their aggregates in plasma, of Freundlich and Abramson (12) on blood cells and their aggregates in serum, of Prideaux and Howitt (21) on egg albumin in $M/50$ buffer, of Abramson and Michaelis (6) on droplets of Nujol, castor oil, benzyl alcohol, and cocoa butter, bare and protein-covered, in electrolyte solutions, and probably also of Freundlich and Abramson (13) on quartz particles in sugar solutions, since considerable electrolyte must inevitably have been added with the sugar. The observations of McTaggart on gas bubbles (17) in water are confined to bubbles so large (60 to 160μ) that the maximum velocity had probably already been attained by the smallest. Burton's experiments with submicroscopic silver sols (8) are not decisive, since there is little evidence that his variations in methods of preparation actually produced sols of different sizes.

van der Grinten (24), whose data have been recalculated by Abramson (4), found the electrophoretic velocity of small particles of glass in distilled water to be very much less than electrosmotic velocity at a flat surface of the same glass. The value for R, as recalculated by Abramson, varied between 2.2 and 2.8. Abramson, however, dismisses this observation with a suggestion that the surface of a broken glass particle is probably chemically different from a fused or polished surface and hence would not be expected to have the same ζ-potential, and later (5) points to the measurements of Sumner and Henry (22) as evidence that when the glass surfaces are identical, R is practically unity. Sumner and Henry, comparing the electrophoretic velocity of a fused glass cylinder with electrosmotic velocity on a flat glass surface, found an average value for R of 1.14. However, since these experiments were not performed in water, but in 10^{-4}

M phosphate buffer, and the cylinder used was 20μ in diameter and 20 cm. long as compared with particles about 3μ in diameter studied by van der Grinten and by Abramson, it is evidently not necessary to suppose that the fused surface studied by Sumner and Henry was chemically different from the broken surfaces of van der Grinten and of Abramson in order to account for the difference in the value of R.

In view of the fact that with the exception of Mooney's work there are no published experiments which furnish even a qualitative test of the late theoretical developments, it seemed desirable to compare the electrophoretic mobility of small particles with electrosmotic velocity on a flat surface of the same material, over a wide range of concentrations, using, in place of the oil emulsion studied by Mooney, solid materials with more stable and easily equilibrated surface properties. It would, of course, be desirable to vary the particle size as well as the concentration, but this introduces great experimental difficulties, and hence has not been attempted in the present work. In the present paper observations on the value of

$$R = \left(\frac{\text{electrosmotic velocity on flat surface}}{\text{electrophoretic velocity of particles } 1\text{–}3\mu \text{ in diameter}}\right)$$

for protein surfaces, found by Abramson and others to be close to unity in concentrated solutions, will be extended to more dilute solutions, and those on the value of R for glass surfaces, found by van der Grinten and Abramson to be greater than unity in water, will be extended to more concentrated solutions.

EXPERIMENTAL

All experiments were carried out in flat electrophoresis cells of the Northrop-Kunitz type. It has been shown by von Smoluchowski (25) that in such cells true electrophoretic velocity is obtained by observing the particles at 0.211 of the distance from the bottom to the top of the cell. True electrosmotic velocity is the algebraic difference, particle velocity at wall minus particle velocity at 0.211 cell depth from wall, where movements toward anode and cathode are given opposite signs. When no movement occurs at the wall the value of R is unity. Since for the purposes of this investigation only the ratio of electrosmotic to electrophoretic velocity was required, the applied field strength was not determined; the voltage drop in any solution was, of course, the same for electrosmosis as for electrophoresis (about 4 volts per centimeter). It was found necessary, in working with unbuffered solutions such as we used, to increase the length of each side arm to about 20 cm. in order to avoid contamination of the cell contents from the electrode reactions. The glass powder was prepared by prolonged grinding of clean Pyrex tubing with a porcelain mortar and pestle. A uniform suspension of any desired particle size can be prepared by fractional sedimentation; in the work reported here the diameter range was from 1 to 3 microns. The cell was illuminated through a dark field condenser and the particles observed through an ocular micrometer. There was no appreciable drift while the circuit was broken. Each recorded velocity is the average of five observations in each direction.

A concentration of 0.01 g. of gelatin per liter was found adequate to coat completely the glass particles, as evidenced by the fact that the isoelectric point of the coated particles was the same as that of the gelatin (pH 4.75). The same concentration is sufficient to coat the cell also (as evidenced by the fact that electrosmosis reverses at the gelatin isoelectric point), if this solution is passed through the cell slowly for approximately an hour. We thus confirm the finding of Abramson (2) and of Dummett and Bowden (11) that this procedure is adequate to insure complete coating. Since this concentration is probably about the minimum which will give a complete coating to the cell in a reasonable time, it was considered better to use 0.1 g. per liter for the present experiments. This solution was passed through the cell slowly for an hour before readings were begun. The salt concentrations investigated were all made up in 0.1 g. per liter gelatin solutions, and each solution remained in contact with both particles and cell for a 15-minute period before observations were begun.

It is necessary that the cell be carefully cleaned in order that normal electrosmosis be exhibited. The criterion adopted of a normal electrokinetic potential at the cell wall was that the electrosmotic velocity in distilled water without protein be at least 2.5 times the electrophoretic velocity with glass particles 1 to 3μ in diameter. In practise, this ratio varied between 2.6 and 3.1,—a range of values which is consistently obtained with proper cleaning. The ratio for gelatin-covered surfaces in distilled water ranged from 1.9 to 2.3. These rather wide variations in the value of R in water and very dilute solutions are probably to be ascribed to differences in electrolyte content of different samples of distilled water, or, in the absence of protein, to variations in the electrical properties of the cell wall, or to both.

Table 1 contains the results of experiments with bare Pyrex surfaces in varying concentrations of potassium chloride. These observations were carried out in a flat Pyrex cell. The sign refers to the pole toward which the particles were moving. Since in potassium chloride the particles are always negatively charged, they move always toward the anode at 0.211 of the distance from the wall. As previously stated, the velocity at this level represents true electrophoretic velocity, V_p. Since, at the bottom of the cell, the particles moved always in the opposite direction if they moved at all, electrosmotic velocity, V_e, is the numerical sum of the observed velocities at the two levels. The absolute magnitude of V_p and V_e

in these experiments is not of quantitative significance, since the field strength may vary slightly from one solution to the next, but the value of R is independent of field strength.

Similar data for gelatin surfaces are given in table 2. No attempt was made to maintain a rigidly constant pH, since the value of R is independent of pH; however, there was no great variation in pH among the different solutions. Table 2 also shows that the same values for electrosmotic velocity are obtained by observing the particles at the wall as by the use of the equation $V_e = 2(V_{\frac{1}{2}} - V_p)$.

Similar observations on both bare glass and gelatin-coated surfaces in contact with thorium chloride are recorded in tables 3 and 4. The tetravalent thorium ion reverses the sign of charge on glass; the isoelectric concentration for electrosmosis and electrophoresis is approximately 3×10^{-6} M. At concentrations near the isoelectric point, the value of R is likely to show irregular variations, but at concentrations other than isoelectric, R approaches unity as the concentration increases.

TABLE 1

Electrophoretic and electrosmotic velocities on bare Pyrex surfaces in potassium chloride

MOLAR KCl CONCENTRATION	μ PER SECOND AT 0.211 FROM BOTTOM = V_p	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+9.7	−16.4	26.1	2.69
5×10^{-5}	+9.9	−11.5	21.4	2.16
5×10^{-4}	+8.5	−5.9	14.4	1.69
1×10^{-3}	+9.0	−4.3	13.3	1.48
1×10^{-2}	+7.9	0	7.9	1.00

Thorium chloride in unbuffered solutions also reverses the sign of charge of gelatin (probably largely a pH effect) at concentrations between 1 and 2×10^{-5} M. Here again the isoelectric point is the same for the particles and the cell, additional evidence that all surfaces are completely coated with protein.

DISCUSSION

The data show that the unqualified statement that electrophoretic velocity equals electrosmotic velocity provided identical surfaces are used is not correct. The equality holds only in relatively concentrated solutions. Conversely, the view that the electrophoretic velocity of unfused bare glass particles must be different from the electrosmotic velocity at a fused flat surface is not correct; the velocities are different in dilute solution (which is also true for protein-covered surfaces) and become the same in relatively concentrated solutions. At a concentration between 10^{-3} and 10^{-2} M the velocities become equal with both bare and protein-covered

TABLE 2

Electrophoretic and electrosmotic velocities on gelatin-coated glass surfaces in potassium chloride + 0.1 g. of gelatin per liter

MOLAR KCl CONCENTRATION	μ PER SECOND AT 0.211 FROM BOTTOM = V_p	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+5.38	−5.50	10.9	2.02
5×10^{-5}	+5.03	−3.79	8.82	1.75
5×10^{-4}	+4.78	−1.47	6.25	1.31
1×10^{-3}	+3.89	−0.81	4.70	1.21
1×10^{-2}	+2.08	0	2.08	1.00

Comparison of two methods for obtaining electrosmotic velocity

MOLAR KCl CONCENTRATION	LEVEL IN CELL	μ PER SECOND	V_p	V_0 AVERAGE TOP AND BOTTOM	V_e $(V_0 - V_p)$	V_e $2(V_{\frac{1}{2}} - V_p)$	V_e AVERAGE	$R = \frac{V_e}{V_p}$
H_2O	Top	−5.74	+7.65	−5.74	13.4	14.9	14.2	1.86
	0.211 from top	+7.94						
	Middle	+15.1						
	0.211 from bottom	+7.36						
	Bottom	−5.74						
10^{-5}	Top	−5.71	+7.98	−5.76	13.7	13.0	13.3	1.67
	0.211 from top	+8.44						
	Middle	+14.5						
	0.211 from bottom	+7.52						
	Bottom	−5.80						
10^{-4}	Top	−4.57	+8.20	−4.90	13.1	12.6	12.85	1.57
	0.211 from top	+8.62						
	Middle	+14.5						
	0.211 from bottom	+7.78						
	Bottom	−5.21						
10^{-3}	Top	—	+6.35	−1.58	7.9	7.3	7.6	1.20
	0.211 from top	+6.43						
	Middle	+10.0						
	0.211 from bottom	+6.27						
	Bottom	−1.58						
10^{-2}	Top	0	+3.52	0	3.52	3.48	3.50	0.99
	0.211 from top	+3.70						
	Middle	+5.26						
	0.211 from bottom	+3.33						
	Bottom	0						

surfaces; at lower concentrations electrosmotic velocity is greater than electrophoretic. The findings are in accord with the theoretical points discussed in the first part of the paper.

We may consider briefly the various factors which might be responsible for the departure from unity of the ratio $\frac{\text{electrosmotic velocity}}{\text{electrophoretic velocity}}$. In the discussion the dielectric constant and viscosity are assigned normal values.

The maximum variation in R, due to variation in K between 4 and 6 as determined by variations in the ratio of particle radius to double layer thickness, could be only between 1 and 1.5, as discussed by Henry (15). Since we have observed R as great as 3.2, this factor alone cannot explain the findings. Moreover, it can be shown that K can never become as great as 6. Henry states that $K = 6$ when double layer thickness, λ, equals particle diameter. However, it is not permissible to substitute $\frac{1}{\kappa}$ for λ when $\kappa r < 5$, according to Müller's treatment (4). Thus, according to Henry, $K = 6$ with a particle of 1μ diameter in pure water, since $\frac{1}{\kappa} =$ 1μ. But according to the equation

$$\lambda = \frac{1}{\kappa}\frac{\kappa r}{1 + \kappa r}$$

(r = particle radius), λ is not identical with $\frac{1}{\kappa}$ but equals 3.3×10^{-5} cm.

TABLE 3

Electrophoretic and electrosmotic velocities on Pyrex surfaces in thorium chloride

In this series the long side arms on the electrophoresis cell had not yet been introduced, hence the field strength was greater

MOLAR $ThCl_4$ CONCENTRATION	μ PER SECOND 0.211 FROM BOTTOM = V_p	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+16.9	−34.0	50.9	3.01
1×10^{-6}	+14.1	−27.8	41.9	2.99
1×10^{-4}	−21.4	+10.0	31.4	1.47
1×10^{-3}	−28.7	0	28.7	1.00
1×10^{-2}	−23.6	0	23.6	1.00

TABLE 4

Electrophoretic and electrosmotic velocities on gelatin surfaces in thorium chloride + 0.1 g. of gelatin per liter

MOLAR $ThCl_4$ CONCENTRATION	μ PER SECOND 0.211 FROM BOTTOM = V_p	μ PER SECOND AT BOTTOM	V_e	$R = \frac{V_e}{V_p}$
H_2O	+5.80	−7.60	13.4	2.31
1×10^{-6}	+6.14	−6.26	12.4	2.02
1×10^{-4}	−13.3	+2.9	16.2	1.22
1×10^{-3}	−10.8	+1.7	12.5	1.16
1×10^{-2}	–	0	–	1.00

The condition that λ equals particle diameter can never be attained, since when $\lambda = r$, $\kappa = 0$, i.e., in any solution possessing a finite ionic strength, $\lambda < r$. Thus K must always be less than 6 even with the smallest particles in dilute solutions, although it can become 4 with large particles in more concentrated solutions, and the operation of this effect can vary R only between 1 and something less than 1.5.

This leads to consideration of the effect of particle size on λ, and therefore on ζ and on electrophoretic mobility. According to the equation

$$\lambda = \frac{1}{\kappa}\frac{\kappa r}{1 + \kappa r}$$

λ becomes significantly less than its normal value of $\frac{1}{\kappa}$ when $\kappa r \leqq 5$. For electrosmosis at flat surface ($r = \infty$), $\lambda = \frac{1}{\kappa}$. Substituting $\frac{1}{\kappa}$ for λ in the condenser equation

$$\zeta = \frac{4\pi\sigma\lambda}{D}$$

(σ = charge density, λ = double layer thickness) for electrosmosis, and $\frac{r}{1 + \kappa r}$ for λ for electrophoresis, it follows that the ratio of electrosmotic to electrophoretic mobilities equals $\frac{1 + \kappa r}{\kappa r}$ or $\frac{1}{\kappa\lambda}$. For distilled water at 25°C., with an estimated ionic strength of 1×10^{-6} and a particle of 1μ radius, $\kappa = 3.25 \times 10^4$, $\kappa r = 3.25$, and the ratio = 1.31. In other words, electrophoretic mobility, *due to the operation of this factor alone*, should be 24 per cent lower than electrosmotic or than the electrophoretic mobility of a particle large enough to escape this effect, or than the electrophoretic mobility of a particle of 1μ radius in a solution strong enough so that $\kappa r >> 5$. In a 5×10^{-5} M potassium chloride solution (ionic strength $= 5 \times 10^{-5}$), $\kappa = 2.3 \times 10^5$, $\kappa r = 23.5$, and the ratio = 1.04. The ratio drops to 1.01 or less, with unity as a limit, in solutions with ionic strength of 5×10^{-4} or greater. In pure water, with a theoretical ionic strength of 1×10^{-7}, $\kappa = 1 \times 10^4$, $\kappa r = 1$, and the ratio becomes 2. It is thus seen that the limiting, and in practise unattainable, value of the ratio for a particle of 1μ radius is 2; for smaller particles the ratio in water of ionic strength 1×10^{-7} could exceed 2. Under the conditions of our experiments the effect of this factor alone is practically negligible with all solutions other than distilled water; with smaller particles the effect should become prominent in solutions of ionic strength[1] greater than 1×10^{-6}.

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[1] A point which seems obscure may be mentioned here. κ is obtained (9) by a series expansion involving

$$\left(e^{-\frac{e\psi}{kt}} - e^{+\frac{e\psi}{kt}}\right)$$

The third factor, the influence of particle size on charge density and therefore on ζ, may be dismissed, since ζ could be changed by only 1 per cent with a particle of 2μ diameter.

The fourth factor, polarization of the double layer, must be invoked to account for the higher values of R we have obtained. The maximum combined influence, as seen in water with an estimated ionic strength of 1×10^{-6}, of the first three factors just discussed may be estimated to raise R to not more than 2; further retardation of electrophoretic below electrosmotic mobility in water may be ascribed to polarization of the double layer by the impressed field, and this latter factor apparently is the predominant one in any solution of ionic strength greater than 1×10^{-6} with particles as large as 2μ diameter. This is contrary to the suggestion of Mooney (18) that such polarization might enhance mobility. A retarding effect seems to us the more probable.

SUMMARY

The influence of electrolyte concentration of medium on the ratio of electrosmotic to electrophoretic velocities with bare glass and gelatin-covered particles of 1 to 3μ diameter has been investigated. The ratio is unity with either type of surface with a concentration between 10^{-3} and 10^{-2} M and at all higher concentrations. With lower concentrations the ratio increases progressively with decreasing concentration, reaching values above 3 in distilled water. A discussion of various factors which may contribute to this result is given.

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where all except the first two terms are neglected, giving $-2\frac{\epsilon\psi}{kt}$. This approximation is justified only when $\frac{\epsilon\psi}{kt} < 1$, which is true only when ψ or $\zeta < 25$ millivolts. Nevertheless, when double layer thickness, λ, is calculated as $\frac{1}{\kappa}$ for 5×10^{-4} M potassium chloride at a plane glass surface at 20°C., where $\zeta = 120$ millivolts, a value of $\lambda = 1.47 \times 10^{-6}$ cm. is obtained. We have recently obtained a specific surface conductivity value of 4.27×10^{-9} mhos for 5×10^{-4} M potassium chloride at a plane glass surface. From this one finds 1.8×10^{13} ions adsorbed per cm.^{2} of surface. If one substitutes the value of ζ, potential, and σ, electric charge density at surface, corresponding to $\zeta = 120$ millivolts and ions per cm.^{2} $= 1.8 \times 10^{13}$, in the condenser equation

$$\lambda = \frac{\zeta D}{4\pi\sigma}$$

one obtains $\lambda = 1.19 \times 10^{-6}$ cm. This is an experimentally obtained value and is subject to no restrictions other than those of experimental error. In view of the above-mentioned restrictions implicit in κ, this correspondence seems surprisingly close.

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A STUDY OF CERTAIN FINELY DIVIDED METALS AND A METHOD FOR THEIR PREPARATION[1]

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INTRODUCTION

More than a century ago attention was directed to the phenomenon of adsorption as an explanation for the phenomenon of catalysis, and the unsaturated forces at solid surfaces were believed to be the real origin of both phenomena. During recent years an intensive study has brought to light the close connection in many cases between catalysis and the specific nature of adsorption (8). In marked contrast to inert adsorbents, metallic catalysts seem to have a definite saturation capacity for certain gases. In the case of the adsorption of hydrogen on nickel this saturation capacity is reached at low pressures (2).

It has been shown that the activity of a catalyst and its adsorptive capacity are greatly affected by the method of its preparation. As it is practically impossible to prepare two catalysts which are exactly alike, it seems very important that adsorption measurements and a study of catalytic activity be made on the same catalyst under the same conditions.

The first work of this nature is that of Pease (5), who has studied the catalytic combination of ethylene and hydrogen on copper by measuring the reaction rate and the adsorption isotherms of the reactants and the product, using the same catalyst for all the measurements. Since then there has been very little work of this kind, although there have been numerous investigations of the adsorption of various gases by several metals which presumably were active catalysts. The metals, which have been used commonly, have been prepared by reducing their oxides with hydrogen.

Metals may be prepared from their amalgams by distilling off the mercury but, so far as the writer is aware, no investigation of the catalytic activity of finely divided metals prepared in this way has been undertaken. Preliminary experiments had shown that metals prepared from the amal-

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gams are active catalysts; therefore it seemed that it would be interesting to study metals prepared in this way.

The hydrogenation of ethylene was selected as the reaction to investigate in connection with these catalysts, and for several reasons. It is a simple reaction, with no side reactions, and it goes to completion. The reactants and the product are reasonably stable, and the course of the reaction may be followed conveniently by measuring the decrease in pressure, the volume remaining constant.

According to Sabatier (6), the hydrogenation of ethylene occurs at the surface of nickel, cobalt, copper, and iron at temperatures about 150°C. Recently it has been shown that this reaction takes place at a readily measurable rate at 0°C. It was decided to measure the velocity of this reaction at 0°C., and to determine the adsorption isotherms of hydrogen, ethylene, and ethane at 0°C. on each of the above metallic catalysts prepared from their amalgams. Furthermore it seemed that it would be interesting to compare the catalysts prepared from the amalgams with those prepared from the oxides. Accordingly metallic catalysts, prepared by reducing the oxides with hydrogen, were studied in the same manner and under the same conditions as those prepared from the amalgams.

After completing the work outlined above it was decided to measure the adsorption of hydrogen on nickel at higher temperatures.

APPARATUS AND EXPERIMENTAL PROCEDURE

The adsorption apparatus (figure 1) was a modified form of the type of apparatus used by Bennett (1) in the adsorption of carbon dioxide on oxide catalysts. The manifold of the apparatus was connected through a mercury cut-off and a trap to a mercury vapor pump, which was backed by a Hyvac oil pump. The trap was at all times immersed in a bath of solid carbon dioxide and alcohol. The manometers and the cut-off were connected through traps to leveling bulbs. The mercury used for these had been purified by acid washing and distilling in the usual manner.

The bulb B, used to measure the hydrogen admitted to the catalyst, was calibrated, surrounded by a water jacket, and sealed in the system so that it could be connected either to the hydrogen reservoir or to the catalyst in bulb A. A three-way stopcock S was inserted so that gases other than hydrogen could be admitted from a gas buret.

Materials

Recrystallized Baker's C. P. salts were used as the source of the metals. The mercury used in forming the amalgams was prepared by decomposing Baker's C. P. mercuric oxide. The hydrogen used in these experiments was prepared by electrolyzing a 15 per cent solution of sodium hydroxide between nickel electrodes. It was passed through a trap surrounded by solid carbon dioxide to remove most of the water carried over from the generator, then over glowing platinized asbestos to remove traces of oxygen, and finally through a long spiral immersed in liquid air to remove traces of water. It was stored in a 2-liter balloon flask. The ethylene was the compressed gas prepared especially for anesthesia by the Kansas City Oxygen Gas Company of Baltimore. The ethane was obtained from the Matheson Company of East Rutherford, N. J. Both the ethylene and ethane were passed through a long U-tube surrounded by solid carbon dioxide to remove any condensible material. Each of these gases was admitted to the catalyst by means of a water-jacketed gas buret.

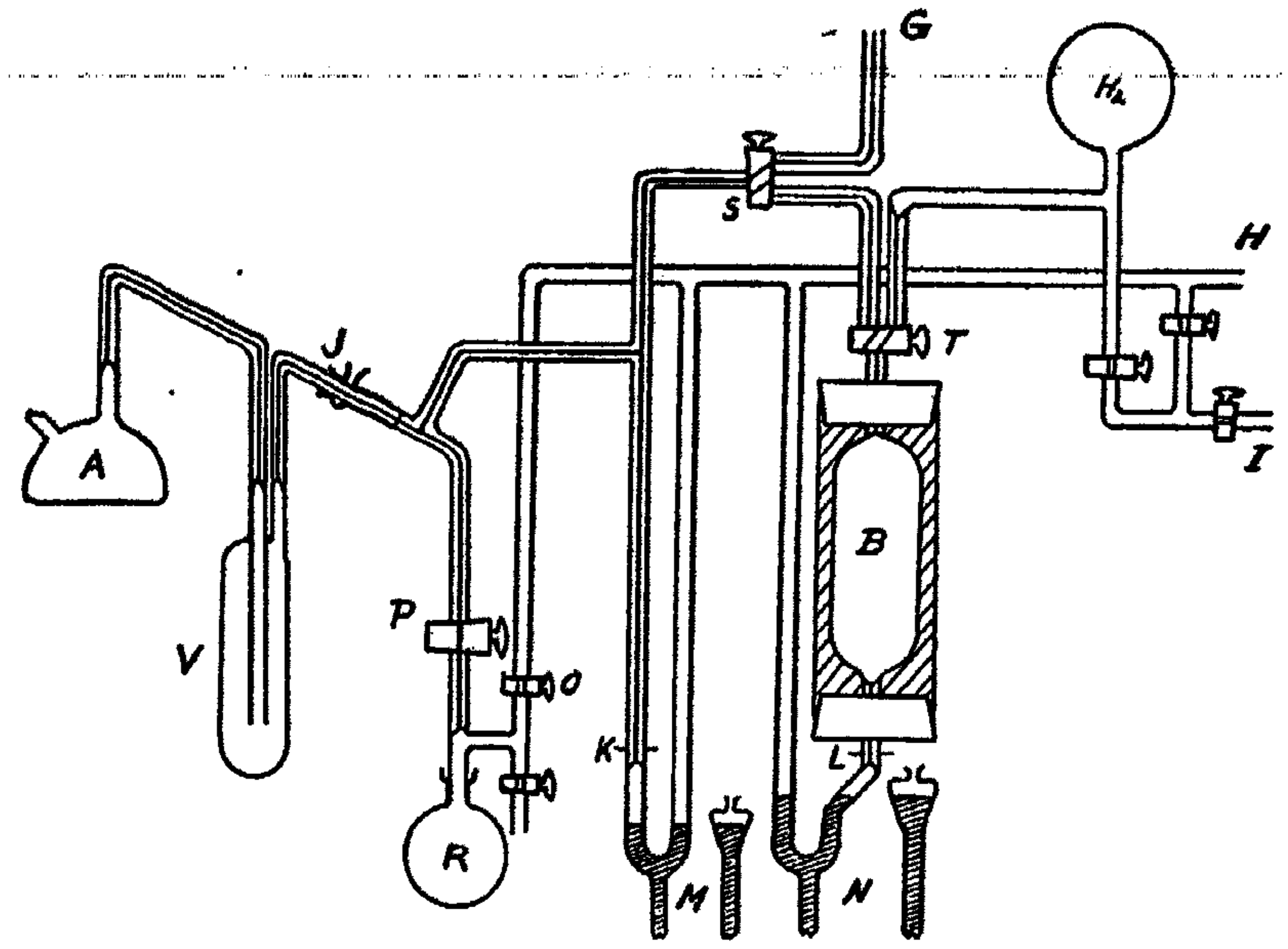

FIG. 1. ADSORPTION APPARATUS
G, to gas buret; H, to high vacuum; I, to hydrogen generator

The metals studied were iron, cobalt, nickel, and copper. Each metal was prepared both from the oxide and the amalgam. The metals prepared from the oxides are referred to as No. 2. Metals referred to by other numbers were prepared from the amalgams. The oxides were reduced in the adsorption bulb by hydrogen for twenty-four hours at the following temperatures: copper No. 2, 200°C.; cobalt No. 2, 390°C.; iron No. 2, 390°C.; nickel No. 2, 275°C.

The amalgams were prepared essentially according to the method given in Smith's *Electrochemistry* for the electrolytic determination of metals using a mercury cathode. About 10 cc. of mercury was put in the cell and connected by a platinum wire in the side arm to the negative side of a

14-volt D. C. line. A solution of the sulfate of the metal, acidified with sulfuric acid, was added to the cell (figure 2), and a platinum anode was then suspended in the solution. In the case of cobalt, iron, and nickel the double ammonium sulfates were used. After the amalgam had been formed, the current was left on, the solution siphoned out, and the amalgam washed with distilled water. Then the amalgam was transferred to the adsorption bulb in the presence of oxygen-free nitrogen, the inlet sealed, and the system evacuated.

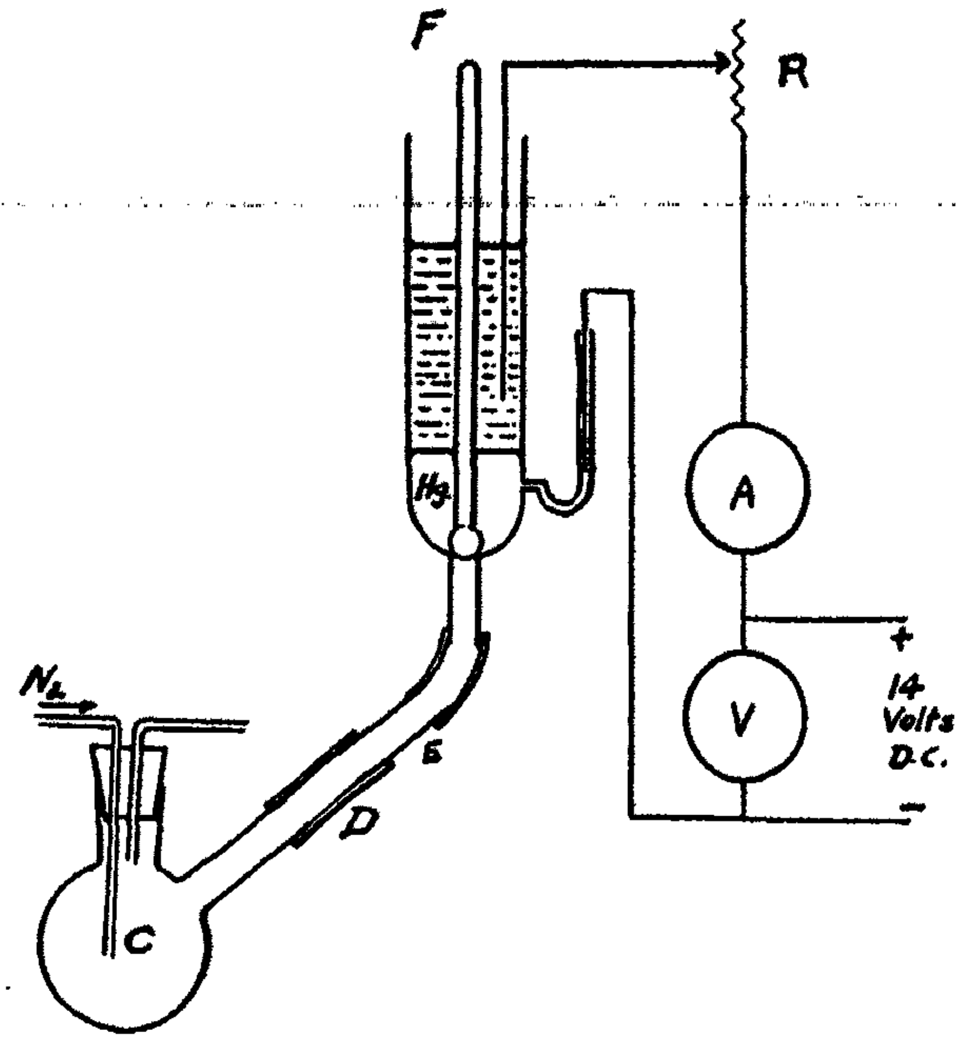

FIG. 2. APPARATUS FOR PREPARING AMALGAM

By means of valve F the amalgam is run into bulb C. Then, closing gum tubing D and removing glass tubing E, the amalgam is transferred to bulb A of the adsorption system. The amalgam is protected by oxygen-free nitrogen.

The capillary tube leading from bulb A (figure 1) was electrically heated by nichrome wire, an electric furnace was placed about bulb A, and the mercury was distilled into trap V. When practically all the mercury had distilled over, the bulb and trap were rotated as a unit about joint J as an axis; the mercury ran down into bulb R. In this way it was possibie to remove the mercury from the adsorption system without breaking the vacuum. The last traces of mercury were removed by immersing the trap V in a bath of solid carbon dioxide and ether, and heating the metals to the following temperatures: copper No. 1, 170°C.; cobalt No. 1, 185°C.; iron No. 1, 220°C.; nickels No. 1, 3, and 4, 170°C.; nickel No. 5, 170°C. The evacuation was continued until the pressure became as low as 1×10^{-5} to 1×10^{-6} mm.

Calibration and method of adsorption measurements

With the adsorption bulb empty, the apparatus was evacuated and bulb A was immersed in a bath of finely shaved ice and distilled water. In all experiments the trap V (figure 1) was immersed to the same depth in a bath of solid carbon dioxide and ether. The temperature, as shown by a pentane thermometer, was −81°C. and was kept very nearly constant by adding small quantities of solid carbon dioxide from time to time.

Keeping stopcock P closed and the mercury level in manometer M (figure 1) near the height K, hydrogen was admitted to bulb A from bulb B. Knowing the temperature of the gas, the volume of bulb B, and the change in pressure in bulb B, the volume of hydrogen admitted to bulb A could be readily calculated. After adjusting the mercury level in manometer M to exactly the height K, the pressure M was measured. In the same manner a number of pressures M, corresponding to various quantities of hydrogen, were measured. When these volumes were reduced to 0°C. and 760 mm. pressure and plotted against the pressures, M, a straight line was obtained from which could be read the calibration volume corresponding to any desired pressure.

In an adsorption measurement the volume of gas admitted to the catalyst was corrected for the volume of gas displaced by the metal. This volume was calculated from the known weight and density of the metal. This method of calibration was used by Nikitin (4) in a study of the adsorption of carbon dioxide on metallic iron, cobalt, and nickel. In the case of nickel No. 5 the system was also calibrated using purified helium. The two calibrations checked within 0.01 cc., which is within the experimental error.

After the catalyst had been prepared and evacuated as described above, a small quantity of hydrogen was admitted to the catalyst, the pressure M was measured, and the volume reduced to standard conditions as described in connection with the calibration above. Then by subtracting from this reduced volume the volume of gas required to give the same pressure in the calibration of the system, the volume of gas adsorbed is obtained. By making a series of pressure measurements, M, corresponding to increasing amounts of gas, the adsorption isotherm could be readily determined.

The adsorption at 0°C. of hydrogen, ethylene, and ethane on each metal was measured. In each case, immediately after determining the adsorption of hydrogen on the metal, ethylene was admitted to the catalyst in an amount approximately equal to that of the hydrogen present. Then the rate of hydrogenation was obtained by measuring the rate of decrease in pressure in the system. After evacuating the catalyst, the adsorption of ethylene was measured, and similarly the adsorption of ethane was measured. Before each adsorption measurement, the catalyst was outgassed in the same manner as was used to prepare the metal for the adsorption of hydrogen. In the case of nickels No. 4 and 5 only the adsorption of hydrogen was studied.

In preparing nickel No. 5 the amalgam was evacuated before being heated. After driving off the mercury, the adsorption of hydrogen on the metal was measured at 0°C. Then the nickel was evacuated at 100°C. and the adsorption and desorption of hydrogen at 99.6°C. was measured. Then the metal was evacuated and the adsorption at 0°C. redetermined. After the system had apparently reached equilibrium the bulb containing the metal was slowly heated, keeping the same amount of hydrogen in the system, and pressure measurements were taken at various temperatures up to 150°C. At each of several different points the temperature was kept constant, and pressure measurements were taken until the system had apparently reached equilibrium.

EXPERIMENTAL RESULTS

The larger part of the results will be presented graphically and the corresponding tables omitted. A brief description of the results, obtained from each metal studied, will be given.

Copper. Neither of the catalysts adsorbed a measurable quantity of any of the gases. Copper No. 2 catalyzed the hydrogenation of ethylene at a readily measurable rate (figure 3), but copper No. 1 was completely inactive.

Cobalt. Cobalt No. 2 showed a much higher adsorption of all the gases (figure 4), but both catalysts were equally effective in catalyzing the reaction (figure 5).

Iron. The quantities of gases adsorbed by both catalysts were small (figure 6), the adsorption of ethylene on iron No. 2 being the largest. Iron No. 2 was a much better catalyst for the reaction than iron No. 1 (figure 7).

Nickel. No nickel catalyst prepared from the amalgam adsorbed a measurable amount of any of the gases. Nickel No. 2 adsorbed a comparatively large quantity of hydrogen and ethylene (figure 8). As is shown in figure 9, nickels No. 1, 2, and 3 displayed the same activity in catalyzing the hydrogenation of ethylene.

Nickel No. 5 adsorbed a large amount of hydrogen at 99.6°C. as is shown in figure 10. When the adsorption at 0°C. was repeated it was found to be very small. Keeping the hydrogen, which was admitted at 0°C., in the system and slowly heating the catalyst, it was found that the pressure began to decrease between 50° and 60°C. The measurements at a series of temperatures between −80° and 150°C. are given in table 1 in the order in which they were obtained.

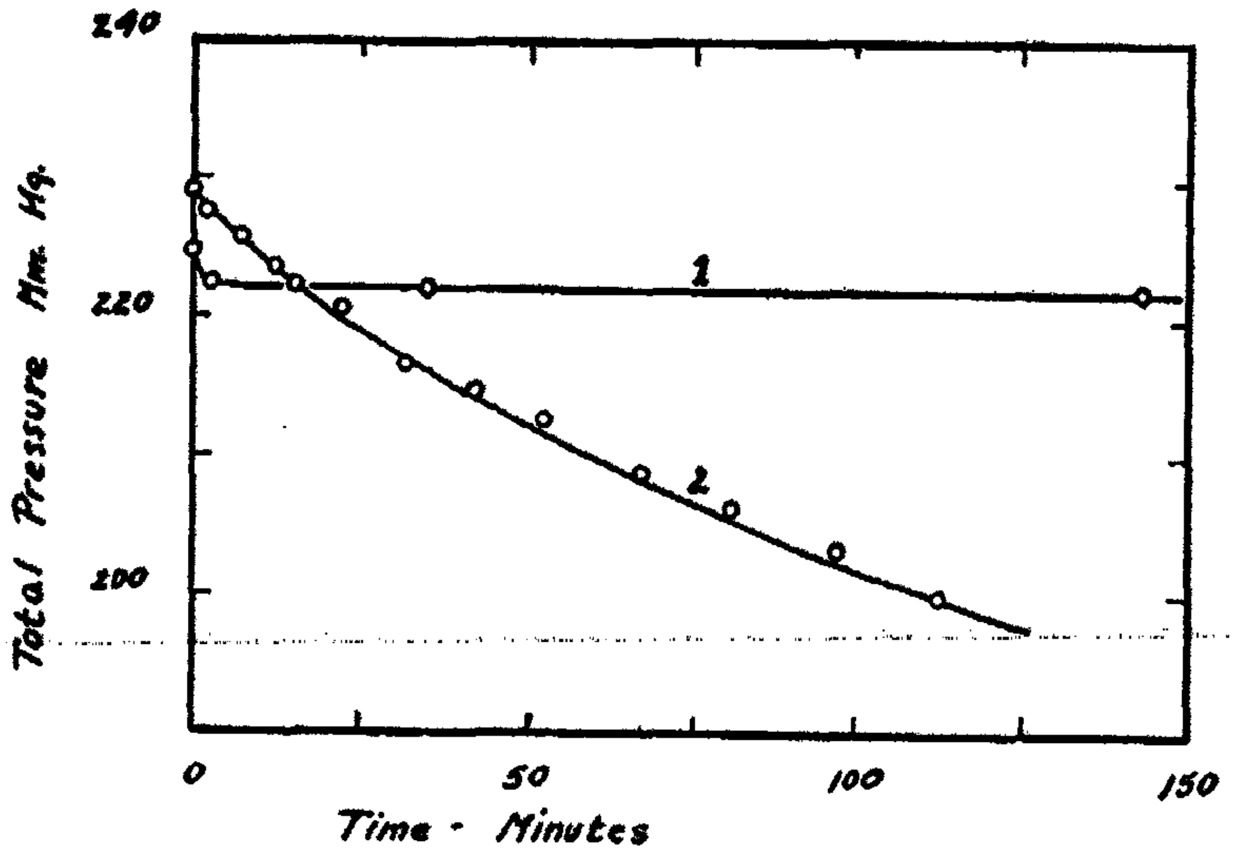

FIG. 3. HYDROGENATION OF ETHYLENE BY COPPER CATALYSTS
Curve 1, copper No. 1 from the amalgam; Curve 2, copper No. 2 from the oxide

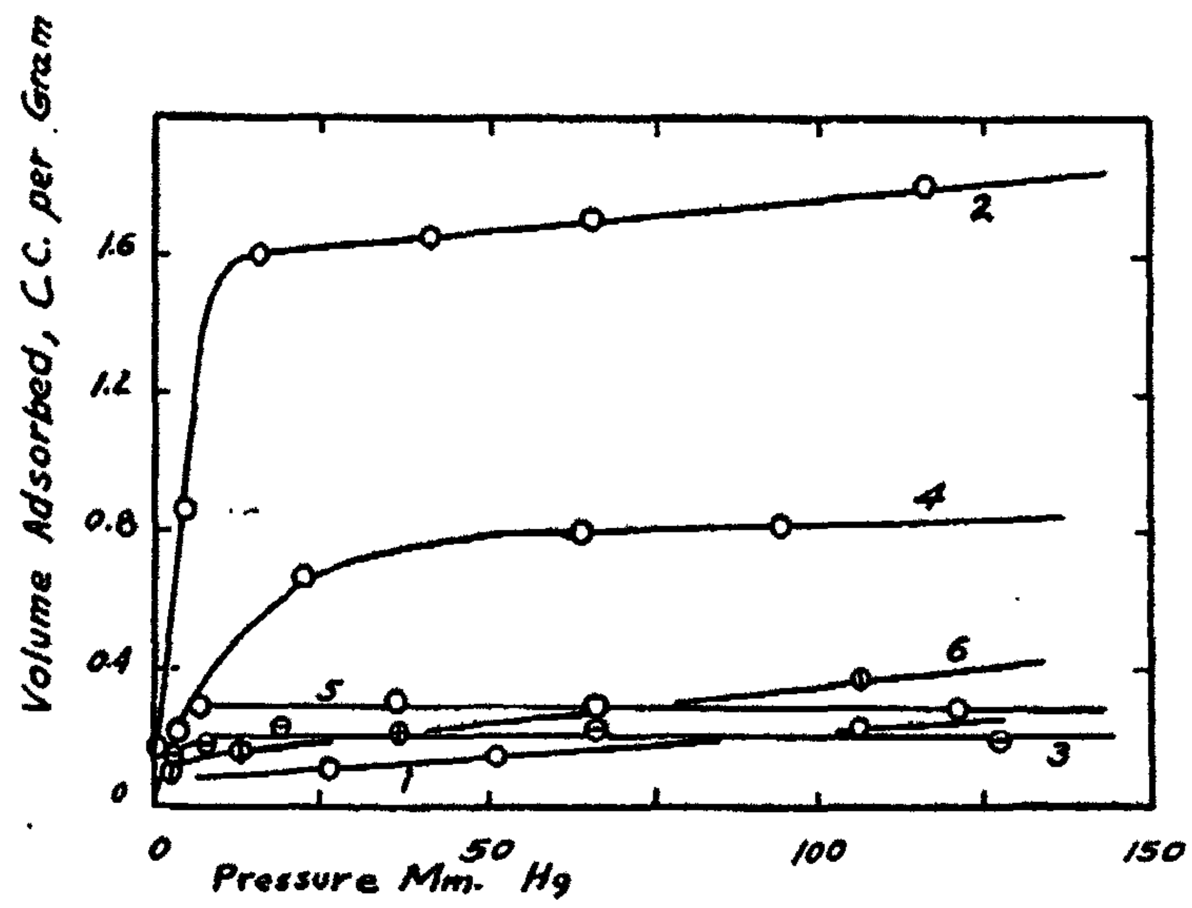

FIG. 4. ADSORPTION BY COBALT CATALYSTS
Cobalt No. 1 prepared from the amalgam; cobalt No. 2 prepared from the oxide. 1, hydrogen on cobalt No. 1; 2, hydrogen on cobalt No. 2; 3, ethylene on cobalt No. 1; 4, ethylene on cobalt No. 2; 5, ethane on cobalt No. 1; 6, ethane on cobalt No. 2.

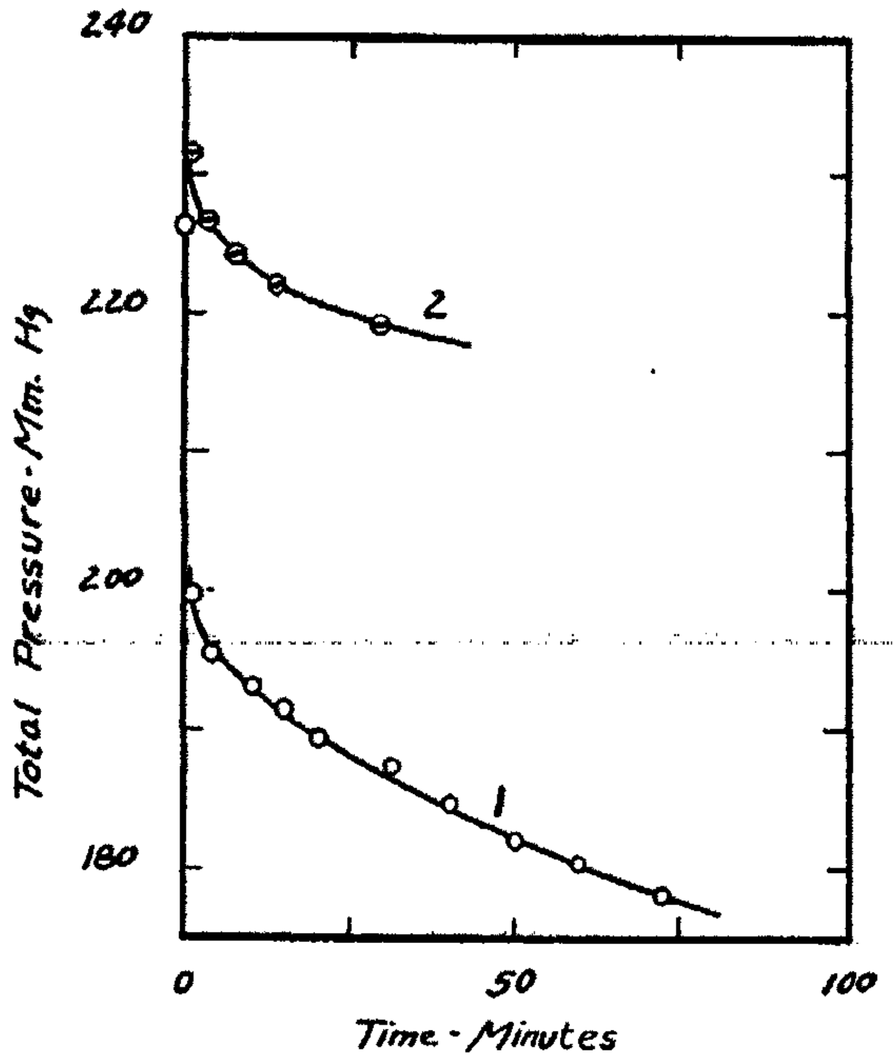

FIG. 5. HYDROGENATION OF ETHYLENE BY COBALT CATALYSTS
1, cobalt No. 1 from the amalgam; 2, cobalt No. 2 from the oxide

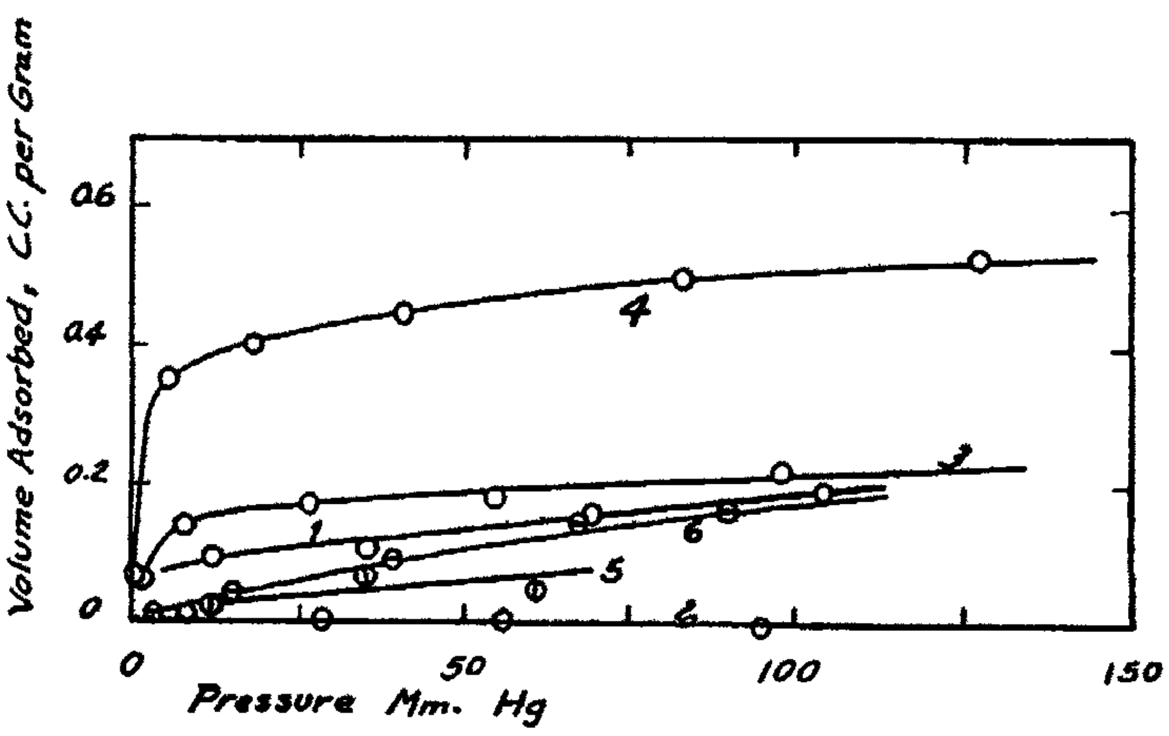

FIG. 6. ADSORPTION BY IRON CATALYSTS
Iron No. 1 from the amalgam; iron No. 2 from the oxide. 1, hydrogen on iron No. 1; 2, hydrogen on iron No. 2; 3, ethylene on iron No. 1; 4, ethylene on iron No. 2; 5, ethane on iron No. 1; 6, ethane on iron No. 2.

DISCUSSION

Adsorption and reaction rates at 0°C.

The adsorption of hydrogen, ethylene, and ethane on the catalysts was in general of the same nature as found by other workers. In the case of the copper catalysts, prepared from both the amalgam and the oxide, and the several nickel catalysts, prepared from the amalgams, the adsorption of the gases was much too small to be accurately measurable. In the case of the other metals studied the amounts of hydrogen and ethylene adsorbed became practically independent of the pressure at fairly low pressures. The amount of ethane adsorbed was approximately proportional to the pressure.

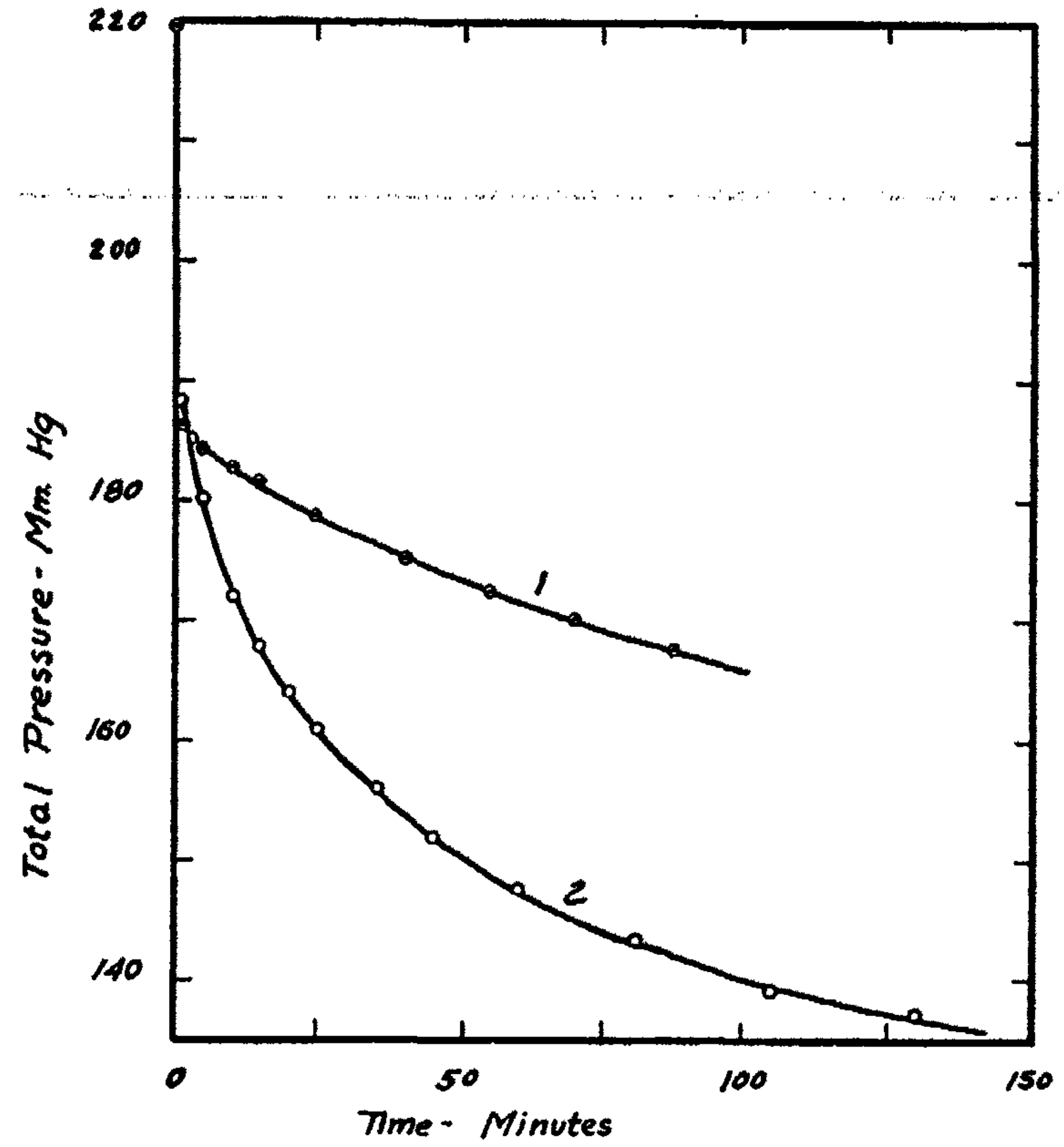

FIG. 7. HYDROGENATION OF ETHYLENE BY IRON CATALYSTS
1, iron No. 1 from the amalgam; 2, iron No. 2 from the oxide

All the metals studied, with the exception of copper No. 1, catalyzed the hydrogenation of ethylene at 0°C. at a readily measurable rate. Copper No. 1 gave practically no reaction even on standing as long as twenty-four hours. This is consistent with the results of Pease (5), who found that mercury poisoned a copper catalyst so that the hydrogenation of ethylene proceeded very slowly and that this poisoning effect was permanent. It

TABLE 1

Adsorption of hydrogen on nickel no. 5

NO.	TEMPERATURE	VOLUME ADSORBED (0°C., 760 mm.)	PRESSURE
	°*C.*	*cc.*	*mm.*
1	0.0	0.02	20.2
2	72.4	3.15	0.0
3	72.4	3.40	19.9
4	99.5	4.04	15.7
5	150.0	4.06	16.2
6	0.0	4.22	12.3
7	0.0	4.23	12.4
8	−80.0	4.30	10.0
9	99.5	4.16	14.6
10	150.0	4.06	16.2
11	150.0	4.13	57.3

Equilibrium had not been reached when measurements No. 3 and 4 were taken. Between readings 6 and 7 the catalyst was kept at room temperature (26°C.) for twenty-six hours. No. 8, no change in adsorption on standing five hours. No. 10, no change in adsorption on standing ten hours. More hydrogen was admitted between Nos. 2 and 3 and between Nos. 10 and 11.

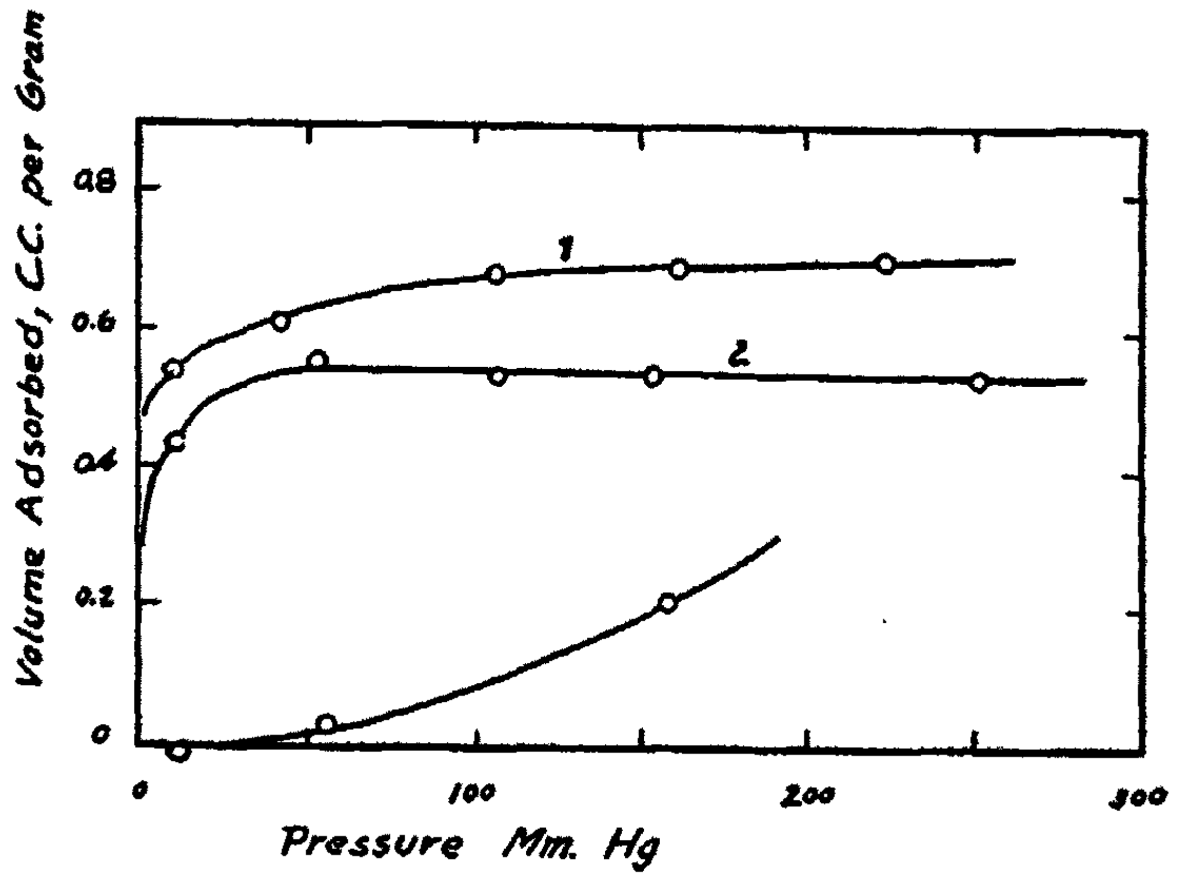

FIG. 8. ADSORPTION BY NICKEL CATALYSTS

Adsorption by nickels No. 1 and 3 (from the amalgam) negligibly small. Adsorption by nickel No. 2 (from the oxide): 1, hydrogen; 2, ethylene; 3, ethane.

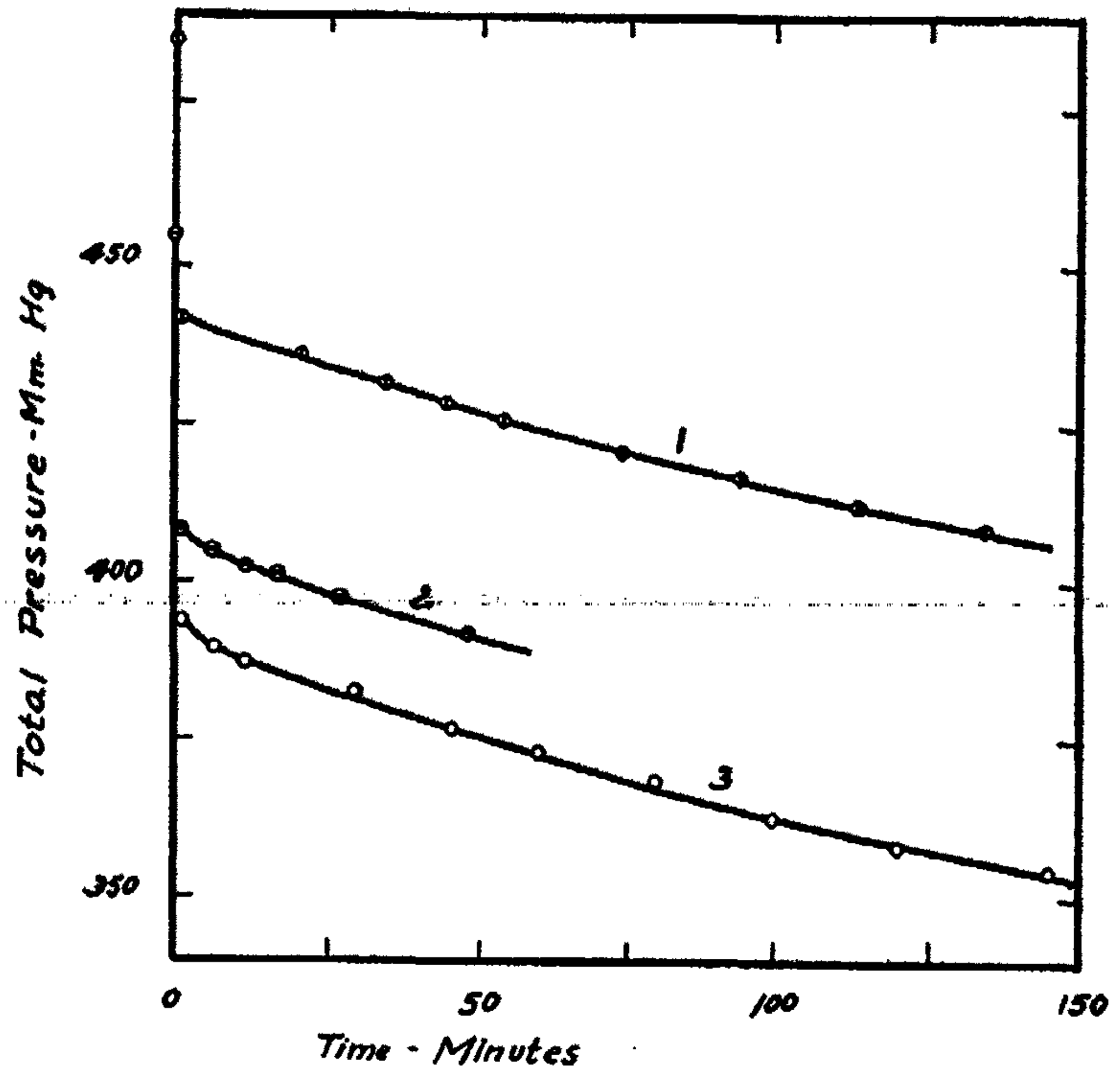

FIG. 9. HYDROGENATION OF ETHYLENE BY NICKEL CATALYSTS

1, nickel No. 1 from the amalgam; 2, nickel No. 3 from the amalgam; 3, nickel No. 2 from the oxide.

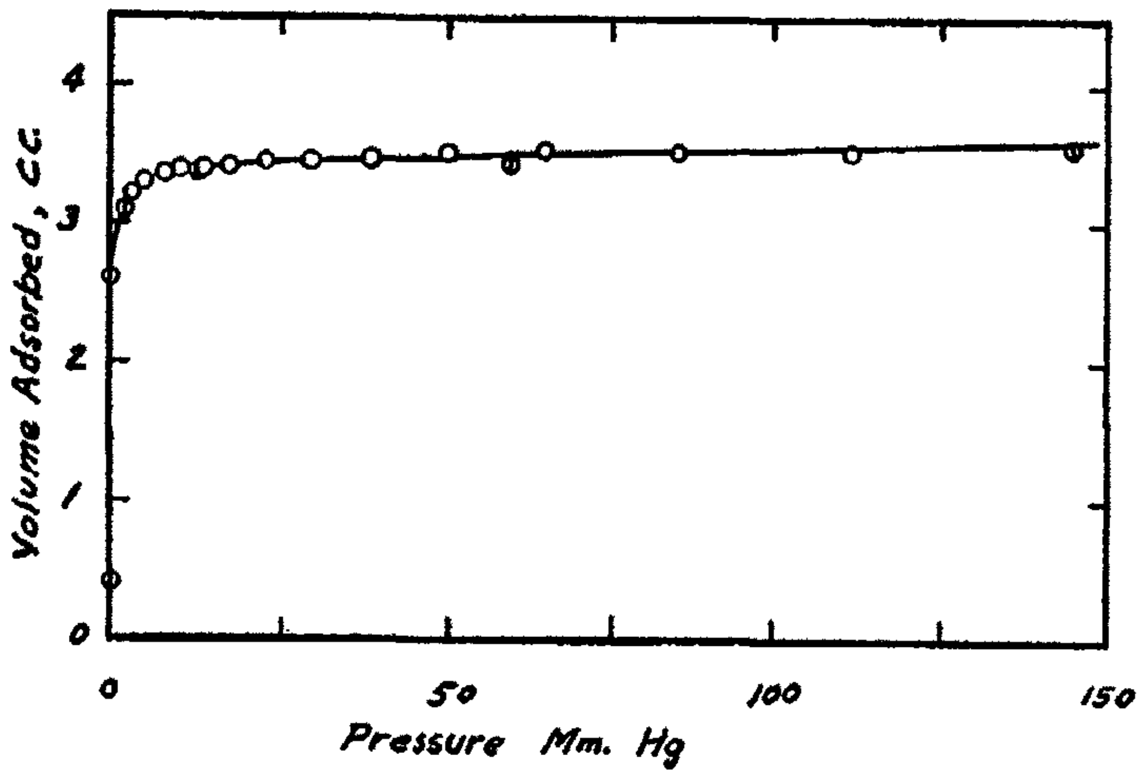

FIG. 10. ADSORPTION OF HYDROGEN ON NICKEL NO. 5 (FROM THE AMALGAM) AT 99.6°C.
⦶, adsorption; ○ desorption

seems that mercury has the effect of destroying the active spots on the catalyst; thus it is not surprising that copper No. 1, prepared from the amalgam, is not an active catalyst. This poisoning effect of mercury was not noticeable in the study of the other metals.

The rate of hydrogenation of ethylene by nickel (figure 9), was the same for the catalysts prepared by the two methods. Both cobalt catalysts (figure 5) gave equally rapid rates of reaction. As nickel and cobalt prepared from the oxides showed much higher adsorption of hydrogen and ethylene than the same metals prepared from the amalgams, it is evident that high adsorption of reactants does not necessarily mean a correspondingly high activity as a catalyst.

The change in total pressure was taken as a measure of the rate of reaction. In the case of iron, nickel, and cobalt from the amalgams, the initial pressures for the reaction rates were calculated from the known volumes of hydrogen and ethylene present and the amounts of the two gases adsorbed. As the quantities of the two gases adsorbed were quite small, it seems that the calculated initial pressures should be fairly accurate. The initial pressures thus calculated are in each of the above-mentioned cases 40 to 60 mm. higher than the first experimentally determined pressure. It is apparent that the initial rate of reaction is very high, for the large decrease in total pressure from its initial value (calculated) to the first experimental value is much too great to be attributed to adsorption, even though the adsorption of the reactants were very high, which is not the case.

Pease (5), in a study of this catalytic reaction, found that when the concentration of hydrogen was kept constant the speed of the reaction decreased as the concentration of ethylene increased. He also found that the deactivation of a copper catalyst by heat treatment or by poisoning resulted in a much larger decrease in the adsorption of hydrogen than of ethylene. This seems to indicate that the adsorption of hydrogen is the more important factor in the hydrogenation of ethylene.

In view of these results an explanation may be offered for the above-mentioned behavior. In all experiments in which the rate of hydrogenation was measured, the adsorption of hydrogen was measured first and then, leaving the hydrogen on the catalyst, an equal volume of ethylene was admitted. Thus at the very first part of the reaction the hydrogen was in large excess. As the ethylene diffused into the catalyst the two gases were competing for the free spaces on the catalyst surface. It seems only reasonable to assume that the amount of hydrogen adsorbed was much greater at the beginning of the reaction than after the gases had become thoroughly mixed. As the reaction rate seems to depend primarily on the amount of hydrogen adsorbed, it seems quite in order that the reaction should be much more rapid at the beginning than after a considerable amount of the adsorbed hydrogen had been displaced by the ethylene.

The above explanation is in agreement with the results of Harker (3), who investigated this same reaction on a supported copper catalyst and found that hydrogen left on the catalyst overnight greatly increased the initial speed of the reaction, while ethylene similarly left on the catalyst greatly reduced the initial speed of the reaction. As Harker has pointed out, the ethylene probably slows down the reaction rate by impeding the movement of adsorbed hydrogen on the catalyst surface to the active centers where the reaction presumably takes place.

The adsorption of hydrogen on nickel at temperatures from −80° to 150°C.

The adsorption of hydrogen on nickel No. 5 (amalgam) at 99.6°C. is very high as compared with the negligibly small adsorption at 0°C. The isotherm (figure 10) shows the adsorption to be completely reversible with respect to pressure.

As is shown by table 1, practically no hydrogen was adsorbed by nickel No. 5 at 0°C., but on slowly heating the catalyst a considerable adsorption began to occur at about 50°C. The adsorption at these temperatures was quite slow; at 72.4°C. more than two hours were required for the system to come to apparent equilibrium. The rate of adsorption seemed to increase with rising temperature. At 100°C. the time necessary to reach apparent equilibrium was less than one hour.

The amount of hydrogen adsorbed was less at 150°C. than at 100°C., and on cooling the catalyst it was found that the amount of adsorbed gas increased steadily down to −80°C. The increase (0.24 cc.) was small in comparison to the total amount adsorbed. On again heating the catalyst the same amount of adsorption was found for each temperature as had been observed at the same temperature in the previous measurement.

From these results it appears that the hydrogen is taken up by the nickel in two ways. The first is ordinary "physical adsorption," which decreases with rising temperature. Numerous measurements had shown the amount of hydrogen adsorbed at 0°C. on this and other nickel catalysts prepared from the amalgam was very small. It was apparent therefore that the amount of "physical adsorption" at 100° to 150°C. was extremely small and practically negligible. The amount of gas taken up in the second manner seems to remain remarkably constant over the range of temperatures studied. The change in adsorption from −80° to 150°C. can be ascribed to the change in the "physical adsorption."

The second manner of "sorption" could be explained by Taylor's (7) theory of "activated adsorption," or by a solution of the gas in the metal or possibly a combination of the two. The time required for the process is in agreement with either explanation. The adsorption isotherm at 100°C. is of the same shape as would be expected on the basis of activated adsorption. However, according to Ward (9), a solution isotherm may have the same form as an adsorption isotherm. The present experimental results do not seem to warrant an attempt to exclude either of these explanations.

SUMMARY

1. The adsorption of hydrogen, ethylene, and ethane has been studied on metallic catalysts prepared from both the oxides and the amalgams.

2. The rate of the hydrogenation of ethylene has been studied on the same catalysts under the same conditions as above.

3. The metals prepared from the amalgams showed a catalytic activity which is quite comparable to that of the metals prepared from the oxides.

4. A very high initial rate of reaction has been found and an explanation has been offered for the same.

5. The adsorption of hydrogen on nickel has been studied at temperatures from −80° to 150°C. It has been shown that only a very small part of the total adsorption is due to "physical adsorption."

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A STUDY OF THE SODA-ALUM SYSTEM. II

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The soda-alum system has been studied by Dobbins and Byrd (2), who determined the 25°C. isotherm and found soda-alum as a stable phase at that temperature. The demonstration of the existence of soda-alum at 25°C. made it seem advisable to continue the investigation further to determine the range of temperature over which it exists as the stable phase. During the progress of the present investigation, Astruc and Mousseron (1) published the data for this system at 5°, 18°, and 42°C., and concluded that soda-alum does not exist below 11°C., nor above 39°C. In the present paper are given the results of a study of the system at 0°, 30°, and 42°C.

EXPERIMENTAL PROCEDURE

Solutions were made, using C.P. sodium sulfate and aluminum sulfate. For each isotherm 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. For the 0° and 30°C. isotherms sodium sulfate decahydrate was used, and for the 42°C. isotherm, anhydrous sodium sulfate was used. The solutions were saturated with the respective salts at temperatures slightly higher than the temperature at which they were to be studied, thus producing equilibrium in a shorter time. Approximately 50 cc. of solution in contact with solid was prepared for each sample, and the bottles placed in the constant temperature bath. The bottles were shaken several times daily, and it was found that equilibrium was reached in less than two weeks. For the 0°C. isotherm, the bottles were kept immersed in a container of crushed ice and water placed in a large refrigerator.

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 and immediately transferred to weighing bottles and weighed. These samples were then diluted to a known volume.

The solid phase presented much difficulty in some cases, owing to the finely divided condition of the solid. In all cases, portions of the solid phase, with adhering liquid, were dipped from the bottles, as much of the liquid as possible was drained off, and the residue transferred to a weighing bottle, weighed, and made up to a known volume.

Methods of analysis

On account of the difficulty of obtaining satisfactory analyses for sulfate in the presence of large amounts of aluminum, it was found advisable to make direct determinations of sodium sulfate and aluminum sulfate. Water was determined by difference.

TABLE 1

0°C. isotherm

SAMPLE NO.	LIQUID		RESIDUE	
	Na_2SO_4	$Al_2(SO_4)_3$	Na_2SO_4	$Al_2(SO_4)_3$
1	6.45	0.00		
2	6.06	3.15	31.44	1.35
3	5.80	5.20		
4	5.55	6.26	29.20	2.36
5	5.40	7.08		
6	5.02	9.33		
7	4.84	9.77		
8	4.70	11.43	31.74	3.71
9	4.38	14.99		
10	4.20	16.47		
11	4.05	19.40		
12	3.85	22.25		
13	2.88	24.23	29.65	8.78
14	2.12	25.55	8.33	39.33
15	1.31	26.42	0.50	44.63
16	0.00	27.97		

Sodium was determined volumetrically by the method of Dobbins and Byrd (3), and aluminum was determined gravimetrically by the method of Dobbins and Sanders (4).

RESULTS

The data for the three isotherms are given in tables 1 to 3 and the results are plotted in figures 1 to 3.

DISCUSSION OF RESULTS

An examination of figure 1 shows that the 0°C. isotherm for this system consists of two solubility curves, with no evidence of compound formation. The composition of the solid phase, determined by means of tie-lines connecting the composition of the liquid phases with the composition of the respective wet residues, shows that the solids in equilibrium with the saturated solutions are sodium sulfate decahydrate and hydrated aluminum sulfate. It is evident that soda–alum does not exist at 0°C.

TABLE 2

30°C. isotherm

SAMPLE NO.	Na_2SO_4	LIQUID $Al_2(SO_4)_3$	RESIDUE	
			Na_2SO_4	$Al_2(SO_4)_3$
1	29.61	0.00		
2	28.10	3.35		
3	27.75	5.14		
4	27.37	6.55	39.20	2.17
5	27.04	8.77		
6	27.00	10.44		
7	26.93	11.42	39.52	3.40
8	26.67	11.73	30.70	11.90
9	24.20	13.55	21.48	19.85
10	15.95	17.73	16.00	24.21
11	12.58	19.49		
13	9.20	22.68		
		25.51		
14	5.43	26.54		
15	5.21	27.20	7.22	29.55
16	3.18	29.56	8.24	32.40
17	2.30	30.87	1.10	44.05
18	1.55	31.21	0.92	42.26
19	0.00	31.99		

TABLE 3

42°C. isotherm

SAMPLE NO.	Na_2SO_4	LIQUID $Al_2(SO_4)_3$	RESIDUE	
			Na_2SO_4	$Al_2(SO_4)_3$
1	32.94	0.00		
2	29.10	6.83		
3	27.13	10.11	75.92	3.86
4	25.70	12.43	76.63	4.07
5	21.12	13.94	20.69	23.77
6	18.74	15.19	18.48	26.31
7	10.31	21.35	12.92	31.45
8	8.03	22.65		
9	5.49	26.94	8.03	31.79
10	2.22	31.32		
11	1.89	32.21	3.26	46.40
12	0.00	34.24		

Figure 2 shows the presence of soda–alum in addition to the two compounds present at 0°C. The limits of concentration between which soda-alum may be prepared are 26.9 per cent sodium sulfate, 11.4 per cent aluminum sulfate, and 4 per cent sodium sulfate, 30.5 per cent aluminum sulfate.

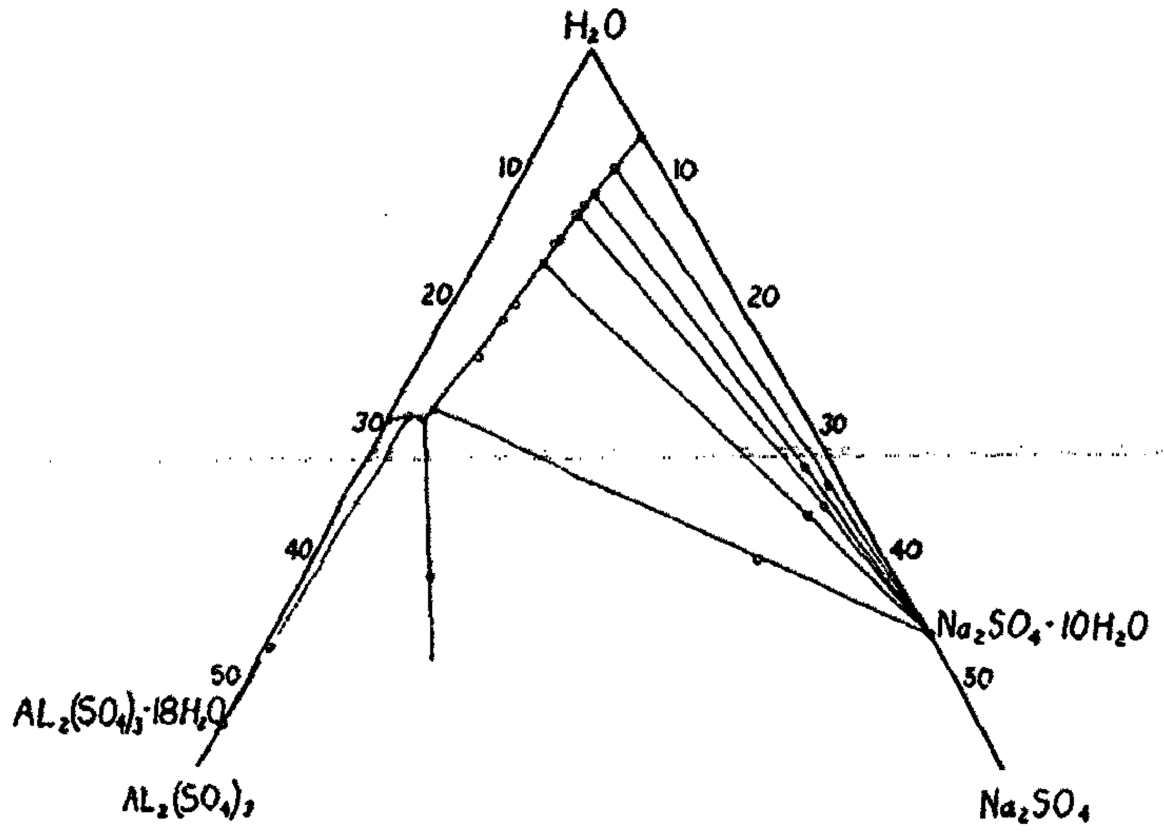

FIG. 1. THE SYSTEM Na_2SO_4–$Al_2(SO_4)_3$–H_2O AT 0°C.

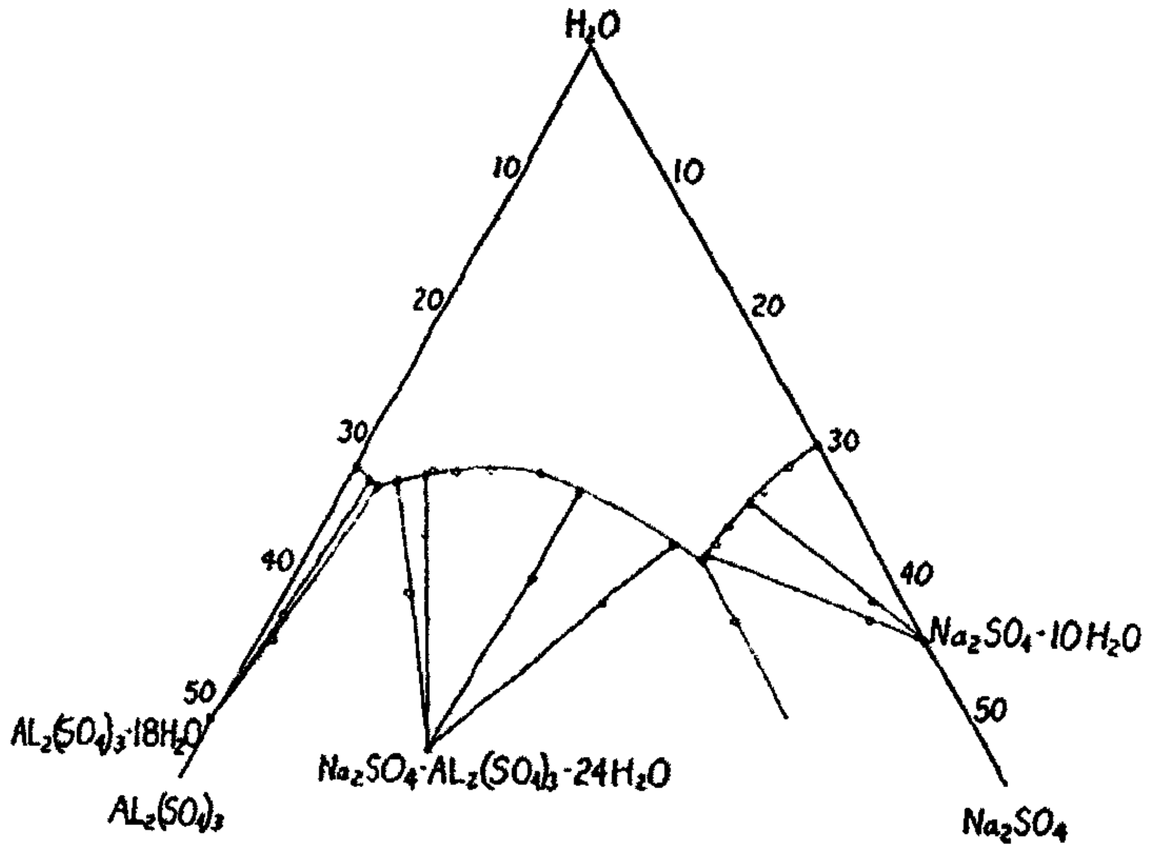

FIG. 2. THE SYSTEM Na_2SO_4–$Al_2(SO_4)_3$–H_2O AT 30°C.

Examination of figure 3 reveals that the 42°C. isotherm is similar to that of the 30°C. isotherm. The solid phases are anhydrous sodium sulfate, hydrated aluminum sulfate, and soda-alum. The determination of the composition of the compound in contact with the middle section of the isotherm presented much difficulty. The solid was very finely divided, and it was impossible to obtain samples comparatively free of the mother liquor. Analysis of the wet residue and extension of the tie-lines to their intersection gave no exact information, since it was impossible to obtain three tie-lines to intersect at one point. Hydrolysis had taken place to some extent, and the excess aluminum present made the intersection of any tie-lines vary greatly from the composition of the alum. The inability to remove the liquid from the residues caused the composition of the residues to be so close to the liquid curve that a small amount of hydrolysis produced a very great effect on the direction of the line.

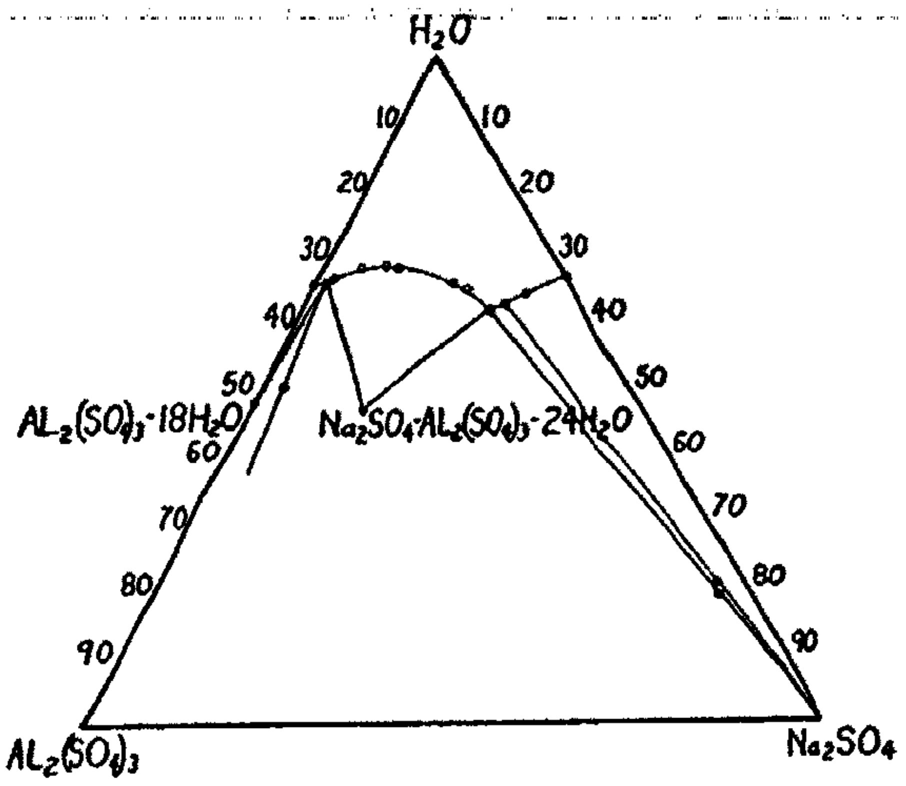

FIG. 3. THE SYSTEM Na_2SO_4-$Al_2(SO_4)_3$-H_2O AT 42°C.

To ascertain the composition of this solid phase, the tell-tale method was used. A small amount of copper nitrate was added to the saturated solutions. Samples of the liquid and the wet residue were taken, and the copper in each was determined electrolytically. From the amounts of copper present, the amount of mother liquor adhering to the solid phase was calculated. Calculations indicated that the solid phase in contact with the middle segment of the 42°C. isotherm consisted of soda-alum with varying excesses of aluminum oxide ranging from 4 per cent to 6 per cent on the extreme left end. On the right portion of this segment of the isotherm, the region of high sodium sulfate concentration, an excess of sodium sulfate was found in the solid. This was most probably due to adsorption.

In order to verify these conclusions as to the composition of the compound in question, a microscopic examination was made of the solid.

This showed conclusively that the substance was composed of small isometric crystals showing the flattened octahedra of the alums.

Since hydrolysis had taken place to some extent, the system should theoretically be treated as a four-component system. However, since the liquid curve is fairly smooth, it is evident that hydrolysis is not a large factor and may be disregarded.

SUMMARY

The 0°, 30° and 42°C. isotherms for the soda-alum system have been determined. There is no alum formation at 0°C. Evidence of the existence of soda-alum as a solid phase at 30°C. and 42°C. was established. Hydrolysis takes place to some extent above 30°C.

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ADSORPTION AND CATALYSIS

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A hot filament of tungsten, iron, molydenum, or platinum placed in vapors of potassium, cesium, or rubidium captures the valency electrons of the atoms surrounding the filament and adsorbs them as ions. The surface thus has ability to cause ionization. By measuring the photoelectric emissivity Brewer (6) showed that the emission curves for iron on which nitrogen, hydrogen, or ammonia has been adsorbed can be duplicated by those obtained from pure iron on which potassium ions have been deposited. This suggests that nitrogen, hydrogen, and ammonia are also adsorbed as ions, and that the strong adsorption on metals, which occurs above certain temperatures, is due to the ability of the surface to cause ionization. As contact catalysis proceeds from the strong adsorption, the ability to cause ionization can be assumed to account for contact catalysis. Coehn and Specht (8) demonstrated that hydrogen adsorbed by palladium is present as ions, since the application of a potential to the metal increases the rate of diffusion of hydrogen to the negative part. This confirms the idea that a metal is able to ionize molecules (atoms) with an ionization potential much higher than the work function of the metal. Since, furthermore, electronic bombardment-synthesis in gas mixtures occurs only when the accelerating voltage is higher than the ionization potential of the molecules most difficult to ionize, and since in the glow discharge it has not been possible to ascribe any reactivity to excited molecules, the mentioned assumption regarding the catalytic effect of the surfaces can be given the following form:—

Postulate I. In a chemical reaction furthered considerably by the presence of a surface, the surface is at the temperatures in question able to ionize those molecules among the reactants most difficult to ionize, and the surface will cause a strong adsorption as ions formed are attracted by the surface.

Postulate II. A surface able to ionize molecules of a gas or liquid, and hence able to yield a strong adsorption, produces an increased adsorption when the molecules are substituted by others having a lower ionization potential, assuming all other conditions to be the same.

As to postulate II the variation in adsorption of different gases on a given

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catalyst is only in the same order as the ionization potential when the ease with which ionization of the molecules takes place and the coefficient of recombination of their ions with electrons are of the same order. Nyrop (17) has calculated the adsorption due to ionization and shown that at a given temperature there is a maximum adsorption and a corresponding saturation pressure. Experiments show that such pressure is a characteristic feature of the strong adsorption in contrast to the van der Waals' adsorption. Nyrop (18) also shows that the positive ion emission from a gas layer adsorbed on a surface having ability to cause ionization is in accordance with the results of Evans (10), and that neutral molecules (atoms) and ions are present on the surface at the same time, since the surface is covered by an electronic gas, the "surface electrons," which is able to neutralize ions formed. The ionization is thus intermittent.

Savard (23) shows that the energy of dissociation of a molecule A_2 or AB_p is $D_A = 2n(I_m - I_a)$ or $D_{AB} = 2nI_m - n_aI_a$, respectively, when $2n$ is the number of linking electrons in the molecule, n_a the number of electrons in A, I_m the first ionization potential of the molecule, and I_a that of the atom. Ionization of a molecule will thus generally decrease the energy of dissociation and, in the same manner, may be able to reduce the energy of activation of a chemical reaction. The ability of a surface to cause ionization will hence be able to reduce the activation energy of a given process.

It has been observed that there is a considerable difference in the ways in which adsorption takes place on a surface at low temperatures and at high. The low temperature adsorption, being of the van der Waals' type, is instantaneous and without a considerable heat of adsorption, whereas above a certain temperature the adsorption is strengthened and takes place with increasing velocity when the temperature is raised. From the velocity at various temperatures an activation energy can be calculated. Taylor has therefore termed such adsorption "activated adsorption." The heat of adsorption in activated adsorption is higher than in the low temperature adsorption. As the temperature is raised there is at very low temperatures the normal decrease in the van der Waals' adsorption, but, when activated adsorption is possible, such adsorption sets in at a certain temperature, increases with temperature, and passes through a maximum.

Considering ionic adsorption, the ability to cause ionization can be represented by an electric field at the surface, the potential barrier hindering the "free" electrons of the metal in escaping. This barrier, P, retards the "free" electrons having the maximum kinetic energy E and the work function becomes

$$\varphi = P - E \tag{1}$$

If the potential barrier shall be able to ionize molecules coming close to the surface, the potential drop must take place inside a certain distance off the surface, a distance varying with the features of the adsorbed molecules. It shall later be demonstrated that this distance decreases with increasing temperature. The ability to cause ionization is thus enlarged with the temperature, although P may remain constant. P and the distance mentioned are thus determining the ability, and above a certain minimum temperature, T_0, the distance becomes so small that ionization takes place. This is in accordance with the wave mechanics result that the time required for an electron to cross a potential barrier decreases rapidly when the thickness of the barrier is decreased. In this connection the radii of the adsorbed molecules (atoms) have influence, as there may be a certain minimum distance between the nuclei of the molecules and the surface. The ionization power of the surface may thus pass through a maximum when the distance between the surface and the outermost part of the surface electrons is decreased.

That the adsorptive power for lead on platinum, as shown by Maxted (15), is 3.5 times that for mercury confirms postulate II, as the ionization potential of lead is 7.38 and of mercury 10.39 volts. If adsorption and catalysis are considered with heed to the postulates the ability to cause ionization, q_0 (in volts), at a given temperature can be estimated. At the same time T_0 can be determined. Table 1 is a synopsis of such estimates.

By A > B is indicated that the adsorption on the metal A is stronger than on B, or that the energy of activation of a given process is less when A is employed. The ability of A to cause ionization should thus be larger than that of B. When T_0 is lower for the adsorption of a gas on A than on B it indicates that the ionizing ability of A is larger than that of B. Considering the postulates and table 1 we obtain table 2, giving the succession of the metals corresponding to a diminishing ability to cause ionization. The succession of the oxides becomes: $MnO > ZnO > Co_2O_3 > CuO > Fe_2O_3 > V_2O_5 > SiO_2 > Cr_2O_3 > Al_2O_3$.

It will be noticed that the dehydrogenation catalysts are able to ionize hydrogen, and the dehydration catalysts water; and that ammonia is decomposed by the synthetic ammonia catalysts but also by copper able to ionize ammonia and not nitrogen.

There are two types of activated adsorption of hydrogen, for instance, on iron, each type occurring in different temperature ranges. The low temperature activated adsorption may be due to H_2^+ ions, the high temperature to H^+ ions.

According to Sommerfeld (25) the "free" electrons of a metal can be regarded as a degenerate gas capable of expanding. The surface will thus be covered by an electronic gas, the "surface electrons" (17, 18). The "maximum" kinetic energy of the electrons is

$$E = 26\, a^{-2/3}\, n_i^{2/3} \tag{2}$$

where a is the volume occupied by a gram-atom and n_i the number of "free" electrons per atom. As only few electrons have energies above E this energy is termed the "maximum." When equation 2 is applied and every atom loses one electron ($n_i = 1$), the value E' of table 3 is obtained for the

TABLE 1

PROCESS	LITERATURE REFERENCE	CATALYST	T_0	φ_0
			°K.	*volts*
Adsorption of H_2 (I.P. = 15.37 v.)	(7)	Ni	83	>15.37
	(7)	Pt	195	>15.37
	(8)	Fe	90–195	>15.37
	(9)	ZnO	273	>15.37
	(10)	Oxides	>400	>15.37
	(4)	Ni > Pd > Cu		>15.37
Adsorption of N_2 (I.P. = 16 v.)	(8)	Fe	273	>16
	(11)	W	293	>16
	(7)	Ni	98–173	>16
Adsorption of CO (I.P. = 14.4 v.)	(8)	Cu	273	>14.4
	(8)	Fe	195	>14.4
Ethylene (I.P. = 12.2 v.) is adsorbed more strongly than hydrogen (I.P. = 15.37 v.) on Cu, Ni, and Pt, but relatively most on Cu		Ni; Pt > Cu		>15.37
Adsorption of H_2 (I.P. = 15.37 v.) and CH_4 (I.P. = 14.4 v.)	(4)	Cu > C		>15.37
Adsorption of CO (I.P. = 14.4 v.) and H_2 (I.P. = 15.37 v.)	(4)	Ni > Pt > Cu		>15.37
Catalytic exchange of atoms between hydrogen (I.P. = 15.37 v.) and water: $H_2^2 + H_2O \rightleftharpoons H_2^2O + H_2$	(15)	Pt		>15.37
Ortho-para hydrogen conversion	(12)	Fe	83	>15.37
	(13)	ZnO	298	>15.37
	(13)	Al_2O_3	580	>15.37
	(4)	Ni > Cu > C		>15.37
Adsorption of H_2O (I.P. = 12.7 v.) on Hg inhibits photoeffect, H_2 (I.P. = 15.37 v.) does not		Hg		15.37 > Hg > 12.7

TABLE 1—*Continued*

PROCESS	LITERATURE REFERENCE	CATALYST	T_0	φ_0
			°K.	*volts*
Hydrogenation of amylacetylene	(21)			
to amyl acetate		Cu } Ni > Cu		>15.37
to heptane		Ni		
Dehydrogenation of	(22)			
piperidine		Pd > Pt		
cyclohexane		Ni > Os > Pt		
decahydronaphthalene		Ni > Pd > Pt		
Hydrogenation (I.P. = 15.37 v.) of organic products	(4)	Cu; Zn; Ni; Co		
		Ni > Co		>15.37
		Ni > Fe		
Synthesis of acetaldehyde from acetylene (I.P. = 11.2 v.) and water (I.P. = 12.7 v.)		Hg		>12.2
Hydrogenation of C_2H_4 (I.P. = 12.2 v.)	(20)	Pd > Pt > Cu		>15.37
	(23)	Ni > Co > Zn		
Synthesis of NH_3 from N_2 (I.P. = 16 v.) and $3H_2$ (I.P. = 15.37 v.)	(4)	Os; Mo; Fe; Ni; Co; Mn; W		>16
		Fe > Pt		>16
		Os > Pt		>16
Decomposition of NH_3 (I.P. = 11.2 v.)	(16)	Cu		>11.2
	(19)	Os > Pt		>11.2
Decomposition of CO (I.P. = 14.4 v.)		Ni > Cu		>14.4
Organic decompositions, etc.		Ni; Co; Fe; Pd, Pt > Cu		
		Ni > Co > Pt; Cu		
Decomposition of ethyl alcohol into aldehyde and hydrogen (dehydrogenation)		Cu; Zn		
Decomposition of ethyl alcohol into ethylene and water (dehydration)		Al_2O_3; W_2O_5		

TABLE 1—*Concluded*

PROCESS	LITERATURE REFERENCE	CATALYST	T_0	φ_0
			°K.	*volts*
By contemporary organic dehydration and dehydrogenation the formation of hydrogen decreases, and that of water increases in the order of the catalysts...	(18)	$MnO > ZnO > Fe_2O_3 > SiO_2 > Cr_2O_3 > W_2O_3 > Al_2O_3$		
Oxidation of CO............	(14)	$Co_3O_4 > CuO > Fe_2O_3 > V_2O_5 > SiO_2$		
	(17)	Al_2O_3	<800	
		Cr_2O_3	<700	
		Fe_2O_3	<600	
Oxidation of methanol......		Pt > Cu Ag		
Combustion of a mixture of H_2 and CO................		Pt > Cu Pt > Cu		

maximum kinetic energy. Now some electrons are more loosely bound to the metallic atoms than the rest; hence it is possible that the atoms will lose so many that a stable electronic shell is left. For iron, chromium, manganese, molybdenum, and tungsten, for instance, there are several possibilities; n_i and the corresponding value of E of table 3 is therefore taken as an average when several possibilities are permissible.[2] By measuring the electronic current from a heated metal the work function φ of the table is calculated.

The number of electrons incident on a surface with a kinetic energy of the electron's motion normal to the surface larger than E is

$$n_s = \frac{8\pi m}{h^3}(kT)^2 \tag{3}$$

In a distance s off the surface where the electrons have lost an energy E, these electrons produce a gas with a density

$$n_g = 20\pi(mkT)^{3/2}\,h^{-3} \tag{4}$$

---

[2] In a previous article (17) n_i was estimated without heed to this uncertainty; thus the discrepancy between table 3 and earlier values.

TABLE 2

Succession of the metals corresponding to a diminishing ability to cause ionization

METALS	ABILITY TO CAUSE IONIZATION	IONIZATION POTENTIAL
		volts
Ni Os Fe Mn Co W Pd Pt	Able to ionize N_2	16
Zn Cu C	Able to ionize H_2	15.37
Ag		
Hg	Able to ionize water	12.7

TABLE 3

METAL	φ	E'	s	n_f	E	$E + \psi$
Ni	5.0	7.47	4	4	18.8	23.8
Os		11.60	2	2	18.4	(23.2)*
Fe	4.8	7.15	2–6	4	18.0	22.8
Cr		6.92	2-4-6	4	17.4	(22.1)
Mn		6.77	3–5	4	17.1	(21.8)
Mo	4.6	5.83	4–6	5	17.0	21.6
W	4.5	5.80	4–6	5	16.9	21.4
Pd	4.5	6.40	4	4	16.2	20.7
Co	4.0	7.30	3	3	15.2	19.2
Pt	4.5	5.97	4	4	15.1	19.6
Zn	3.3	5.96	2–6	4	15.0	18.3
Cu	3.7	7.10	1–5	3	14.8	18.5
C	4.1	8.50	2	2	13.5	17.6
Al	3.9	5.63	3	3	11.7	15.6
Au		5.60	1–5	3	11.4	(14.6)
Ag	2.9	5.47	1–5	3	11.3	14.2
Hg		4.42	2–6	4	11.2	(14.0)
Pb	3.9	3.78	4	4	9.5	13.4
Mg	3.0	4.62	2	2	7.3	10.3
Ca	2.2	3.17	2	2	5.0	7.2
Li		3.82	1	1	3.8	(5.8)
Na	1.8	3.14	1	1	3.1	4.9
K	1.2	2.14	1	1	2.1	3.3

---

* Parentheses indicate that the value has been estimated.

In a zone quite close to the surface and in a distance a off the surface the density is

$$n_a = \frac{8\pi(2m)^{3/2}}{3h^3}(E - E_a)^{3/2} \tag{5}$$

where E_a is the kinetic energy lost by the electrons in moving the distance a. ($E_a < E$). Near the outermost zone in a distance $x < s$ the density is expressed by an equation similar to equation 4, but the density is somewhat larger. The density of the outermost part of the surface electrons is thus increasing with $T^{3/2}$. Approximately[3] the distance between the outermost zone and the surface, viz., a plane through the exterior nuclei of the metallic ions, is

$$s = 3.6 \times 10^{-6}\, a^{-1/6}\, n_i^{1/3}\, T^{-1/2} \tag{6}$$

and

$$E/s = 7 \times 10^{6}\, a^{-1/2}\, n_i^{1/3}\, T^{1/2} \tag{7}$$

For $T = 100$ we have for silver $E/s = 3.3 \times 10^{6}$.

As to the field accounting for φ, this is strongest at distances not much larger than s off the surface, but the strength will decrease as the density of the outermost part of the surface electrons is enlarged, i.e., with raising temperature. A part of φ equal to

$$\varphi' = \mu\, T^{-3/2}\varphi \tag{8}$$

may thus be able to assist in the ionization. ($\mu\, T^{-3/2}\varphi < \varphi$.) At high temperatures the maximum ability of a surface to cause ionization is thus equal to E, but at lower temperatures to $E + \varphi'$.

T_0 is the minimum temperature at which the activated adsorption by a given experimental technic is measurable. If T_1 and T_2 are the minimum temperatures for the same gas adsorbed on two surfaces having the ability to cause ionization $E_1 + \varphi_1'$ and $E_2 + \varphi_2'$, we should in accordance with equation 6 have approximately

$$\sqrt{\frac{T_2}{T_1}} = \frac{E_1 + \varphi_1'}{E_2 + \varphi_2'} \tag{9}$$

The adsorption of hydrogen on nickel and platinum mentioned in table 1 gives, when the values of table 3 for E and φ are applied, a minimum temperature for the adsorption on iron of 110°K. Considering equation 9, the minimum temperatures mentioned in table 1 are in agreement with

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[3] In calculating s it has been estimated that the electronic density at the surface is equal to that at the interior of the metal, although the density is somewhat less at the surface and just below. The electrons crossing the surface are thus accelerated slightly just before the retardation sets in and $P = (E + \Delta E) + \varphi$.

table 3. Further, the succession of the metals of table 2 is the same as that of table 3.

Taylor suggested that so-called peak areas were associated with special activity. Steacie and Elkin (26) demonstrated, however, that the rate of decomposition of gaseous methyl alcohol over solid and liquid zinc was directly dependent on the temperature, there being no discontinuity at the melting point. It was therefore concluded that the entire surface is uniformly active. A progressive removal of the postulated peak areas by poisoning causes, furthermore, no change in the activation energy of the decomposition of hydrogen peroxide on platinum. It seems thus that the catalytic activity is not bound to certain areas of the surface of a single metal. The ionic adsorption described does not involve any assumption regarding peak areas. A heterogeneous catalyst will, however, have crystal surfaces with different activity.

When ionic adsorption of a gas takes place, the positive ions formed neutralize part of the effect of the surface electrons whereby the distance between the outermost part of the surface electrons and the surface increases, viz., the average field close to the surface is weakened, although the potential difference between any point of the metal and points at some distance from the surface may remain constant. At a certain adsorption the field may thus be weakened to such degree that the surface no more is able to ionize the molecules. The ionic adsorption is hence limited, and molecules with ionization potentials lower than that of the gas will, when admixed, act as poison. Bredig (5) showed that in the decomposition of hydrogen peroxide on platinum, hydrogen sulfide destroyed the activity to a much larger degree than hydrogen cyanide. The ionization potential of hydrogen sulfide is 10.4 and of the cyanide 14.8 volts. Besides the limit of the adsorption set by the weakening of the field, impinging molecules and the presence of the surface electrons counteract the adsorption; the adsorption may thus never reach the limit set by the field. At high temperatures the field is strengthened so much that the influence of the adsorbed positive ions is decreased. Poisons are thus more active at low than at high temperatures; this is a well-established fact. A given reaction may also be self-poisoning. The temperature will therefore have to be above a certain value before the reaction takes place with a considerable velocity. Now the catalysts with high ionizing power are more exposed to poisoning than those with lower. In hydrogenation processes, for instance, platinum and palladium are thus active at room temperature, whereas the more active iron and nickel require a higher temperature. That argon is not as strongly adsorbed as nitrogen although their ionization potentials are of the same order is due to a difference in requirement to the distance over which the potential drop at the surface take place, argon demanding a smaller distance than nitrogen. (Argon has, for instance, a smaller effective sectional area than the nitrogen molecule.)

As mentioned, a too narrow potential barrier in relation to the dimensions of the adsorbed molecules may weaken the power of ionization. In that case a very small concentration of poison will be able to cause an increase in adsorption at lower pressures.

The use of relatively weak catalysts in the hydrogenation of coal, tars, and oils and assisting the hydrogenation by hydrogen sulfide (7), added in the free state or formed *in situ*, may depend on a reaction between the sulfide (I.P. = 10.4 volts) and the organic matters, which in many cases have an ionization potential less than 11 volts. Hydrogen sulfide, on the other hand, poisons, for instance, the reaction between acetylene and water, which takes place on several catalysts, as its ionization potential is lower than that of acetylene (11.2 volts) and water (12.7 volts).

In catalytic hydrogenation of oleic acid the double bond is at low pressures saturated and the carboxyl group is not affected. At high pressure the latter is reduced and the double bond is largely unattacked. The ionization potential of ethylene is 12.2 volts and of carbon monoxide 14.4 volts. It may thus be justifiable to assume that the radicals close to the double bond of oleic acid are more easily ionized than the carboxyl group and are thus hydrogenated preferably at low pressures where the molecules lie flat on the surface. At high pressure, however, the carboxyl group comes more easily into contact with the catalyst, as compression causes the molecules to stand at a fairly steep angle to the surface, hence the preferential hydrogenation of this group. In the hardening of oils, linoleic, linolenic, and other highly unsaturated acids are hydrogenated in preference to oleic acid. When the adsorbed molecules lying flat on the surface are highly unsaturated they are attracted to the surface at two or more points; they are thus adsorbed preferentially to oleic acid having one double bond only. This preferential adsorption is the cause of the preferential hydrogenation.

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THE SOLUBILITY OF LEAD IN MERCURY

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The purpose of this investigation was to determine the solubility of lead in mercury from 20°C. to 70°C., using the general method developed earlier in this laboratory (3, 14), but preliminary work gave indication that special technique and special apparatus would be necessary because liquid lead amalgams oxidize rapidly in the presence of air. Since the free energy of formation of lead oxide from the elements is −41,000 calories (7), this compound would be very stable when once formed.

A critical survey of the existing solubility data for lead–mercury revealed that very little work has been done on this binary system below 100°C. The work of Jänecke (6) extends downward to only 106°C., while Puschin (9) is apparently the only investigator who has reported a series of values below 100°C. However, Puschin's values are few in number, with the precision of these determinations apparently unstated. Hence a careful and precise set of solubility data for lead–mercury at the lower temperatures should be a welcome addition to our knowledge of lead amalgams.

MATERIALS

The lead used in this investigation was from a standard sample prepared by the U. S. Bureau of Standards. The Bureau has quoted no analyses for this material, but its melting point (1) is 327.3°C. as against 327.5°C., the reported value for pure lead (5). Spectrographic analysis of the lead using a Bausch and Lomb Littrow spectrograph indicated that antimony, bismuth, cadmium, copper, iron, magnesium, silicon, and silver were present in amounts varying from a trace as in the case of bismuth, silver, and sodium to faint, very faint, and exceedingly faint quantities with respect to the other elements above mentioned. Calcium was the only impurity found to be present in more than a trace, while titanium and vanadium could not be definitely determined because of the presence of these two elements in the carbon electrodes. It has been concluded therefore, that the impurities present in the lead introduce no appreciable error in the results.

The mercury used was purified by passing it several times through a 5-ft. Meyer column containing 6 *N* nitric acid and then triple distilling the material according to the method of Hulett and Minchin (4). After this purification, 30-g. samples of this mercury when evaporated in an atmosphere of hydrogen yielded residues averaging 0.2 mg. high in the weighed capsules in which the samples were heated.

APPARATUS

Considerable time and effort were spent in perfecting a solubility tube adapted to the elimination of experimental error due to oxidation of the lead amalgams during any part of the experimental procedure. An illustration of the perfected solubility tube employed in this investigation is given in figure 1. The tubes were made from Pyrex glass. The lead amalgams were prepared *in vacuo* in these solubility tubes by keeping the lead and mercury separated until after each tube had been pumped out. The lead was cut into small cubes, about 2 mm. on an edge, and inserted into the nib A through the open end of the tube B; then mercury was added to the tube by means of a funnel and allowed to collect in the end of the tube at C, after which the tube was sealed up near B. The tube was evacuated through the capillary, D, which was subsequently sealed. The function of the tube E, with its end drawn to a fine tip, was to afford a means of breaking the vacuum in the solubility tube when the amalgam was to be filtered. F indicates the filter section of the tube where the lead amalgam, after passing through glass wool and a fine capillary, was conducted by means of the guiding tube, G, into the receiving section H. After the solubility tube was evacuated, the lead and mercury could be brought together by merely tipping the tube so that the lead would fall out of the nib A into the mixing tube BC.

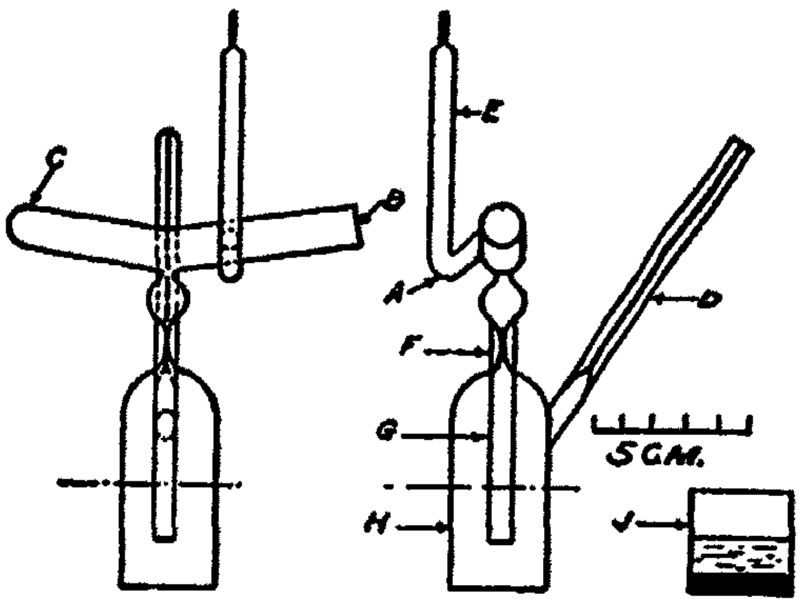

Fig. 1. The Solubility Tube

The thermostat and mechanical equipment used in this investigation were employed previously by other workers in this laboratory (3, 14), and the oven in which the mercury was vaporized in the analysis of the amalgams has also been described (3). The rate of oscillation of the shaking mechanism was adjusted to eleven times per minute to eliminate spattering of the small volume of amalgam in the mixing tube in order that all portions of the mercury should become saturated with lead.

The thermometers employed were of good quality, reading directly to 0.1 and 0.2°C., respectively, and were calibrated against other thermometers certified by the Bureau of Standards. The analytical weights were calibrated by Richards' method and compared with a 10-g. weight certified by the Bureau of Standards.

EXPERIMENTAL PROCEDURE

Before quantitative measurements on solubility were made, the precision of the analytical procedure for lead amalgams was determined. Solubility tubes were cleaned with boiling 6 *N* nitric acid, rinsed with water, and dried in an oven at above 100°C., after which treatment they were charged with a weighed amount of lead, which was placed in the nib A, figure 1, and a weighed amount of mercury, placed in the tube at C. The tubes were then evacuated and sealed at pressures varying from 0.033 to 0.002 mm. as measured by a McLeod gauge, but in a majority of cases the pressure at sealing was not far from 0.01 mm. The data of Puschin were here used to prepare amalgams so that all the lead placed in the tubes would be dissolved.

The solubility tubes were then placed in the thermostat and shaken for several hours, after which the tubes were then rotated through 180° and the amalgams filtered. Filtration was produced by breaking the tip of the tube E, figure 1, to admit purified hydrogen to the previously evacuated solubility tubes, through rubber tubing slipped over the tube E. The sudden change of pressure was sufficient to cause the amalgam to be filtered.

The next step was to analyze the amalgam sample that collected in the receiving part of the tube, H. The analyses were made according to the method of Sunier and Gramkee (12), which consists in the vaporization of the mercury from an amalgam, weighing the residue as the amount of metal dissolved in the mercury.

Special tests have shown that there is less than 0.1 mg. change in weight when 0.3-g. samples of lead are heated in an atmosphere of hydrogen to above 440°C. for at least eight hours.

The experiments summarized in the data of tables 1 and 2 indicate that the average deviation of the analytical concentration from the known value was 2 parts per thousand or below, and that this analytical method is entirely adequate for the analysis of lead amalgams having concentrations of the order studied in this investigation.

The precautions to be taken during the analysis of lead amalgams by this method are (1) protection of the amalgam from oxidation at all times, and (2) heating the lead amalgam during the process of vaporization of mercury from it to not over 350°C., so that bumping of the amalgam may be eliminated.

Details of the handling of the amalgam after filtration were as follows: (1) the entire solubility tube with contents was weighed; (2) the solubility tube was opened by a hot glass rod applied to a file mark along the dashed line as in figure 1; (3) the amalgam in the lower part of the tube was covered with benzene (figure 1J) and then placed in the oven for vaporization of mercury from the amalgam; (4) the part of the solubility tube above the dashed line was weighed on the analytical balances to the nearest milligram; (5) the lower section of the tube with its residue of lead was removed from the oven and weighed; (6) afterwards the lead was quantitatively removed by dilute boiling nitric acid, and the emptied tube was dried and

TABLE 1

The solubility of lead in mercury

TUBE	LEAD TAKEN	MERCURY TAKEN	ATOMIC PER CENT TAKEN	ATOMIC PER CENT FOUND	DEVIATION IN PARTS PER THOUSAND
	grams	*grams*			
1	0.2577	36.057	0.6872	0.6874	0.3
2	0.2593	37.524	0.6646	0.6672	3.9
3	0.2580	34.807	0.7125	0.7139	1.9
4	0.2569	35.727	0.6914	0.6931	2.5
Average			0.6889	0.6904	2.2
Deviation of average composition					2.2

TABLE 2

The solubility of lead in mercury

TUBE	LEAD TAKEN	MERCURY TAKEN	ATOMIC PER CENT TAKEN	ATOMIC PER CENT FOUND	DEVIATION IN PARTS PER THOUSAND
	grams	*grams*			
1	0.6041	28.575	2.006	2.006	0.0
2	0.6093	27.892	2.071	2.071	0.0
3	0.6097	28.569	2.025	2.019	3.0
4	0.6079	29.363	1.965	1.966	0.5
Average			2.017	2.016	0.9
Deviation of average composition					0.5

weighed empty. The difference between the value of operations No. 1 and No. 4 determined the weight of the lower part of the tube, J, plus the weight of the amalgam taken. Operation No. 3 was for the purpose of protecting the lead amalgam from the air until the tube was placed in the oven in an atmosphere of hydrogen. From the measurements outlined above, the atomic per cent of lead in the amalgam was calculable, and it is seen from this description that the easily oxidized amalgams were exposed to oxygen for only a few seconds, from the time the hydrogen-containing solubility tubes were opened until the amalgams in the lower sections were covered with benzene. It is to be pointed out here that the analyses reported in table 1 were made using a somewhat different type of tube than the perfected apparatus, and that the results in table 2, excepting tube 4, were obtained using a tube differing from the one illustrated, in that a small crucible was sealed inside of the tube H. However, it is believed that the high precision of the blank analyses, as well as the precise results in subsequent solubility determinations using the solubility tube shown in figure 1, are proof enough of the validity of the analytical method and of the efficacy of this type of tube.

The procedure when measurements of the solubility at a given temperature were to be made differed from the procedure in the study of the analytical method in that there was at least a 100 per cent excess of lead present in the mixing tube, using Puschin's data as a guide. The earlier runs appeared to indicate that the attainment of equilibrium was rather slow when the amalgam, at a given temperature, was nearly saturated with lead. For that reason, practically all of the runs were made at constant temperature for a considerable length of time, necessitating for practical reasons that equilibrium be approached, for a given run, from one side only.

EXPERIMENTAL RESULTS

In table 3 are presented complete data for a typical run, while table 4 gives a summary of data for all runs. Because there was some duplication of determinations at various temperatures, it seems desirable that the more accurate and reliable data should be indicated, and the mean probable error for each group of such determinations stated. This information has been compiled in table 5. In the calculation of atomic percentage, 200.61 was used for the atomic weight of mercury and 207.20 for the atomic weight of lead.

DISCUSSION OF RESULTS

Criteria which were employed in the selection of the best data were (1) length of run, (2) temperature control, (3) number of determinations, and (4) the precision of the various measurements. As has been previously indicated, the attainment of equilibrium was found to be moderately slow,

—much slower in fact than was found to be true in the determinations of gold solubility in mercury by other workers in this laboratory (12, 13, 14).

TABLE 3

Complete data for run J

Time of run, 115 hours; equilibrium from the low side; temperature, 39.9°C.

TUBE	WEIGHT OF LEAD	WEIGHT OF AMALGAM	ATOMIC PER CENT LEAD	DEVIATION FROM MEAN IN PARTS PER THOUSAND	REMARKS
	grams	*grams*			
1	0.5277	23.214	2.203	0	
2	0.6090	26.769	2.204	0.5	
3	0.6051	26.363	2.224	x	Exclude
4	0.5391	23.737	2.201	0.9	
5	0.6495	28.511	2.207	1.8	
6	0.5847	25.700	2.204	0.5	
7	0.5926	26.092	2.201	0.9	
8	0.6216	27.394	2.199	1.8	
Average............................			2.203 ±.001	0.8	

TABLE 4

Summary of solubility data for all runs

RUN	TEMPERATURE	ATOMIC PER CENT LEAD	DEVIATION IN PARTS PER THOUSAND	NUMBER OF TUBES	TIME
	°*C.*				*hours*
AA	16.1†	1.372	30	4	8
M	19.7	1.469	11	8	286
K	30.7	1.811	2	8	120
J	39.9	2.203	1	7	115
A	46.5†	2.509	2	3	5
D	47.4	2.592	7	5	22
C	47.4	2.559	11	5	8
B	47.4	2.567	4	3	29
H	48.2	2.631	1	7	115
E	60.5	3.425	2	3	41
F	60.6*	3.438	2	5	34
L	69.2	4.279	4	6	203
G	70.2	4.340	5	3	23

* Equilibrium approached from both sides.

† Uncalibrated thermometers used in these two runs.

Hence no run was considered to be reliable in which the time of the run was less than twenty-two hours. In all of the accepted runs the temperature was automatically controlled by a mercury thermoregulator of the type employed by Clark (2) and constant temperatures within 0.01° and 0.02°C. limits could be maintained over a period of days, and to within 0.005°C. over a period of hours. No run was included among the selected data unless the total number of acceptable determinations was at least five, and exclusion of doubtful or wild values was made on the principle that many small variations occur with higher frequency than do larger variations from the mean, and the general criterion for elimination of values having large deviations was followed (8, 11).

In table 5 the mean for the B and D determinations has been presented because the two runs were made at the same temperature within the limits of experimental error, and the runs were made for nearly the same length of time. Moreover an average of many determinations under practically identical conditions should be more reliable than the two sets of values reported separately, because the value of a mean determination increases with the number of precise observations.

TABLE 5

Summary of best data on solubility

RUN	TEMPERATURE	MEAN VALUE ATOMIC PER CENT LEAD	MEAN PROBABLE ERROR	PROBABLE ERROR OF SINGLE DETERMINATION	NUMBER OF DETERMINATIONS
	°C.		*± per cent*	*± per cent*	
M	19.7	1.469	0.005	0.013	8
K	30.7	1.811	0.001	0.003	8
J	39.9	2.203	0.001	0.002	7
B D	47.4	2.588	0.005	0.012	7
H	48.2	2.631	0.001	0.003	7
F	60.6	3.438	0.003	0.006	5
L	69.2	4.279	0.006	0.015	6

The solubility curve (see figure 2), log N_{Pb} versus $1000/T$, was drawn in such a manner that the most reliable values were given the greater weight, with the line of the curve following the more precise observations more closely than the observations whose accuracy and precision, for one reason or another, were regarded as the less reliable. The dotted line in the graph is that drawn for Puschin's data, and was made with due regard for other values from his work which lie beyond the scale of this graph.

In table 6 the solubility of lead in mercury at rounded temperatures as read from the log N_{Pb} versus $1000/T$ plot is presented. The equation for the solubility versus temperature curve, between the limits 19.7°C. and 69.2°C., is

$$N_{\mathrm{Pb}} = 0.5893 - 0.004115T + 0.0000073547^{2}$$

where N_{Pb} is the atomic fraction of lead dissolved and T is the absolute temperature. The equation was calculated by least squares from the data in table 5, and is useful for determining solubility with moderate accuracy, but for the closest estimation the use of a large plot of the data is recommended.

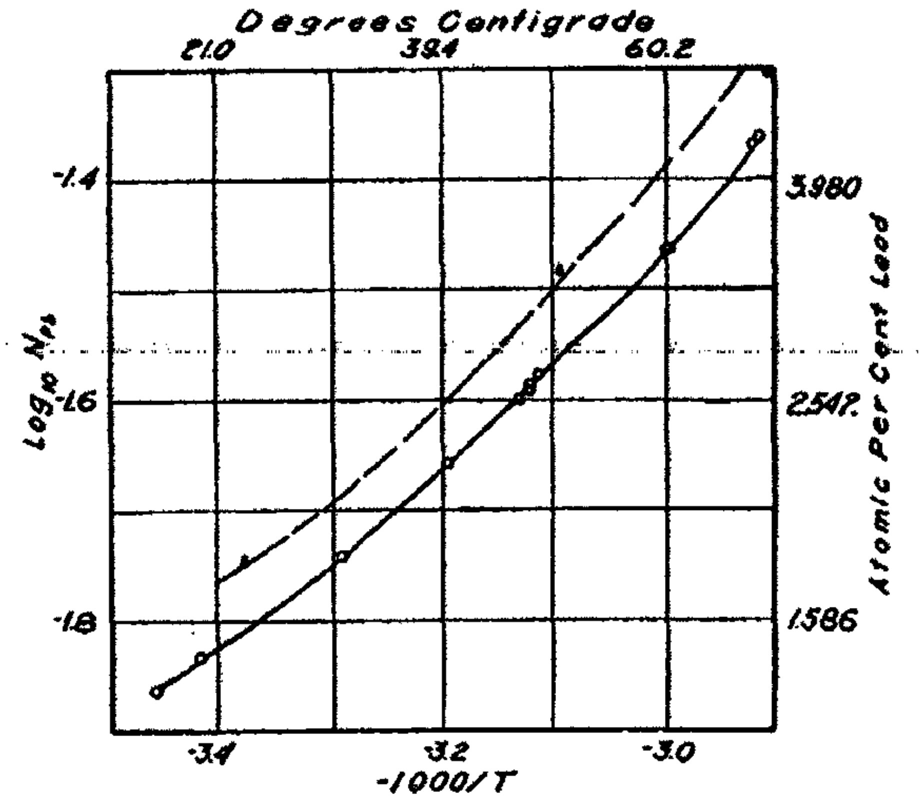

FIG. 2. LOG N VERSUS 1000/T PLOT
△, results of Puschin; ○, results of author

TABLE 6

Solubility of lead in mercury at rounded temperatures

(From log N versus 1000/T plot)

TEMPERATURE	ATOMIC PER CENT LEAD (FROM CURVE)	ATOMIC PER CENT LEAD (CALCULATED)	ERROR IN PARTS PER THOUSAND
°C.			
20	1.476	1.50	16
30	1.780	1.76	11
40	2.199	2.18	9
50	2.742	2.74	1
60	3.419	3.46	12
70	4.330	4.31	5

Examination of the curve shows that the author's data give lower values for the solubility than those of Puschin for corresponding temperatures. This may be due to the fact that in making a solubility curve for amalgams, using a thermal method as Puschin did, supercooling, particularly at lower temperatures, might be more apt to occur, yielding high values for the solubility. On the other hand, it is difficult to conceive how the author's data can be much lower than the true value, because such an extraordinary length of time has been allowed for equilibrium to be attained. There is no evidence to indicate that lead amalgams are colloidal in character within the concentrations studied, if the high precision of the determinations may be used as a criterion of homogeneity.

The curvature apparent in the log N_{Pb} versus $1000/T$ plot, instead of the straight line which is obtained when there is strict conformation to Raoult's law, may be due to the fact that the solid phase is not the one indicated, or to the fact that the latent heat of fusion of lead is some unknown function of the temperature and cannot be considered as constant. No tests have been made in this study to determine the nature of the solid phase in equilibrium with the liquid solution, but Puschin (9), after reviewing previous work, presents evidence of his own to indicate that solid solution is the solid phase.

In a paper by Richards and Garrod-Thomas (10) on electrochemical measurements of amalgams, it is stated that a 1.02 per cent lead amalgam by weight, corresponding to 0.997 atomic per cent, is an unsaturated amalgam at 0°C. Extrapolation of the author's curve verifies this statement, and indicates the saturation value to be 1.072 atomic per cent lead at 0°C.

SUMMARY

1. Special solubility apparatus has been designed and special experimental technique developed for the efficient handling of the rapidly oxidized lead amalgams. This type of apparatus and technique may be of use also in studies of other easily oxidized amalgams.

2. About seventy determinations of the solubility of lead in mercury have been made in the temperature range 20°C. to 70°C., with an average deviation of about 5 parts per 1000 for the final runs.

3. The experimental results are adequately represented by the following equation within the temperature range studied:

$$N_{Pb} = 0.5893 - 0.004115T + 0.000007354T^2$$

To Professor Arthur A. Sunier the author is indebted for counsel and assistance, and to the University of Rochester for making this research possible. The author is also indebted to Mr. T. J. Zak of the Bausch and Lomb Optical Company for the spectrographic analysis of the lead from the Bureau of Standards.

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PHYSICAL CHEMISTRY OF THE PROTEINS IN NON-AQUEOUS AND MIXED SOLVENTS. II

Electrochemical Properties of Protein Solutions in Certain Glacial Organic Acids

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INTRODUCTION

In general the proteins are insoluble in the most commonly used organic solvents, but there are known a few anhydrous and a larger number of mixed solvents which will dissolve many of the proteins. These solvents consist largely of a number of alcohols and hydroxy compounds, some aliphatic carbon acids, and certain not very closely related nitrogen compounds. The separation of the prolamines by alcohol mixtures is the best example of the use of a mixed solvent in protein chemistry.

In the first paper of this series a study was made of the state of aggregation of certain proteins in mixtures of urea and water and of glycerol and water (1). In this communication there will be presented the results of experiments on the electrochemical properties of protein solutions in the aliphatic carbon acids, formic, acetic, and lactic.

GLACIAL ALIPHATIC CARBON ACIDS THAT ARE PROTEIN SOLVENTS

Formic, acetic, lactic, and pyruvic acids have been reported to be solvents for proteins. The earlier literature of the subject contains the information that gelatin dissolves in glacial acetic and lactic acids (see ref. 12), that Mathewson (13) prepared solutions of gliadin in glacial acetic acid, and that Robertson (16) found that casein would dissolve in anhydrous formic acid with ease. A more systematic survey of the subject has recently been published by Loiseleur (10). In the course of the present work, most of Loiseleur's observations were confirmed, but in a few instances there was a disagreement with his statements. With Loiseleur, it was observed that anhydrous formic acid readily dissolves most proteins in the cold, including such diverse members as gelatin, casein, fibrin, edestin, gliadin, egg albumen, zein, etc. Apparently the only proteins not dissolved are certain of the keratins.

Loiseleur states that acetic acid dissolves gelatin in the cold and edestin on heating, but does not dissolve the other mentioned proteins. The only dry protein we were able to dissolve in acetic acid was gelatin, and in the course of this there was noted the paradox that solutions could be prepared and were stable when the gelatin concentration was above a certain critical value, but that it could not be brought into solution in concentrations below this critical level (9). Attempts to dissolve edestin in acetic acid were unsuccessful even after prolonged heating on a water bath.

According to Loiseleur, propionic acid dissolves none of the proteins, but the substituted propionic acids, lactic and pyruvic, readily dissolve many proteins. In our experience casein and edestin swell and slowly go into solution in lactic acid at room temperature. Heating markedly accelerates the rate of solution. Shreds of fibrin become hugely swollen in cold lactic acid, but only on being heated do they completely disperse.

Loiseleur emphasizes the point that protein solutions in the organic acids do not have the usual properties characteristic of colloidal solutions in water. They are not turbid, do not foam, have a low viscosity, and are not coagulated by the protein precipitant acids, tannic, trichloroacetic, and picric, nor by salts of such heavy metals as iron, chromium, and lead. However, by merely diluting these organic acid protein solutions with water, the characteristic colloidal properties are at once restored.

Because of these effects, Loiseleur takes the point of view that in the anhydrous solutions the proteins are actually in "true" solution. Just what is implied by this is somewhat ambiguous, since no further elaboration of the author's conception of the distinction between true and colloidal solutions is given. We assume it is implied that these acid solvents cause a disaggregation of the proteins into units of low molecular weight, since it is generally accepted that colloidal properties are associated with a high molecular size. If this hypothesis is correct, and it were possible to demonstrate that the proteins disaggregate into small units in any group of solvents, it is readily seen that it would be a matter of great importance for chemical theories of the structure of the proteins. One class of substances, namely the soaps, is known to exist as aggregated colloidal micelles in aqueous solution and as simple molecules in alcoholic solution (11). If we interpret Loiseleur correctly, he views the change of properties from aqueous protein solutions to those in the glacial acids as a similar transformation. This conception is not completely novel. Similar suggestions have been proposed, for example, by Herzog and Kobel (7) and by Troensegaard and Schmidt (21). Experimental evidence for such a transformation was offered in what was supposed to be the low molecular weight, 200 to 600, obtained by freezing point measurements of proteins in phenol solution. However, Cohn and Conant (4), who reëxamined the question, showed that the above measurements actually were in error owing to the traces of moisture which were introduced with the protein samples. When this error is eliminated, no disaggregation of proteins in liquid phenol can be demonstrated.

The claim that proteins dissolved in the aliphatic carbon acids lose all of their colloidal properties, moreover, is not completely correct. Concentrated solutions of casein in formic acid, dissolved by heating, set to gels on cooling, and these solutions also show a distinct turbidity. One of the colloidal precipitants, phosphotungstic acid, is able to precipitate proteins even from formic acid. Moreover, the lack of the properties usually associated with colloidal solutions is not a sufficient criterion for invariably assuming a change in the state of aggregation. A similar lack of colloidal properties is found with protein solutions in concentrated urea, which also show no turbidity, do not foam, and are not coagulated by heat. Yet, as was shown by Burk and Greenberg (1) and by Burk (2), many of the proteins have the same molecular size in urea as they do in aqueous solution.

The experiments reported here were undertaken because of their interest to the subject of the structure and the physicochemical state of the proteins, and also for their significance to theories of solubility. Since most of the solvent mixtures for proteins are weak acids or bases, it has been proposed that the solvent properties depend upon the formation of electrically charged protein ions by the interaction with the solvent acid or base. This is undoubtedly the case in many instances, but is by no means universally true. Burk and Greenberg have shown that urea does not act as a protein solvent because of basic properties, and in this communication it will be shown that the same is true of certain of the glacial acids.

EXPERIMENTAL

The conductivities were measured by the Kohlrausch telephone method, using a General Radio Company oscillator as the alternating current source. The semi-micro cell of 2.5 ml. volume shown in figure 1 was employed in all the measurements. An interesting feature of the cell, aside from its size, is that the electrodes, indicated by "s" in the drawing, were formed by spiraling 22 gauge platinum wire. These electrodes were coated with platinum black electrolytically, and the cell constant was determined against standard solutions of potassium chloride in the usual manner. The solvent materials used for preparing the solutions were as follows: Kahlbaum's 100 per cent formic acid, specific conductance about 10^{-4} mhos; Baker or Merck's 85 per cent glacial lactic acid[1] with a conductance of around 5×10^{-5} mhos; and Baker's 99.5 per cent glacial acetic acid with a conductance of less than 10^{-7} mhos.

The proteins used were purified preparations of low ash content. Casein

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[1] Completely anhydrous lactic acid cannot be used for solvent purposes, as it is a crystalline solid at ordinary temperatures.

was prepared by the method of Van Slyke and Baker (22), edestin by that of Osborne (14). The gelatin was an Eastman Kodak Company's electrolytically deashed preparation, and deaminized gelatin was prepared from this as described by Hitchcock (8).

All of the protein concentrations are recorded in the tables on the basis of grams of dry protein per liter of solvent. Wherever necessary for this purpose, a correction has been applied for the moisture content of the protein.

Conductivity measurements

The conductivity data obtained in this investigation are recorded in tables 1 to 5. The observations in glacial lactic and acetic acid, which are given in table 1, may well be considered together, separately from the results in formic acid.

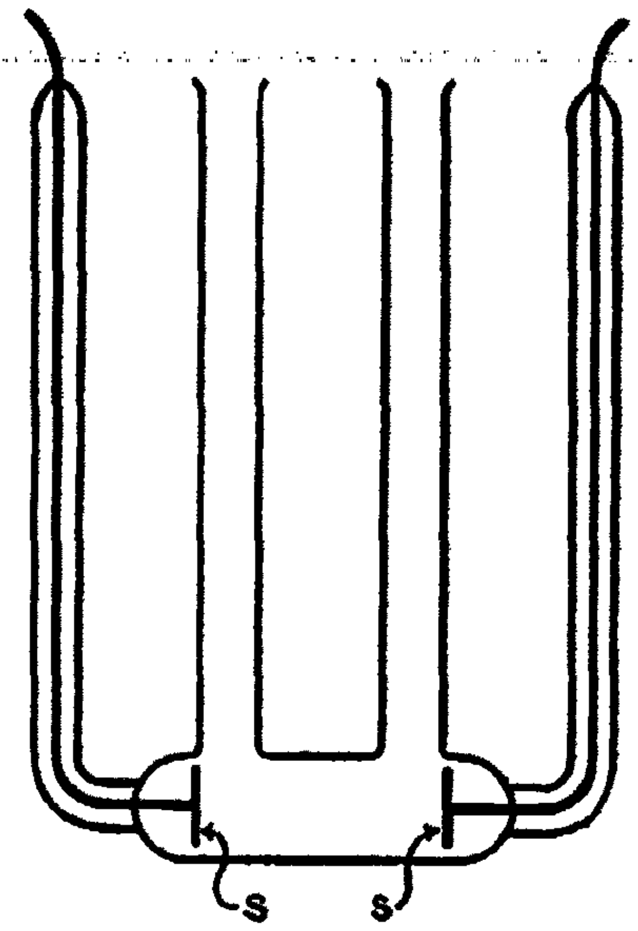

Fig. 1. Semi-micro Conductivity Cell

The three proteins, casein, edestin, and gelatin, as noted in table 1, add practically nothing to the conductance of glacial lactic acid. In acetic acid, gelatin increases the conductivity to values more than a hundredfold that of the solvent, but even so, the magnitude of the conductance is comparatively small. The inference to be drawn from this is that the solvent power of these two acids for proteins is not dependent upon an ability on their part to react with the proteins to form protein ions. From the conductivity values of table 1, there can be no question regarding this view about lactic acid. However, to accept the same viewpoint for acetic acid, the increased conductance produced by gelatin, even though small, has to be explained.

That the increased conductivity in these solutions is probably not due to protein salt formation follows from the fact that the conductivity increases

TABLE 1

Specific conductivity of certain proteins in glacial lactic and acetic acids

CASEIN IN LACTIC ACID		EDESTIN IN LACTIC ACID		GELATIN IN LACTIC ACID		GELATIN IN ACETIC ACID	
Concentration	Specific conductivity	Concentration	Specific conductivity	Concentration	Specific conductivity	Concentration	Specific conductivity
g. per liter of solvent	*mhos* × 10^5	*g. per liter of solvent*	*mhos* × 10^5	*g. per liter of solvent*	*mhos* × 10^5	*g. per liter of solvent*	*mhos* × 10^5
0	5.14	0	5.25	0	7.37	0	0.01 (about)
2.80	5.06	2.85	5.24	4.30	7.48	27.0	1.22
5.65	4.95	5.70	5.23	8.60	7.53	36.0	1.97
8.45	4.93	8.55	5.30	13.00	7.75	45.0	2.75
11.25	4.90	11.40	5.34	17.30	8.03	54.0	3.64
14.05	4.88	14.25	5.46	21.60	8.11	63.0	4.71
16.90	4.87	17.10	5.49	26.00	8.52	72.0	5.79
19.70	4.86	19.95	5.53	30.30	8.82		
22.50	4.96	22.80	5.56	36.10	9.03		
25.30	4.97						
28.15	5.04						

TABLE 2

Conductivity of casein in formic acid

CONCENTRATION	χ SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 990$ (MEAN OF DYE TITRATION AND HEXONE BASE CONTENT)	Λ	CONCENTRATION	χ SPECIFIC CONDUCTIVITY†	EQUIVALENT CONCENTRATION $N = 990$ (MEAN OF DYE TITRATION AND HEXONE BASE CONTENT)	Λ
Casein I				Casein II			
g. per liter of solvent	*mhos* × 10^5		*mhos*	*g. per liter of solvent*	*mhos* × 10^5		*mhos*
4.55	17.3	0.0046	37.7	1.90	7.2	0.0019	38.0
9.30	37.6	0.0094	40.0	4.70	17.3	0.0047	36.8
13.90	55.1	0.0140	39.3	9.45	39.9	0.0095	42.0
18.55	73.2	0.0187	39.1	14.15	56.6	0.0143	39.6
23.20	95.8	0.0235	41.7	18.90	74.6	0.0191	39.1
25.10	102.8	0.0254	41.5	23.60	91.6	0.0239	38.3
27.85	110.6	0.0282	39.2	28.30	109.1	0.0286	38.2
32.50	121.1	0.0328	36.7	33.10	126.7	0.0334	38.0
39.10	138.8	0.0395	35.2	37.85	140.4	0.0382	36.8
46.40	169.8	0.0470	36.2	47.20	170.5	0.0477	35.8
55.70	200.0	0.0563	35.5	56.65	198.4	0.0572	34.7

* Specific conductivity of solvent = 14.0 × 10^{-5} mhos has been subtracted from the total.

† Specific conductivity of solvent = 10.15 × 10^{-5} mhos has been subtracted from the total.

much more than proportionally to the gelatin concentration. Doubling the gelatin content produces about a threefold increase in conductance. This increase may well be due to the effect of the moisture added with the gelatin. In qualitative tests it was found that small quantities of water markedly increased the conductance of glacial acetic acid. The gelatin employed had a 10 per cent moisture content.

TABLE 3

Conductivity of edestin in formic acid

CONCENTRATION	X SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 640$ (DYE TITRATION VALUE)	Λ	EQUIVALENT CONCENTRATION $N = 750$ (HEXONE BASE CONTENT)	Λ
g. per liter of solvent	*mhos* × 10^6		*mhos*		*mhos*
4.75	29.7	0.0074	40.1	0.0063	47.2
9.50	55.9	0.0148	37.8	0.0127	44.0
14.25	85.4	0.0223	38.3	0.0190	45.0
19.00	115.3	0.0297	38.9	0.0254	45.4
23.80	144.7	0.0372	38.9	0.0318	45.5
28.50	165.1	0.0445	37.1	0.0380	43.5
33.30	195.7	0.0518	37.8	0.0444	44.0
38.10	216.8	0.0595	36.5	0.0508	42.7

* Specific conductivity of solvent = 10.15 × 10^{-6} mhos has been subtracted from total.

TABLE 4

Conductivity of gelatin in formic acid

CONCENTRATION	X SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 950$ (MEAN OF DYE TITRATION AND HEXONE BASE CONTENT)	Λ
g. per liter of solvent	*mhos* × 10^6		*mhos*
9.0	37.5	0.0095	39.5
18.0	77.0	0.0190	40.5
27.0	116.1	0.0285	40.8
36.0	151.9	0.0379	40.0
45.0	185.4	0.0475	39.0
54.0	217.1	0.0568	38.2

* Specific conductivity of solvent = 10.8 × 10^{-6} mhos has been subtracted from the total.

Even if it were granted that the conductivity increase is due to protein ionization, a rough calculation shows that the density of charge produced must be very small. Assuming the equivalent conductivity of gelatin acetate would be of the same order as of gelatin formate (table 4), it is calculable from the data of table 1 that the gelatin would have one equivalent of charge for each 75,000 to 100,000 grams. This figure can hardly be as much as one charge per protein molecule. From this evidence another explanation must be sought for the ability of lactic and acetic acids to dissolve proteins than through an interaction to form protein ions. The true explanation of the solvent power remains to be determined.

Conductivity in formic acid

On the other hand, it can hardly be doubted that formic acid reacts with proteins to give ionized protein salts. In tables 2 to 5 are recorded the conductivity values of solutions of casein, edestin, gelatin, and deaminized gelatin in 100 per cent glacial formic acid. These proteins all markedly increase the specific conductivity of the formic acid, the increase being nearly proportional to the amount of protein in solution. The casein measurements were carried out on two separately prepared samples and in different lots of the solvent. The good agreement between the two series is evidence that the conductivity is an intrinsic property of the protein and not of any contamination therein. The magnitude of the conductivity values attained is quite considerable, being nearly of the same order as is found with solutions of the alkali and alkaline earth formates in formic acid. While the ionization reaction is probably no more essential to account for the solvent properties of formic acid than for the other organic acids, still it must be beneficial in this respect and it indicates why formic acid is a so much more powerful solvent than either lactic or acetic acid.

TABLE 5

Conductivity of deaminized gelatin in formic acid

CONCENTRATION	X SPECIFIC CONDUCTIVITY*	EQUIVALENT CONCENTRATION $N = 1705$ (DYE TITRATION VALUE)	Λ	EQUIVALENT CONCENTRATION $N = 1515$ (HEXONE BASE CONTENT)	Λ
g. per liter of solvent	*mhos* × 10^5		*mhos*		*mhos*
10.0	25.7	0.0059	43.6	0.0066	39.0
20.0	53.4	0.0117	45.6	0.0132	40.4
30.0	77.1	0.0176	43.8	0.0198	38.9
40.0	90.8	0.0235	38.6	0.0264	34.4
50.0	126.0	0.0294	42.9	0.0331	38.1
60.0	147.4	0.0352	41.9	0.0397	37.2

* Specific conductivity of solvent = 10.8×10^{-5} mhos has been subtracted from the total.

To obtain a more quantitative picture of the electrochemical nature of the protein solutions, it is desirable to evaluate the values for the equivalent conductivity. But to obtain these physical quantities for the proteins in formic acid is a problem offering formidable difficulties because of the uncertainty of the equivalent weights of the proteins.[3]

We were aware of no means by which it would be possible to determine the equivalent weights of proteins in these solutions directly. The extent of the interaction between the proteins and formic acid is unknown, and in aqueous solutions of acid or alkali the equivalent weight of a protein is not a constant but instead varies with the pH, so an estimate is not readily obtained in this way.

The only possible method of approach appears to be through the application of plausible assumptions regarding the equivalent weight, derived from other sources. With such an approach, to obtain what seemed a reasonable estimate of the equivalent weights, recourse was had to the following: From the many studies on the acid combination of proteins in aqueous solution, it has become probable that the maximum combining capacity in this medium is determined by the content of the amino acids, arginine, histidine, and lysine, in a protein. Chapman, Greenberg, and Schmidt (3) have shown that the titration of proteins with acid dyes is in good agreement with this view. Because of the huge excess of formic acid it may be reasoned that the basic groups of the proteins are completely neutralized in formic acid solution. Accordingly, it seems not improbable that the equivalent weight of a protein in formic acid solution may be measured by the value given by the content of arginine, histidine, and lysine or, what usually closely agrees with it, the dye titration figure.

On the basis of this assumption, the equivalent conductivities of casein, edestin, gelatin, and deaminized gelatin were calculated from the content of the hexone bases as determined by Van Slyke (see ref. 3) and, where there was a significant difference, also from the dye titration data of Chapman, Greenberg, and Schmidt. The results of these calculations are incorporated in tables 2 to 5 for each of the proteins respectively under the columns designated by the symbol Λ. The equivalent weight chosen for casein in table 2 is 990, which is the average of the value from the dye titration of 1000 and the hexone base content of 980. The equivalent weight of 950, chosen for gelatin (table 4), also is the mean of the figures from dye titrations and the hexone base content. For the other two proteins separate calculations are given, using values of equivalent weight derived from both of the above sources.

The equivalent conductivity of all four measured proteins has nearly the same calculated values. This correspondence upholds the choice of the equivalent weights, since because of their closely related properties, it may well be expected that the mobility of the proteins in formic acid would be

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[3] This is an illustration of the great importance which the equivalent weights have for the solution of electrochemical problems and of how baffling the formulation of the electrochemical state is without these constants.

virtually the same. An erroneous basis for the selection of the equivalent weights would be expected to lead to widely varying calculated values of Λ. The close correspondence in equivalent conductivity, it is true, is mainly determined by the high value of the mobility of formate ion in comparison with the mobilities of other ions in formic acid. The work of Schlesinger and coworkers (19, 20) shows that a similar condition prevails among the alkali and alkaline earth formates. The magnitude of the equivalent conductances obtained with the proteins seems plausible when compared with the values for the alkali and alkaline earth formates.

Most interesting are the results with gelatin and deaminized gelatin. The calculated values of the equivalent conductivities are about the same for each, and both agree well with the figures obtained for casein and edestin even though it is to be remembered that the equivalent weight of the deaminized gelatin has been deliberately altered by the removal of the ε-amino group of lysine through interaction with nitrous acid. That the calculations based on this known change should give such harmonizing results is strongly in favor of the reasoning given here.

The results obtained lead to the picture that the proteins in formic acid form ionizable salts rather analogous in electrochemical behavior to the alkali and alkaline earth formates in formic acid. The proteins behave in a manner that might be expected of formic acid salts of rather high valency.

Electrical transference

Since the conductivity curves of the proteins are not satisfactory for the purpose of evaluating the limiting equivalent conductivities at infinite dilutions, a number of electrical transference experiments were carried out to get at this data. The Hittorf method was employed in the first instance. The cell, with some slight modifications, was the type introduced by Landsteiner and Pauli (15). Five electrode portions were obtainable for analysis, but experience soon showed that only in the outermost anode and cathode portions was there produced any concentration change. The electrodes were of platinum wire and no correction was applied for the hydrogen evolved at the cathode and carbon dioxide at the anode, which have been shown by Schlesinger and Bunting (17) to be the main products of the electrode reactions. The current passing through the cell during the course of an experiment was measured with an iodine coulometer. A motor generator developing a D. C. current at a voltage of 250 supplied the current for electrolysis.

Naturally, the change in formate ion was not measurable, so only the change in protein content could be followed. This was determined by Kjeldahl analysis of the nitrogen content. The results obtained on each of the proteins are given in table 7. As the table shows, very closely agreeing figures were obtained from both cathode and anode portions in repeated experiments. From the transference numbers the Λ^0 values of the proteins shown in table 6 were calculated, using the value of 51.6 for the equivalent conductivity of formate ion as given by Schlesinger and Bunting (19). Compared to the figures in aqueous solution, the protein-

TABLE 6

Electrical transference of proteins in formic acid

Temperature, 25°C.

a. Casein

EXPERIMENT NO.	CASEIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	CASEIN CHANGE IN COMPARTMENT		T^+_{casein}
	g. per liter	*milliequivalents*		*ml.*	*milliequivalents*	*mg.*	*milliequivalents*	
1	30.0	0.455	Anode	17.5	0.443	−42.4	−0.043	0.095
		0.455	Cathode	17.0	0.430	+41.6	+0.042	0.092
2	30.0	1.065	Anode	19.6	0.995	−95.5	−0.097	0.090
		1.065	Cathode	17.5	1.025	+97.5	+0.099	0.093
Average								0.093
Λ^{0+}_{casein}								5.5

b. Edestin

EXPERIMENT NO.	EDESTIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	EDESTIN CHANGE IN COMPARTMENT	EDESTIN CHANGE $N = 640$	$T^+_{edestin}$	EDESTIN CHANGE $N = 750$	$T^+_{edestin}$
	g. per liter	*milliequivalents*		*ml.*	*milliequivalents*	*mg.*	*milliequivalents*		*milliequivalents*	
3	27.0	1.360	Anode	20.1	1.68	−121	−0.189	0.14	−0.161	0.12
4	28.5	0.775	Anode	18.8	1.00	−76	−0.1175	0.15	−0.1015	0.135
		0.775	Cathode	18.6	0.99	+75	+0.117	0.15	+0.1000	0.13
Average								0.15		0.13
$\Lambda^{0+}_{edestin}$								9.0		7.7

c. Gelatin

EXPERIMENT NO.	GELATIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	GELATIN CHANGE IN COMPARTMENT $N = 950$		$T^+_{gelatin}$
	g. per liter	*milliequivalents*		*ml.*	*milliequivalents*	*mg.*	*milliequivalents*	
5	30	1.27	Anode	17.8	0.554	−153	−0.160	0.125
	30	1.27	Cathode	16.4	0.562	+144	+0.150	0.12
Average								0.12
$\Lambda^{0+}_{gelatin}$								7.2

TABLE 6—*Concluded*

d. Deaminized gelatin

EXPERIMENT NO.	DEAMINIZED GELATIN CONCENTRATION	COULOMETER CURRENT	COMPARTMENT	VOLUME OF COMPARTMENT	NITROGEN TITRATION CHANGE OF COMPARTMENT	DEAMINIZED GELATIN CHANGE IN COMPARTMENT	DEAMINIZED GELATIN CHANGE $N = 1705$	$T^{+}_{\text{deaminized gelatin}}$	DEAMINIZED GELATIN CHANGE $N = 1515$	$T^{+}_{\text{deaminized gelatin}}$
	g. per liter	*milliequivalents*		*ml.*	*milliequivalents*	*mg.*	*milliequivalents*		*milliequivalents*	
6	30	1.27	Anode	16.8	0.444	−121	−0.071	0.056	0.08	0.063
	30	1.27	Cathode	18.8	0.419	+127	+0.0745	0.059	0.084	0.066
Average								0.058		0.064
$A^{v+}_{\text{deaminized gelatin}}$										3.5

TABLE 7

Electromotive force cells and transference of sodium formate in formic acid

Temperature = 25°C.; reference concentration = 0.147 molal sodium formate

CONCENTRATION OF SODIUM FORMATE		E (MEASURED)	T_{Na^+}
per cent	*moles per liter of solvent*	*volts*	
0.10	0.0147	0.0286	0.241
0.15	0.0220	0.0236	0.241
0.20	0.0294	0.0197	0.238
0.25	0.0367	0.0164	0.232
0.30	0.0441	0.0142	0.230
0.35	0.0514	0.0123	0.236
0.40	0.0588	0.0110	0.236
0.45	0.0662	0.0090	0.220
1.00	0.1470	0.0000	
Average			0.236

ion mobility in formic acid is astonishingly low, but it is quite concordant with the figures for the mobility of the cations of the alkali and alkaline earth elements in formic acid obtained by Schlesinger and associates.

It was also attempted to determine the transference numbers of formic acid solutions through the use of electromotive force cells with transference. Since Hall and Conant (6) have shown that certain oxidation-reduction couples can be used to measure the hydrogen-ion activity in such non-aqueous solvents as acetic acid, it seemed not unlikely that the quinhydrone electrode could be used for this purpose in formic acid. Tests showed that this electrode worked well in the presence of the alkali formates, but unfortunately, not with solutions of proteins in formic acid. This may be due to an interaction between quinone and the proteins, similar to the reaction which occurs in the quinone leather tanning process (see ref. 23).

Although no valid results were obtained with the proteins, the data obtained with sodium formate will be presented, since the method offers an independent means of obtaining such information that has hitherto, as far as we are aware, not been employed for non-aqueous solutions.

The cell set-up for the measurements is given by the equation,

$$\mathrm{Pt} \underset{E_1}{|} \text{Quinhydrone}, [\mathrm{NaOOCH}]_1 \underset{E_3}{|} [\mathrm{NaOOCH}]_2, \text{Quinhydrone} \underset{E_2}{|} \mathrm{Pt} \qquad (1)$$

The electromotive force of this cell (5), as can be readily shown, is given by equation 2 below, provided the mass law relationship, $[H^+]\,[HCOO^-] = k$ holds in formic acid.

$$E = E_2 - E_1 + E_3 = 2T_c \frac{RT}{F} \ln \frac{[\mathrm{NaOOCH}]_2}{[\mathrm{NaOOCH}]_1} \qquad (2)$$

where T_c is the cation transference number. At 25°C., using numerical values of the constants, the equation becomes

$$E = 0.118\ T_c \log \frac{[\mathrm{NaOOCH}]_2}{[\mathrm{NaOOCH}]_1} \qquad (3)$$

In carrying out the measurements, the liquid junction in the cell was established by plugging a stopcock which connected the two arms of the cell with cotton wool so that only a slow diffusion of liquid obtained. With this arrangement it was found that after a few minutes to allow for the attainment of diffusion equilibrium, a very steady and reproducible electromotive force was established. Since quinhydrone is quite soluble in formic acid, it was introduced just before the start of an experiment in amounts required to make the concentration in each arm of the cell the same.

The results obtained with the sodium formate solutions are recorded in table 7. With the concentrations of sodium formate employed of between 0.0147 and 0.066 molal, the transference numbers found for sodium ion are reasonably constant. The average value of 0.236 for the sodium ion transference number, while not identical with the value of 0.22 obtained by Schlesinger and Bunting by the Hittorf method, is perhaps in as good agreement as might reasonably be expected, since no great degree of refinement marks the results by either procedure.

SUMMARY

1. Measurements of the conductivity of solutions of proteins in the glacial carbon acids, lactic, acetic, and formic have been carried out. In lactic and acetic acids this is increased but little. On the other hand, a marked

conductivity increase is produced in anhydrous formic acid, so that the solutions become nearly as good conductors as are solutions of the alkali and alkaline earth formates in formic acid.

2. On the basis of certain plausible appearing assumptions the equivalent conductivity of the proteins casein, edestin, gelatin, and deaminized gelatin in formic acid has been calculated.

3. Transference numbers of the protein formates have been determined by the Hittorf method. The results of the conductivity and transference measurements lead to the picture that the proteins in formic acid form ionizable salts having electrochemical properties which would be expected of formic acid salts of rather high valency.

4. Measurements of the transference numbers of sodium formate in formic acid have been carried out by means of an electromotive force cell with transference.

5. The solvent action of the three glacial acids used in this work for proteins does not appear to be particularly dependent upon their ability to form electrically charged protein ions.

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THE ADSORPTION OF THE VAPORS OF CERTAIN KETONES AND ESTERS BY ACTIVATED CHARCOAL[1]

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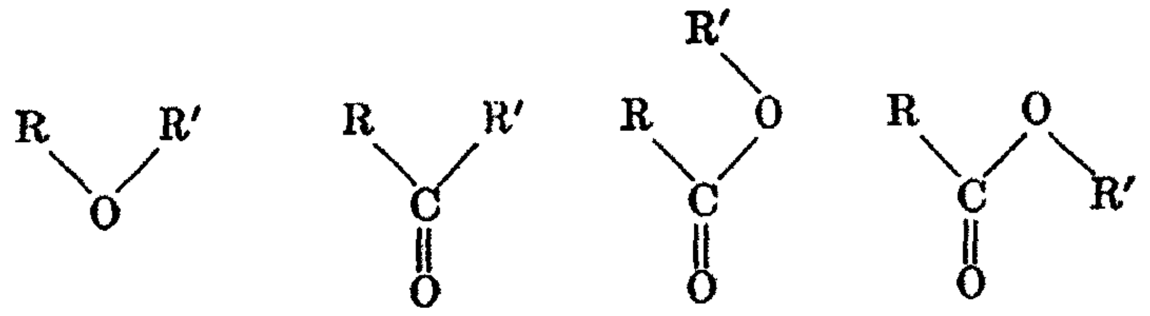
Previous investigations (4) have dealt with the adsorption of vapors of various types by activated charcoal. These have been studied with special reference to the influence of the position and the nature of substituent groups in the vapor molecules upon adsorption magnitudes. In this paper we present the results obtained in the study of the adsorption of certain ketone and ester vapors by charcoal. If these are considered in conjunction with the vapors of ethers previously studied (6), we have three types of oxygen compounds to consider, namely,



I II

Ether Ketone Ester

The mobility of the molecules on an adsorbing surface supports the view that adsorption is a phenomenon due to physical attraction. These forces may be simply van der Waals forces or they may be of an electrical nature, depending upon the dipole nature of the vapor molecules. Under the influence of the powerful surface forces the molecular dipoles will be definitely oriented and attracted by the surface atoms.

According to Eucken and Meyer (2), the dipole moment of a molecule is the vector sum of the partial moments of the individual linkages of the

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[1] A brief extract of a dissertation presented by Arthur C. Hanson to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

atoms in the molecule. They have calculated the moments of the following typical linkages:

Linkages......	H—C	H—O	C═O	C—C	C—OH	$C—C^{O}_{H}$
$\mu \times 10^{18}$ E.S.U.	0.4	1.6	2.3	0.7	1.6	1.0

They have added vectorially the four moments in the ester molecule, R·COO·R′, and they have found the moments for formulas I and II to be 3.4×10^{-18} and 1.1×10^{-18} E.S.U., respectively. Since the moment of the H—(C) should be the same as that of CH_3—(C), or of $CH_3 \cdot [CH_2]_n$—(C), the moments should be independent of the nature of the radical R, provided it consists of hydrogen atoms, or of alkyl groups only.

Except as modified by the remaining linkage moments, the C═O moment is the one specifically active in the adsorption of ketone vapors. Its value should be affected considerably by the presence and the manner of rotation of the R—O— dipoles in the ester molecule. The moments of the fatty acids are approximately 1.4×10^{-18} and of most esters about 1.8×10^{-18} E.S.U.

According to Debye (1), the two possible angles between the two H—O linkages of the water molecule are 64° and 110°, respectively; the corresponding moments calculated for these angular dimensions are 1.34×10^{-18} and 4.34×10^{-18} E.S.U. The actual observed moment lies between these at about 1.8×10^{-18}. It is conceivable that by repulsion between substituted groups the moments of the ether molecules, R_2O, should be different from that of their prototype, H_2O, and yet be only slightly affected by the size of the alkyl groups.

With these considerations in mind, it should be quite evident that whether we consider the ethers, the ketones, or the esters separately as a class, the magnitude of the adsorption due to the dipole moment will be but slightly modified by the complexity of the molecules of the given type.

While the moments of the molecules are undoubtedly effective in adsorption, the relative amounts adsorbed for the different vapors of any one class will depend to a large degree upon certain other physical properties. Among these are the cross-sectional area of the molecules, the ease of condensation, or the boiling points of the pure liquids, and the van der Waals constants "*a*."

If it is assumed that the vector moment is the same in the ether and ketone molecules oriented at the surface, it is evident that the surface covering power of dimethyl ether should be practically the same as that of dimethyl ketone. The surface covering power of either one must be less than that of the corresponding diethyl compound. With either type the covering power must increase with increase in the complexity of the substituted alkyl groups.

In so far as the previous work has shown, the adsorption of any vapor at low pressures is greater the higher the boiling point of the pure liquid.

TABLE 1

The adsorption of acetone vapor by charcoal at various temperatures

At 0°C.												
p......	0.00	0.00	0.20	0.55	1.24	3.52	5.16	12.41	28.19	33.69	44.87	50.58
x/m...	12.23	25.40	60.88	75.45	85.48	94.20	97.94	102.80	109.06	110.64	114.59	116.90
p......	61.00	64.58	70.08									
x/m...	120.87	122.74	131.67									
At 40°C.												
p........	0.10	0.35	0.55	0.69	0:79	1.55	2.28	3.52	4.46	9.03	12.02	
x/m......	6.33	20.17	25.48	31.10	34.74	45.57	60.65	67.59	72.28	83.13	86.93	
p........	18.02	24.07	27.00	37.72	52.12	78.42	89.89	154.47	243.51	288.68		
x/m......	91.83	95.28	96.10	99.34	101.45	104.36	105.49	109.62	114.48	116.51		
p........	337.92	388.26	420.91	421.50	412.17							
x/m......	119.29	121.26	128.10	129.74	122.93							
At 56.3°C.												
p............	0.30	0.89	1.89	4.25	6.70	12.57	16.88	17.22	24.80	37.67	45.54	
x/m..........	10.01	19.12	31.05	49.98	58.97	70.50	75.06	75.20	80.57	86.30	88.65	
p............	56.14	80.38	112.92	158.29	164.64	228.62	281.32	421.51	437.04			
x/m..........	91.12	93.93	96.64	99.37	99.81	102.21	103.84	108.90	109.07			
At 99.48°C.												
p.....	1.09	1.84	4.17	8.79	15.29	17.52	32.61	39.21	56.58	58.72	75.60	86.82
x/m..	5.88	7.76	13.77	22.90	31.36	33.68	44.74	47.57	53.85	56.05	62.80	66.15
p.....	88.00	88.45	112.77	137.49	169.01	183.60	204.10	233.59	288.09	358.12	422.64	
x/m..	66.56	66.56	71.38	75.06	77.94	79.21	80.73	82.35	84.49	86.95	89.58	
At 138.27°C.												
p........	2.00	7.69	10.32	35.24	66.11	112.72	161.56	248.53	297.72	315.48	405.97	419.95
x/m.....	4.38	10.68	13.21	25.63	36.32	46.48	52.98	60.66	63.38	64.24	68.93	71.50
At 183.10°C.												
p........	14.14	38.09	76.08	125.16	183.66	248.20	308.35	370.85	415.00	420.93		
x/m......	4.46	9.29	15.48	22.11	28.09	32.57	36.50	40.20	42.80	46.47		

Here, also, the cross-sectional area exerts a specific influence. The first molecules admitted to the surface are adsorbed without definite arrangement with respect to the surface atoms. Before the surface can become completely covered at saturation there must be a movement of the molecules along the surface, or a rotation about their points of attachment. For this reason more time is required for the attainment of adsorption equilibrium (5), and this influence will be greater, the greater the cross-section and the complexity of the molecules.

TABLE 2

The adsorption of methyl ethyl ketone vapor by charcoal at various temperatures

At 0°C.												
p..........	0.00	0.00	0.25	0.74	0.86	2.45	3.92	6.50	8.28	12.25	17.99	21.21
x/m........	43.47	44.22	60.98	83.50	83.72	89.39	91.91	94.26	96.17	98.40	102.79	105.85
p..........	24.93	25.27										
x/m........	108.43	112.91										
At 50°C.												
p..........	0.79	3.12	3.72	5.95	8.72	16.60	30.23	65.36	160.10	220.30	290.10	295.92
x/m........	27.82	53.73	57.60	64.04	67.72	76.03	80.15	84.56	90.48	92.50	94.05	96.08
At 79.5°C.												
p..........	0.15	0.60	1.85	5.75	8.42	9.32	19.28	29.68	52.77	105.47	172.40	237.20
x/m........	9.98	19.66	35.34	50.04	56.54	57.00	65.27	69.44	72.95	76.80	80.00	81.88
p..........	279.27	297.43										
x/m........	83.33	85.57										
At 139.15°C.												
p..........	4.71	13.33	24.25	43.31	62.69	63.23	91.97	98.11	98.56	125.56	165.56	184.94
x/m........	16.86	27.60	36.45	45.63	51.24	51.31	55.97	56.96	57.36	59.95	62.94	64.11
p..........	274.34	298.22										
x/m........	68.45	76.65										
At 181.2°C.												
p..........	6.84	20.05	39.84	82.41	139.35	217.70	275.92	295.20				
x/m........	9.59	21.03	30.33	37.54	45.19	51.49	54.41	55.03				

The apparatus, charcoal, and the technique involved are the same as that employed in all of the previous work. The ketones and esters were Eastman's products of highest purity. They were further purified according to approved standard methods and several times fractionally distilled, using the apparatus designed by Loveless (3). Only the final middle fractions distilling over within a range of 0.01° to 0.10°C. at the correct boiling point were used.

The complete experimental data, including all duplicate series, are collected in the following tables. In these p is the equilibrium pressure

TABLE 3

The adsorption of diethyl acetone vapor by charcoal at various temperatures

At 0°C.											
p	0.00	0.30	0.64	1.30	1.65	5.35	7.91	9.61	9.68		
x/m	40.18	73.43	76.40	81.66	83.28	88.39	91.49	97.39	98.85		
At 40°C.											
p	0.00	0.10	0.35	0.70	2.61	4.43	11.68	16.93	21.39	28.13	30.08
x/m	24.09	34.39	50.18	55.09	65.31	68.68	74.22	76.19	77.31	78.83	79.23
p	31.87	53.02	56.14	63.74	68.45	70.49	95.20	120.15	120.68		
x/m	79.60	83.61	84.32	85.62	86.35	87.35	90.85	95.30	97.72		
At 99.4°C.											
p	0.35	0.84	1.78	1.95	4.02	5.43	9.81	10.79	14.42	23.06	
x/m	28.00	35.19	42.34	43.16	49.57	52.45	57.65	58.36	60.29	62.93	
p	24.89	36.22	69.28	93.90	115.46	119.77					
x/m	63.28	65.11	67.87	69.25	70.15	72.62					
At 139.09°C.											
p	0.40	1.55	2.79	5.85	5.92	6.95	8.68	11.01	14.42	16.67	19.00
x/m	10.34	21.19	28.68	37.25	39.66	39.66	42.57	45.62	48.57	49.66	51.38
p	21.82	34.04	39.15	59.02	90.00	117.94	118.68				
x/m	52.49	55.02	55.48	57.36	60.30	62.26	64.37				
At 182.4°C.											
p	0.80	1.88	4.08	5.49	9.06	10.40	15.61	22.30	26.22	39.62	50.64
x/m	9.73	15.43	21.58	24.58	29.87	31.01	34.95	38.03	39.06	43.60	45.64
p	77.31	102.03	114.08	119.70							
x/m	49.17	51.38	53.09	55.40							

in millimeters and x/m is the number of cubic centimeters (N.T.P.) of vapor adsorbed by 1 g. of charcoal.

For want of a better method we have made use of the Langmuir equation for adsorption on a plane surface and we have plotted the values of $p/(x/m)$ against the corresponding pressures, p. The Langmuir isotherms thus obtained for low pressures at various temperatures are shown in figures 1 and 2; those for the boiling points at higher pressures are shown in figure 3. Within the range indicated by the experimental points, the Langmuir equation satisfactorily expresses the adsorption relations. At still higher pressures, however, the experimental points deviate widely from the straight line plot.

The influence of the structure and molecular complexity of the ether, ketone, and ester vapor molecules is perhaps best shown by the natural boiling point isotherms, $x/m = ap^n$. At the boiling point the tendency of the vapors to condense is practically eliminated. The only forces prevailing are those between the adsorbent and the vapor molecules and the van der Waals forces between the molecules in the vapor phase.

TABLE 4

The adsorption of ethyl formate vapor by charcoal at various temperatures

At 0°C.												
p.......	0.10	0.20	0.60	2.98	7.25	12.91	21.94	30.58	40.95	50.33	59.47	69.94
x/m....	37.79	60.69	82.01	92.61	96.96	99.47	102.39	104.74	107.65	110.27	112.53	114.55
p.......	73.41											
x/m....	117.88											
At 40°C.												
p........	0.05	0.25	1.25	3.57	6.66	7.89	13.10	17.62	29.63	44.77	89.89	
x/m......	16.89	30.56	44.06	59.54	71.13	74.50	79.47	81.27	85.79	88.86	93.14	
p........	129.01	172.24	238.75	300.01	322.99	377.64	397.49	448.37	448.72			
x/m......	94.90	96.83	99.41	102.18	103.12	105.68	106.24	108.64	110.85			
At 54.4°C.												
p.........	0.30	0.50	1.09	1.24	2.43	3.91	4.21	7.53	10.40	12.82	17.08	
x/m.......	9.50	13.52	22.90	24.01	35.30	44.28	46.42	56.76	61.63	65.52	69.75	
p.........	25.05	33.52	47.53	63.08	80.80	88.08	176.56	224.94	243.25	370.85		
x/m.......	74.74	78.55	81.51	84.75	86.27	87.55	91.13	92.62	93.68	96.40		
p.........	371.84	464.97	580.33									
x/m.......	96.82	98.21	100.55									

The natural boiling point isotherms, figure 4, show definite characteristic regularities. Ethyl formate is less adsorbed at all pressures than is methyl acetate. At pressures below 0.2 mm. the order of increasing adsorption for the acetate vapors is: methyl < ethyl < propyl. At higher pressures the order is exactly reversed. Methyl propionate is less adsorbed than are ethyl and propyl acetates at pressures below 0.8 mm.;

it is more highly adsorbed than methyl acetate below 1.5 mm. The higher boiling *n*-propyl acetate is the most highly adsorbed of all the esters at low and least at high pressures. The order of adsorption of all the esters at pressures below 0.8 mm. is

TABLE 5

The adsorption of methyl acetate vapor by charcoal at various temperatures

At 0°C.												
p...........	0.10	0.20	0.35	0.40	2.38	6.16	16.08	16.63	33.31	48.50	55.40	
x/m........	38.94	59.99	71.10	78.71	92.66	97.61	102.94	103.05	108.75	114.11	115.95	
p...........	59.56	63.04	63.34									
x/m........	116.65	123.81	123.12									
At 40°C.												
p........	0.20	0.30	1.29	5.91	7.15	23.08	26.91	54.26	78.43	125.84		
x/m......	20.85	35.51	54.07	75.42	77.59	87.98	88.64	92.91	95.25	97.88		
p........	190.51	234.80	309.78	332.67	360.69	391.44	394.94					
x/m......	101.62	103.49	108.22	109.58	110.26	112.65	121.08					
At 57.10°C.												
p........	0.10	0.94	3.67	7.13	17.39	24.91	40.96	71.22	109.26	258.99		
x/m......	6.52	35.96	55.88	65.24	76.49	81.41	85.82	88.79	91.29	96.59		
p........	351.66	428.08	447.96	573.13	754.03							
x/m......	99.08	101.21	101.89	105.66	110.91							
At 99.71°C.												
p........	1.04	3.20	12.75	16.03	28.69	43.18	60.46	76.14	129.40	184.25		
x/m......	13.12	22.70	41.50	43.75	52.66	58.91	63.74	66.81	72.20	76.55		
p........	244.16	310.98	380.27	402.26								
x/m......	79.01	81.56	82.98	85.52								
At 139.46°C.												
p.......	6.16	10.92	15.88	38.07	68.35	135.91	177.65	221.47	261.34	327.06	376.55	405.43
x/m....	16.14	21.84	26.06	38.11	45.76	56.26	60.41	64.10	65.93	68.97	70.07	72.50

Ester...........	*n*-AcOPr >	AcOEt >	PrOMe >	AcOMe >	FOEt
$a \times 10^5$(atms.)[2]....	5144	4076	4027	3137	3128
$\mu \times 10^{18}$ (E.S.U.)...	1.78	1.81	1.69	1.76	1.92

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[2] The van der Waals constants, *a*, were taken from or calculated by formulas given in Landolt-Börnstein, Physikalische-Chemische Tabellen, 5th edition, Vol. I, p. 253. Springer, Berlin (1923).

TABLE 6

The adsorption of ethyl acetate vapor by charcoal at various temperatures

At 0°C.

p	0.00	0.05	0.10	0.30	0.40	2.63	2.98	6.30	9.58	10.82	15.88
x/m	17.06	34.28	40.13	66.88	75.21	81.59	82.36	85.08	87.69	88.60	91.97
p	17.37	20.50	24.47								
x/m	92.85	94.09	99.01								

At 40°C.

p	0.00	0.05	0.10	0.50	0.98	1.24	1.54	8.49	14.74	15.19	32.41
x/m	6.90	20.39	21 68	47.54	50.86	63.69	64.57	71.92	75.26	75.55	78.50
p	43.09	49.64	50.13	83.39	104.34	111.58	117.14	135.36	141.81		
x/m	79.26	79.99	80.33	83.12	84.60	85.62	85.37	87.83	87.88		
p	143.29	166.58	183.66								
x/m	88.36	89.91	91.29								

At 76.06°C.

p	0.05	0.20	0.25	0.35	0.89	3.18	4.67	9.78	18.47	48.15
x/m	7.93	18.25	21.85	29.46	38.56	52.32	55.63	61.39	66.03	70.30
p	50.48	100.37	115.06	150.30	180.88	184.95				
x/m	70.54	73.49	74.15	75.21	76.50	77.48				

At 99.48°C.

p	0.40	1.54	3.97	8.34	20.95	33.01	41.40	67.21	115.80	132.08
x/m	19.24	31.02	40.41	47.49	55.35	58.67	60.28	63.27	66.03	66.64
p	153.68	174.03	186.64							
x/m	67.27	67.89	69.24							

At 139.48°C.

p	0.30	2.98	6.16	13.01	22.24	40.75	48.25	48.60	58.22	87.51
x/m	13.55	22.61	28.15	34.51	40.83	46.25	48.33	48.76	50.20	53.23
p	122.90	142.86	167.33	178.59	189.66					
x/m	55.56	57.07	58.08	58.37	61.57					

At 180.53°C.

p	1.49	6.01	16.13	37.92	66.51	85.23	141.02	170.01	191.65
x/m	9.61	18.34	27.05	36.00	41.78	44.41	49.15	50.68	53.24

This is exactly the order of decreasing boiling points of the liquids; it is also the same order as that of the van der Waals constants.

The order of adsorption at higher pressures is

Ester	AcOMe	>	FOEt	>	AcOEt	>	PrOMe	>	AcOPr
$a \times 10^6$ (atms.)	3137		3128		4076		4027		5144

With slight variations due to cross-sectional influences the order here is the reverse of the order of increasing values of the van der Waals a.

TABLE 7

The adsorption of n-propyl acetate vapor by charcoal at various temperatures

At 0°C.											
p	0.00	0.00	1.09	3.77	6.54	7.83					
x/m	24.85	52.27	68.52	73.23	76.48	79.98					
At 40°C.											
p	0.00	0.00	0.20	0.30	0.50	1.04	2.03	5.26	10.67	17.27	
x/m	19.72	26.13	37.94	52.34	54.63	58.17	59.86	63.33	65.23	66.70	
p	22.63	28.09	34.50	38.77	44.52	55.19	58.27	67.60	69.09	71.08	
x/m	67.88	68.86	69.72	70.79	71.21	73.25	73.72	74.74	75.17	76.95	
At 99.54°C.											
p	0.05	0.64	1.88	5.55	11.45	25.96	55.20	75.32	94.00	115.85	116.54
x/m	16.00	29.87	41.43	47.96	51.50	54.83	57.38	58.35	59.29	60.51	62.00
At 139.53°C.											
p	0.25	0.74	2.53	4.66	11.50	35.78	61.84	79.78	100.69	116.54	
x/m	11.02	20.08	28.94	33.52	40.62	47.12	49.82	50.88	51.98	52.96	
At 181.54°C.											
p	0.50	1.19	3.22	7.68	10.36	15.36	28.24	47.12	68.98	101.38	117.93
x/m	5.69	11.13	16.92	23.20	25.11	28.38	33.28	36.71	39.32	41.20	42.99

Similar relations also were found to exist for the adsorption of ketone and ether vapors. The order of adsorption at low pressures is

Ketones	Et_2CO	>	EtCOMe	>	Me_2CO
$a \times 10^6$ (atms.)					
$\mu \times 10^{18}$ E.S.U.			2.74		2.74

Ethers	Pr_2O	>	Et_2O	>	Me_2O
$a \times 10^6$			3464		1609
$\mu \times 10^{18}$			1.14		1.29

TABLE 8

The adsorption of methyl propionate vapor by charcoal at various temperatures

At 0°C.											
p	0.00	0.05	0.10	0.15	0.25	0.70	0.75	2.98	7.89	9.78	14.00
x/m	14.94	29.99	55.85	64.05	67.87	76.68	77.77	82.23	86.43	87.59	90.26
p	17.72	18.81	21.94	22.14							
x/m	92.79	93.26	95.74	98.51							
At 40°C.											
p	0.05	0.10	0.20	0.84	3.90	7.15	26.01	37.28	54.55	74.65	98.08
x/m	16.41	33.31	48.30	61.16	70.02	73.33	78.21	79.63	81.47	83.32	85.63
p	127.72	156.21	168.91								
x/m	88.25	90.63	93.18								
At 79.85°C.											
p	0.15	0.45	1.74	3.03	7.00	8.84	11.17	18.96	33.21	45.77	60.26
x/m	11.20	24.85	43.87	49.78	57.25	59.10	60.90	64.30	67.52	68.92	69.99
p	93.47	108.90	123.80	153.13	168.22						
x/m	71.82	72.63	73.09	74.04	76.52						
At 90.88°C.											
p	0.25	0.35	1.04	2.98	7.55	12.41	24.92	30.78	48.50	67.36	85.13
x/m	12.14	20.61	27.10	38.68	47.98	52.48	58.30	60.22	63.16	65.06	66.60
p	116.90	152.29	168.87								
x/m	68.03	69.11	70.41								
At 138.73°C.											
p	0.25	0.75	2.13	4.27	6.35	12.56	17.77	25.07	31.22	37.03	48.25
x/m	8.25	12.30	18.54	24.51	27.87	34.97	38.16	41.96	44.07	46.00	48.31
p	53.06	87.16	100.22	103.10	146.53	147.42	174.87				
x/m	49.30	53.46	54.69	54.98	57.54	58.22	59.48				

TABLE 9

Heats of adsorption calculated from the isosteres

VAPOR	ΔH	VAPOR	ΔH
	cal.		cal.
Acetone	−10690	Methyl acetate	−11520
Methyl ethyl ketone	−11224	Ethyl acetate	−11960
Diethyl ketone	−11020	*n*-Propyl acetate	−13200
Ethyl formate	−13140	Methyl propionate	−14030

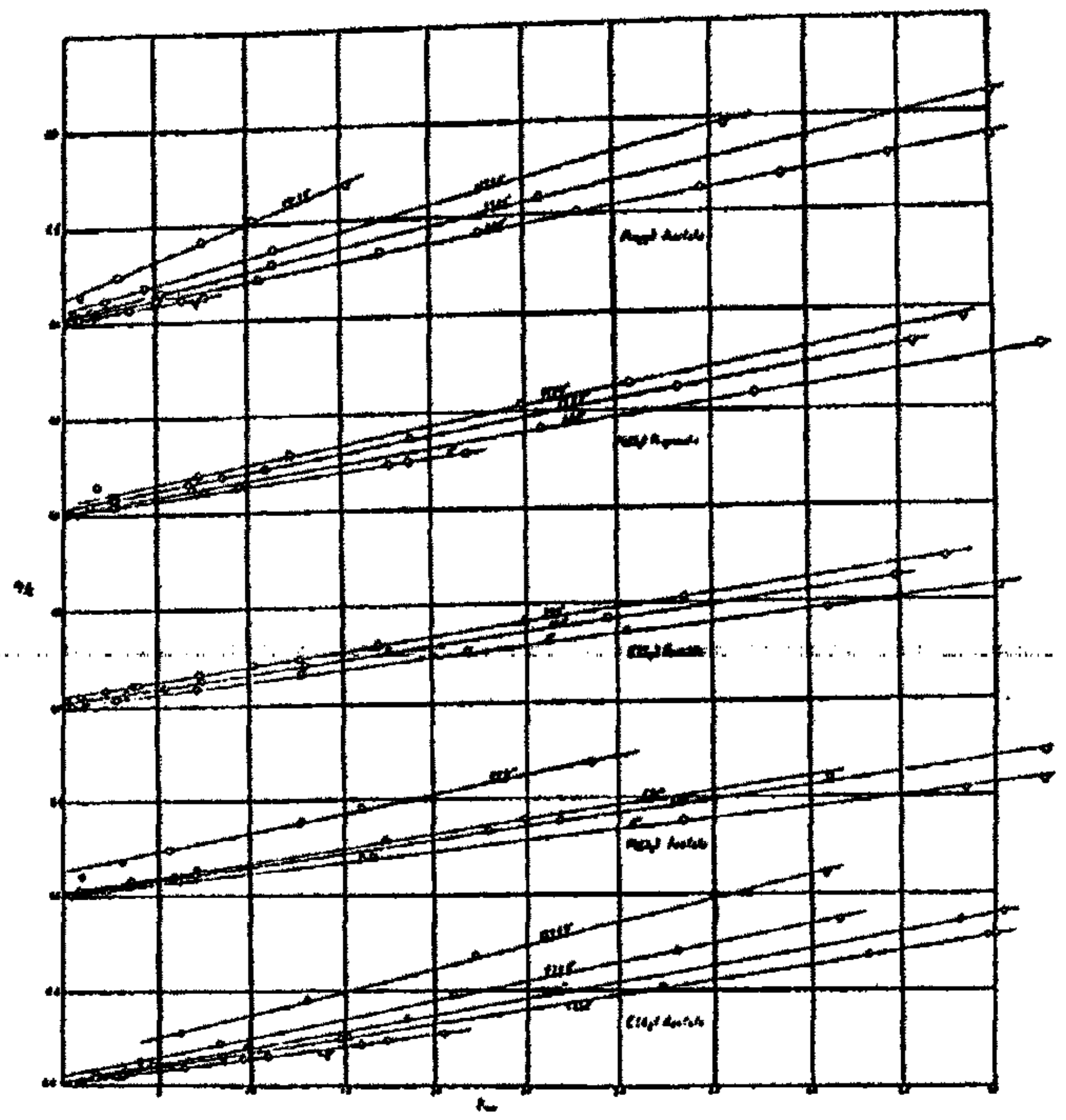

FIG. 1. LANGMUIR ISOTHERMS FOR VARIOUS ESTERS AT DIFFERENT TEMPERATURES

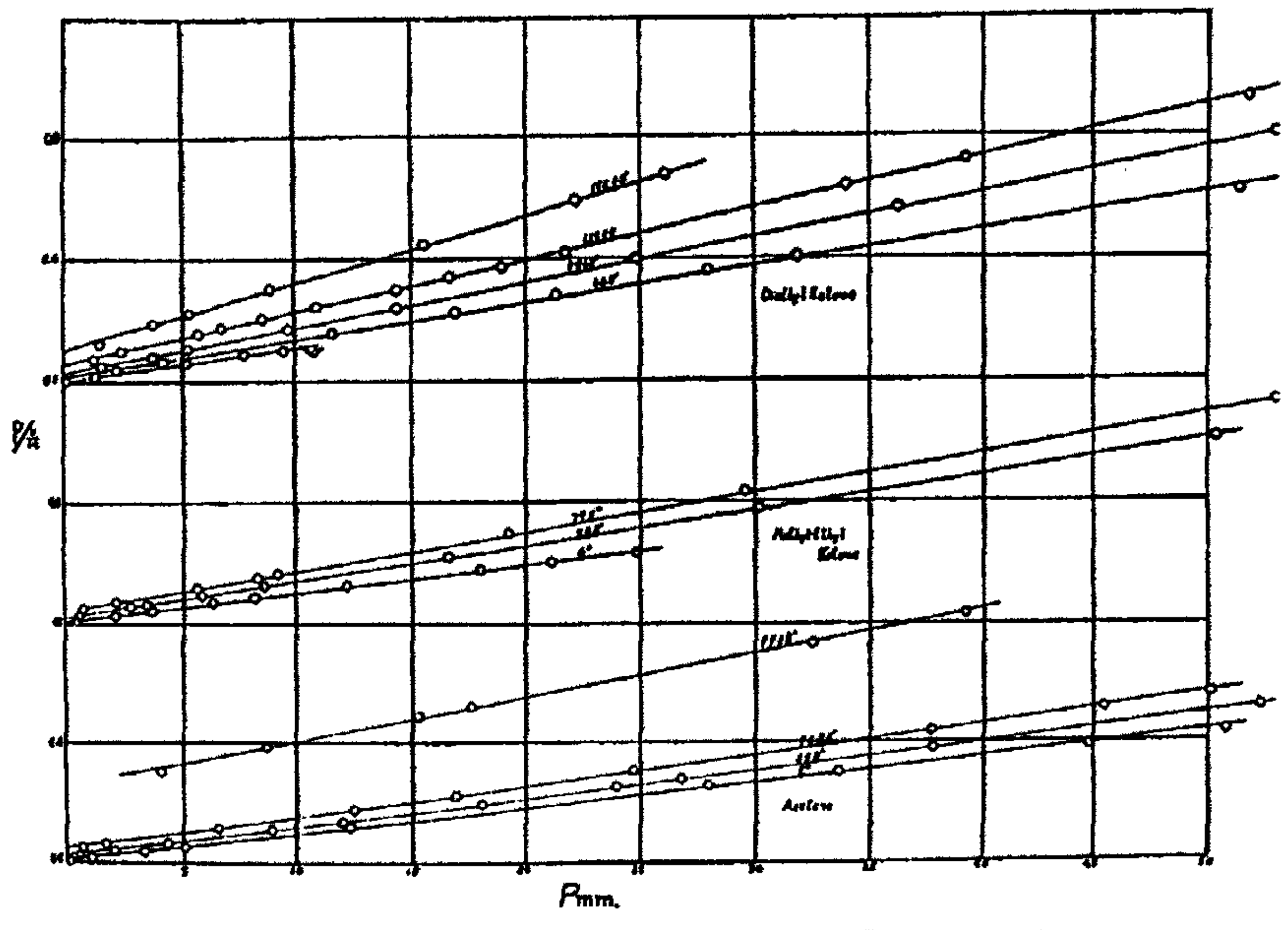

FIG. 2. LANGMUIR ISOTHERMS FOR CERTAIN KETONES AT DIFFERENT TEMPERATURES

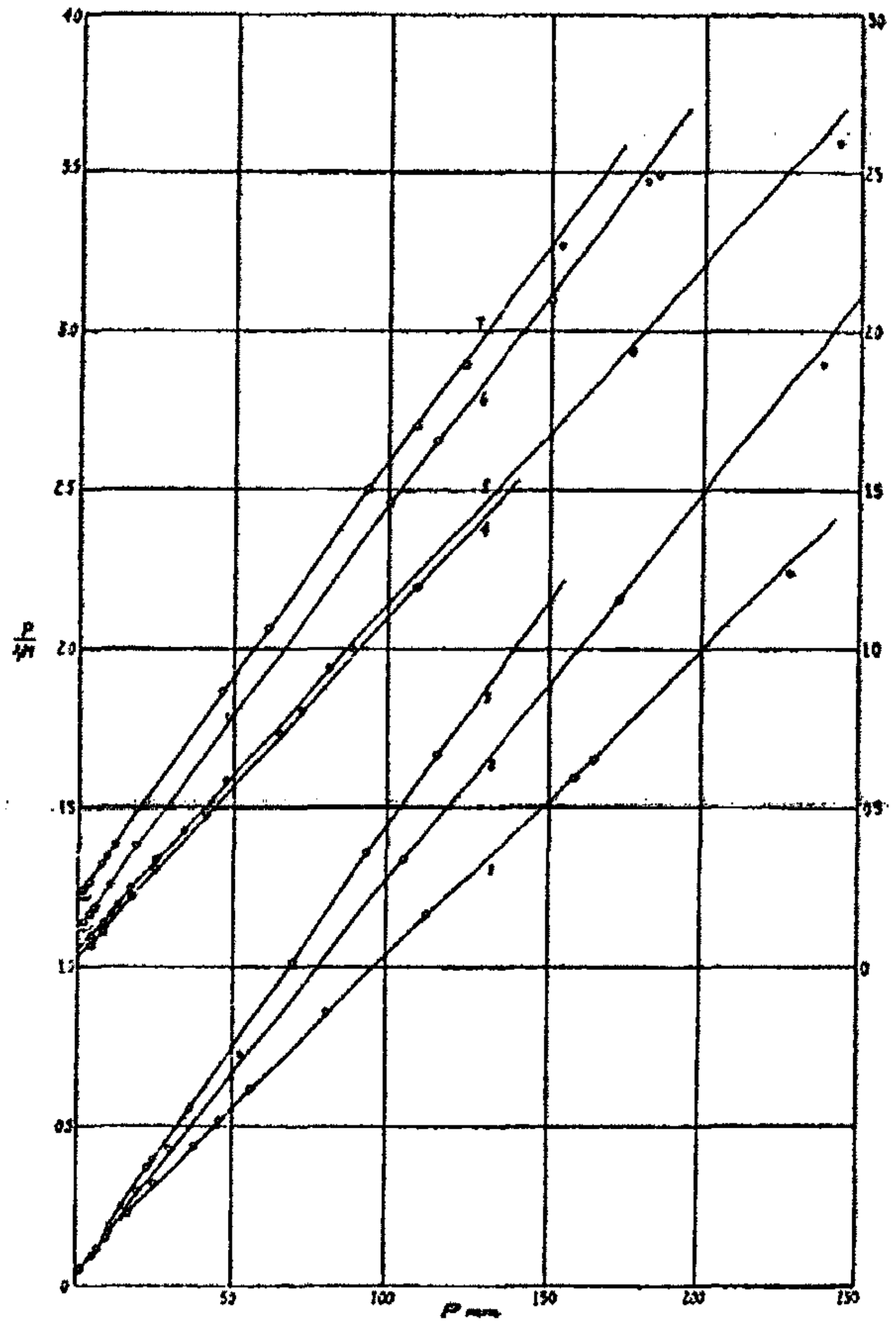

Fig. 3. Langmuir Boiling Point Isotherms

1, Acetone; 2, methyl ethyl ketone; 3, diethyl ketone; 4, methyl acetate; 5, ethyl formate; 6, ethyl acetate; 7, methyl propionate.

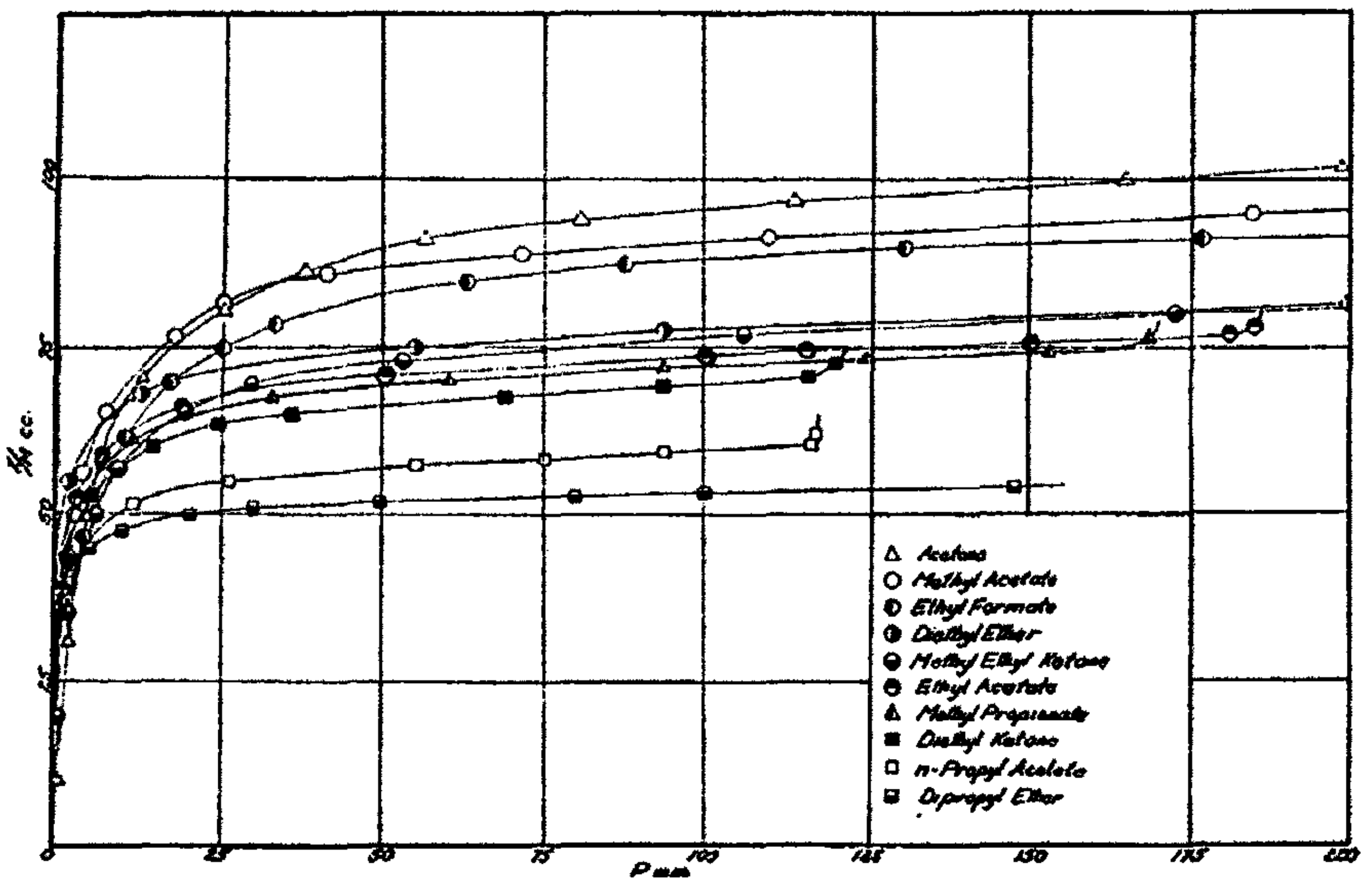

Fig. 4. Natural Isotherms at the Boiling Points

For both the ketones and the ethers the order is again reversed at high pressures. The values of *a* for the ketones are not available, but they should increase with increase in molecular complexity.

The relations obtained from the study of the natural boiling point isotherms appear to permit two definite conclusions: first, for all vapors of any one class the magnitude of the adsorption is directly dependent upon the van der Waals constant *a*; second, the magnitude of adsorption is independent of the dipole strength of the vapor molecules, or their influence is masked by other factors.

The isosteres were plotted for the ketone and ester vapors. With the exception of the lowest concentration, the experimental points fall exceedingly well upon straight parallel lines. The heats of adsorption calculated from the slopes of the isosteres are given in table 9.

SUMMARY

The adsorption of certain ketone and ester vapors by activated charcoal has been measured at several temperatures between 0°C. and 182°C.

The Langmuir equation for adsorption on plane surfaces applies for pressures up to approximately 200 mm.

For any series the amount of vapor adsorbed at low pressures is always greatest for the vapor having the highest boiling point; it is less for the simpler low-boiling liquids. At higher pressures the order of adsorption is reversed. Adsorption increases with increase in the value of the van der Waals *a*, and it appears to be independent of the dipole strength of the vapor molecules.

The heats of adsorption have been calculated from the slopes of the isosteres.

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THE SURFACE BEHAVIOR OF ZEOLITES

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The authors wished to study the surface behavior of zeolites during dehydration by the method previously applied to aged hydrous alumina (2). Accordingly the water content of samples of scolecite and analcite of different average particle sizes was determined under the same conditions. The large particle samples (3×10^3 cm.^{2} apparent surface per gram) and small particle samples (5×10^3 cm.^{2} apparent surface per gram) were kept in weighing bottles in a desiccator at various temperatures and vapor pressures. A few of the many results obtained are given in table 1. As far as the authors could tell these were all equilibrium values, with the exception of sample g, since the water content–time curve had become level.

These results become of special interest when applied to the equation derived earlier (1)

$$c = (w_l w_s' - w_s w_l')/(w_l + w_s' - w_s - w_l')$$

w_l and w_s represent water percentages contained by a pair of zeolite samples (large and small particles) at a given temperature and vapor pressure. w_l' and w_s' represent the percentages of water in the same two samples under different conditions. c will then be the calculated percentage of water in the zeolite when no water adsorption has taken place. Several values for c are given in table 2.

Several interesting conclusions can be drawn from these results. The c values for scolecite are remarkable for their constancy. This fact, coupled with the data in table 1, leads to the conclusion that the water variation of this zeolite was due to a change in surface adsorbed water. The water content within the scolecite lattice did not change appreciably under the conditions of the experiment.

The c values for analcite are also essentially constant. From the data in table 1 the change in water content at the higher vapor pressures was essentially due to a change in positively adsorbed surface water. But at the lower vapor pressure the water content of the small particle analcite sample is lower than that of the large particle sample. This fact, together with the calculated c values, clearly indicates that a surface dehydration took place. Water was lost from the surface portions of the zeolite lattice, forming a zone of skeleton lattice at the surface of the particles. As far as present experiments could show, this was an equilibrium condition.

This case of surface dehydration is an example, on a larger scale, of what the authors believe happens during the dehydration of hydrates and related compounds. It seems likely that with such compounds a condition of surface dehydration may be a stable one, in which true equilibrium can be reached. This conception is discussed more completely in an earlier paper (2).

TABLE 1

Water content of zeolites under various conditions

ZEOLITE	PAIR	WATER PERCENTAGE		SUBSTANCE IN DESICCATOR	TEMPERATURE °C.
		Large particle	Small particle		
Scolecite	a	16.09	16.34	$CuSO_4 \cdot 5H_2O$	23
Scolecite	b	16.15	16.44	$Na_2HPO_4 \cdot 12H_2O$	24
Scolecite	c	15.78	15.90	BaO	50
Scolecite	d	15.56	15.58	BaO	126
Analcite	e	9.388	9.402	$CuSO_4 \cdot 5H_2O$	24
Analcite	f	9.491	9.512	$Na_2HPO_4 \cdot 12H_2O$	23
Analcite	g	9.214	9.143	P_2O_5, vacuum	22
Analcite	h	9.135	9.056	P_2O_5, vacuum	21

TABLE 2

Calculated water content for zeolites when no adsorption takes place

ZEOLITE	PAIRS	*c*	ZEOLITE	PAIRS	*c*
Scolecite	a, c	15.54	Analcite	e, h	9.35
Scolecite	b, c	15.52	Analcite	f, h	9.42
Scolecite	a, d	15.48	Analcite	e, g	9.36
Scolecite	b, d	15.48	Analcite	f, g	9.43

These results throw a somewhat different light upon the variation of the water content of zeolites, particularly at lower temperature. Such data as those of Tammann (3) may now be interpreted somewhat differently.

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USE OF THE PHOTOELECTRIC CELL IN THE STUDY OF PHOSPHORESCENCE

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In the course of investigations in this laboratory on the preparation of phosphorescent zinc sulfide, a need arose for a convenient method of measuring luminous intensity of the preparations. While the photometric method has been used extensively in work of this type (1, 2, 5, 7, 8), it was thought that the photoelectric cell might prove adaptable and at once offer possible advantages. Pospielow (4) made photoelectric measurements of the response of phosphorescent materials to cathode rays and ultra-violet light. Schwarz and Urbach (6) have measured the phosphorescence of alkali halides photoelectrically.

Measurements recorded in this paper were made on ZnCuS phosphors all of which were prepared here except samples 1, 2, and 3, which represent commercial materials of the highest grade we could obtain. Our samples were chosen from about one hundred fifty products representing different methods of preparation. So far, we have confined ourselves principally to the problem of measuring response of the phosphorescent materials to excitation by α-particles from a source kept separate from the samples.

APPARATUS

Simple cell-galvanometer hook-up. The Visitron, type F-2, cell generates its own E.M.F., hence the circuit in this case consists of only the cell and a sensitive wall-type galvanometer. Of course, with this type of cell it is important that the galvanometer have low resistance as well as high sensitivity. Our galvanometer had a resistance of 110 ohms and sensitivity of 1.265×10^{-9} amperes. The scale was placed 230 cm. from the galvanometer. The negative terminal of the cell was grounded.

The General Electric P.J.15 cell was used in direct hook-up with a sensitive galvanometer and an E.M.F. of 240 volts.

Amplifier hook-up for P.J.23 cell. The General Electric P.J.23 cell is not sensitive enough to allow satisfactory readings with the simple circuit described above, even for measurement of response to strong α-particle excitation. It was therefore necessary to develop an amplifier for use with this cell (figure 1). In the figure, G_1 is a three-button galvanometer,

G_2 is a Leeds and Northrup type P galvanometer, having a sensitivity of 100 megohms, and L is a 4-dial 10,000-ohm resistance box.

METHOD OF EXCITATION OF PHOSPHORS WITH SEPARATE SOURCE

The samples were spread on 3 in. × 3 in. glass plates. In order to insure uniform thickness and smoothness of surfaces, celluloid strips were held rigidly along two edges of the glass surface while a straight edge was run along the strips, spreading a layer of zinc sulfide about 0.5 mm. thick. The α-particle source was prepared by transferring precipitated radiothorium hydroxide to a 3 in. × 3 in. glass plate and spreading it over a circular area about 3.4 cm. in diameter. The remainder of the surface of the plate was coated with a thick layer of paraffin to keep reflected light from entering the cells. After this deposit had thoroughly dried, it was covered with a layer of collodion and one thickness of cellophane. The strength of the source was between 2 and 3 mg. radium equivalent. The collodion and cellophane served to guard against contamination of the samples and the dark room; however, they reduced the effective strength of the source to about 0.1 its real value.

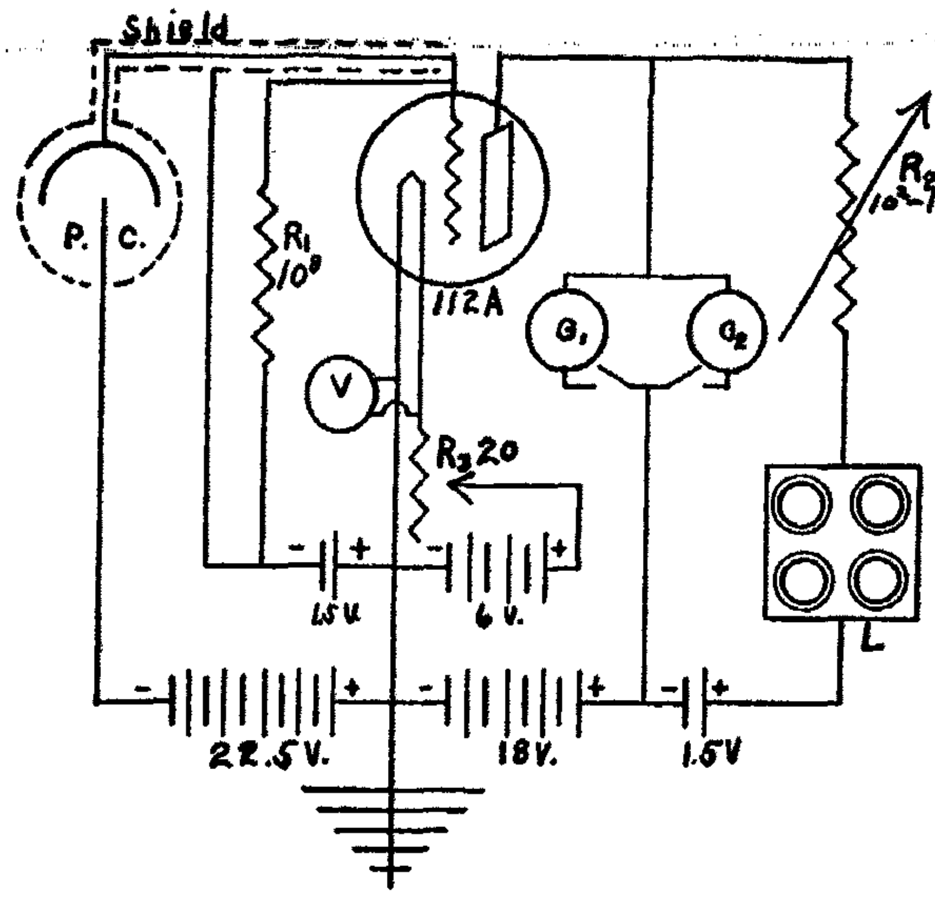

FIG. 1. AMPLIFIER HOOK-UP FOR P.J. 23 CELL

A shallow box was provided with guides on the inside bottom for placing the plates holding the samples so that all had the same position when measured. The source plate was secured, source down, to the under side of a removable shelf which had a centered opening slightly larger than the deposit of radioactive source, through which the light to be measured emerged. When the shelf was placed in position in the box, the α-particle source was directly over the center of the sulfide sample and about 3 mm. distant. Thus most of the measured light passed through the radioactive material, which was not so opaque but that a large part of the emitted light reached the cells. Early measurements disclosed that there was a steady increase in intensity of light up to about ten minutes after the source was placed in position above the samples. Increases after that length of time were so small that any differences of rate of increase among the various samples were negligible. Hence we adopted the procedure of exposing samples to the source ten minutes before making measurements. Care was taken in placing the cells over the opening in the shelf to insure uniformity in exposure of sensitive surface to illuminated area. All measurements were made in the dark room on samples which had been in the dark long enough so that light emission resulting from previous excitation was not appreciable. Because of its convenient form, the Visitron cell was handled in the open. However, in making transfers to and from the shelf, the cell case was not touched on account of the large temperature coefficient of the cell. The P.J.15 cell was permanently mounted in a light-tight box so that the cell was directly over the shelf opening.

TABLE 1

Response of phosphorescent materials to excitation by α-particles

SAMPLE	GALVANOMETER DEFLECTION IN CENTIMETERS			RELATIVE RESPONSE (SAMPLE 1 = 100)			RANK		
	P.J. 23	F-2	P.J. 15	P.J. 23	F-2	P.J. 15	P.J. 23	F-2	P.J. 15
1	22.90	1.90	16.25	100	100	100	3	4	2
2	15.10	1.40	11.80	63.9	73.7	72.6	9	9	5
3	16.70	1.50	13.70	73.0	78.9	84.3	8	8	4
4	16.70	1.60	14.30	73.0	84.2	88.0	6	6	3
5	21.60	2.00	16.80	94.3	105.3	103.4	4	3	1
6	25.50	2.25		111.4	118.4		1	1	
7	23.10	2.05		100.9	107.9		2	2	
8	14.70	1.20		63.8	63.2		10	10	
9	19.10	1.65		83.4	86.8		5	5	
10	16.70	1.50		73.0	78.9		7	7	

Essentially the same arrangement was used for measurements with the P.J.23 cell. The cell was permanently mounted directly over an opening in a shelf which was built into a light-tight box. The source plate was attached to this shelf exactly as described above. Samples were placed in the box under the source by way of a sliding floor which could be slid into and out of the box after raising a sliding door on the side of the box. The shelf and cell were so placed that source and cell occupied the same positions relative to the samples as in the other method. The convenience of this method makes it superior to any other tried.

The results of the measurements are given in table 1.

DISCUSSION OF RESULTS

Measurements with the P.J.15 cell were not completed because of failure of the cell. Exact agreement between the three cells should not be expected, because the samples differ somewhat in color and the cells differ in relative response to different wavelengths of light. In fact, it is surprising that the results show only one discrepancy in ranking. Choice of a cell may be governed by the particular phase of the problem of phosphorescence under consideration. If the problem is comparison of products with a view to use in luminous paint, then the ideal cell would be one whose curve of spectral response coincides with that of the eye. The Visitron cell meets this condition rather satisfactorily, but it does not lend itself well to use with an amplifier, so that one is forced to work with feeble currents. However, the results show that under the conditions of our experiments the currents are large enough for purpose of comparison. Although it is probably safe to assume that measurement of response of phosphorescent material to separate source excitation is a reliable indicator of its usefulness in paint, we plan to extend our method to direct measurement of luminous paints.

By slight modification of the set-up described above for the P.J.23 cell, the photoelectric cell may be used conveniently for measurement of response of the samples to light. We made enough measurements of this kind to confirm the reports of other investigators (3), who have found that response to α-particles cannot be predicted from study of light response.

SUMMARY

1. We have used three types of photoelectric cells in measuring the response of samples of phosphorescent zinc sulfide to α-particle excitation.
2. Difference in spectral response of the cells probably accounts for some differences in results.
3. The photoelectric cell is readily adaptable to measurement of luminous intensity of phosphorescent substances and offers the advantages of simplicity and freedom from the personal element over the ordinary photometric method.

We gratefully acknowledge our indebtedness to Dr. Herman Schlundt, who sponsored this investigation. We are grateful also to Dr. R. T. Dufford for the loan of certain apparatus and to Mr. C. C. Carrol for preparing the radioactive material.

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THE SOLUBILITY OF SODIUM BROMIDE IN ACETONE

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The measurement of the relative solubility of a sparingly soluble salt in a pure solvent, and in the presence of other salts using the same solvent, affords a ready measure of the change in potential or of the activity coefficient of the saturating salt. These changes should be accounted for by any adequate theory of solutions. The interionic attraction theory of Debye and Hückel (2) has achieved considerable success in describing the properties of strong electrolytes in aqueous solutions. The experimental data, using water as a solvent, are quite extensive.

Since the interionic attraction theory is premised on the fact that all effects are due to the electrostatic attraction between ions, it is to be expected that the validity of this assumption and the equations derived by Debye and Hückel (2) could be subjected to a quite rigorous test by employing solvents of lower dielectric constants, since the electrostatic forces between ions vary inversely as the dielectric constant of the medium containing the ions.

The experimental data on the mutual solubility relations in solvents with dielectric constants lower than that of water are limited (1), but cover a range of solvents with dielectric constants ranging from 64 for water at 75°C. (1a) to 6 for acetic acid (1j, 1l). Several types of solvent and saturating salts have been used.

When interpreted in terms of the interionic attraction theory, the results of these investigations are somewhat conflicting. The deviations, as might be expected from the assumptions and approximations made in the development of the equations used, are larger for the solvents of lower dielectric constants and for the higher or more unsymmetrical valence types of salts concerned.

The simple Debye-Hückel equation relating the solubility of a uni-univalent salt to the ionic strength of the solution may be written in the following form:

$$\log \frac{S}{S_0} = \frac{A\epsilon^2\kappa}{2DRT(1 + \kappa b)} - \frac{A\epsilon^2\kappa_0}{2DRT(1 + \kappa_0 b)} \tag{1}$$

where $K^2 = \dfrac{8\pi\epsilon^2 A\mu}{1000\,DRT}$; S_0 and S are the solubilities (in moles per liter) of the pure saturating salt and of the saturating salt in the presence of solvent salts, respectively; μ_0 and μ the corresponding ionic strengths; A, Avogadro's number; ϵ, the unit charge; D, the dielectric constant of the medium; T, the absolute temperature; R, the gas constant; and b, the mean ionic diameter.

Taking the value of the dielectric constant of acetone at 25°C. as 20.8 (6), substituting the values of the constants, and considering the ions as point charges, equation 1 reduces to

$$\log \frac{S}{S_0} = 3.718\,\mu^{\frac{1}{2}} - 3.718\,\mu_0^{\frac{1}{2}} \tag{2}$$

In equation 2, $\mu_0^{\frac{1}{2}}$ is a constant, hence the equation is linear in $\log \frac{S}{S_0}$ and $\mu^{\frac{1}{2}}$. A plot of $\log \frac{S}{S_0}$ against $\mu^{\frac{1}{2}}$ should yield a straight line with a slope of 3.718 if this simple form of the Debye-Hückel equation holds for solutions of salts in acetone. Solubility measurements of a sparingly soluble salt in acetone will afford a ready means of testing the theory.

MATERIALS

A commercial grade of acetone was dried over anhydrous calcium chloride. Best results were obtained by adding about 35 g. of the anhydrous salt to 1 liter of acetone, and allowing the mixture to stand for about six days with occasional shaking. The acetone, thus treated, was distilled in a vacuum-tight, all-glass still with a fractionating column 125 cm. in length, filled with glass beads. The last third of the distillate was rejected. The distillation was carried out in a darkened room. The product thus prepared showed a density of 0.7845 at 25°C. and an index of refraction of 1.3560 at 25°C., using the D line as standard. Seventy-five per cent of this product distilled in a temperature range of 0.05°C., the entire sample showing a range of 0.10°C.

A standard brand of C.P. sodium bromide was twice recrystallized from distilled water, and dried to constant weight at 300°C. in a current of dry air.

Lithium perchlorate was prepared by the method of Richards and Willard (4). The salt was dried to constant weight by prolonged heating at 150°C. in a current of dry air. The anhydrous salt tested neutral and was free from ferric, calcium, magnesium, potassium, sodium, fluoride, and chloride ions.

Calcium perchlorate was prepared by the method of Willard and Smith (7). The salt was dried to constant weight by heating at 260°C. in a current of dry air. The anhydrous salt tested neutral and was free from ferric, magnesium, and chloride ions.

Every precaution was taken to exclude moisture in the storing and handling of these materials.

METHOD

Half-liter, reground, glass-stoppered flasks were "steamed" with acetone vapor. The required amount of the solvent salt was weighed into the container, and about 450 cc. of acetone was then blown into the flask with a current of dry, carbon dioxide-free air. The weight of the acetone added was noted. After the solvent salt had completely dissolved, a comparatively large excess of sodium bromide was added, after which the glass stopper was sealed in place with a mixture of beeswax and rosin.

The sealed containers were placed in a mechanical shaker and agitated vigorously for from forty-eight to sixty hours, the containers being covered to exclude light. During this period of shaking, the containers were removed several times from the shaker and cooled in an ice bath to expedite the saturation process.

After from forty-eight to sixty hours on the mechanical shaker, the containers were transferred to a constant temperature bath, maintained at 25°C. ±0.02°C., and permitted to remain, with occasional shaking, for an additional twenty-four hours.

After equilibrium had been established, as much as possible of the clear supernatant liquid was blown into a weighed flask by a current of dry, carbon dioxide-free air. The weight of the sample was determined, the acetone distilled off over a water bath, and the residue taken up with distilled water.

The sodium bromide present in each sample was determined by the Volhard method (5) for bromide ion estimation.

EXPERIMENTAL RESULTS

The solubility data for sodium bromide in acetone in the presence of lithium and calcium perchlorates are shown in tables 1 and 2, respectively. Figure 1 shows the measured solubility of the sodium bromide as a function of the ionic strength of the solution. The solubilities calculated from equation 2 are also shown. In figure 2, the log $\frac{S}{S_0}$ data from tables 1 and 2 are shown, plotted against the one-half power of the ionic strength. The theoretical lines for acetone (slope 3.718) and for water (slope 0.5) also have been included.

The slope of the best straight line through the experimental points, in the smaller ionic strength region, is about 8.5. Points for the more dilute solutions are closely grouped about this line, indicating that both sets of data give slopes approaching the same limiting slope. The value of the experimentally observed slope is more than twice as large as the theoretical slope for acetone. It would be necessary to assume a dielectric constant of about 10, for the more dilute solutions, to bring the theoretical slope into agreement with the experimental slope.

From equation 1 the slopes, obtained by plotting the $\log \frac{S}{S_0}$ values against the one-half power of the ionic strength, for two different solvents, should vary inversely as the three-halves power of the ratio of the dielectric constants for the two solvents, both being at the same temperature. For water and acetone, this ratio is 7.4 at 25°C. The increase in solubility due to a salt with a non-common ion should be 7.4 times greater in acetone than in water. Our experimental data show the increase to be about 17 times greater, which is hardly of the right order of magnitude to be ex-

TABLE 1

The solubility of sodium bromide in acetone at 25°C. in the presence of lithium perchlorate

$LiClO_4$ MOLES PER LITER $\times 10^3$	SOLUBILITY (S) OF NaBr IN MOLES PER LITER $\times 10^3$	$\frac{S}{S_0}$	$\log \frac{S}{S_0}$	$\mu \times 10^3$	$\mu^{\frac{1}{2}}$
0.0000	1.1841	1.0000	0.00000	1.1900	0.03449
0.0000	1.1959				
0.3103	1.3786	1.1585	0.06390	1.6889	0.04109
0.5469	1.4523	1.2204	0.08650	1.9992	0.04471
0.7847	1.5820	1.3294	0.12362	2.3667	0.04865
1.9740	1.9259	1.6148	0.20908	3.8999	0.06245
3.5910	2.2461	1.8875	0.27593	6.1971	0.07872
19.2390	3.5754	3.0045	0.47777	22.8144	0.11790
38.1470	5.2067	4.3754	0.64102	43.3537	0.20823
78.2210	8.2430	6.9269	0.84054	86.4640	0.29405
392.6900	21.5747	18.1300	1.25840	414.2647	0.24363

TABLE 2

The solubility of sodium bromide in acetone at 25°C. in the presence of calcium perchlorate

$Ca(ClO_4)_2$ MOLES PER LITER $\times 10^3$	SOLUBILITY (S) OF NaBr IN MOLES PER LITER $\times 10^3$	$\frac{S}{S_0}$	$\log \frac{S}{S_0}$	$\mu \times 10^3$	$\mu^{\frac{1}{2}}$
0.3057	1.6118	1.3546	0.13182	2.5289	0.05029
0.5535	1.9070	1.6025	0.20480	3.5675	0.05973
0.7716	2.2246	1.8694	0.27170	4.5394	0.06738
1.9680	3.6428	3.0612	0.48589	9.5468	0.09771
4.1290	5.9969	5.0394	0.70238	18.3839	0.13558
8.4210	9.4767	7.9636	0.90111	34.7397	0.18649

pected. The divergence noted here is of the same order of magnitude as that shown by the data of Robinson (1h).

Using equation 1, in which the ionic diameters are not neglected, but only the first terms of the series in the expansion of the hyperbolic sine are retained, several values for the mean ionic diameter b, were calculated from the experimental data. These values are all negative, the average being about -10×10^{-8}. This corresponds to a value of about 0.5×10^{-8} when the next two terms of the expansion, as developed by Gronwald,

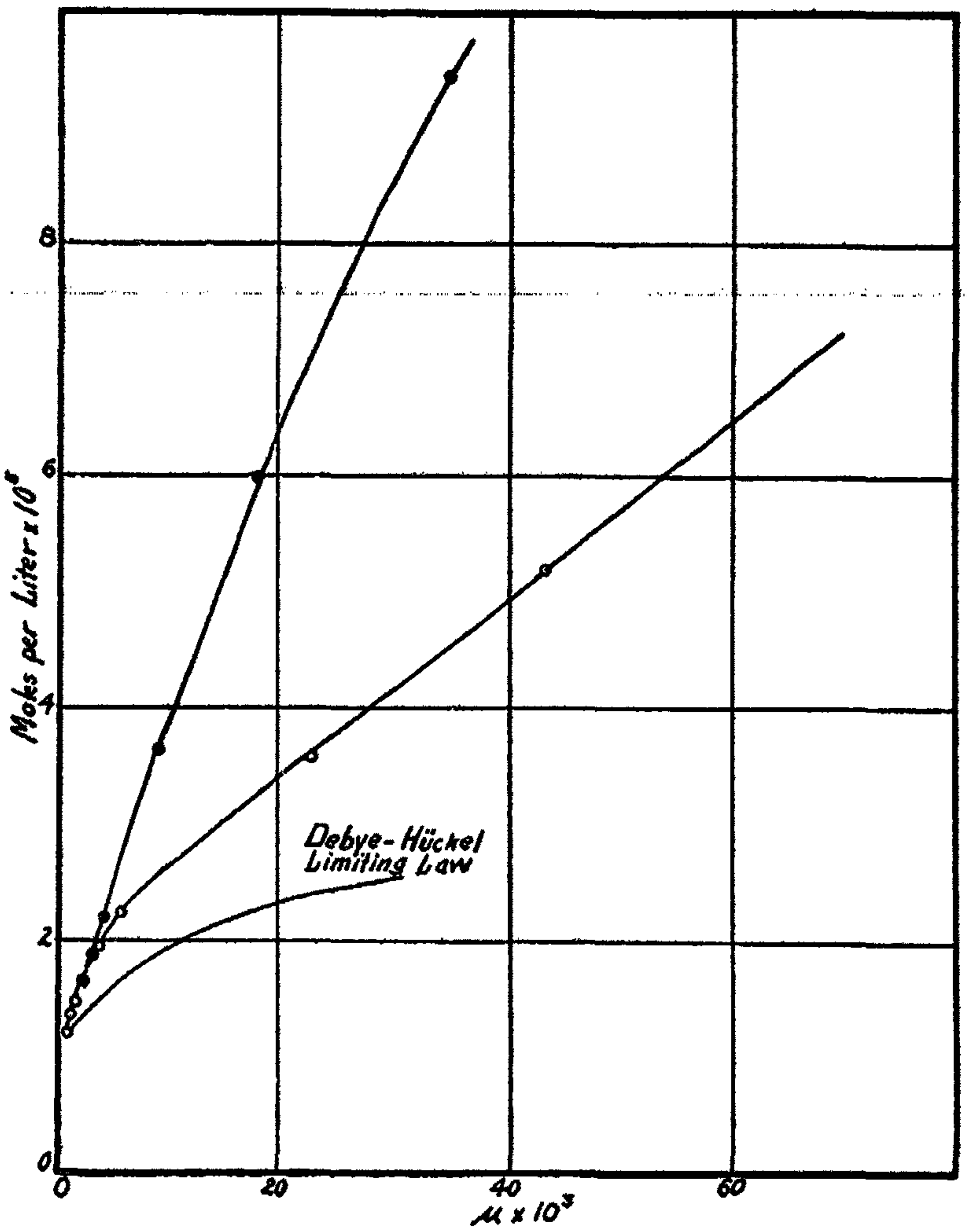

FIG. 1. THE SOLUBILITY OF SODIUM BROMIDE IN ACETONE
○ $LiClO_4$; ● $Ca(ClO_4)_2$

LaMer, and Sandved (3), are included. No positive values of the ionic diameter will bring the experimental data and theory into agreement.

We believe that this marked divergence between the theory and experimental results, not only in the case of our data but also in the case of those of Kraus and Seward (1f) and Robinson (1h), is the result of too great a solubility of the saturating salt in acetone. It is reasonable to expect that as the dielectric constant of the solvent becomes smaller, the highest total salt concentration at which the interionic attraction theory will be obeyed must also decrease. Seward and Hamblet (1l) and Scholl, Hutchison, and Chandlee (1j), using glacial acetic acid as solvent (dielectric constant about 6), have found rather good agreement up to a total salt concentration of about 0.0006 mole per liter. In view of this, it appears

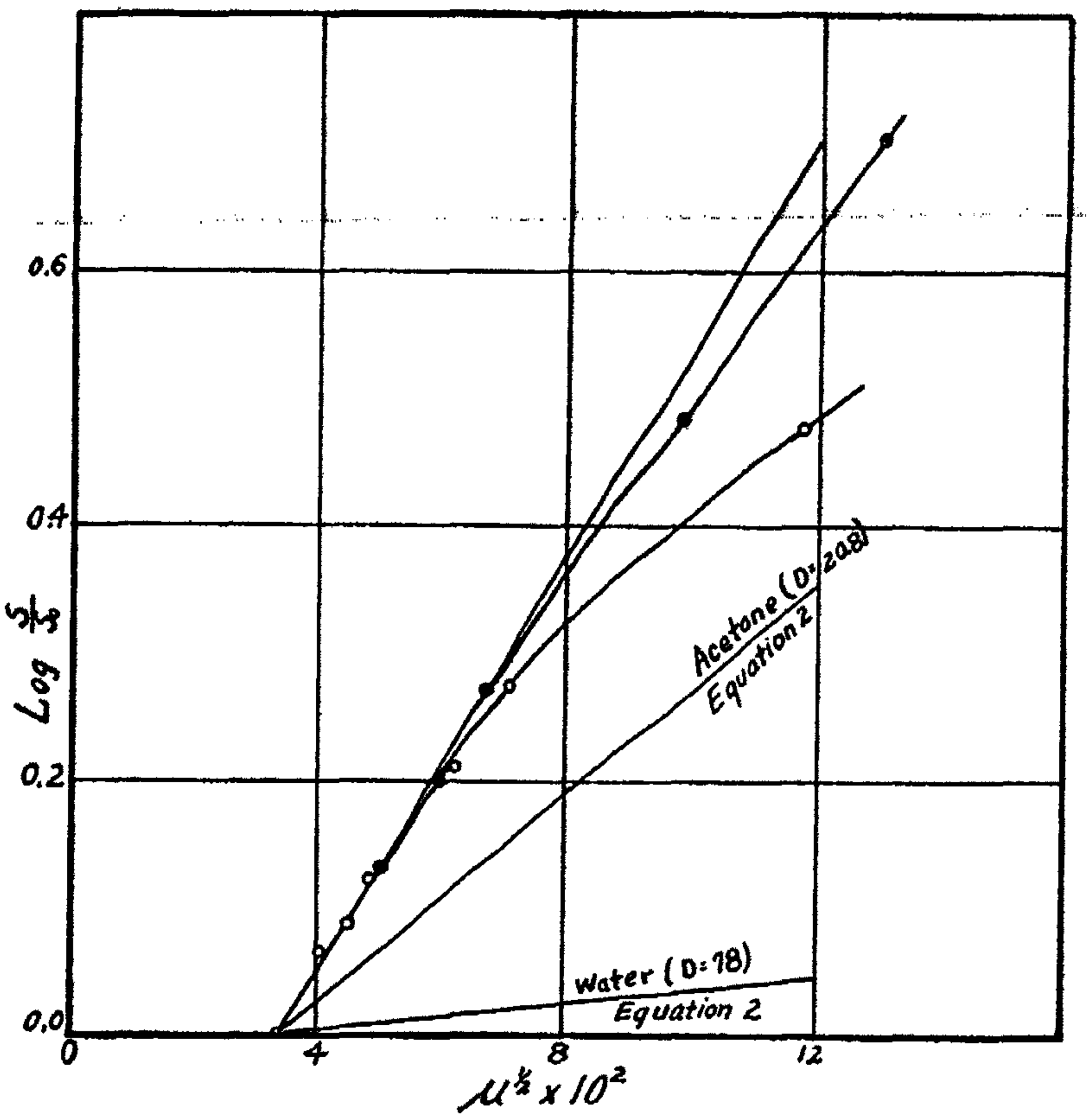

FIG. 2. THE SOLUBILITY OF SODIUM BROMIDE IN ACETONE COMPARED WITH THE INTERIONIC ATTRACTION THEORY

○ $LiClO_4$; ● $Ca(ClO_4)_2$

that the total salt concentration should not exceed 0.001 molar, if agreement between the theory and experimental data is to be obtained, using acetone as the solvent.

SUMMARY

The solubility of sodium bromide in acetone, in the presence of lithium and calcium perchlorates, has been determined.

The presence of these solvent salts produces a marked increase in the solubility of the sodium bromide in acetone.

The results have been examined from the point of view of the interionic attraction theory of Debye and Hückel. The observed solubilities are much larger than those predicted by the theory.

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THE SYSTEM ANILINE-FORMIC ACID-WATER

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A study of mixtures of aniline, formic acid, and water was made by the methods commonly used for heterogeneous systems in equilibrium, and the results were summarized in a triangular graph in the usual manner. The region in which the components separated into two liquids was mapped out, and the distribution of the formic acid between the two liquid layers was found. The region in which crystals were deposited was also mapped out, and the crystals were proved to be aniline formate, $C_6H_7N \cdot CH_2O_2$. This work was done at 15°C.

However, these liquid mixtures and also the solid crystals were not in equilibrium; they changed continuously, producing formanilide and water. Thus crystals first formed in a given system of the components redissolved; and liquid mixtures at one time homogeneous, in time separated into two layers. Moreover the crystals of aniline formate were unstable in two directions, dissociating into aniline and formic acid on the one hand and giving formanilide and water on the other.

Goldschmidt and Wachs (3) studied the rate of formation of anilides, proving it to be in general bimolecular, while Davis and Rixon (2) studied the equilibrium, formic acid + aniline $\rightleftharpoons$ formanilide + water, in a solution of aqueous pyridine at 100°C., but they do not mention aniline formate. This equilibrium was confirmed in the course of the present work. Also a study of some properties (density, etc.) of certain mixtures of these three components was made by Pound and Russell (5).

The aniline was purified by distillation. The formic acid-water solutions, containing from 5 to 87 per cent formic acid, were made from the best commercial acids, 40 per cent and 87 per cent; from the latter acid, by treatment with the calculated amount of phosphorus pentoxide and by subsequent distillation *in vacuo*, there was obtained the 99 per cent acid, (see ref. 4). The formic acid content of these solutions and of the mixtures was found by titration with standard baryta water, using phenolphthalein; with this process the presence of aniline or of formanilide did not interfere. Such direct titrations of the mixtures gave the free formic acid and the acid present as aniline formate, the latter evidently dissociating in the process; such formic acid will be referred to as "free acid." By boiling solutions containing formanilide with an excess of caustic soda and then cooling and titrating with acid, the "total acid" was obtained, i.e., formic acid free and as aniline formate and as formanilide. The difference, "total acid" – "free acid," or "fixed acid," gave the formic acid fixed as formanilide. "Fixed acid" was also obtained in the solution after the neutralization of the "free acid" by boiling with excess caustic soda, etc., and this procedure gave the same results as the former.

Aniline was determined in the mixtures by titrating the warm acidified solutions containing potassium bromide with potassium bromate solution, using starch-potassium iodide as outside indicator; the bromate solution was standardized against pure aniline. This method gave the total aniline in the mixture, i.e., aniline free and as formate and as formanilide.

TABLE 1

FORMIC ACID USED	COMPOSITION OF THE CRITICAL MIXTURE		
	Aniline	Formic acid	Water
per cent	*per cent*	*per cent*	*per cent*
5.164	13.55	4.45	82.0
9.73	21.7	7.6	70.7
12.91	34.65	8.45	56.9
16.17	50.1	8.1	41.8
20.29	67.05	6.7	26.25
22.79	78.7	4.85	16.45
	95.09		4.91
	3.61		96.39

The percentages (weight) of aniline, formic acid, and water will be referred to as per cent aniline, per cent formic acid, and per cent water. Per cent formic acid without qualification means per cent of "free acid" (as defined above).

I. DETERMINATION OF THE UNOBTAINABLE LIQUID MIXTURES, I.E., OF THE LINE *BSSC*

This was got by the direct titration of the following formic acid solutions by aniline. The critical mixture, shown by characteristic opalescence, could be found to within a drop of aniline, the total amount of which varied from 5 to 40 cc. (see table 1). The critical mixtures of aniline and water were taken from Applebey and Davies (1), and from other workers (see ref. 6). The above critical mixtures are marked ☐ in the graph.

II. THE DISTRIBUTION OF THE FORMIC ACID

The distribution of the formic acid between the aniline and the aqueous layers gave the following results:

	per cent formic acid in aniline layer	*per cent formic acid in aqueous layer*
From 5.164 per cent formic acid	0.65	4.0
From 9.73 per cent formic acid	1.45	5.75
From 20.29 per cent formic acid	3.75	7.1

The three resulting tie lines are drawn in the graph.

III. DETERMINATION OF THE CURVE *DPG*

The curve *DPG*, bounding the region in which crystals separated, was determined by three methods:

a. Mixtures were made up from known weights of aniline and of formic acid solutions, and the resulting crystals and solutions were agitated in a thermostat at 15°C. for ¾ hour or more, and then separated and analyzed for "free acid" and aniline. The crystals were needle-shaped and long, especially if formed slowly or on the sides of the vessel above the main mixture. Rapid mixing gave small and entangled crystals and a semisolid mass which disentangled on agitation. On long agitation squat and compact crystals sometimes took the place of the needles. Both these kinds of crystals were aniline formate (see later). On further agitation the crystals in some experiments disappeared altogether.

TABLE 2

COMPOSITION OF SOLUTION			COMPOSITION OF CRYSTALS		
Aniline	Formic acid	Water	Aniline	Formic acid	Water
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
79.6	7.2	13.2	68.7	29.5	1.8
64.8	11.3	23.9	66.9	30.4	2.7
51.9	12.5	35.6	63.2	29.9	6.9
38.5	18.4	43.1	64.0	31.8	4.2
36.8	24.0	39.2	61.1	31.4	7.5
35.1	33.1	31.8	60.6	32.7	6.7
38.1	41.1	20.8	62.7	33.6	3.7

The method of residues was used thus to give the points on the curve *DPG* and the tie lines leading to the point *H*, representing aniline formate. The results were only approximate: long agitation meant that much formanilide was formed, which of course vitiated the result, and short agitation meant that the solution and crystals had not perhaps reached equilibrium at 15°C. Mixtures of aniline with the more concentrated formic acids were the most affected by the former complication, but all of the results were somewhat so affected. Hence especially the percentage of free acid in the solutions was lower than it should have been. A few typical results were those given in table 2. These points are marked O in the graph.

b. Various formic acid solutions were titrated by aniline, at 15°C., until crystals permanently remained in the mixtures. This method gave points along the curve *PG*. These crystals were squat. The points obtained in this manner probably tend to lie below the true solubility curve, i.e., crystals appeared momentarily as the aniline was run in and subsequently did not dissolve within a short time. When the 99 per cent formic acid was thus titrated with aniline, crystals remained when the mixture contained 34.4 per cent aniline,—obviously low. By taking aniline formate and finding the amount of 99 per cent acid which would just dissolve it, the point *G* was found at 37 per cent aniline,—a value which is still probably low. Thus 10 cc. (11.87 g.) of 76.08 per cent formic acid required 6.86 cc. (7.07 g.) of aniline, and the mixture then contained 37.3 per cent of aniline. It was found that for crystals to persist in the mixtures the following percentages of aniline were required:

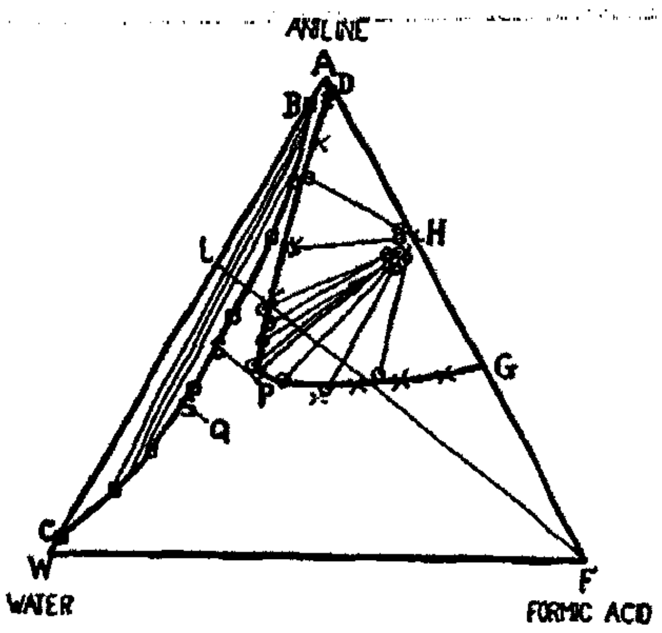

FIG. 1. THE SYSTEM ANILINE-FORMIC ACID-WATER

48.9 per cent formic acid solution required 33.2 per cent aniline
61.44 per cent formic acid solution required 35.9 per cent aniline
76.08 per cent formic acid solution required 37.3 per cent aniline
87.23 per cent formic acid solution required 38.2 per cent aniline

These points are marked × in the graph.

c. Aniline was titrated with various formic acid solutions at 15°C. until crystals persisted in the mixtures. Thus points along the curve *DP* were obtained. The crystals formed were generally needle-shaped. Thus 28.7 g. of aniline take 1.00 g. of 48.9 per cent formic acid solution, and the per cent of aniline in the mixture is thus 96.6. The mean results indicate that for crystals to persist in the mixtures the following percentages of aniline were required:

30.5 per cent formic acid solution required 54.2 per cent aniline
35.67 per cent formic acid solution required 65.1 per cent aniline
43.8 per cent formic acid solution required 86.9 per cent aniline
48.9 per cent formic acid solution required 96.1 per cent aniline
76.08 per cent formic acid solution required 97.9 per cent aniline

These points too are marked × in the graph.

IV. CHANGES IN THE LIQUID MIXTURES ON KEEPING

Mixtures containing appreciable formic acid and water showed a pink color on addition of the aniline; this increased in intensity for a few minutes and then decreased after ten minutes or more.

Mixtures of the three components were kept for many days at room temperatures, about 10°C., some in stoppered flasks in desiccators, others in sealed tubes; they were analyzed from time to time. In all of them the "free formic acid" plus the "fixed formic acid" equalled the original "free formic acid." The "free acid" decreased roughly in accordance with the bimolecular action, i.e., the formic acid fixed as formanilide in a given time was roughly proportional to the product of the aniline and formic acid percentages (concentrations). Moreover the speed of this action rapidly increased as the water-content decreased; a lowering of the water by about 14 per cent trebled the speed of action, other conditions being equal. Also a state of equilibrium was obtained after ten days or so, if the solution remained homogeneous; no satisfactory equilibrium constant was obtained however. A few typical results are given in table 3.

The formation of formanilide may be taken as equivalent to adding more aniline to the mixtures. Thus a mixture originally containing p per cent aniline, q per cent formic acid, and r per cent water, when the per cent of free formic acid falls to $(q - x)$, becomes $(p - 2.02\,x)$ per cent aniline, $(q - x)$ per cent formic acid, $(2.63\,x)$ per cent anilide, and $(r + 0.39\,x)$ per cent water, which behaves as $(p + 0.61\,x)$ per cent aniline, $(q - x)$ per cent formic acid, and $(r + 0.39\,x)$ per cent water, or the mixture moves to states along lines parallel to PS and QS, i.e., parallel to the line from the formic acid corner to the (61 per cent aniline, 39 per cent water) mixture, FL. Thus mixture P, No. 27, on the eighth day when it had just separated, contained only 8.6 per cent "free acid," and thus the "fixed acid" was 10.6 per cent, which was equivalent to 21.4 per cent of fixed aniline, as 27.9 per cent of anilide, and to 4.15 per cent of extra water; and the mixture then contained 8.6 per cent of "free acid," 15.8 per cent of free aniline (the dissociable aniline formate being included in these figures), with 27.9 per cent of anilide and 47.7 per cent of water; this mixture behaved as one with 8.6 per cent formic acid, 43.7 per cent aniline, and 47.7 per cent water, and therefore separated into two layers.

TABLE 3

NO.	MIXTURE			FORMIC ACID OBTAINED AFTER TIME GIVEN	
	Aniline	Formic acid	Water	Time	Formic acid
	per cent	*per cent*	*per cent*	*days*	*per cent*
3	19.95	39.15	40.9	35	30.9
				61	31.0
				71	30.9
6	25.65	36.35	38.0	40	25.3
				68	25.4
10	26.75	35.82	37.43	$\frac{1}{24}$	35.26
				$\frac{1}{2}$	29.93
				2	27.2
				4	24.8
				9	24.21
				27	24.17
				34	24.18
				42	24.18
				63	24.28
				74	24.27
24	9.15	4.69	86.15	2	4.20
				8	4.13
				16	4.02
				26	3.92
25	19.8	10.36	69.85	2	9.96
				8	8.64
				11	8.16
				14	Separated
26	28.0	14.6	57.4	2	12.9
				8	9.44
				9	Separated *QS*
27	37.2	19.2	43.6	2	14.25
				8	8.58, separated *PS*
31	78.65	5.35	16.0	2	4.11, separated
32	30.7	52.6	7.7	$\frac{1}{8}$	46.5
				2	36.9
				9	34.4
				17	34.1
				30	34.12

TABLE 3—*Concluded*

NO.	MIXTURE			FORMIC ACID OBTAINED AFTER TIME GIVEN	
	Aniline	Formic acid	Water	Time	Formic acid
	per cent	*per cent*	*per cent*	*days*	*per cent*
35	20.3	49.0	30.7	2	44.8
				9	41.5
				17	41.0
				30	40.0
39	18.9	70.7	10.4	$\frac{1}{8}$	68.5
				4	65.5
				11	63.1
				16	62.7
				25	62.66

Undoubtedly this hypothesis was in general accordance with the facts observed. Thus mixtures like Nos. 3, 6, 10, 32, 35, and 39 came to equilibrium and never separated into layers; mixtures near the line *BSSC*, like Nos. 31, 25, 26, 27, soon separated, and at points *S* as calculated above. Mixtures within the area *DPG* formed crystals, which dissolved in time, and these mixtures then separated in a similar manner to the former ones. Mixture No. 24 shows the influence of water, and mixture No. 31 that of aniline, on the rate of change, on the equilibrium, and on the final separation into two layers.

V. THE CRYSTALS, ANILINE FORMATE, AND THEIR CHANGES ON KEEPING

The crystals of aniline formate were not readily soluble in benzene, toluene, carbon tetrachloride, or petrol; they readily dissolved in water, methyl and ethyl alcohols, acetone, ethyl acetate, chloroform containing 2 per cent alcohol (B.P. chloroform), and in ether. They recrystallized as the ether evaporated. The crystals when kept beneath petrol soon became brown, and simple washing with petrol made them brownish. The white crystals remained unchanged beneath toluene for a few days, but then changed rapidly and soon a brown liquid, aniline or formanilide, was left. When kept in the air or dried in a current of air, the crystals acquired a pinkish or yellowish or brownish tinge.

Many samples of these crystals were made and were washed with one or other of the first four solvents, dried in desiccators over sulfuric acid or calcium chloride, and examined from time to time. Two white samples of the acicular crystals, analyzed at once, both gave 33.2 per cent formic acid and 66.1 per cent aniline, thus per cent of moisture by difference was 0.7; another sample gave 33.8 per cent formic acid, but smelt of free formic acid. Theoretically aniline formate contains 33.1 per cent formic acid and 66.9

per cent aniline. When dry crystals of the aniline formate were kept over sulfuric acid, the smell of formic acid could be detected after some hours and aniline could be detected in the sulfuric acid after some days. The dissociation into aniline and formic acid is therefore appreciable at room temperatures.

The crystals were usually in long needles, but (see above) occasionally there were obtained more compact forms (squat monoclinic prisms); these had the same composition as the needle-shaped crystals. Microscopic examination of freshly formed samples of the crystals indicated the presence of some compact crystals along with the main mass of acicular crystals. These last apparently changed the more quickly (surface effect?), leaving the compact forms. A second crop of crystals formed from a mixture of formic acid and aniline also tended to consist of compact forms.

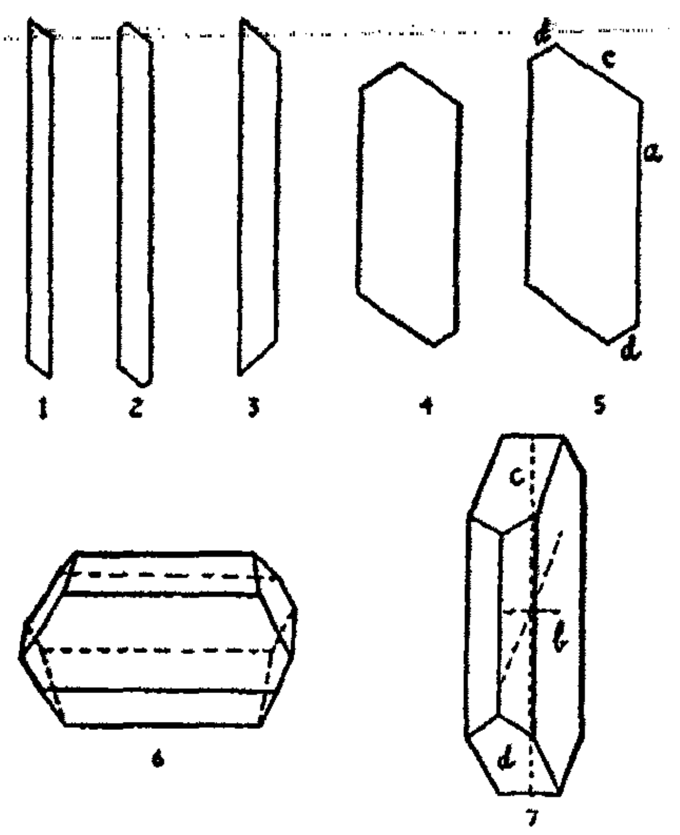

FIG. 2. CRYSTALS OF ANILINE FORMATE

The authors owe thanks to Mr. H. Yates, who examined and sketched these crystals and who supplied the following notes on the accompanying sketches (figure 2): "In the graph the figures 1, 2, and 3 are various shapes of acicular crystals, showing three types of crystal-face, of which two are developed in 1, and all three in 2, while in 3 the vertical faces are fully developed but there is only one of each type of inclined face. Crystal 1 was actually seen to grow into form 2 by developing of the third type of face. The angle between the two faces in 1 is 52°.

"Figures 4 and 5 represent tabular crystals lying on the clino-pinacoid plane. From these shapes the interfacial angles are: ac = 57°20′; ad = 59°; cd = 63°40′.

"Figure 6 is an actual sketch of a typical prismatic crystal under the microscope.

"Figure 7 is the same crystal correctly oriented, showing its monoclinic symmetry and the positions of the crystallographic axes."

The melting point of the crystals was 62°C. (maximum value), with average values about 60°C. The values varied as might be expected; also a remelting was always at a lower temperature than the original.

The crystals on keeping gradually became sticky; then very small crystals above or apart from the main lot became yellowish and liquefied; in a sealed vessel after several days a film of liquid (droplets) could be seen between the crystals on the walls of the vessel. Then the stickiness increased and the sample became yellowish or brownish, and finally free liquid (solution) accumulated, and in a couple of days more the crystals had disappeared. These changes took in all about seventeen days in a closed vessel at room temperatures (about 10°C.).

The petrol-washed samples changed very quickly. One such sample after nine days over calcium chloride had formed a yellowish liquid, and after twenty-four days a brown liquid; after sixty days new crystals had formed. The liquid was drained from these crystals, which were then washed and recrystallized from xylene; they gave a melting point of 43°C., indicating that they were (impure) formanilide (m.p. = 46°C.).

The crystals kept in contact with the mother liquor changed the fastest of all; they took but two or three days to disappear.

Many samples of crystals were kept in sealed vessels or over various drying agents and other reagents, but the changing to liquid was never stopped, though it might have been retarded by the absence of moisture. The free formic acid content diminished, and the fixed formic acid content increased continuously. In general, the (free *plus* fixed) formic acid in old crystals equalled the original free acid; in some samples there may have been some adsorption of water, and in other samples some preferential loss of formic acid over loss of aniline; but the loss of acid by volatilization was insignificant as compared with loss of acid by change into formanilide. Thus the crystals A (see table 4) gave a final liquid containing 7.3 per cent of free acid and 25.1 per cent of fixed acid; total = 32.4 per cent, original = 32.2 per cent. The crystals O gave on the fourth day 32.7 per cent of free acid and 1.0 per cent of fixed acid; total = 33.7 per cent, original = 33.8 per cent. The crystals L, from the third experiment reported in section IIIa, gave a final liquid containing 4.7 per cent of free acid and 26.9 per cent of fixed acid; total = 31.6 per cent, original = 29.9 per cent. However they were put in a desiccator overnight before sealing. After nine days crystals N were nearly all liquefied, and the sample went 16.2 per cent of free acid, 8.4 per cent of fixed acid,—indicating that much water had been picked up; the outer water contained both aniline and formic acid. Allowing for the water picked up, the rate of fixation of acid as formanilide was found to be the same as for the first six days.

The free acid content of some samples of crystals kept at room temperatures varied as shown in table 4.

TABLE 4

CRYSTALS WASHED WITH	SAMPLE	CONDITION OF KEEPING	ORIGINAL PER CENT FORMIC ACID	AFTER DAYS	PER CENT FORMIC ACID	FINAL STATE	CHANGE IN PER CENT FORMIC ACID PER DAY
CCl_4, petrol, and dry air........	A	In sealed tube	32.2	12	7.3	Liquid	2.08
	B	Over $CaCl_2$	32.2	12	24.1	Quite sticky	0.68
CCl_4, toluene, and dry air.....	E	In sealed tube	34.6	6	11.7	Liquid	3.8
	C	Over H_2SO_4	34.6	14	9.3	Two-thirds liquid	1.8
	D	Over P_2O_5	34.6	14	15.2	One-third liquid	1.4
CCl_4 and dry air..	F	In sealed tube	32.5	13	7.9	Liquid	1.9
	G	Over H_2SO_4	32.5	13	28.8	Sticky	0.28
	H	Over KOH	32.5	13	27.3	Sticky	0.40
Toluene, CCl_4, and dry air.....	O	In air	33.8	6	32.5	Slightly sticky; yellowish	0.22
	N	Over water	33.8	6	26.2	Very moist; white	1.25
	M	Over NaOH solution	33.8	6	26.4	Quite moist; white	1.2
	Q	Over $CuSO_4$	33.8	6	29 6	Sticky; brownish	0.7
	R	Over H_2SO_4	33.8	7	32.2	Slightly sticky; white	0.23
	P	Over P_2O_5	33.8	6	—	Slightly sticky; white	—
			33.8	9	31.2	Slightly sticky; white	0.29
Toluene..........	K	In sealed tube	33.0	15	7.2	Liquid	1.7
(Only drained from liquor)....	L	In sealed tube	29.9	24	4.7	Liquid	1.05

The samples A, E, F, K, and L had just liquefied completely in the time shown. This liquefaction took, on the average, seventeen days, and then the per cent of free acid had fallen to the average value of 6.2 (seven samples). The original condition of the crystals evidently had an influence on their subsequent rate of change. Possibly the presence of excess of formic acid in the crystals E, C, and D accelerated their changing. Also the crystals passed to liquid and lost more free acid in sealed vessels than in the open air. The average loss in per cent of free acid, excluding samples C, D, and E, in sealed samples was 1.6 per cent per day (seven samples); in samples over sulfuric acid, 0.22 per cent per day (five samples); and in samples over calcium chloride, 0.66 per cent per day (three samples). The drier the atmosphere about the crystals the slower seemed to be the rate of change of free acid, but even with excess of phosphorus pentoxide, as in sample P, the characteristic changing to formanilide still went on. The crystals, apart from the consequences of this changing, did not appear to be deliquescent.

In conclusion, the crystals of aniline formate change according to both the reactions:

$$\text{Aniline} + \text{Formic acid} \underset{(1)}{\rightleftharpoons} \text{Aniline formate} \underset{(2)}{\rightleftharpoons} \text{Formanilide} + \text{Water}$$

Probably change 2 is accelerated by water and by formic acid (see ref. 2); this change indeed may only occur in solution. Moreover as the products of the dissociation 1 may both provide such a solvent and are also both hygroscopic, the difficulty of stabilising the compound, aniline formate, will be realized.

SUMMARY

1. The authors have studied the behavior of mixtures of aniline, formic acid, and water at room temperatures.

2. The region of partially miscible mixtures has been mapped out.

3. The distribution of formic acid between the aniline and the aqueous layers has been found.

4. The region in which crystals of aniline formate separated has been mapped; no other solid phase was found.

5. The change of the liquid mixtures into formanilide was studied.

6. The change of the solid crystals of aniline formate into formanilide was studied.

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INTERMITTENCY AND THE HERSCHEL EFFECT[1]

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DISCUSSION

Many hypotheses have been advanced to explain the effects produced by exposure of photographic emulsions to radiant energy. One of the more fruitful of these hypotheses assumes that the action of light on the photographic emulsion is photochemical, and postulates the coëxistence of forward and reverse reactions. The forward reaction causes the silver halide grains in the emulsion to pass from the original undevelopable state to a developable state. The reverse reaction causes the exposed grains to return to an undevelopable state somewhat similar to that which existed before exposure. When light falls on the emulsion, the forward process causes grains to become developable. As soon as an appreciable number of grains becomes developable, the reverse reaction causes some of them to become undevelopable. After the exposure has proceeded for some time, a statistical equilibrium between the two reactions may be reached when just as many grains are being made undevelopable as are being made developable.[2] This condition corresponds to the horizontal portion of the characteristic time–density curve, that is, the portion of the curve where further exposure produces no further increase in density.

The magnitude of the equilibrium density attained on any given emulsion is a function of the wavelength and intensity of the radiation. In general the greater the intensity of the incident illumination, the greater will be the resulting equilibrium density. The effect of the wavelength of the incident radiation is dependent on the spectral sensitivity of the emulsion. Exposure to blue light produces high developable density on

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[1] Paper read before the Twelfth Midwest Regional Meeting of the American Chemical Society, held at Kansas City, Missouri, May 3, 1934.

[2] The system of reactions occurring when energy falls on a photographic emulsion is not always as simple as that outlined above. It has been shown that developable grains are not always capable of being returned to an undevelopable state by the reverse reaction. Such grains are said to be in a "non-reversible state." The amount of non-reversible density existent at any one time appears to be a function of the total developable density concomitantly existent. We hope to discuss this relationship and its implication more fully in a future paper.

ordinary chloride emulsions, while orange or red light produce low developable densities. It seems then that with blue light the forward reaction greatly predominates over the reverse reaction, while with red light this predominance is not so great. If an emulsion is given an exposure to blue light sufficient to produce a relatively high developable density and is subsequently given an exposure to red light, the density produced by the first exposure may be somewhat reduced by the second. This reduction in developable density by reëxposure to light of the longer wavelength is known as the Herschel effect. By means of the above considerations the Herschel effect may be explained[3] as being brought about by predominance of the reverse reaction during the exposure to red light.

Numerous studies have been made of the relative efficacy of continuous and intermittent primary photographic exposures. Intermittent exposures, to the same illumination and for the same effective length of exposure time, have been found in general to be less effective in producing density than continuous exposures, although it has been found that for exposures to extremely high light intensities and for very short intervals of darkness, intermittent exposures may be more efficient than continuous exposures in building up density. This difference in the density produced by intermittent exposures and by equivalent continuous exposures is known as the intermittency effect. As with the Herschel effect, the intermittency effect may be explained on the hypothesis of simultaneous forward and reverse reactions if we also assume the existence of photochemical lags in these reactions (1, 2, 3).

EXPERIMENTAL

It is supposed that, when the illumination is interrupted,—as it is during the periods of darkness in intermittent exposure,—a definite interval of time must elapse before the two reactions cease. Upon this hypothesis Blair and Hylan have suggested that those factors which accentuate the forward reaction, such as (1) strong illumination, (2) short wavelength, and (3) fast emulsion, should make an intermittent exposure more efficient than a continuous one. They also suggest that those factors which accentuate the reverse reaction, such as (1) faint illumination, (2) long wavelength, and (3) slow emulsion, should make an intermittent exposure less efficient than a continuous one. These suggestions are in keeping with experimental data. Intermittent exposures usually produce less developable density than do equivalent continuous exposures. This fact is

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[3] For an historical summary and bibliography of the concept of the Herschel effect as a regression phenomenon, see LÜPPO-CRAMER (Proc. 7th Intern. Congr. Phot. (London), p. 45 (1928)). For a more precise treatment, see JOEHNCK AND BLAIR (J. Optical Soc. Am. **23**, 67 (1933)), JAMES (J. Chem. Physics **2**, 132 (1934)), and the forthcoming paper mentioned in footnote 2.

explained by supposing that the terminal lag of the reverse reaction predominates over that of the forward reaction.[4] The result, then, is that the density which has been built up during the period of exposure is reduced slightly during the period of darkness. That is, density is not built up at so great a rate by intermittent exposure as by continuous exposure. Moreover, the equilibrium density resulting from intermittent exposure is less than that resulting from continuous exposure.

Factors which accentuate the reverse reaction, such as faint illumination, long wavelength, and slow emulsions, tend to produce a reduction of density during the periods of darkness in intermittency. It is ordinarily necessary that these same conditions be present in order that the Herschel effect may be produced. These considerations enable us to predict that, when the above-mentioned factors are present, intermittent exposures will be more effective in producing the Herschel effect than equivalent continuous exposures.

In order to test the above-mentioned prediction, a series of experiments was made on a slow, contrasty emulsion which is particularly subject to the Herschel effect (Azo F No. 5 paper). The paper was exposed to white light from an incandescent lamp for 48 seconds, the energy intensity at the surface of the paper being 1550 ergs per square centimeter per second. This exposure produced a high developable density approximating that shown on the ordinate at $t = 0$ in the figures. Successive sheets of the exposed paper were then reëxposed, some intermittently and others continuously, to a second radiation of intensity 1700 ergs per square centimeter per second. The intermittent exposures were made in a sensitometer employing a sector wheel of 120 degrees opening and rotating at a speed of 28 R.P.M. Three separate wavelength bands of secondary radiation, as given by appropriate Wratten filters, were employed,—orange, red, and short infra-red. The filters employed were No. 72 (600 and 700 mμ), No. 70 (700 mμ), and No. 88 (over 700 mμ). Each filter was used in conjunction with a water-cell which passed 90 per cent of radiation of wavelength 800 mμ, 50 per cent of 900 mμ, and only 10 per cent of 1000 mμ. The sheets were developed for 90 seconds in (Eastman formula) "D-73" developer (diluted 1 part of developer to 3 of water) at 21°C., fixed in acid hypo, washed, and ferrotyped. The normal reflection densities remaining after stated reëxposure intervals were measured with a photoelectric cell reflection densitometer.

The results are depicted in figures 1, 2, and 3, where the normal reflection densities are plotted against the corresponding intervals of exposure to the "herschelizing" light. It is apparent from the figures that intermittent

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[4] Davis (2) suggests that, during the period of the terminal lags, the "strength" of both the forward and reverse reactions falls off exponentially, so the resultant effect is a difference between two exponential functions.

exposure, under the conditions of the experiment, produces a relatively greater Herschel effect than corresponding intervals of continuous exposure to the "herschelizing" light. There is not sufficient data at hand to enable any explanation of why the observed "spread" between the curves for intermittent and for continuous exposure is apparently greater for orange light than for the longer wavelengths. This variation of "spread" with wavelength was found in all of several different determinations.

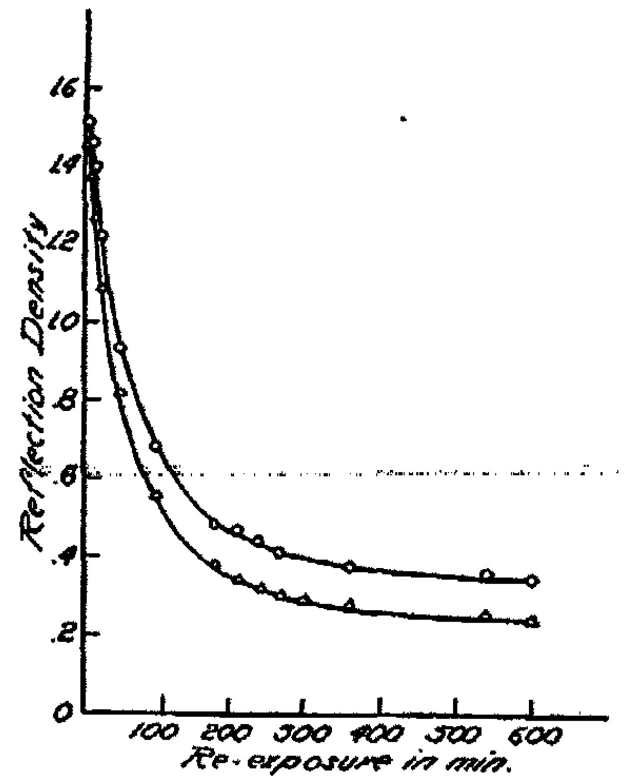

Fig. 1. Intermittency and the Herschel Effect in Orange Light
O, continuous reëxposure; △, intermittent reëxposure

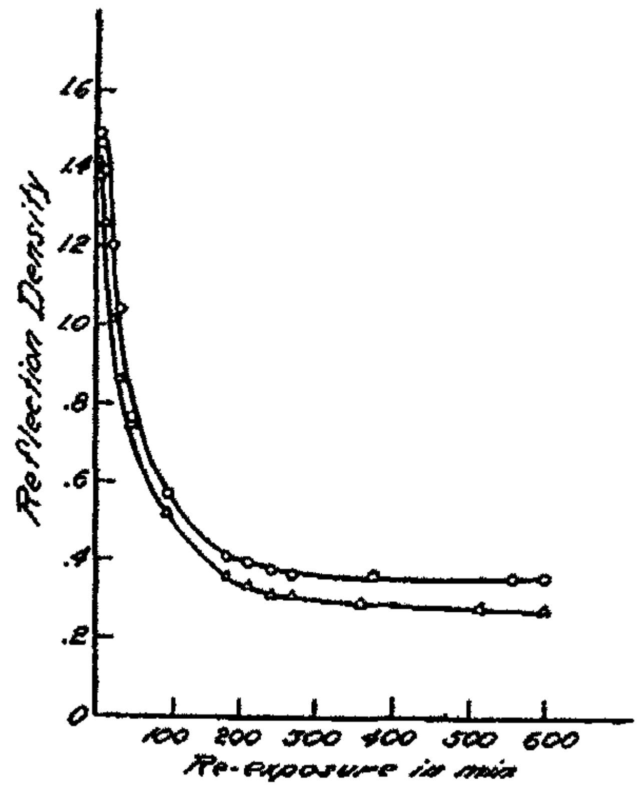

Fig. 2. Intermittency and the Herschel Effect in Red Light
O, continuous reëxposure; △, intermittent reëxposure

Though perhaps not apparent from the extent of the curves, there seems to be a tendency for prolonged infra-red exposure to yield slightly lower equilibrium densities than those obtaining for orange light. In any event absolute density comparisons, for much prolonged exposure times and for low densities, are rendered difficult both by natural regression of the latent image with time (in the dark) and because of the fact that at low densities variations introduced by slight differences in development conditions are relatively more important than at higher densities.

SUMMARY

The interpretation of the Herschel and intermittency effects is briefly discussed on the basis of the familiar hypotheses of simultaneous forward and reverse reactions with accompanying photochemical lags. From a consideration of certain implications of these hypotheses a new effect is predicted. The existence of this effect—namely, that intermittent exposure to the "herschelizing" light will be more efficient in producing Herschel effect than equivalent continuous exposure—has been amply proven by laboratory results employing three different wavelength bands of "herschelizing" light.

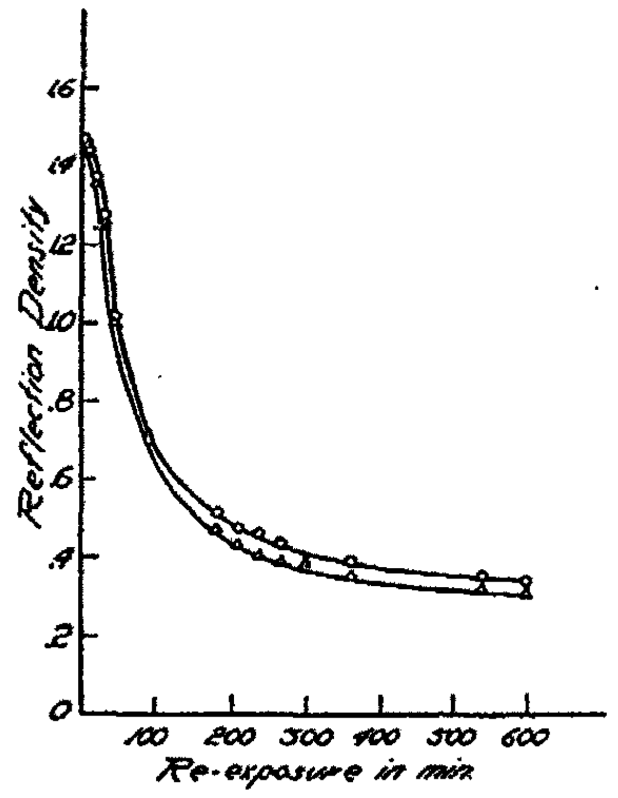

FIG. 3. INTERMITTENCY AND THE HERSCHEL EFFECT IN INFRA-RED LIGHT
O, continuous reëxposure; △, intermittent reëxposure

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A STUDY OF THE BENZOIN REACTION. I

The Reaction between Pure Benzaldehyde and Pure Potassium Cyanide

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INTRODUCTION

Smith (8) in 1899 stated that potassium cyanide and benzaldehyde yield benzoin in the absence of water. This statement was later contradicted by Lachmann (4), who considered that Smith's experiments had been vitiated by contamination with atmospheric moisture. More recently Morton and Stevens (7) have again stated that water is unnecessary for the production of benzoin.

This discrepancy in the published results on the place of water in the benzoin reaction is important, as the most widely accepted view of the mechanism of the reaction (6) involves the formation of a cyano ion. In addition an insight into the innate nature of the benzoin reaction may be obtained by a study of the kinetics of the heterogeneous reaction between alkali cyanide and benzaldehyde, assuming that the reaction can proceed in the absence of all solvents and reagents.

ANALYTICAL METHODS

The method used by Stern (9) is accurate, but not rapid. The methods of Lachmann (5), Morton and Stevens (7), and Anderson and Jacobson (2) are not sufficiently accurate, as they make no allowance for the solubility of benzoin in benzaldehyde even in the presence of water. Ten grams of wet benzaldehyde dissolve about 0.9 g. of benzoin. As a result of a number of control experiments the following technique was finally standardized.

The reaction mixture from 10 g. of benzaldehyde and varying amounts of cyanide is treated with 20 cc. of glacial acetic acid, and warmed until solution is complete. The liquid is then mixed with 35 cc. of water and allowed to stand overnight to ensure complete separation of benzoin. This is filtered off, dried, and weighed. Benzaldehyde is extracted from the filtrate with ether, and the extract dried over calcium chloride. The liquid after removal of ether is distilled at 2 mm. pressure at 110°C. The solid residue is dissolved in 10 cc. of glacial acetic acid, which is then diluted with 100 cc. of water. The precipitated benzoin is filtered off after twelve hours, dried, and weighed.

The benzoin as weighed was relatively pure, having a melting point not lower than 129°C. Little side reaction occurred under the conditions of the experiments, as may be seen from the high yields on prolonged heating (figure 1) and from the fact that the benzoin did not lose weight on extraction with sodium carbonate solution, showing the absence of benzoic acid.

MATERIALS EMPLOYED

Benzaldehyde

Kahlbaum's "purest" benzaldehyde was first used. It was confirmed that the experimental results were not altered when this benzaldehyde was washed with sodium carbonate solution, dried over calcium chloride, and distilled in a current of nitrogen which had been treated with pyrogallol solution, soda lime, and sulfuric acid. Merck's "purest" benzaldehyde gave identical results in trial experiments and was also used. Technical benzaldehyde, even when purified by washing with alkali and with water followed by distillation in a current of pure nitrogen after drying, gave variable results.

The sensitiveness of the benzoin reaction to traces of impurities in the benzaldehyde used has been commented on by Stern (9). Slight contamination of the hydrogen in which the benzaldehyde was distilled inhibited the reaction. The nature of the impurity was not traced, but it may have been hydrogen sulfide.

It is essential that the benzaldehyde should be free from benzoic acid, since this directly attacks the cyanide (1). To avoid oxidation, the aldehyde was stored in small lots in an atmosphere of purified nitrogen.

The formation of acid in any lot was detected by a fall in the yield in check experiments. Quinol cannot be used to inhibit oxidation as it is a negative catalyst for the benzoin reaction (see Part II[1]).

Potassium cyanide

Kahlbaum's or Merck's "purest" potassium cyanide was used. As received, these cyanides contained traces of moisture, but after drying at 110°C. at 2 mm. for 2 hours (11) analysis showed 100 ±0.05 per cent potassium cyanide. The dried material was stored in small lots out of contact with carbon dioxide and water, and was weighed in a closed bottle.

EXPERIMENTAL METHODS

The benzaldehyde was weighed in a closed bottle and poured into the glass reaction bottle, an allowance, experimentally determined, being made

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[1] To appear in the next issue.

for the benzaldehyde adhering to the sides of the weighing bottle. The reaction bottle was previously washed with pure acetone and with distilled water and heated at 107°C. in an oven; the bottle had a heat capacity such that on adding the benzaldehyde its temperature fell close to 100°C.

Immediately the benzaldehyde had been poured in, the necessary amount of potassium cyanide was added, and the reaction bottle sealed with a glass stopper, a rubber washer, and a spring clip. Each washer was thoroughly cleaned with acetone and distilled water before use, and was discarded after it had been used thrice.

The sealed bottle was shaken in a thermostat at two vibrations per second at 100 ± 0.2°C. The time of shaking was controlled by a stop watch.

No difficulty was experienced in repeating experiments to within 0.1 g. benzoin.

SOLUBILITY OF POTASSIUM CYANIDE IN BENZALDEHYDE

Experiments have shown that benzaldehyde even at 100°C. does not dissolve potassium cyanide (cf. Stern (9)).

SOME PRELIMINARY EXPERIMENTS

A number of experiments were made to examine the effect of certain external factors on the course of the reaction. It was found that the rate of reaction was not affected by addition of ground glass, by increasing the rate of shaking, or by using a sealed reaction vessel of thin glass which was previously evacuated at 2 mm. pressure. It can be concluded therefore that the reaction was not affected by the glass surface nor by the rubber washer, nor by the presence of air in the reaction vessel.

It should be emphasized that in spite of these experiments there is present a constant factor which poisons about 0.17 g. of potassium cyanide. Experiments in which smaller quantities of cyanide were used to trace this factor will be discussed later.

THE ACTION OF PURE POTASSIUM CYANIDE ON PURE BENZALDEHYDE

It will be clear from the experiments mentioned above that pure potassium cyanide and pure benzaldehyde readily yield benzoin. As will be described later, the reaction is inhibited by impurities present in the potassium cyanide; this phenomenon explains the failure of Lachmann to obtain benzoin except in the presence of water or of benzoin itself.

Figure 1 shows the results of experiments on the rate of formation of benzoin at 100°C. The points and dotted curves refer to experimental results; the full curves have been calculated (see below).

An examination of the curves shows that: (a) The reaction is autocatalytic. (b) The initial rate of reaction depends on the quantity of potassium cyanide present. (c) Once normal reaction has begun the rate is almost independent of the quantity of potassium cyanide present; thus, when rapid reaction has set in, the slope of the curve for 0.2 g. of potassium cyanide is almost the same as that of the curve for 6.2 g. (1 mol. proportion of potassium cyanide). (d) The autocatalyzed stage of the reaction is succeeded by a period of deceleration most marked with the smaller quantities of potassium cyanide.

We are evidently dealing with two concurrent reactions. The presence of potassium cyanide is necessary to produce benzoin, because if benzoin and benzaldehyde are shaken together at 100°C. the quantity of benzoin does not increase. Once benzoin is formed a second reaction sets in, in which benzaldehyde, potassium cyanide, and benzoin together yield benzoin.

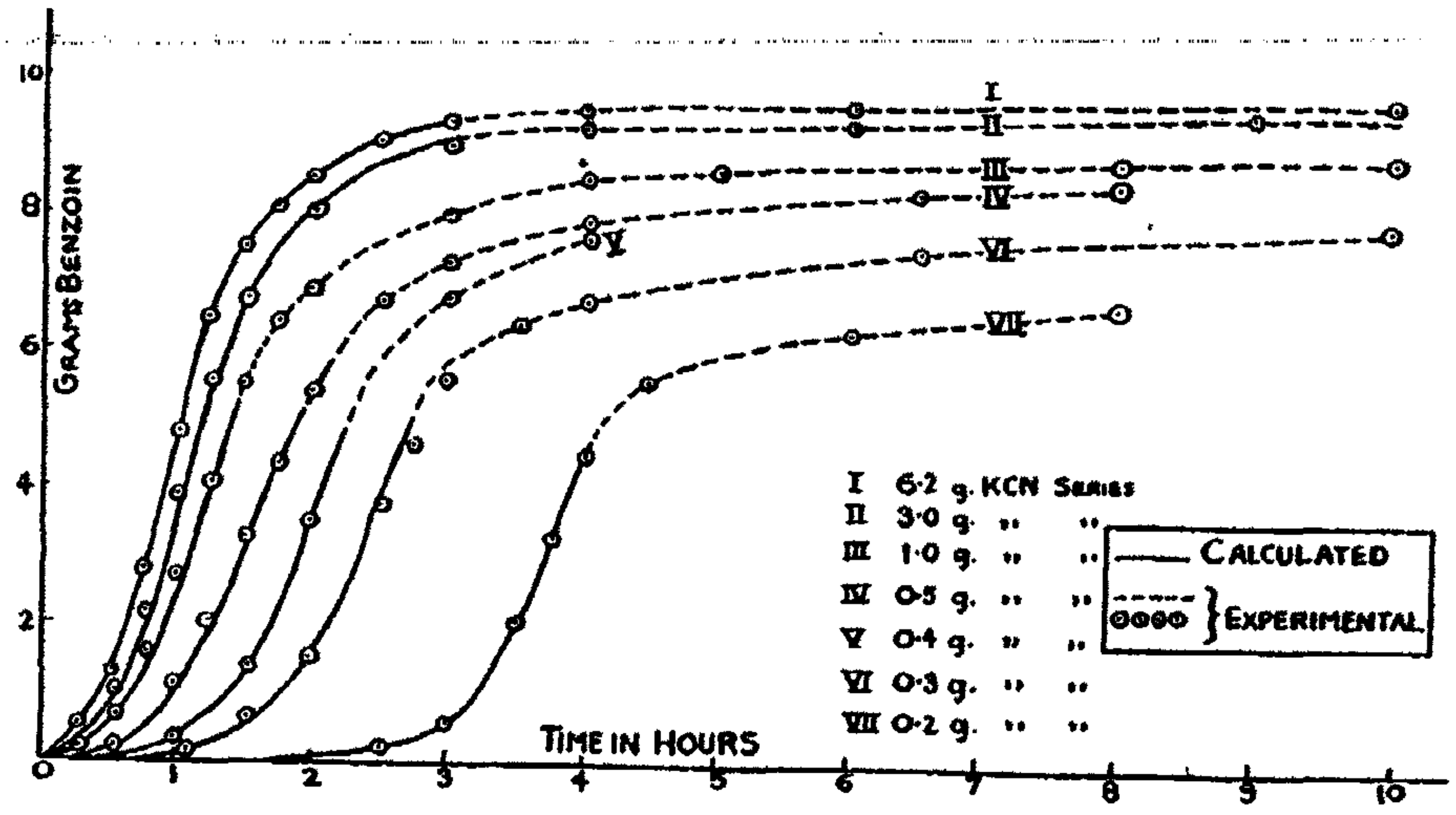

FIG. 1

Experiments in which 1 g. of benzaldehyde was replaced by 1 g. of benzoin showed that added benzoin behaves in the same manner as benzoin formed in the reaction.

THE QUANTITY OF POTASSIUM CYANIDE EFFECTIVE IN PRODUCING REACTION

Experiments at 100°C., some lasting up to 30 hours, with 10 g. of benzaldehyde and increasing quantities from 0.1 to 0.2 g. of potassium cyanide, benzoin being added to serve as a catalyst, showed that the formation of benzoin began only with 0.18 g. potassium cyanide.

Experiments were then made in which 20 g., 10 g., and 5 g. of benzaldehyde were shaken, respectively, with 1.0 g., 0.5 g., and 0.25 g. of potassium cyanide. The results are plotted in figure 2, the quantities obtained from

20 g. of benzaldehyde being halved and those with 5 g. being doubled. The three curves do not coincide but instead, as the quantity of cyanide decreases, the relative rate of reaction falls off.

On the same figure there are plotted the results of an experiment with 10 g. of benzaldehyde and 0.3 g. of potassium cyanide; the results correspond closely with the doubled quantities from 5 g. of benzaldehyde and 0.25 g. of potassium cyanide.

A study of figure 2 indicates that we can assume that 10 g. of benzaldehyde and about 0.33 g. of potassium cyanide yield twice as much benzoin in a given time as 5 g. of benzaldehyde and 0.25 g. of potassium cyanide. If then y is the quantity of potassium cyanide rendered inactive we have

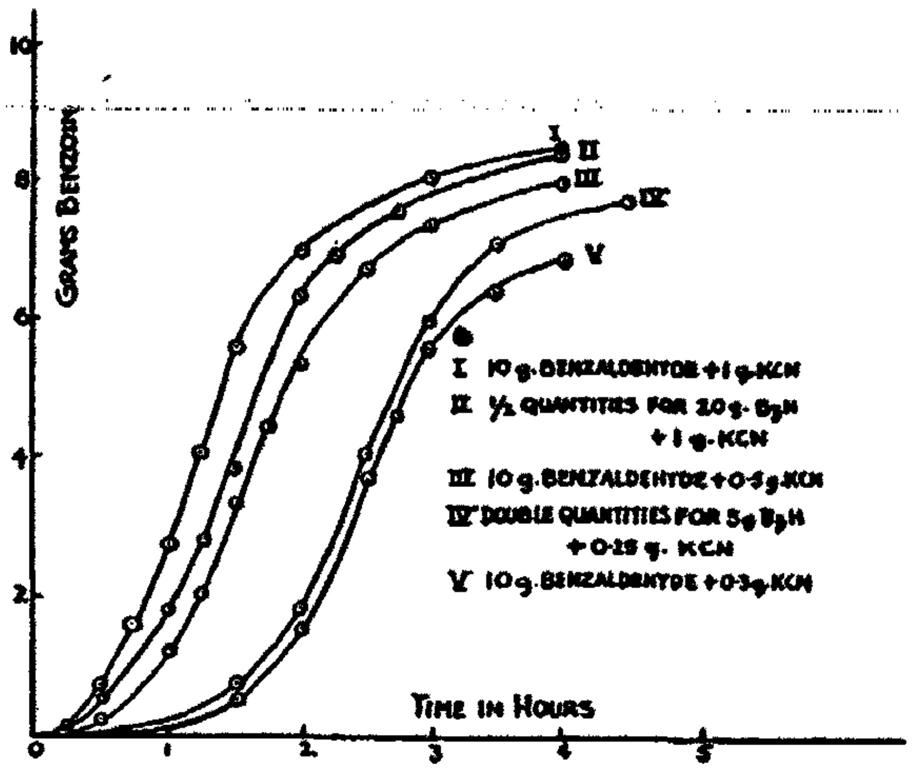

FIG. 2

$$0.33 - y = 2\,(0.25 - y)$$

whence

$$y = 0.17$$

This is in agreement with the results of the direct determination.

In what follows we subtract 0.17 g. from the "gross" quantities of potassium cyanide used in each experiment to obtain "net" effective quantities.

The inhibiting factor

Having established the fact that in some way up to 0.17 g. of potassium cyanide was poisoned in each experiment, attempts were made to determine the cause of this.

In the preliminary experiments (p. 729) made in the early stages of the research, 1 g. of potassium cyanide was used. As figure 1 shows, with this quantity of cyanide the rate of reaction is not sensitive to small changes in the amount of cyanide, so that it became advisable to repeat such experiments with smaller quantities of cyanide (table 1).

Three factors might be responsible for the poisoning: (a) the glass of the bottle; (b) the rubber ring used to seal it; and (c) small quantities of oxygen enclosed in the bottle.

It will be seen from table 1 that if the rubber washer is removed, benzoin can be obtained from 0.15 g. of potassium cyanide. In the presence of 1 g. of rubber no benzoin is obtained from 0.15 g. of potassium cyanide. It is possible that the effect of rubber is due to the sulfur it contains for, as will be shown later (Part II), sulfur is a powerful anticatalyst for the reaction.

TABLE 1

EXPT. NO.	BENZALDEHYDE USED	KCN USED	TIME OF SHAKING AT 100°C.	SPECIAL CONDITIONS	YIELD OF BENZOIN	CONCLUSION
	grams	*grams*	*hours*			
1	10	0.15	4	Sealed in an atmosphere of nitrogen	1.69	Oxygen of air or rubber appears to stop the reaction
2	10	0.15	4	Sealed in air	1.70	Oxygen does not stop the reaction
3	10	0.15	4	Sealed in air with rubber pieces (1 g. present)	Nil	Rubber stops the reaction
4	10	0.10	5	Sealed in air	0.2	
5	10	0.10	5	Sealed in an atmosphere of nitrogen	0.17	
6	10	0.05	5	Sealed in air	Nil	Residual inhibiting factor present
7	10	0.08	5	Sealed in an atmosphere of nitrogen	Nil	

Even with a reaction vessel sealed in an atmosphere of nitrogen, no benzoin is yielded by less than 0.10 g. of cyanide. The reason for this is still obscure.

THE ACCELERATED STAGE OF THE REACTION

In the mathematical formulation of these reactions in highly condensed systems, of the type in which a solvent itself is undergoing reaction, it has seemed to us preferable to use molecular concentrations (mole fractions) rather than volume concentrations. This is unusual, but may be justified by the following consideration: If in a reacting mixture of benzaldehyde and benzoin, one imagines a benzaldehyde molecule surrounded by a closely packed mixture of benzaldehyde and benzoin molecules, then the number of collisions it will make in a given time with surrounding benzoin molecules depends not so much on the total volume of the liquid, which will not vary greatly as benzaldehyde is converted into benzoin, but on the fraction of benzoin molecules among the surrounding molecules, that is, on the mole fraction.[2]

It is admitted that this consideration has only approximate validity, since the molecules of benzoin are larger than those of benzaldehyde, but it forms an approach to what is practically a new branch of chemical kinetics, in which there is little precedent to follow.

An examination of the curves obtained with small quantities of potassium cyanide when the autocatalytic[3] reaction is predominant indicates that the total rate of this reaction in a given system is independent of the quantity of potassium cyanide present (p. 729), but is proportional to the total amount of benzoin present, and to the square of the molecular fraction of benzaldehyde. This can be interpreted to mean that the rate of this homogeneous reaction is proportional to the number of collisions of molecules of benzoin each with two molecules of benzaldehyde (p. 737). We may write therefore,

$$\text{Total rate of homogeneous reaction in a given system} = K_1 [C_6H_5CHO]^2 \underline{C_6H_5COCHOHC_6H_5} \qquad (1)$$

where $C_6H_5COCHOHC_6H_5$ stands for the total amount of benzoin present in the system.

Since this reaction which is accelerated by benzoin requires the presence of potassium cyanide, but is not affected by the total quantity present, it would seem that it is the trace of potassium cyanide dissolved in benzaldehyde which induces the reaction.

The slower reaction involving the initial production of benzoin, is found by analysis of the reaction velocity curves to have, in a given system, a total rate proportional to the total quantity of potassium cyanide present, and to the square of the molecular concentration of benzaldehyde. Since potassium cyanide is practically insoluble in benzaldehyde at 100°C., it is evident that the proportionality factor for the quantity of potassium cyanide is in reality a factor for the total surface of potassium cyanide present, as this with uniform cyanide is proportional to the total quantity present. We may therefore (see p. 738) regard the reaction as heterogeneous, and as having a total rate proportional to the total surface of cyanide present, to the fraction of the surface covered, and to the rate at which benzaldehyde molecules collide with unit area of surface.

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[2] It is assumed that a given molecule is always surrounded by the same number of neighboring molecules.

[3] A discussion of the mathematical treatment of simple autocatalytic reactions (logistic equation) is given by Reed and Berkson (J. Phys. Chem. 33, 760 (1929)).

We have consequently,

$$\text{Total rate of heterogeneous reaction} = k[\mathrm{C_6H_5CHO}]^2\,\underline{\mathrm{KCN}}$$

where $\underline{\mathrm{KCN}}$ stands for the total amount of potassium cyanide present. For a given quantity of potassium cyanide in the system we may write,

$$\text{Total rate of heterogeneous reaction} = k_2[\mathrm{C_6H_5CHO}]^2 \tag{2}$$

We may now proceed to write the differential equation for the concurrent reactions.

Let n be the number of moles of C_6H_5CHO remaining at time t, and N = the number of moles of benzaldehyde initially taken. Then $\frac{N-n}{2}$ = the number of moles of benzoin present at time t, $\frac{N+n}{2}$ = total number of moles present, and molecular fraction of benzaldehyde $= \frac{2n}{N+n}$.

Then the total rate of reactions 1 and 2 is given by

$$-\frac{dn}{dt} = k_1\left(\frac{2n}{N+n}\right)^2\left(\frac{N-n}{2}\right) + k_2\left(\frac{2n}{N+n}\right)^2 \tag{3}$$

so that,

$$-2k_1(t-c) = \frac{-N^2}{(N+X)n} + \frac{N(3N+2X)\ln n}{(N+X)^2} - \frac{(2N+X)^2\ln(N+X-n)}{(N+X)^2} \tag{4}$$

where $X = 2k_2/k_1$, and c is a constant.

For calculation purposes it is more convenient to express quantities in grams than in moles, and for a system containing initially 10 g. of benzaldehyde, equation 4 becomes, when x is small,

$$t - c' = -\frac{1}{k_1}\left[-\frac{5}{n'} + 3.45\log n' - 4.60\log(10 + X' - n')\right]$$

where c', n', X' refer to gram-units; k_1 is independent of the units in which the benzaldehyde is expressed.

For the experiments under consideration, $k_1 = 5.7$, and k_2' for 1 g. of effective potassium cyanide per 10 g. of benzaldehyde = 0.185. Hence we have the values given in table 2.

The equations to be employed for (a) 0.2 g. of potassium cyanide and for (b) 6.2 g. of potassium cyanide for 10 g. of benzaldehyde are, respectively,

$$\text{(a)}\quad -5.7(t-3.70) = \frac{-5}{n'} + 3.45\log n' - 4.60\log(10.002 - n')$$

$$\text{(b)}\quad -5.7(t-0.75) = \frac{-4.8}{n'} + 3.3\log n' - 4.4\log(10.4 - n')$$

Equations for other quantities of potassium cyanide are obtained in a similar manner.

The application of these equations to calculate the course of the time reaction curve for the accelerated stage is shown in figure 1. During the accelerated stage of the reaction the experimental and calculated results are in satisfactory agreement. It should be stated that the homogeneous catalyzed reaction is much the faster of the two reactions involved.

THE LATER STAGES OF THE REACTION

The rapid decrease in the rate of reaction when about half of the benzaldehyde present has been converted is a striking feature of the experimental curves.

TABLE 2

KCN USED (a)	KCN EFFECTIVE ($b = a - 0.17$)	$k_2' = 0.185b$	$X' = \frac{2k_2'}{k_1} = \frac{2k_2'}{5.7}$
grams	*grams*		
0.2	0.03	0.006	0.002
0.3	0.13	0.024	0.01
0.33*	0.16	0.030	0.011
0.4	0.23	0.043	0.015
0.5	0.33	0.061	0.02
0.59†	0.42	0.08	0.030
1.0	0.83	0.15	0.05
3.0	2.83	0.53	0.20
6.2	6.03	1.12	0.40

* Double quantities for 5 g. of C_6H_5CHO + 0.25 g. gross KCN.

† Half quantities for 20 g. of C_6H_5CHO + 1 g. gross KCN.

This consideration led to the determination of the solubility of benzoin in benzaldehyde at 100°C.; 10 g. of benzaldehyde at 100°C. dissolve 10.4 g. of benzoin, so that when about 50 per cent of the benzaldehyde has been converted, saturation of the remaining aldehyde with benzoin occurs, and any further formation of benzoin involves precipitation of this substance. This consideration, while it explains a falling-off in the rate of reaction, does not show why this decrease is more rapid with the smaller quantities of potassium cyanide.

This phenomenon can be explained by assuming that the precipitated benzoin adsorbs dissolved cyanide from the solution. With a small quantity of cyanide a small quantity of benzoin will remove all from solution; with a large quantity of cyanide a large quantity of benzoin must be precipitated before all the cyanide is removed. We expect, therefore, that with a large quantity of cyanide the fall in the rate of reaction will be due for the most part to a contraction in the amount of saturated solution and not to the stoppage of the homogeneous reaction. We can, accordingly, calculate the rate of reaction as follows:

Let B = number of moles of benzoin soluble in 1 mole of benzaldehyde at 100°C. If the solution first becomes saturated when m moles of benzaldehyde remain, we have then $\left(\frac{N - m}{2}\right)$ moles of benzoin, and hence

$$Bm = \frac{N - m}{2}$$

and

$$m = \frac{N}{2B + 1}$$

The total rate of reaction when the solution becomes saturated is (see equation 3)

$$-\frac{dm}{dt} = k_1 \left(\frac{2m}{N + m}\right)^2 \left(\frac{N - m}{2}\right) + k_2 \left(\frac{2m}{N + m}\right)^2 = \frac{k_1}{(B + 1)^2} \left(\frac{BN}{2B + 1} + \frac{X}{2}\right)$$

If now for convenience in calculation we work in grams and put B' = number of grams of benzoin soluble in 1 g. of benzaldehyde at 100°C., and assume that the solution first becomes saturated when m' grams of benzaldehyde remain, we have

$$\frac{B'}{2} = B$$

and

$$\frac{-dm'}{dt} = \frac{2k_1}{(B' + 2)^2} \left(\frac{B'N'}{B' + 1} + X'\right)$$

Putting $k_1 = 5.7$, $N' = 10$, $X' = 0.4$,[4] and $B' = 1$, we have

$$\frac{-dm'}{dt} = \frac{11.4}{9}\,(5 + 0.4)$$

As a first approximation, we can neglect the heterogeneous reaction with potassium cyanide and write

$$-\frac{dm'}{dt} = \frac{11.4 \times 5}{9} = 6.4$$

Since it is a uniform saturated solution of benzoin in benzaldehyde which is undergoing reaction we have,

$$-\frac{dn'}{dt} = -\frac{n'}{m'} \times -\frac{dm'}{dt} = \frac{6.4n'}{m'}$$

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[4] This corresponds to 6.2 g. of potassium cyanide (table 2).

And since $m' = 5$,

$$-\frac{dn'}{dt} = 1.28n'$$

whence,

$$-t + c = 0.78 \ln n' = 1.80 \log n'$$

When $t = 1, n' = 5$, so we have

$$-t + 2.26 = 1.80 \log n'$$

The application of this equation to calculate the course of the reaction velocity curve for 6.2 g. of potassium cyanide from 5 g. of benzoin onwards is shown by curve 1 in figure 1. The agreement is satisfactory. When the quantity of benzoin formed is large, the homogeneous reaction is affected by removal of potassium cyanide and the actual rate decreases more rapidly than the calculated rate.

The agreement with the calculated equation for 3 g. of potassium cyanide is also found satisfactory (see figure 1, curve 2, from 5 g. of benzoin onwards).

With smaller quantities of potassium cyanide, i.e., quantities less than 3.0 g., the dissolved cyanide is removed too rapidly to enable the above equations to apply.

EXPERIMENTS WITH POTASSIUM CYANIDE AND BENZALDEHYDE AT 30°C.

Curves in figure 3 show the results of some experiments at 30°C. They are of interest as showing that pure benzaldehyde and pure potassium cyanide can yield benzoin at room temperature.

THE MECHANISM OF THE HOMOGENEOUS BENZOIN REACTION IN THE ABSENCE OF WATER

The experimental results show that the total rate of this reaction is proportional to

$$[C_6H_5CHO]^2\underline{C_6H_5CHOHCOC_6H_5}$$

molecular fractions being used in place of concentrations. If the reaction involved is of the type

$$C_6H_5CH(OK)(CN) + C_6H_5CHO + C_6H_5CHOHCOC_6H_5 \rightarrow C_6H_5C(OK)(CN)CHOHC_6H_5 + C_6H_5CHOHCOC_6H_5$$

then if, as is likely, the concentration of $C_6H_5CH(OK)CN$, that is, of dissolved potassium cyanide, is proportional to the concentration of benzaldehyde, we can write the rate of reaction as proportional to

$$[C_6H_5CHO]^2\underline{C_6H_5CHOHCOC_6H_5}$$

The mechanism necessary to explain these kinetic results is essentially the same as that suggested by Lapworth (6).

While the un-ionized form of the cyanohydrin compound has been written, it may be that even in benzaldehyde solution the trace present is always ionized. On the other hand, as regards the mobility of the hydrogen atom in the cyanohydrin compound, it would not appear to be important whether it is or is not ionized.

The necessity for the presence of benzoin before the homogeneous reaction can proceed is not easy to explain.

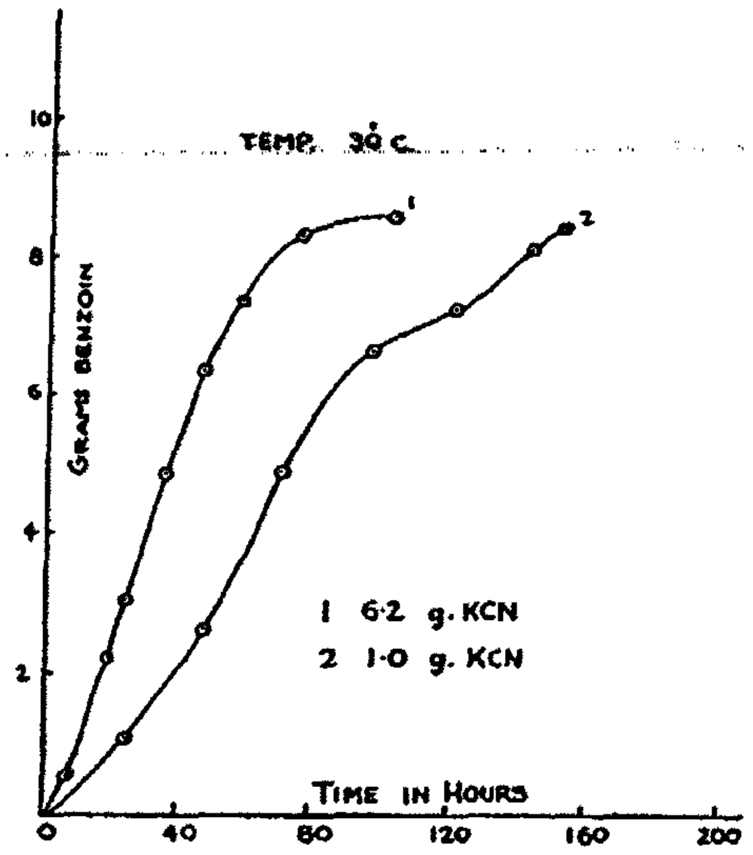

FIG. 3

THE MECHANISM OF THE HETEROGENEOUS BENZOIN REACTION IN THE ABSENCE OF WATER

This reaction obviously takes place at the surface of the undissolved potassium cyanide. The total rate of formation of benzoin in this reaction may be regarded as proportional to the number of collisions of benzaldehyde molecules on that portion of the potassium cyanide surface which is covered by similar molecules. If the adsorption is small, then the fraction of the surface covered by the benzaldehyde molecules will be proportional to the concentration of benzaldehyde in the liquid phase (3), the number of collisions on the whole surface is also proportional to the benzaldehyde concentration, while the area of the whole surface varies with the amount of potassium cyanide present. Accordingly the rate of formation of benzoin under these conditions is proportional to

$$[C_6H_5CHO]^2\underline{KCN}$$

which is the equation deduced from the kinetic data (p. 734).

The mechanism of this reaction is much the same as that postulated for the homogeneous reaction. We assume that the adsorbed benzaldehyde is present as the cyanohydrin compound, and that when collision occurs, condensation to the benzoin cyanohydrin compound takes place. This then eliminates benzoin. In the formation of the cyanohydrin compounds the potassium and cyanogen ions may remain partly attached to the potassium cyanide lattice, reverting to it when eliminated from the potassium cyanide compound.

SUMMARY

1. It is shown that pure potassium cyanide and pure benzaldehyde react in absence of water to give benzoin.

2. Two concurrent reactions take place—a fast homogeneous autocatalytic reaction and a slow heterogeneous reaction.

3. The results have been treated mathematically on this basis.

4. The mechanisms of the reactions in the absence of water have been discussed.

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NEW BOOKS

Line Coördinate Charts for Vapor Pressure-Temperature Data. By Frank E. E. Germann and Odin S. Knight. 2 charts, 22.9 x 61 cm. University of Colorado, Boulder, Colorado. Price: $2.00.

One of the great obstacles in physical, organic, and industrial laboratories has been the lack of at least approximate vapor pressure-temperature data. The authors have supplied this need by the production of a line coördinate chart based on the integrated form of the Clausius-Clapeyron equation. The reciprocals of the absolute temperatures have been plotted against the logarithms of the vapor pressures over the range of 500 to 900 mm. The vapor pressures obtained by various authors have been studied, and weighted curves drawn. In all cases the individual variations among the results for a given compound are greater than the possible error made in assuming the lines to be straight.

The 183 compounds given are conveniently separated into chain and ring compounds. Each class is provided with two scales: chain compounds, 0° to 125°C. and 105° to 230°C.; ring compounds, 65° to 225°C. and 185° to 390°C. The use of these charts makes calculations for corrections in boiling points due to variation in pressure unnecessary. The charts permit temperature readings within 0.25°C. if the pressure is known, or pressures within 2 mm. if the temperature is known. A knowledge of the prevailing barometer pressure only is required.

Ample directions are given for the interpolation of boiling point or of vapor pressure values, and for the insertion of new data as it may appear. These charts will meet a long-felt want in all laboratories, whether at sea-level or at higher altitudes.

J. N. Pearce.

The Solid Products of the Carbonization of Coal. Chemical Department, South Metropolitan Gas Co. Paper cover; 123 pp.; 41 figures; 45 tables. London: South Metropolitan Gas Co., 709 Old Kent Road, S.E. 15, 1934.

This monograph gives the results of an original investigation conducted by the chemical staff of the South Metropolitan Gas Co. over a period of several years in an endeavor to increase the use of coke as a domestic fuel. Following a short introduction, Chapter II, on an investigation into the possibility of producing by the carbonization of coal a smokeless solid fuel suitable for the domestic grate fire, describes test methods for determining the ignition temperature, combustibility, reactivity to carbon dioxide, steam, and sulfuric acid, and electrical conductivity of cokes and chars. Application of these tests to a series of cokes made at increasingly higher carbonizing temperatures, ranging from 500 to 1050°C., showed that reactivity to air, carbon dioxide, steam, and sulfuric acid decreased and electrical conductivity increased with increasing temperature of carbonization. These changes in coke characteristics were most marked at about 700°C. carbonization temperature and coincided with the change in appearance from a dull black to the characteristic silvery sheen of high temperature coke. The absorptive capacity of the cokes for carbon dioxide increased sharply with increasing temperature of carbonization up to a maximum at 700°C., and then fell rapidly. Deposition of graphitic carbon reduced slightly the reactivity of the high temperature cokes but seemingly was not the major cause of the large difference between low and high temperature cokes. Alteration of the physical structure produced by any modification of the high temperature carbonizing process likely to be practicable was quite ineffective in producing a substantial improvement in the combustibility of the coke.

As a result of this investigation the authors believe that the difference in reactivity between low and high temperature coke is due to a profound change in chemical rather than physical structure. Assuming that the benzene ring nucleus plays an important part in the chemical structure of coal, they believe that in the low temperature carbonization of coal, i.e., below 700°C., side chains are stripped from the nucleus without coalescence of these nuclei; whereas, in carbonization above 700°C., the single nuclei coalesce to form complex polycyclic compounds coincident with a marked evolution of hydrogen. The closer association of the carbon atoms without the frequent interposition of hydrogen atoms suggests a plausible explanation of the reduced chemical activity.

Chapter III states the characteristics of a satisfactory low temperature fuel as having a size between 1 and 2 inches, low ash, not over 5 per cent moisture, about 13 per cent volatile matter, and an electrical resistivity of not less than one million ohms. In order that the coke may be readily ignitable and freely burning in the ordinary domestic grate the coal must be carbonized below 700°C.

Chapter IV, on the use of high temperature coke as a domestic fuel, describes the "metro" coke grate which was developed for use of high temperature gas cokes. Burning tests and the effect of residual volatile matter, size, ash, and volume of ash on the performance in grates and domestic hot water boilers are given. Optimum characteristics are size 1 to 2 inches, moisture 3 per cent, volatile therms per ton 2½, and as low ash volume as possible.

Although high combustibility is not of the same importance in American practice because coke is used in central heating furnaces rather than open grates, yet American fuel technologists will find this monograph worthy of careful study. Physical chemists will be interested in the theory advanced in explaining the reduction of reactivity with increasing temperature of carbonization.

A. C. FIELDNER.

ERRATUM

Vol. 39, pp. 432-5: The ordinates of figures 1 to 4 should be labelled "cu. mm. of pyridine per square centimeter of membrane."

THE ELECTROKINETIC POTENTIAL AND THE STABILITY OF COLLOIDS[1]

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Received June 14, 1934

Experimental evidence (6) shows that the stability of hydrophobic colloids is determined by the electrokinetic potential of the particles. In the case of hydrophilic colloids, however, the experiments indicate (1,4) that coagulation depends primarily on the amount of hydration, while the ζ-potential seems to be of much less importance. The question arises, therefore, whether the electric forces are sufficient to explain the stability of hydrophobic colloids. This problem has been investigated by A. March (3). He finds that the observed electrokinetic potentials are at least ten times too small to account for the existence of colloids with microscopic particles. March comes to the conclusion that the stability of colloids is essentially due to the existence of a protecting skin around every particle. This result is in agreement with the fact that colloidal particles do not grow or flow together during coagulation. Even liquid particles remain separated after coagulation. In view of the experimental facts, it seems natural to assume that in the case of hydrophilic colloids this protecting skin is formed by the hydrated water molecules.

For hydrophobic colloids this explanation can obviously only be accepted if we can understand the origin and nature of this protecting skin. We must prove that the energy necessary to destroy this skin is larger than the energy of the temperature motion of the partices. Finally its existence must be closely connected with the electrokinetic potential in such a way that its influence vanishes with small ζ-potentials.

In a recent paper (5) I have proposed the following explanation of the origin of this protecting skin: The electric double layer creates a very strong inhomogeneous electric field around each particle. This field produces by electrostriction a large hydrostatic pressure in the range of the double layer. We find, therefore, around each particle a thin shell where the water is under considerable pressure. It is this shell which acts as the protecting skin. According to this theory the mechanism which produces

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

the stability of colloids is very similar for hydrophilic and hydrophobic sols. The difference lies in the fact that in hydrophilic colloids the water molecules are "attached" to the surface of the micelle by chemical (adsorption) forces and hence coagulation is to a large degree independent of the ζ-potential. In hydrophobic colloids the water molecules are only "attracted" to the surface by the electrostatic forces of the double layer, and hence their stabilizing influence diminishes as the ζ-potential gets smaller.

The energy of this electrostatic effect can be calculated by means of the same considerations as given by Zwicky (7) for the electric field around ions. We consider a plane diffuse double layer. If the ζ-potential is not larger than 50 millivolts the electric potential φ at a distance x from the surface of the particle is given by

$$\varphi = \zeta e^{-Kx}$$

where $\frac{1}{K} = \lambda$ is the effective thickness of the double layer. The electric field at the distance x is

$$E = \mathrm{K}\zeta e^{-Kx}$$

and the dielectric polarization

$$P = \frac{D-1}{4\pi} E$$

where D is the dielectric constant of water. We use the value $D = 80$. Dielectric saturation effects can be neglected. According to A. H. Lorentz and Dällenbach (2) the force exerted on 1 cc. of the dielectric is then

$$F = \frac{1}{4\pi}\left[1 + \frac{(D-1)(3D+7)}{5}\right] E \frac{\mathrm{d}E}{\mathrm{d}x}$$

and hence the hydrostatic pressure p at the distance x from the surface

$$p = \int_x^\infty F\,\mathrm{d}x = 155\,\zeta^2 K^2 e^{-2Kx}$$

The maximum pressure exists along the surface $x = 0$ and reaches the value

$$p_0 = 17K^2\zeta^2\,10^{-10} \text{ kg. per cm.}^2$$

In this formula ζ is the value of the potential in volts and has usually values smaller than 0.1. For a monovalent electrolyte K^2 has, according to Debye and Hückel, the value

$$K^2 = \gamma \cdot 1.07 \times 10^{15}$$

where γ is the molar concentration of the electrolyte. Using $\zeta = 0.1$, $\gamma = 1/1000$ we get therefore a maximum pressure of about 18 atmospheres.

Five to ten times larger values of this pressure can be calculated if we take into account the curvature of the surface of small colloidal particles. In the case of a spherical particle the potential decrease is given by

$$\varphi = A\frac{e^{-Kr}}{r}$$

and since the pressure depends on $E = -\frac{\partial\varphi}{\partial r}$ and $\frac{\partial E}{\partial r} = -\frac{\partial^2\varphi}{\partial r^2}$ one realizes that this more rapidly decreasing potential gives rise to a larger pressure.[2]

It is intended to show here only that the proposed theory gives results of the correct order of magnitude. We shall, therefore, consider only the case of the plane double layer, keeping in mind, however, that for colloids the numerical values of all results will usually be considerably larger.

This hydrostatic pressure will result in a volume contraction of the colloid and leads to the conclusion that agglutination produces an increase of the volume. This increase is given by

$$\Delta V = 4\pi N \int_r^\infty \kappa p(r) r^2 \, dr$$

where $\kappa = 45 \cdot 10^{-6}$ is the compressibility of water and N the number of colloidal particles in one liter. The calculation gives, with the most favorable assumptions, an increase of 10^{-3} to 10^{-4} cc. for one liter of colloid. Linder and Picton (8) observed an expansion of this order of magnitude for a sol of ferric hydroxide.

While the work of compression $\int p dV$ is small and can be neglected, Zwicky has pointed out that this electrostrictive effect produces an appreciable change of the free energy of the water. According to measurements of Bridgman the specific heat of water at room temperature decreases under the influence of pressure, and the free energy diminishes likewise. For small pressures the energy decrease is nearly linear and has the approximate value

$$\Delta U = 1.34 \cdot 10^{-3} \text{ cal. per gram} = 5.6 \cdot 10^{4} \text{ ergs per gram}$$

for a pressure of 1 kg. per cm^2.

The layer of compressed water on the surface of a colloidal particle is

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[2] The calculation of this case has been carried out, but since the result cannot be given in analytical form, it will not be given here. The above expressions for φ are only valid for small values of ζ. The solution for large values of ζ leads to even larger values of $\frac{d\varphi}{dr}$ and hence to still larger pressures.

therefore the seat of a negative free energy. The amount of energy necessary to destroy 1 cm.^{2} of this film is given by

$$U = \int_0^\infty 5.6 \cdot 10^4 p \, dx = 4.8 \cdot 10^{-5} K \zeta^2 \text{ ergs per cm.}^2$$

Introducing again $\zeta = 0.1$, $\gamma = 1/1000$ gives

$$U = 0.5 \text{ erg per cm.}^2$$

If we use the accurate solution for the plane double layer (5) for a Z-Z valent electrolyte the expression for U is

$$U = 4.8 \cdot 10^{-5} K z \zeta^2 \left(\frac{\sinh \psi}{\psi} \right)^2$$

where

$$\psi = \frac{ze}{4kT} \zeta$$

k = Boltzmann's constant, and e = electronic charge. This gives for $Z = 3$, $\gamma = 1/1000$, and $\zeta = 0.1$

$$U = 3 \text{ ergs per cm.}^2$$

Taking into account the curvature of the surface we can expect values of 10 ergs per cm^2. This is almost of the same order of magnitude as the surface tensions of liquid-liquid interfaces, and we can readily understand that this surface layer of compressed water is able to stabilize the colloid.

If we assume that coagulation can occur only if this surface layer is destroyed in the area of contact, and if we assume that for large particles this area of contact is larger than 10^{-14} cm.^{2}, we see that the temperature motion of the particles is not large enough to destroy the protecting skin. Hence, the colloid is stable. A small reduction of the ζ-potential decreases the energy necessary to produce coagulation, and since U is proportional to ζ^2 the stability of a colloid is very sensitive to small changes of the electrokinetic potential.

Making allowance for the approximations used, the proposed theory is therefore able to explain the dependence of the stability of hydrophobic colloids on the electrokinetic potential.

It is interesting to note that the theory leads to the conclusion that the degree of stability of hydrophobic colloids should decrease rapidly for temperatures above 80°C. Bridgman's measurements show that above 80°C. the free energy of water decreases only slightly with pressure. For pressures larger than 1000 kg. per cm.^{2} the energy increases at this temperature. It seems possible that the coagulation produced by heating of certain hydrophobic colloids (Pt) is a consequence of this effect.

The electrostrictive effect will also reduce the specific heat of colloids. This effect can be calculated with the method given by Zwicky (7) for electrolytes, but owing to the small number of colloidal particles this effect is too small to be measured.

The magnitude of the electrostrictive effect depends on the type of electric double layer, but it will exist even for a Helmholtz double layer.

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THE INFLUENCE OF SALTS ON THE POTENTIAL AND CHARGE OF INERT AND PROTEIN SURFACES[1]

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INTRODUCTION

At a previous Symposium (1) I have had the pleasure of reviewing the theory and experiments pertaining to the influence of size, shape, and conductance of microscopically visible particles on their electric mobilities. Since that time publications by Mooney (14), by Henry (13), and by Bikerman (10) have given further information which has increased our perception of the difficulties involved in correlating theory with experiment and which is suggestive of further experimentation. At this Symposium rather than review these advances it seems desirable to consider certain other developments in the treatment of the ζ-potential and the net charge density, σ, of the surfaces of large particles. If large particles in simple salt solutions are considered, much of the difficulty met in applying the theory of electrokinetics to small particles is avoided. It has been found that if the effects of *salts not reversing the sign of surface charge* are investigated in the light of modern electrolytic theory, certain simplifications result. These simplifications have consisted of a study of surfaces the charges of which depend primarily upon: (1) adsorption of ions (quartz, graphite, etc.); (2) ionization (amorphous proteins).

Although the complex arrangements existing at cell surfaces have, as yet, prevented our obtaining a picture suitable for all cells, in certain instances, the study of biological materials like blood cells, bacteria, and immune substances indicates that surfaces with properties somewhat similar to these two limiting types may be encountered (2). With the glimpses of possible arrangements obtained by means of the simpler chemical models to be presented here, it is hoped that an appreciation of the simpler models will justify our dissatisfaction with mere glimpses, and that further study of these models in connection with experiments on the biological materials themselves will enable us to find the constitution and properties of cell surfaces more comprehensible.

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

IONS

If the concentration of an aqueous solution of, say, potassium chloride is increased, the electric mobilities of the ions, K^+ and Cl^-, decrease. This typical decrease in the ionic electric mobility, v, is depicted in figure 1, where the change in v_{K^+} with the molar concentration, c, of potassium chloride is given. Note that the value of v_{K^+} is greatest at infinite dilution, and that the decrease in v_{K^+} can be approximately described by the equations of the Debye-Onsager theory. The case of ionic electric mobility of this type represents the limiting case of a very small particle, the charge of which remains constant while the electric mobility changes.

"INERT" SURFACES

In the cases of inert and of protein surfaces, and also, of biological systems, the problem becomes more general in nature, for we must deal with particles having diameters from the order of 1×10^{-7} cm. to those of the order of macroscopically visible particles including flat surfaces. The effects of salts on the electric mobility of microscopic and ultramicroscopic particles can be readily studied by the method of electrophoresis; or, analogously, streaming potentials and electroösmotic mobilities can be measured in tubes and diaphragms. These measurements lead to the calculation of the electrokinetic potential, ζ, by means of the equations for large particles (13, 14):

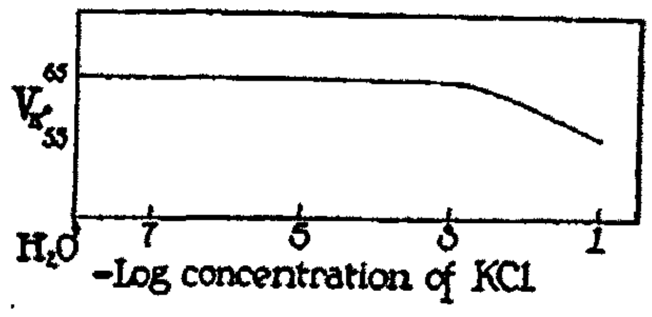

FIG. 1

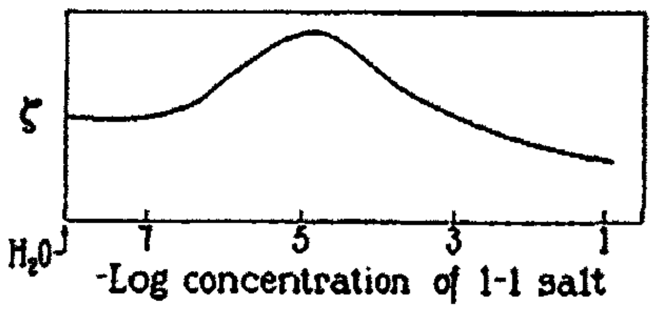

FIG. 2

FIG. 1. SCHEMA GIVING CHANGE IN THE ELECTRIC MOBILITY OF AN ION WITH INCREASING CONCENTRATION OF THE ELECTROLYTE

FIG. 2. TYPICAL CURVE SHOWING EFFECT ON ζ OF INCREASING THE CONCENTRATION OF A SIMPLE SALT

$$\zeta_E = \frac{4\pi\eta v}{D} \tag{1a}$$

$$\zeta_S = \frac{4\pi\eta}{D}\,\frac{E}{PR} \tag{1b}$$

$$\zeta_O = \frac{4\pi\eta u}{D} \tag{1c}$$

Here ζ_E, ζ_S, and ζ_O refer to values of the electrokinetic potential calculated from measurements of v, the electric mobility, of E, the streaming potential, and of u, the electroösmotic mobility, respectively; η is the coefficient of viscosity and D the dielectric constant of the medium; P is the pressure, and R is the specific resistance of the liquid in the tube or diaphragm. All units are C.G.S. electrostatic. For reasons stated elsewhere it is reasonable to assume that the values of D and η in the electric double layer approximate those in the bulk. When the radius of the particle is not large compared with the effective thickness of the electric double layer, the constant 4π in equations 1a to 1c must be modified (13, 14).

For the past two decades, quantitative measurements of the effect of salts on v, $\frac{E}{PR}$, and u have been studied on "inert" surfaces like glass, quartz, paraffin oil, collodion, cellulose, and graphite.[2] If we restrict our present discussion to salts not reversing the sign of surface charge, and calculate ζ by means of equations 1a to 1c as the mode of experimentation may determine, the shape of the ζ–c curve is usually that given by figure 2. This typical ζ–c curve on comparison with the v–c curve in figure 1 differs markedly from the typical v–c curve for ions. On the addition of salt, a maximum in the ζ–c curve (figure 2) is observed (3), usually at concentrations of the order $1 \times 10^{-5}\,M$. The ζ-potential $\left(\text{or } v,\ u, \text{ and } \frac{E}{PR}\right)$ then decreases in much the same way that simple ionic mobility decreases. How can we explain this curious type of curve? Theoretical consideration of this problem by Gouy (11), Stern (16), and Gyemant (12) indicated that the charging process of the surface must be considered. The charge of the simple ion K^+, as has been mentioned, remains constant as v_{K^+} decreases. This is by no means the case with "inert" surfaces. The net surface charge density, σ, changes as more ions are added to the solution (5, 6, 14, 15). In general, for an infinite plane surface, σ can be calculated by combining the Poisson and Boltzmann equations. The integrated equation for σ is, in systems consisting essentially of two ions,

$$\sigma = \sqrt{\frac{\mathbf{N}D\mathbf{k}T}{2\pi \times 1000}\, c_{1[2]}\, z_{1[2]} \left[\frac{1}{z_2}\left(e^{+z_2\frac{\mathbf{e}\zeta}{\mathbf{k}T}} - 1\right) + \frac{1}{z_1}\left(e^{-z_1\frac{\mathbf{e}\zeta}{\mathbf{k}T}} - 1\right)\right]} \quad (3)$$

where $\mathbf{N}$ is Avogadro's number, $\mathbf{k}$ Boltzmann's constant, c the molar concentration, e the base of the natural logarithm, $\mathbf{e}$ the electronic charge, z the valence, and T the absolute temperature. In case $Z_1 = -Z_2 = Z_3$ in aqueous media, equation 3 reduces to

$$\sigma = 2\sqrt{\frac{\mathbf{N}D\mathbf{k}T}{2\pi \times 1000}}\,\sqrt{c}\,\sin h\, z\,\frac{\mathbf{e}\zeta}{\mathbf{k}T}$$

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[2] References to these publications may be found in the citation, Abramson and Mueller, or in detail in Chapters VI, VII, and VIII of the writer's monograph (2).

or

$$\sigma = 2\alpha \sqrt{c} \sin h \frac{z\zeta}{2\beta} \tag{3a}$$

where $\alpha = 17{,}650$ and $\beta = 0.025$ volt at 18°C. Equations 3 and 3a give us a means of following changes in the net surface charge as the number of ions in the solution increases.

Keeping in mind the complex form of the ζ–c curve (figure 2), examine the σ–c curves (figures 3 to 8). It is important to bear in mind that values of σ given in these curves have been corrected for the original charge due to the ions in distilled water (7). In each case the total charge, σ_T, has first been calculated. This total charge is due both to the ions of the solvent and dissolved carbonic acid and to the ions of the added salt. If σ_W is that due to the ions of the solvent and carbonic acid alone, the charge due to the salt is evidently

$$\sigma_T - \sigma_W = \sigma$$

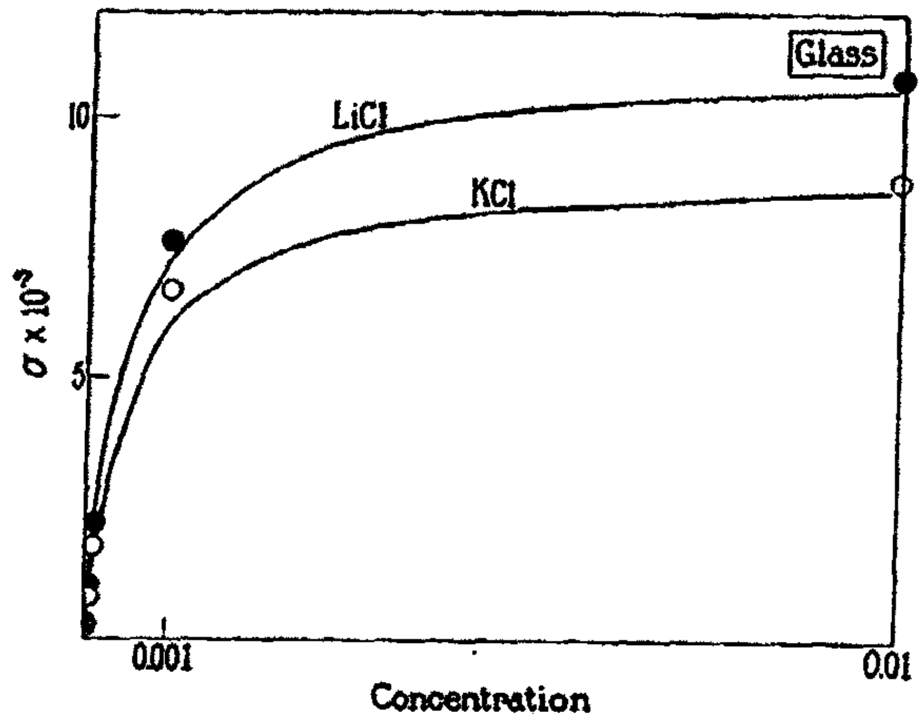

FIG. 3. THE EFFECT OF SALTS ON THE SURFACE DENSITY OF NET CHARGE ON GLASS

The points have been calculated by means of equation 3 from data of Furutani, Kurokochi, and Asoda. The smooth curves have been drawn according to the form of the Langmuir isotherm similar to equation 4.

In every example calculated from the data in the literature (5, 6) for surfaces of glass, paraffin oil, silica gel, collodion, graphite, and cellulose, irrespective of the nature of the material and irrespective of differences in the salts themselves, the type of curve obtained is the same. In each instance σ increases sharply and almost linearly at low concentrations with the charge density apparently reaching a limiting value at about $c =$

$0.001M$. The descending part of the ζ–c curve given in figure 2 has frequently been taken to represent a "discharge" of the surface or of particles, since aggregation frequently occurs in this concentration range.

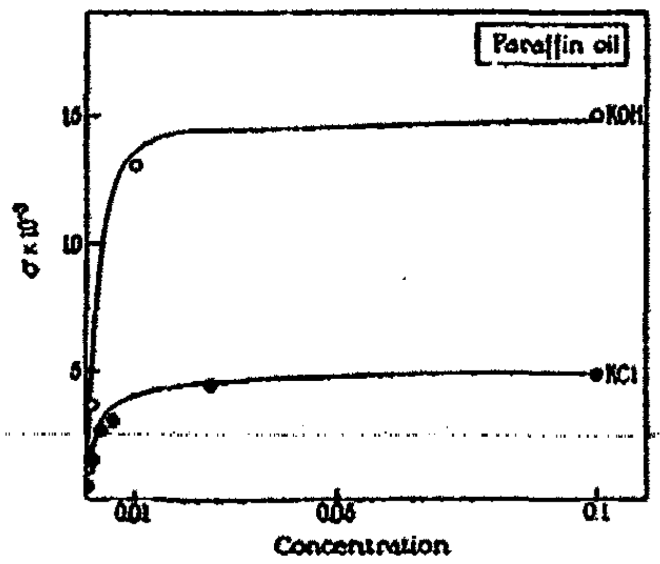

Fig. 4

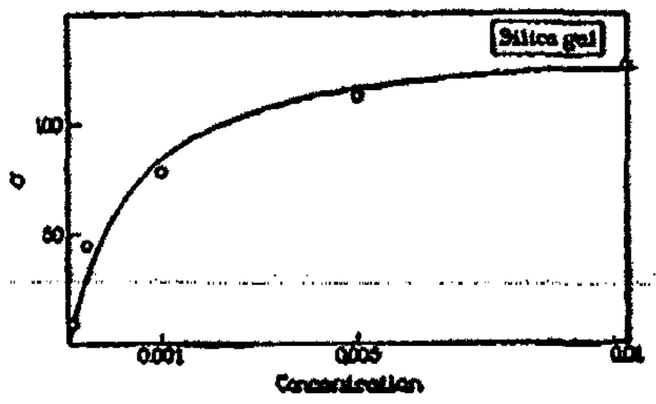

Fig. 5

Fig. 4. The Points on the σ–c Curve Have Been Calculated from Data of Ellis Published in 1911, and from Data of Mooney (1931)

The smooth curves have been calculated by means of equation 4

Fig. 5. The Effect of a Simple Salt on Silica Gel Calculated from Data of Glixelli and Wiertelak

The smooth curves are typical isotherms

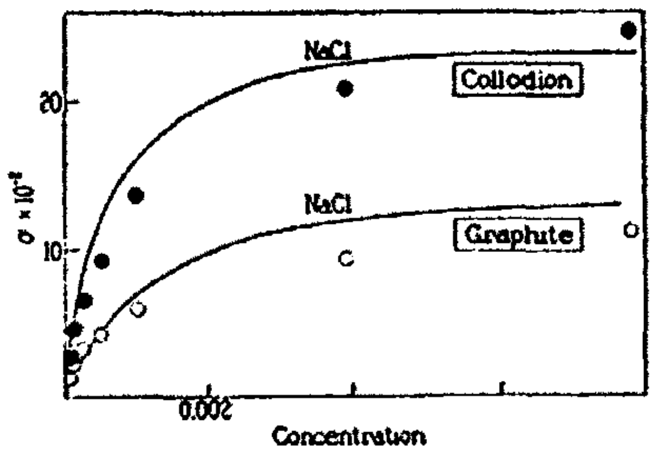

Fig. 6

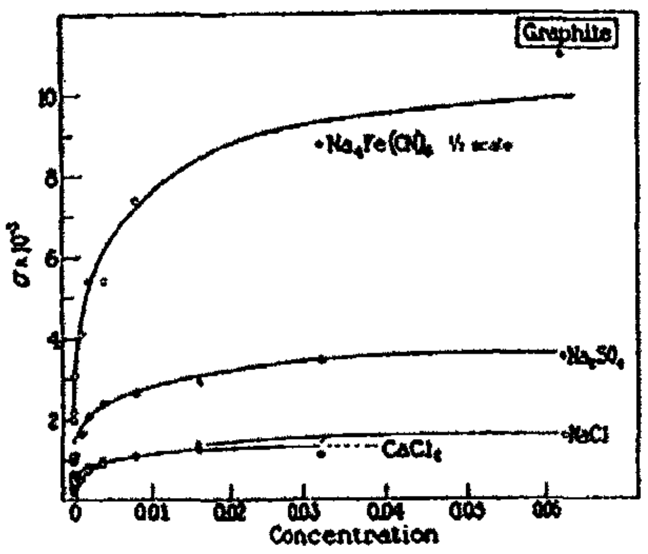

Fig. 7

Fig. 6. Similar to the Preceding Three Figures and Calculated from Data of Loeb

Fig. 7. The Effect of Salts not Reversing the Sign of Charge Calculated by Means of Equation 6a from Data of Loeb

Figures 3 to 8 demonstrate that, contrary to this notion, the addition of salt may actually be accompanied by an increase of the net charge even in the region of rapid coagulation. The complicated course of the ζ–c curve is due to the fact that ζ depends upon two variables, σ and κ (the "reciprocal thickness" of the diffuse ionic atmosphere), both of which depend on c.[3] We have here done what is tantamount to assuming the validity of the theory of the diffuse double layer to obtain the dependence of κ on c, permitting the calculation of σ (c).

σ and ζ presumably vary quite differently with c. As c increases $1/\kappa$ decreases. When c is small the increase in σ is more important, but as c increases the decrease in $1/\kappa$ becomes more important, flattening out the σ–c curve.

The reader will have noted that the form of all the σ–c curves bears a strong resemblance to the simple Langmuir adsorption isotherm. The smooth curves of figures 3, 4, 5 and 6 have actually been plotted by an equation of this form,

$$\sigma = \sigma_M \frac{Bc}{1 + Bc} \tag{4}$$

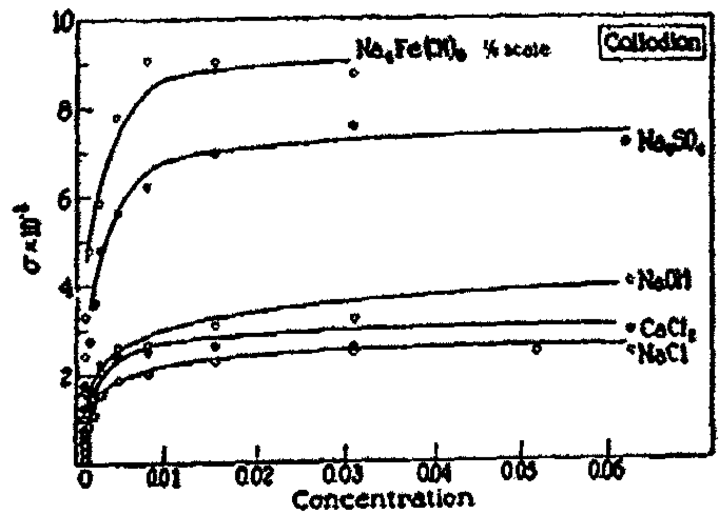

FIG. 8. SIMILAR TO FIGURE 7, CALCULATED FROM DATA OF LOEB

where $\sigma_M B$ is the initial slope of the σ–c curve and σ_M is equal to the limiting value of σ within the concentration range. The agreement is excellent and indicates that selective adsorption of the negative ion takes place. The curves for the different alkali halogens and alkaline earth halogens show fewer variations than the curves for potassium bromide, iodide, and chloride. Especially large values of the charge are reached for the sulfates and ferrocyanides. The data indicate that for glass, graphite, and

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[3] The value of κ is

$$\kappa = \sqrt{\frac{4\pi N e^2}{1000\, DkT}}\ \sqrt{\Sigma c_i z_i^2}$$

where N is Avogadro's number, e the electronic charge, k Boltzmann's constant, c the concentration in moles per liter, and z the valence. The quantity $\Sigma c_i z_i^2$ is equal to twice the ionic strength, μ, of Lewis.

collodion, the adsorption potential increases in the series

Cl^-, Br^-, I^-;
Li^+, Na^+, K^+, Rb^+, Cs^+;
Mg^{++}, Ba^{++}, Ca^{++};
I^-, $(SO_4)^=$, $[Fe(CN)_6]^{\equiv}$

and that in general for these surfaces the adsorption potentials of the positive ions are considerably smaller than those of the negative ions.

The initial slope of the σ–c curves leads to values of the adsorption potentials of the same order of magnitude as found for the adsorption of gases.

It is of interest to calculate (neglecting the adsorption of positive ions) the fraction of the area occupied by ions in connection with the limiting value of σ. To take the case of glass, $\sigma_M = 9000$ E.S.U., representing about 2×10^{13} ions per cm.^{2} If the area occupied by each ion is taken as 5×10^{-16} cm.^{2}, the limiting area occupied by the free negative is 0.01 cm.^{2} or 1 per cent of the surface. This is a rather higher value than that deduced by previous investigators, but is compatible with the type of adsorption postulated by Langmuir's simple theory of adsorption.

In a future communication we shall give results of calculations by means of equation 3 for the σ–c curve for non-symmetrical cases of polyvalent ions not reversing the sign of charge. Using the Debye approximation for surfaces where $\frac{e\zeta}{kT}$ is relatively small, we have obtained preliminary indications that the form of the curve is exactly the same as that obtained by the rigorous expression (equation 3) for uni-univalent salts. Some of the curves obtained by the approximate formula are given in figures 7 and 8 (graphite and collodion). Compare these curves with the σ–c curves for the same substances using the full equation. There is obviously no difference in the shape of the curves.

PROTEINS

The study of the effect of salts on the charge of protein surfaces is simplified by the fact that the net charge of protein molecules dissolved in simple mineral acids can be determined by a thermodynamic method. Thus in a protein-HCl solution, we have, for example,

$$(Cl^-)_{Pr} = (Cl^-)_{Total} - \frac{a_{Cl^-}}{\gamma_{Cl^-}}$$

where the subscript Pr refers to the ions bound by the protein, the parentheses represent concentrations, and a and γ are activity and activity coefficient, respectively. If n is the time average of the net charge of the protein molecule, the expression,

$$n = (\mathrm{H}^+)_{\mathrm{Pr}} - (\mathrm{Cl}^-)_{\mathrm{Pr}}$$

gives a simple means of determining the net charge. Evidently the net charge of proteins having known molecular weights can be very closely determined from suitable electrometric measurements by making certain assumptions in regard to the activity coefficients of the ions present in the solution.

It has been found that the changes in charge as determined by thermodynamic methods agree with the changes in charge calculated by means of the Debye approximation (8). That is, in solutions of the same ionic strength the electric mobility of the same protein at different hydrogen-ion activities is directly proportional to the number of hydrogen (hydroxyl) ions bound. The theoretical expression predicting this relationship is to be found in the Debye-Henry approximation for the potential at the surface, where, for particles the size of protein ions,

$$v = \frac{1}{6\pi} \frac{\zeta_B D}{\eta}, \qquad (\kappa r > 30) \tag{5}$$

and

$$\zeta = \frac{Q}{Dr} \frac{1}{(1 + \kappa r)} \tag{6}$$

and

$$Q = 4\pi r^2 \sigma \tag{6a}$$

Consider in the light of these equations the special case of a uni-univalent salt not shifting the isoelectric point (9). Since the charge of proteins seems to depend mainly on the pH in the absence of salts, at any given pH a certain number of hydrogen ions over a time average are bound to the protein molecule. Assume then that v depends only on (κ) if the pH is fixed. ζ_K, and consequently v, which is proportional to ζ_B, will depend only upon κ if all other terms are considered constant, giving

$$v = v(\kappa)_{\sigma_{\mathrm{pH}} = \mathrm{const.}} \tag{7}$$

By assuming that σ remains constant we do not by any means imply that no change in σ occurs incidental to changes in κ. It is merely postulated that the change in v with σ, due to the variation of κ, is very small compared with the change in v due to explicit variation of κ. Addition of salt under these conditions, then, should cause only a diminution in v without a maximum in the curve. We have used our empirical form of equation 6

$$\zeta = \frac{Q}{Dr}\frac{1}{(2.4 + \kappa r)} \tag{8}$$

or

$$\zeta = \frac{Q}{Dr}\frac{1}{f(\kappa r)} \tag{8a}$$

to plot the theoretical form of the v–c curves in figure 9, by evaluating $f(\kappa r)$ for $r = 4 \times 10^{-7}$ cm. and various values of v for gelatin. Note the following points of interest in these curves.

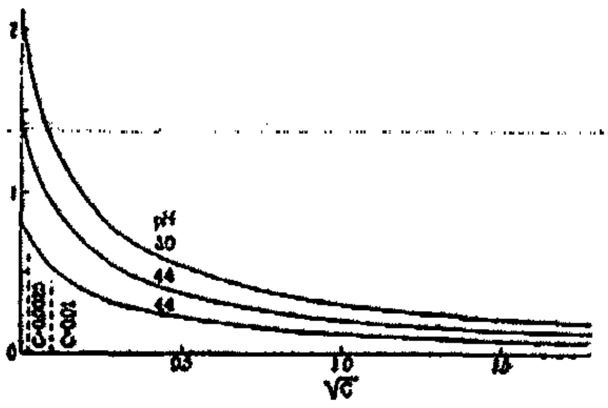


FIG. 9. THEORETICAL v–c CURVES FOR GELATIN AT DIFFERENT VALUES OF pH

The two short vertical dotted lines at the lower left corner show the limits of extrapolation when the pH is sufficiently low to have appreciable amounts of acid present.

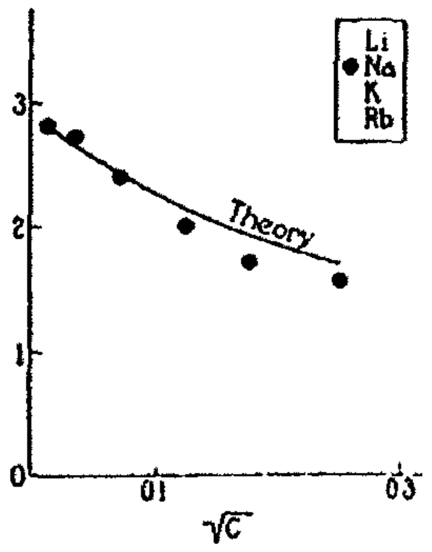


FIG. 10. DATA OF LOEB FOR PARTICLES OF DENATURED EGG ALBUMIN IN 0.0002 *M* SODIUM HYDROXIDE

The smooth curve is calculated by means of the theory here proposed

The curves should in reality not cut the ordinate at $c = 0$, for, in order to fix Q, a certain amount of acid must be present even though the concentration of protein and of salt is vanishingly small. In other words, v is always measured in the presence of a finite value of κ, which is given for strong acids by the concentration, and not by the mean activity, of the acid. The dotted lines indicate, for example, the limiting position of the ordinate for $c = 0.0025$ *M* and $c = 0.01$ *M*.

In more concentrated salt solutions the validity of equation 6 decreases; however, the curves indicate that v should be, as in the case of ions, still appreciable even in 4 M salt solutions. Technical difficulties at present prevent measurements of v in salts of this concentration, but values of the proper magnitude have been observed by Hitchcock in $M/25$ acetate buffers for gelatin and by the author for serum proteins in $M/7$ salt solutions. It would be most desirable to devise methods to discover if the available form of the theory is confirmed, in the prediction $v > 0$, by observations in concentrated salt solutions.

In figure 10 are values of v for denatured egg albumin particles in $M/5000$ sodium hydroxide. At this pH, in the absence of salt, v is rather high, 2.8μ per second. The smooth curve is the theoretical curve calculated by means of equation 8, taking $r = 2.2 \times 10^{-7}$ cm. and making the usual assumptions in regard to η and D.

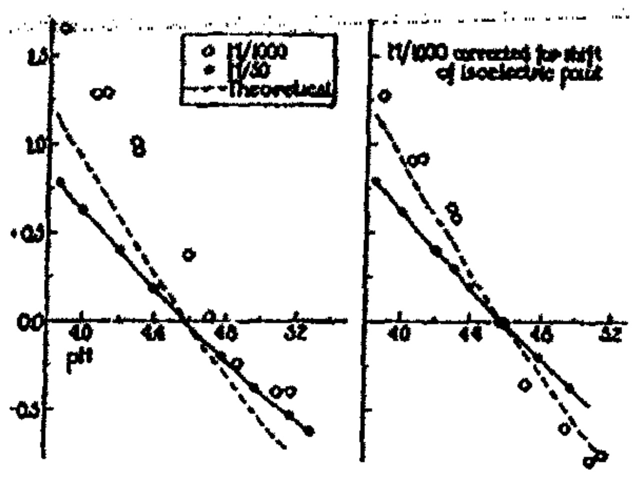


FIG. 11

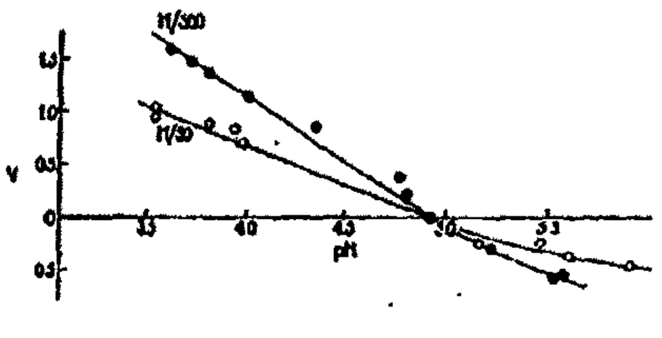


FIG. 12

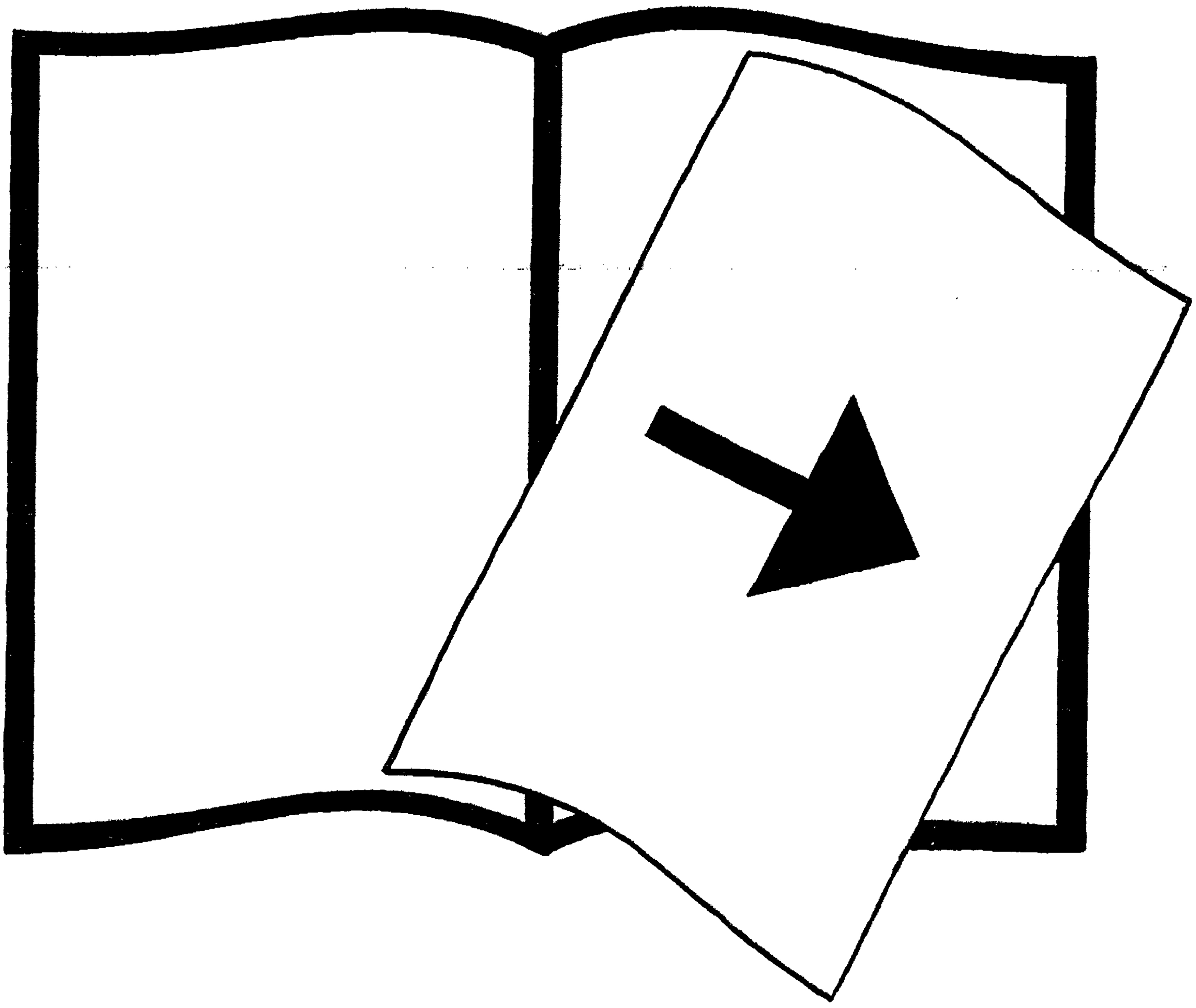
FIG. 11. THE EFFECT OF THE CONCENTRATION OF ACETATE BUFFERS ON THE MAGNITUDE OF THE ELECTRIC MOBILITY

By correcting for the shift in the isoelectric point the effect of diluting the buffer is predicted.

FIG. 12. THE ELECTROPHORESIS OF GELATIN-COATED QUARTZ PARTICLES

The decrease in electrophoretic mobility is approximately predicted by the theory here proposed.

It is noteworthy that the courses of the theoretical and experimental curves are almost identical. Figure 11 gives the results of similar experiments and calculations for egg albumin in acetate buffers, a correction having been made for the shift in the isoelectric point with variation in c. Comparable results were obtained for egg albumin in hydrochloric acid and for gelatin in acetate buffers (figure 12). To summarize: by assuming that the electric charge of proteins is primarily determined by the hydrogen-ion activity of the medium and by making corrections when necessary for shift of the isoelectric point, it is possible to derive a simple relationship between v and the concentration of uni-univalent electrolytes. This relationship, namely, that v depends upon κ in a way which indicates



PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS. IX

SOME BINARY FREEZING POINT DIAGRAMS AND A STUDY OF THEIR IDEALITY

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Received October 8, 1934

It was recently pointed out (16) that the errors inherent in the usual Beckmann method of determining binary freezing point diagrams may be very considerable, causing a shift in the eutectic temperature and composition and in some cases causing false indications of compound formation. For the present investigation a number of systems which are reported in the literature as showing compound formation were reconstructed, using more recent and more reliable freezing point methods, with the added purpose of making a study of the degree of deviation from the ideal freezing point laws. The heats of fusion of four of the compounds involved were also experimentally determined.

PURIFICATION OF MATERIALS

In each case the compound was finally recrystallized, using a centrifugal filtration tube (13), until the sample gave cooling curves indicating suitable purity (1).

Eastman Kodak Co. benzamide was recrystallized from water four times and dried at 110°C. for two and one-half hours. *m*-Nitrophenol, made from *m*-nitroaniline, was supplied to us by Professor John Donleavy; it was fractionally distilled at 4 mm. pressure and then recrystallized from benzene. Acenaphthene, supplied to us by Dr. Lorenz P. Hansen, was vacuum sublimed, using a plug of glass wool to prevent particles from being carried into the sublimate mechanically; it was then recrystallized from alcohol. Kahlbaum's β-naphthylamine after fractional distillation at 12 mm. pressure proved to be suitably pure.[2] The *m*-dinitrobenzene used was purified as described previously (14).

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[2] The final sample melted to a water-white liquid which gradually developed a pink coloration, probably due to a slight oxidation. A small sample was heated in an open tube in a Thelco oven at 120°C. for twenty hours. Although the liquid now had such a deep red color that it was practically opaque, its freezing point was only 0.14°C. lower than that of the pure product. Since this treatment was much more drastic than would be undergone by any freezing point sample, it was obvious that exclusion of air was unnecessary.

FREEZING POINT METHODS AND RESULTS

The freezing point measurements were made in part by the method and apparatus already described (15) and in part by the visual method of Johnston and Jones (5). The data obtained for three binary systems are given in table 1.

DISCUSSION OF FREEZING POINT DATA

A comparison of these results with those in the literature brings out the fact that binary freezing point data obtained by means of the Beckmann method are likely to be very much in error. The values here reported are in some cases as much as 10°C. above those reported by the previous authors. That the error is also partly due to the presence of impurities in the original samples is shown by the fact that the freezing points reported for the supposedly pure substances are often too low.

The system benzamide–*m*-nitrophenol affords a good example of a system in which the errors in the freezing point data caused a simple eutectic system to be mistaken for a case showing compound formation (8). There is actually only a single eutectic point, having the composition 56.5 mole per cent of *m*-nitrophenol and the freezing point 42.1°C. The results of Puschin and Rikovski (12)[3] for this system show fair agreement with ours, but they report their freezing points only to the nearest 0.5°C. and their eutectic halts to the nearest 1.0°C. Their diagram, which is based on melting point as well as freezing point measurements, falls above ours on the benzamide side, 0.8°C. higher for the pure substance and about 1.5°C. higher for the 70 mole per cent mixture. On the other hand, their eutectic temperature lies about 1°C. below ours. In order to verify our curve a sample containing 70.0 mole per cent of benzamide was agitated in a thermostat at 100.5°C., at which temperature it melted completely. Another sample containing 48.51 mole per cent of benzamide melted completely by the same method when the thermostat was at 57.2°C., but not when it was kept at 57.0°C. for fifteen minutes.

The diagram for the system acenaphthene–*m*-dinitrobenzene shows the

[3] In a previous paper (14) the binary freezing point data for the system naphthalene–*m*-dinitrobenzene were reported to show that Puschin's (11) supposed correction of the diagram of Kremann (6) was entirely incorrect. Although Puschin has evidently not seen our paper he has now (12) repeated the determinations on that part of the diagram which we called in question and he now agrees that a 1:1 compound does exist, but he gives 50.5°C. for the freezing point of the compound, which is 0.6°C. lower than our value. That there must still be a slight error in his results here is shown by the fact that the freezing point of his 1:1 compound is lowered by adding naphthalene but is not lowered by adding *m*-dinitrobenzene, so that there is no eutectic on that side of the 50:50 composition, but a "transition point." The questionability of such freezing point behavior has been pointed out by Kremann (7).

formation of a stable 1:1 compound freezing at 71.9°C. with two eutectics, 68.7°C. and 66.5°C., at the compositions 36 and 68 mole per cent *m*-dinitrobenzene, respectively. The agreement of previous authors (3, 10) with our results is rather erratic. Most of their points fall below ours, but a few points on the acenaphthene branch and Giua's (3) values in the region of compound formation show good agreement. The freezing point reported by Giua for pure acenaphthene, 94.5°C., must certainly be in error, since our value, 93.3°C., was obtained from cooling curves which showed our sample to be amply pure.

TABLE 1

Binary freezing point data

SYSTEM BENZAMIDE-*m*-NITROPHENOL		SYSTEM ACENAPHTHENE-*m*-DINITROBENZENE		SYSTEM β-NAPHTHYLAMINE-*m*-DINITROBENZENE	
Mole per cent of benzamide	Freezing point °C.	Mole per cent of acenaphthene	Freezing point °C.	Mole per cent of β-naphthylamine *	Freezing point °C.
100.0	127.2	100.0	93.3	100.0	109.5
90.6	120.5	94.5	90.5*	57.4	70.6 (55.0*c*)
70.7	101.1	89.2	87.5*	36.5	58.5 (53.5*c*)
58.1	80.1*	85.0	84.9*	29.7	66.4
56.3	74.5	83.8	84.3*	0.0	90.1
53.9	66.7	81.4	82.8*		
51.0	63.7*	73.4	78.0 {(68.6*c*) (68.7*h*)		
46.7	51.7*	72.4	76.5*		
44.7	44.8*	67.3	72.6* {(68.7*c*) (68.7*h*)		
		(64)	68.7		
44.2	—— (42.2*h*)†	61.6	69.9*		
43.7	42.3*	54.9	71.6*		
(43.5)	42.1				
43.3	—— (42.1*h*)	50.0	71.9		
40.6	48.9*	34.9	68.4*(66.7*h*)		
		(32)	66.5		
40.0	50.3*	28.0	70.2*(66.5*c*)		
35.5	58.4	26.3	{71.8(66.4, 66.3*c*) 71.7*(66.5*h*)		
34.0	60.4*	17.5	78.4		
19.4	81.2	00.0	90.1		
00.0	96.8				

* By visual method.

† The temperatures in parenthesis are the temperatures of the eutectic halts. The letters *h* and *c* designate whether heating or cooling curves, respectively, were employed to determine the eutectic temperature. The percentages in parentheses are the estimated eutectic compositions.

Only three binary freezing points were determined for the system β-naphthylamine–*m*-dinitrobenzene. Our results show that the diagram reported by Kremann and Grasser (9) is essentially correct down to about 65°C., although their sample of β-naphthylamine had a freezing point 0.5°C. lower than ours. Our 58.5°C. point, however, is a little more than a degree higher than their values, and the eutectic halts which we obtained in the heating curves of the samples on the β-naphthylamine and the *m*-dinitrobenzene sides of the diagram were 55.0°C. and 53.5°C. as against their 53.3°C. and 51.8°C., respectively. The fact that there are two eutectics is additional proof that a compound forms, as Kremann and Grasser claim. There seems to be no basis for the statement (4) that the compound has an incongruent melting point.

TABLE 2

Heat content data for liquid and solid states

STATE	NO. OF OBSERVATIONS	TEMPERATURE RANGE °C.	a	b	c	ΔH AT t_f CALORIES PER MOLE
m-Nitrophenol						
Solid	5	74	−795	34.63	0.0680	5100
Liquid	5	45	2954	49.38	0.0581	
Benzamide						
Solid	8	105	−652	27.17	0.1113	4900
Liquid	5	40	2323	46.83	0.0765	
Acenaphthene						
Solid	7	71	−925	40.16	0.0852	4950
Liquid	6	50	2898	55.81	0.0447	
β-Naphthylamine						
Solid	5	88	−880	37.71	0.1036	5250
Liquid	4	50	3616	41.67	0.1290	

THE HEATS OF FUSION

Direct calorimetric measurements of the differences between the heat contents of the liquid and solid forms of *m*-nitrophenol, benzamide, acenaphthene, and β-naphthylamine and the solid forms at 22°C. were made by the method described by Andrews, Lynn, and Johnston (2). Following their usage the heat content of the solid and of the liquid have been expressed by empirical equations, valid over a short temperature range in the neighborhood of the melting point, of the form $H = a + bt + ct^2$.

In this equation H is expressed in gram-calories per mole at $t°$, the heat content of the solid at 22°C. being taken as zero. The value of H for the liquid minus that for the solid is the heat of fusion, ΔH. For *m*-nitrophenol it is $\Delta H = 3748 + 14.76t - 0.0100t^2$; for acenaphthene it is $\Delta H = 3823 + 15.65t - 0.0404t^2$; for benzamide it is $\Delta H = 2975 + 19.66t - 0.0348t^2$;

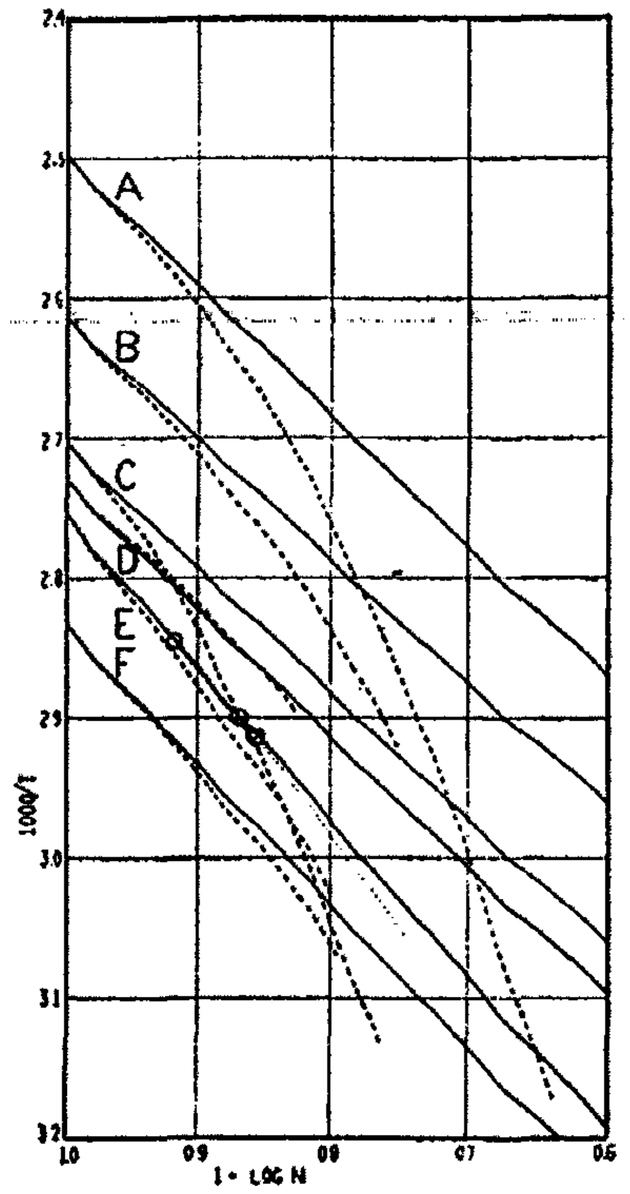

FIG. 1. PLOT OF $1000/T$ AGAINST $1 + \log N$ FOR THE BINARY SYSTEMS AC, BE, DE, AND FE

A = benzamide; B = β-naphthylamine; C = *m*-nitrophenol; D = acenaphthene; E = *m*-dinitrobenzene; F = naphthalene. The full lines = ideal curves; the broken lines = experimental data. In curve A the second component was *m*-nitrophenol; in B, *m*-dinitrobenzene; in C, benzamide; in D, *m*-dinitrobenzene; in E ----, β-naphthylamine; in E ....; naphthalene; in E ○○○○, acenaphthene; in F, *m*-dinitrobenzene.

and for β-naphthylamine it is $\Delta H = 4496 + 3.96t + 0.0254t^2$. The values of ΔH calculated at the freezing point, t_f, are given in table 2.

DISCUSSION

The above data and those for the system naphthalene-*m*-dinitrobenzene (14) have been plotted in figure 1 to show how far the freezing point curves deviate from ideal behavior. The heavy straight lines represent the changes in $1000/T$ with $1 + \log N$ in case the ideal freezing point relationship

$$\frac{d \ln N}{dT} = \frac{\Delta H}{RT^2}$$

holds. In this equation, T is the freezing point in degrees Absolute of a sample of the composition N, expressed in terms of the mole fraction of the pure component crystallizing out at that temperature. ΔH, the heat of fusion of that component, is assumed to be constant[4] and equal to the calorimetrically determined values as given in table 2 and previously (2). The broken lines in figure 1 represent the experimental freezing point data for the systems in question. In all cases N was calculated without assuming any compound formation. The values for the compound region of the diagrams are of course not considered.

An examination of figure 1 reveals the very interesting but rather paradoxical fact that for the four binary systems under consideration the greatest deviation from ideality occurs in the case of that one for which the diagram shows no compound formation, viz., the system *m*-nitrophenol–benzamide. On the other hand, practical ideality is displayed by the system acenaphthene–*m*-dinitrobenzene, in which it is definitely known from the freezing point diagram that a stable 1:1 compound forms. The cause of these anomalies cannot be given definitely, but the *m*-nitrophenol–benzamide case could be explained by assuming that a compound does form but that solubility relations are such that it does not crystallize out.[5]

In both of the other systems the deviation is such as would be normally expected in the case of compound formation. In all four binary systems the extent of deviation can be seen to be roughly the same for the two branches of the diagram.

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[4] Since the expression for ΔH in terms of T is not applicable over the wide range in question.

[5] If we assume ideal freezing point lowering by the compound, the proportion present at the eutectic point can be calculated from the deviation on each side of the diagram. Thus a mixture made from 0.433 mole of benzamide and 0.567 mole of *m*-nitrophenol could be calculated from the ideal benzamide curve to have the actual composition 0.133 mole of benzamide, 0.267 mole of *m*-nitrophenol, and 0.300 mole of 1:1 compound. This shows very poor agreement, however, with the corresponding results for the same point calculated from the ideal *m*-nitrophenol curve, viz., 0.052, 0.186, and 0.381, respectively.

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FERRIC OXIDE AND AQUEOUS SULFURIC ACID AT 25°C.

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INTRODUCTION

In a series of papers by Recoura (7), another series by Scharizer (8), and in papers by Niggli and Faesy (5), Grimm and Ramdohr (3), Weinland and Ensgraber (10), and by others, there are described many compounds containing varying proportions of ferric oxide, sulfur trioxide, and water. That all are *stable* solids under the conditions described is more than doubtful, but any of them may have been actually realized. Metastable equilibria are common and persistent in the system, Fe_2O_3–SO_3–H_2O, where diffusion is slow, liquids viscous, crystallizing forces weak, supersaturations common, and colloidal dispersion frequent.

Cameron and Robinson (2), Wirth and Bakke (11), and Appleby and Wilkes (1) found that at 25°C. the solubility of ferric oxide in aqueous solutions increased steadily with increasing concentration of sulfuric acid to a well-defined maximum. As to the concentrations at this maximum, they disagree among themselves, with earlier determinations by Scharizer, and with those to be given presently. All observers found the solid phases in contact with the liquid solutions containing less than 26.4 per cent sulfur trioxide varied continuously in content of ferric oxide and sulfur trioxide. Cameron and Robinson and Appleby and Wilkes regarded the solids as members of a series of solid solutions, while Wirth and Bakke thought they formed two series with an ill-defined transition point. They avoided defining them as solid solutions. Similar results were obtained at 18°C. by Appleby and Wilkes. Posniak and Merwin (6), who worked on the system at higher temperatures but *not* at 25°C., objected to the conclusion that these solids form a series of solid solutions, and regarded them as adsorption complexes.

With increasing concentration of sulfuric acid beyond that at which the ferric oxide is most soluble, the solubility of the ferric oxide decreases, at first very rapidly, then more and more slowly. At very high concentrations of sulfuric acid, there is no detectable iron in the liquid phase and apparently no water in the solid. There are several transition points with change in the composition of the solid in contact with the liquid solutions. So much is agreed upon by all observers. There is, however, very wide divergence among these observers regarding position of the solubility curves and transition points and the composition of the corresponding solid phases.

EXPERIMENTAL WORK

Preparation of residues

It is quite impracticable to make complete separations of solids from their corresponding mother liquors in this system; hence the necessity of using indirect methods to determine the composition of the solids. The "telltale" method of van Bijlert (9) was discarded, since a suitable telltale was not found. The method of "residues" was employed by Wirth and Bakke, plotting their results on the right-angled isosceles triangle and by Appleby and Wilkes, plotting on the 60°-angled isosceles triangle (the conventional equilateral triangle). Owing to the character of the tie line fans or fasceaus in this system, the right-angled isosceles triangle is preferable in the interest of clarity; also, statement of the results in grams rather than in reacting weights. Undoubtedly, a principal factor making for confusion in the work of previous investigators was their inability to separate the mother liquors from the residues with any approach to completeness, with consequent uncertainties in the directions of the tie lines. In this investigation the solutions were filtered through multiple paper mats under several hundred pounds pressure. The residues thus obtained were dry to the touch and friable, though yet containing appreciable amounts of adhering mother liquor.

Results obtained in a study of six series of solutions

Series 0. Six series of solutions were studied (see data in table 1). In series 0, the bottles containing the suspensions were heated in a water bath until the contents were completely liquefied. On cooling, they were continuously agitated in a large constant temperature bath. From time to time during a period of about nine months, they were removed from the bath to transfer some of the solid from one bottle to another for a thorough re-seeding of each. Finally they remained in the bath four to five months before the contents were analyzed.

The plot shows the liquid solution data falling on or very close to a straight line, and the tie lines between these and the corresponding residue data form a spreading fan, indicating a series of solid solutions with ferric oxide (probably hydrated) as one limiting member, and, as the other limiting member, a compound approaching in composition the definite solid ($Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$) appearing at a concentration of sulfuric acid higher than that at which the ferric oxide is most soluble.

Series A. The solid employed in preparing series A was made by oxidizing with nitric acid a solution of ferrous sulfate and ferric chloride in equally

TABLE 1

Composition of solutions, corresponding residues, and solid phases in the system Fe_2O_3–SO_3–H_2O at 25°C.

SERIES	SOLUTIONS		RESIDUES		SOLID PHASES
	SO_3	Fe_2O_3	SO_3	Fe_2O_3	
	per cent	*per cent*	*per cent*	*per cent*	
0	9.59	7.04	16.70	47.20	Solid solution
	23.38	18.76	29.04	49.36	Solid solution
	25.45	20.04	31.56	43.27	Solid solution
	25.62	20.19	31.61	45.31	Solid solution
	26.37	20.45	35.53	30.37	Solid solution
	27.01	18.32	36.31	28.55	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
A	12.55	9.86	11.59	71.73	Solid solution
	18.51	13.87	10.46	82.54	Solid solution
	23.96	17.19	7.77	79.89	Solid solution
	28.95	17.95	4.54	83.80	Solid solution
B	12.98	10.19	15.55	51.94	Solid solution
	19.21	15.52	25.82	40.98	Solid solution
	25.22	19.08	26.15	41.27	Solid solution
C	3.55	2.45	7.23	65.25	Solid solution
	6.83	4.86	7.81	63.37	Solid solution
	13.79	9.91	29.85	55.56	Solid solution
D	8.02	4.76	2.67	81.60	
	18.17	12.33	5.66	77.57	
	24.67	16.67	5.02	67.59	
	30.07	18.98	12.49	77.88	
	26.4	*20.5*			Solid solution and $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
E	26.71	19.06			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	26.60	18.76	36.35	27.95	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	26.85	18.21			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	27.11	17.70	36.92	27.61	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	27.45	17.31			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	27.45	17.16			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.00	16.70	36.93	28.01	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.20	*16.4*			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$ and $Fe_3O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.88	15.94	37.74	28.67	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.95	15.40	37.01	27.52	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	29.15	15.10	38.15	27.55	$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$
	28.28	14.49	39.26	25.06	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.30	13.92	38.39	23.90	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.88	12.18	38.84	23.85	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	28.80	11.90	38.56	23.88	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$

TABLE 1—*Concluded*

SERIES	SOLUTIONS		RESIDUES		SOLID PHASES
	SO_3	Fe_2O_3	SO_3	Fe_2O_3	
	per cent	*per cent*	*per cent*	*per cent*	
E	28.92	11.06	38.78	23.53	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	29.00	10.87	39.66	24.63	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	29.64	9.31	39.64	24.31	$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$
	32.1	*7.2*			$Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$ and $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	32.06	6.96	47.03	22.40	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	32.10	6.82	48.38	23.39	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	32.08	4.70	44.09	23.26	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
			44.25	23.58	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	34.34	2.03	46.76	20.35	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	38.72	0.26	47.35	19.13	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	45.28	0.06	48.14	14.40	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	51.40	0.03			$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	56.79	0.03			$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	30.3	*14.7* (Metastable)			$Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$ and $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	30.96	10.34	41.50	25.62	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.20	9.55	41.75	25.78	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.47	8.95	42.62	26.43	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.54	8.94	42.26	26.32	$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$
	31.8	*8.4* (Metastable)			$Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$ and $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	31.88	8.11	47.79	23.99	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	31.83	7.97	45.76	24.22	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
	31.86	7.76	46.46	22.33	$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$

molar quantities, drying, and washing the residue to remove chlorine and nitric acid. It was a grayish tan colored product, containing 30.60 per cent sulfur trioxide and 58.45 per cent ferric oxide. The suspensions were agitated at constant temperature for four months, the liquids analyzed, and agitation resumed for three months, and the liquids again analyzed. No significant change in the composition of the liquid phases having taken place, the corresponding residues were prepared and analyzed. The data for the two liquid solutions of lowest concentration fall on the right line plotted from series 0. The data for the solution of next higher concentration fall somewhat below the line, and the data for the solution of highest concentration fall in another field. The tie lines all slant towards the axis of ferric oxide composition. It appears that this series had not come to final equilibrium. For the sake of clarity the data are not shown in the accompanying chart.

Series B. The solid used in preparing series B was made by bringing into solution with hydrochloric acid a mixture of ferric oxide and ferric sulfate in the proportion of 2 moles to 1, slowly evaporating to dryness, and washing the residue until free from chlorides. It was light yellowish tan in color and contained 26.89 per cent sulfur trioxide and 54.95 per cent ferric oxide. The solutions were analyzed after four months and again after seven months agitation at constant temperature. No significant changes having taken place, the residues were prepared and analyzed. The data for the liquids fall on the right line found from series 0 and the corresponding tie lines form a spreading fan.

Series C. The solid used in preparing this series was obtained by extracting some of the solid prepared for series B with dilute ammonia water and washing the residue free of ammonia. It was dark red in color and contained about 1 per cent sulfur trioxide and 94.2 per cent ferric oxide. The series was agitated for seven months at constant temperature, and the liquids analyzed at the end of four months and seven months. No significant changes having taken place meanwhile, the residues were prepared and analyzed. The results harmonized with those obtained from series 0 and B.

Series D. In preparing this series, a standard brand of analyzed ferric oxide was employed. It was blood-red in color. The series was agitated for seven months. The data for the liquids give points somewhat below the right line plotted from the results obtained from series 0, B, and C, the discrepancy being the greater the greater the concentration. The tie lines for solution and residues are important. They all slope towards the axis of ferric oxide, and show the solid phase was essentially ferric oxide in each case, slowly absorbing sulfur trioxide and water. They do not converge to a point nor give any evidence of the formation of a definite compound.

Series E.[1] For this series several solids were prepared, hydrated ferric oxides and basic ferric sulfates. They were prepared from aqueous solutions, and great care taken to remove contaminations and to avoid overheating. The suspensions were agitated continuously at 25°C. for seventeen months, then allowed to settle for two months, analyses of liquids and residues being made during the latter period. A plot of the data for liquids and corresponding residues shows four solubility curves were realized: one, corresponding to stable conditions only; one, to metastable conditions only; and the other two partly to stable and partly to metastable conditions. Transition points were found with approximate accuracy by interpolation. Attempts to realize them experimentally are impracticable.

The fasceau or bundle of tie lines in three cases is too narrow to permit a definite convergence, so the composition of the solid phase in equilibrium

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[1] The analytical data for series E are taken from a dissertation submitted by E. W. Constable in May, 1934, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The authors of this paper are responsible for the interpretation of the data.

with the several solubility curves was determined in another way. Since, in any group of points representing residues, the individual points lie close together, it may be assumed that the ratio of ferric oxide to sulfur trioxide in them approximates that in the corresponding solid. Actually, the residues all contained a slight excess of acid, due to adhering mother liquor. A straight line through the origin and at the angle whose tangent corresponds to this ratio, must pass through the point corresponding to the composition of the solid phase. This point must lie within the limits of the fasceau and must also correspond to a rational formula. The procedure proved to be easy and satisfactory in application.

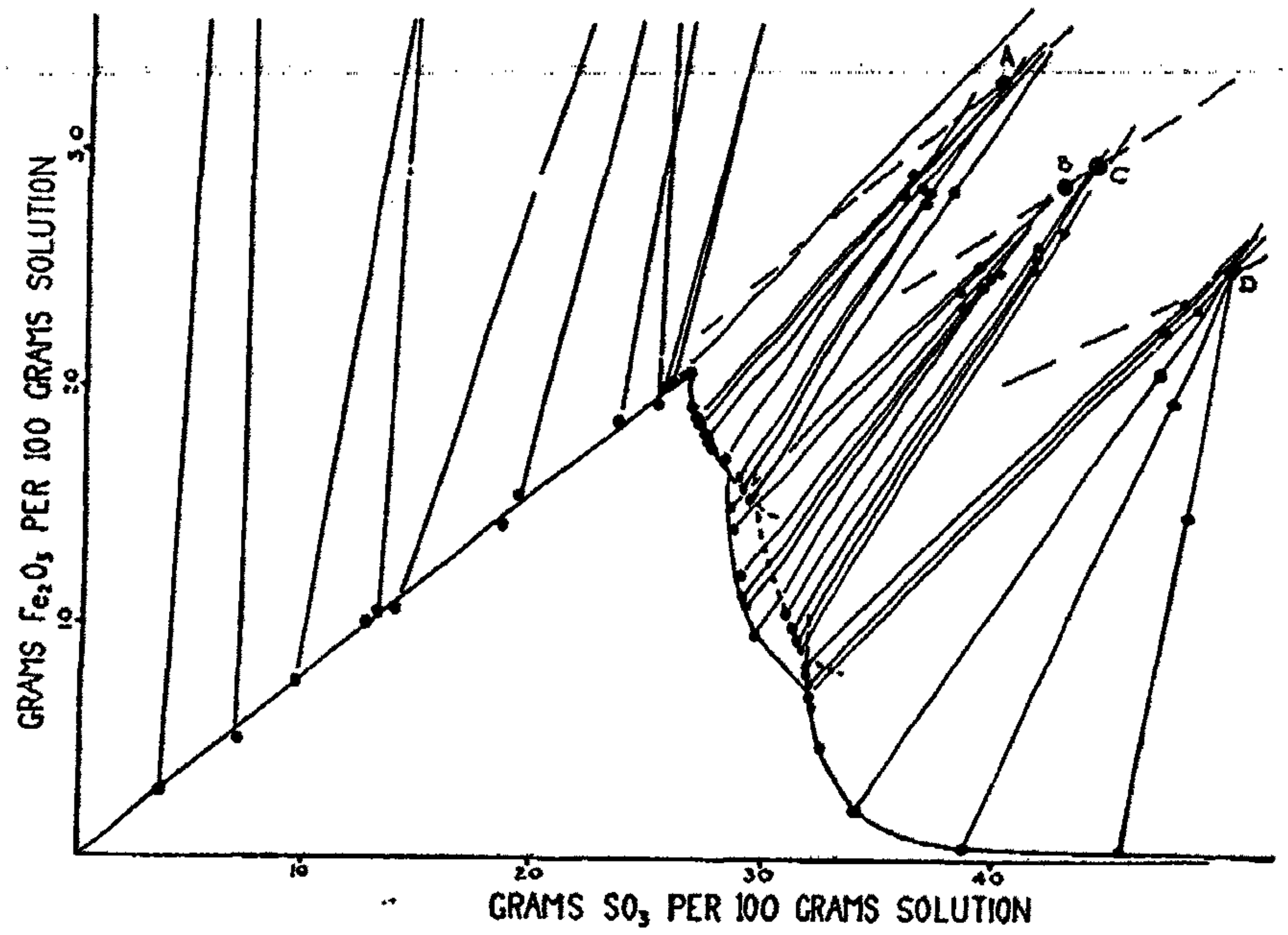

FIG. 1. SOLUBILITY CURVES, RESIDUES, TIE LINES, AND SOLID PHASES IN THE SYSTEM FERRIC OXIDE–AQUEOUS SULFURIC ACID AT 25°C.

A, $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$. B, $Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$. C, $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$. D, $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$.

Specific gravity and viscosity of solutions

To investigate further the possible existence of a transition point in the solubility curve corresponding to the series of solid solutions, specific gravity determinations of the liquid phases were made with a Westphal balance. The results are assembled in table 2. When plotted against content of sulfur trioxide or ferric oxide, the points corresponding to the solutions presumed to have reached equilibrium fall on a smooth curve passing through the origin. A curve passing through the most possible of all points does not indicate any intermediate transition point.

For the same purpose viscosities were estimated by timing the rate of flow of the solutions through a capillary and comparing with the rate of flow of water through the same capillary. These results are also assembled in table 2. When plotted they fall on a smooth curve, nor is there any indication of an intermediate transition point. There is some uncertainty attaching to the higher viscosities, a solution from which the dispersed solid has long settled showing a slightly higher viscosity than one which has recently been vigorously agitated with the suspension.

Colloidal dispersions

Abnormally high viscosities, with other observations, suggested that ferric oxide, or substances corresponding to basic sulfate formulas, might be dispersed as sols. Therefore solutions in contact with their respective solid phases were set aside in a quiet place in the laboratory for a year. Probably the temperature variation was within the limits 25° to 30°C.

TABLE 2

Comparison of specific gravity and coefficient of viscosity with sulfur trioxide and ferric oxide content of aqueous solutions of ferric hydrates at 25°C.

PER CENT OF		SPECIFIC GRAVITY	VISCOSITY COEFFICIENT	PER CENT OF		SPECIFIC GRAVITY	VISCOSITY COEFFICIENT
SO_3	Fe_2O_3			SO_3	Fe_2O_3		
3.55	2.45	1.052	0.0095	18.51	13.87	1.364	0.0206
6.83	4.86	1.104	0.0101	19.21	15.52	1.397	0.0241
8.02	4.76	1.118	0.0101	23.96	17.19	1.500	0.0501
12.55	9.86	1.229	0.0127	24.67	16.67	1.471	0.0406
12.98	10.19	1.242	0.0129	25.22	19.08	1.550	0.0756
13.79	9.91	1.243	0.0136	28.95	17.95	1.590	0.0930
18.17	12.33	1.328	0.0187				

In no case was the solution completely empty, optically, although the transmitted light beam showed but little solid to be present. Microscopic examination of these solutions with a dark field illumination showed, in each case, particles exhibiting Brownian movements. In some cases these particles appeared to have definite forms, but were too small to admit of precise description, and their total mass in any case must have been negligible in comparison with the dissolved constituents. No doubt the presence of colloidal dispersions may account, in part at least, for the difficulties and discrepancies noted by investigators of this system, but its importance has been exaggerated.

X-ray spectrographs of the solids

Diffraction x-ray spectrograms were made of the residues corresponding to the series of solid solutions; also, for comparison, of ferric oxide and of the normal sulfate, $Fe_2O_3 \cdot 3SO_3$, made by the directions of Recoura. Recording the many readings of the lattice spaces would require a table beyond reasonable dimensions. The photographs seem to fall, more or less clearly, under one or the other of two types, which may be designated as alpha and beta. The alpha type approaches the spectrogram for ferric oxide, while the beta type approaches that for the normal sulfate. The distinction is none too sharp, for certain lines appear in both the ferric oxide and the normal sulfate spectrograms, and some lines from both are to be found in the individual spectrograms of most of the residues. Two of these, because of the small number of lines which can be definitely measured, are in doubt. Practically every line they show which can be definitely measured is found in the spectrogram of ferric oxide, also in that of the normal sulfate. In table 3, the first column records the series to which the residue belongs; the second the mole ratio of sulfur trioxide to ferric oxide in the residue as shown by analysis; the third column the type of spectrogram given by the residue; and the fourth column the slant of the tie line, whether to the left towards the ferric oxide axis, or contrariwise. Clearly, the two sets of observations are in reasonable agreement. Further study of the observations may reveal more definite results, but for the present it may be said that the x-ray spectrograms support the view that the residues are mixtures. Since we may have but one solid phase in the residue, under equilibrium conditions, each of these mixtures would seem to be a member of a series of solid solutions. It is reasonable to think one limiting member of the series is ferric oxide or a hydrate of it. The composition of the other limiting member of the series lies between $Fe_2O_3 \cdot 1.25SO_3 \cdot nH_2O$ and $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$; and probably near the latter.

DISCUSSION

The solubility of ferric oxide at 25°C. was found to be directly proportional to the concentration with respect to sulfuric acid, in solutions containing less than 26.4 per cent sulfur trioxide. The results of previous investigators are in fair agreement. The rate at which equilibrium was reached between the solutions and the corresponding solids was slow, the more so in the more viscous and highly concentrated solutions. The rate of solution was found to be dependent on the composition, the physical character, and previous treatment of the solid brought into contact with the liquid.

The conclusion of Wirth and Bakke that there is a transition point corresponding to the liquid containing 22.1 per cent sulfur trioxide and 19.7 per cent ferric oxide was disproved. The stable solids in equilibrium with the liquids were found to form one single series of solid solutions, one limiting member being ferric oxide probably somewhat hydrated and the other probably approaching in composition the basic salt $Fe_2O_3 \cdot 2.5SO_3 \cdot$

$7H_2O$, which is the stable solid when the liquid reaches a concentration beyond 26.4 per cent sulfur trioxide. The residues in contact with two of the liquids in series B approximated the composition of a basic salt $Fe_2O_3 \cdot 1.25 SO_3 \cdot nH_2O$, and the chart shows the limiting solid is yet more acid in composition. Posniak and Merwin argue these solids to be adsorption complexes because they follow Freundlich's law. They do, and should if they be solid solutions. They do not appear to be crystalline, but all solid solutions are not mixed crystals. It would be necessary to assume unbelievably thick films if they be adsorption complexes. The character of the tie lines would seem to prove that the solids are solutions, a view supported by consideration of the x-ray spectra.

Increasing the concentration of sulfur trioxide beyond 26.4 per cent, the new solid phase appearing was found to be the basic salt, $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$. Wirth and Bakke reported it as α-copiapite, $Fe_4S_5O_{21} \cdot 18H_2O$, the laboratory-made product having been studied by Scharizer and the naturally occurring product by Linck, Geroth, and McCaughey (4). They also reported a β-copiapite $Fe_3(OH)(SO_3)_4 \cdot 13H_2O$ as stable solid for a part of the solubility curve, although there is no inflection in the curve when the beta variety replaces the alpha salt. They were probably misled by analyses of their very wet residues. Appleby and Wilkes reported the stable solid over this range of concentration to be a basic salt $5(FeO_3 \cdot 3SO_3) \cdot 2Fe_2O_3$. Very wet residues and misplaced confidence in the use of the equilateral triangle misled them.

TABLE 3

Comparison of data from tie lines and spectrograms of residues for the system Fe_2O_3–SO_3–H_2O *at 25°C.*

SERIES	COMPOSITION	TYPE	SLANT	SERIES	COMPOSITION	TYPE	SLANT
A	0.108	Alpha	Left	D	0.320	Alpha	Left
D	0.146	Alpha	Left	A	0.330	Alpha	Left
D	0.149	Alpha	Left	B	0.580	Beta	Right
A	0.194	Alpha	Left	C	1.08	Beta	Right
C	0.227	?	Right	B	1.26	Beta	Right
C	0.247	?	Right	B	1.27	Beta	Right
A	0.250	Alpha	Left				

Over the next range of concentration of sulfuric acid the solid phase in contact with stable liquids was found to be the normal salt $Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$. This salt, known as coquimbite in natural occurrences, was reported by Wirth and Bakke, but Appleby and Wilkes reported the stable solid over this range of liquid concentrations to be the heptahydrate, $Fe_2O_3 \cdot 3SO_3 \cdot 7H_2O$.

Over a yet higher range of concentration of sulfuric acid, the stable solid was found to be the acid salt $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, which was reported by Wirth and Bakke and by Appleby and Wilkes. The former reported it to be replaced by the trihydrate in contact with solutions containing upwards of 34 per cent sulfur trioxide, which the present investigation contradicts.

Wirth and Bakke found the solubility curves corresponding to the basic salt and the acid salt to extend into metastable regions. The present investigation goes further. A complete metastable solubility curve was found, one transition point quite definitely, the other with fair precision, and the solid phase in equilibrium with the solution represented by the curve was shown to be the normal salt, $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$.

It is futile to compare the data reported by previous investigators for the solutions in contact with the above cited solids, the several sets of observations disagreeing widely.

Finally, attention is directed to the fact that in no case does the right line connecting the origin with a point representing a definite salt intersect the solubility curve corresponding to that salt. There are no congruent points in the system. This fact explains many of the difficulties reported in earlier investigations.

SUMMARY

In regard to the system Fe_2O_3–SO_3–H_2O at 25°C. the following observations have been made:

1. Ferric oxide, Fe_2O_3, has a maximum solubility of 20.5 g. in a solution containing 26.4 g. of sulfur trioxide.
2. Solution is slow, depending much upon the composition, physical characteristics, and previous history of the solid brought into contact with the solution.
3. Approach to equilibrium is slower the more concentrated, therefore the more viscous, the liquid phase.
4. From zero concentration to 26.4 per cent sulfur trioxide the solubility of ferric oxide is directly proportional to the concentration in sulfur trioxide. The solids in contact with these solutions form one continuous series of solid solutions.
5. Solubility curves were found in equilibrium with the solids: $Fe_2O_3 \cdot 2.5SO_3 \cdot 7H_2O$, $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$, $Fe_2O_3 \cdot 3SO_3 \cdot 9H_2O$, and $F_2O_3 \cdot 4SO_3 \cdot 9H_2O$. The system of solutions in equilibrium with solid $Fe_2O_3 \cdot 3SO_3 \cdot 8H_2O$ was found to be metastable. Transition points were determined by interpolation.
6. There are no congruent points in the system.

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THE ATOMIC MASS OF POTASSIUM. II

The Potassium Chloride–Silver Ratio

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The following report summarizes a determination of the potassium chloride–silver ratio by the new and now fully developed standard solution method (2).

PURIFICATION OF REAGENTS

The general criterion of acceptable purity for any reagent used in this work was that it should introduce no impurities equivalent to more than 0.005 mg. of silver into any single analytical system or 1500 g. of standard solution.

Potassium chloride. The potassium materials were obtained from five different manufacturers. The salts were purified by rapid crystallization from hot or cooling solutions in 500-cc. platinum dishes. In a few of the early crystallizations, and whenever free chlorine was present in the solutions, quartz vessels were used. As a general rule (applying also in the purifications of silver, lime, sugar, potassium nitrate, sodium nitrite, and ammonium chloride) small head and tail fractions were rejected in each crystallization or precipitation. The central fraction was always drained for about fifteen minutes at 1500 R. P. M. in a centrifuge attachment in which the salt was inclosed entirely in platinum. Fusions which were part of the potassium chloride purification were made in a 180-cc. platinum cup in an electrically heated 200-cc. porcelain beaker. After these fusions the salt was dissolved in water and filtered through a platinum Munroe crucible.

Sample 1 (40 g.) was separated from a 500-g. quantity of potassium oxalate from a Norwegian source. This material was crystallized six times, changed to the chloride by one treatment of the solution with chlorine gas, crystallized once, and fused. Sample 2 (42 g.) was obtained from a kilogram of potassium nitrate from a German source. This material was recrystallized ten times, then precipitated three times from solution with hydrogen chloride gas. After each of the three precipitations the potassium chloride was fused and crystallized once from water. Sample 3 (43 g.)

was taken from 500 g. of potassium chlorate from a German source. The chlorate was recrystallized ten times and carried cautiously through the two stages of decomposition to a state of clear fusion. Rejected liquors from subsequent crystallizations (*vide infra*) contained less than 0.01 mg. of chlorate and perchlorate. Sample 4 (67 g.) was separated from 500 g. of potassium chloride from a German source. After one crystallization from water the material was precipitated twice from solution with hydrogen chloride gas. After each precipitation the salt was crystallized once from water, fused, and again crystallized from water. It was next crystallized from constant-boiling hydrochloric acid, then from water, and fused. Sample 5 (78 g.) was taken from an 1100-g. quantity of 98 per cent muriate of potash from Searles Lake, California. This salt was crystallized once from dilute aqua ammonia, twice from water, and once from 1 *M* hydrochloric acid made from recrystallized Searles Lake potassium chloride. It was then crystallized eight times from water and fused.

To complete the above purifications, each of the five potassium chloride samples was crystallized three times from water, filtered through a Munroe crucible, and then crystallized, centrifuged, and dried with especial care to avoid the introduction of platinum scrapings. The centrifuged crystals were dried in a platinum dish for three hours at 180°C., and then desiccated over broken pieces of fused potassium hydroxide at pressures less than 0.002 atmosphere for at least three days.

By weighing all of the platinum before and after use in these final procedures it was found that a maximum of 0.14 mg. of platinum could have been present in the five samples (270 g.).

Silver. Three silver samples were purified independently at different times. Sample 1 (526 g.) was prepared from 1500 g. of C. P. silver nitrate. After one crystallization from water this material was precipitated from saturated solution by slow addition of 15 *M* nitric acid, using 0.38 cc. of acid per gram of silver nitrate. The crystallization and precipitation with acid were repeated, and the 925 g. of material remaining was made up to a liter with water and neutralized with ammonia. The dissolved salt was then reduced to silver by addition of 1.5 liters of solution made by neutralizing formic acid with ammonia, using 0.50 cc. of 78 per cent acid per gram of silver. The mixture was kept slightly alkaline with ammonia and warmed toward the end of the reduction. Sample 2 (465 g.) was prepared from 750 g. of heterogeneous silver residues, which were reduced to silver with zinc and sulfuric acid. The silver was thoroughly washed and dissolved in 7.5 *M* nitric acid, using 1.85 cc. of acid per gram of silver. It was next precipitated as silver chloride. This compound was reduced to silver with a warm concentrated solution containing 1.80 g. of sucrose and 0.50 g. of sodium hydroxide per gram of silver. The silver was thoroughly washed, dried, and fused on lime in a current of methane. The solution in nitric acid, precipitation as chloride, reduction to silver, and fusion were then repeated. The etched silver bars were dissolved in nitric acid and reduced to silver with ammonium formate solution containing an excess of 0.5 cc. of 5 *M* aqua ammonia per gram of silver. Sample 3 (528 g.) was prepared from a kilogram of C. P. silver nitrate. The material was precipitated as silver chloride and recrystallized once from freshly prepared 5 *M* aqua ammonia. The crystals were digested in 6 *N* hydrochloric acid and aqua regia, washed, and reduced to silver with sucrose and sodium hydroxide. The 565 g. of silver remaining was washed, fused, etched, dissolved in nitric acid, and made up to 8 liters in a solution containing 100 g. of excess ammonia. The compound was reduced to silver by addition of a solution made by collecting 300 g. of sulfur dioxide in 1.5 liters of solution containing 160 g. of ammonia. The mixture was warmed to complete the reduction.

Occasional filtrations were an essential part of the above purification schemes. All precipitations were made from dilute solutions. Precipitated silver and silver chloride were washed twenty to thirty times with 1-liter portions of water.

To complete the above purifications each of the three silver samples, supported on lime in a current of hydrogen, was fused in a quartz muffle into 50-g. to 100-g. bars. The bars were deeply etched, then transported at 0.02 to 1.0 amperes across a cell made entirely of quartz. The electrolytic crystals were thoroughly washed, dried in quartz, and fused into 0.1-g. to 10-g. buttons, supported on lime in a 5-ampere current of electrolytic hydrogen, in a clean quartz muffle (3).

The formation of silver with the necessary smooth unbroken surface was favored by the following conditions. The current was first passed at 8.5 amperes, then held at 9.2 amperes until the silver had melted. After five to fifteen minutes, during which the furnace was rocked occasionally, the current was lowered to 7.0 amperes until the silver had solidified. The silver was cooled completely before removing it from the hydrogen atmosphere. The buttons were deeply etched, washed, dried in quartz, and finally heated for two hours in a quartz tube at 400° to 500°C. in a 2×10^{-8} atmosphere vacuum. They were kept in desiccators over fused potassium hydroxide until ready for use.

Potassium nitrate. Two samples of potassium nitrate were each crystallized ten times from water. When portions of these samples were subjected to nephelometric tests capable of revealing unmistakably one part in a million of silver or its chloride equivalent, they showed no trace of these impurities. Approximately 9.4-g. portions of the material, fused in platinum and weighed to the nearest 0.1 mg., served as the starting point in the synthesis of the standard solutions.

Lime. Three samples of lime were prepared from C. P. calcium nitrate by variations of a procedure including several crystallizations of the nitrate, electrolysis to remove traces of iron or heavy metals, and two precipitations from solution with freshly prepared ammonium carbonate solution, followed by ignition in a quartz muffle.

Water. The water used in the purification and analysis of samples 2 and 4 of the potassium chloride was obtained by distilling the ordinary distilled water of the laboratory without addition of reagents until the main fraction had a specific conductance of about 0.20×10^{-6} ohm^{-1} cm.$^{-1}$ when treated with pure nitrogen at 25°C. For all other work water from the same source was redistilled in succession from dilute alkaline permanganate solution and very dilute sulfuric acid.

Other reagents. Phosphorus pentoxide was resublimed in a current of purified oxygen in an all-glass apparatus. Aqua ammonia, formic acid, nitric acid, and hydrochloric acid were purified by one to three distillations of the C. P. concentrated or suitably diluted reagents in quartz apparatus. Sugar, sodium nitrite, and ammonium chloride were crystallized once from water. Solutions of sodium hydroxide were filtered through a Munroe crucible and electrolyzed in a platinum dish until free from iron and heavy metals. Commercial methane, carbon dioxide, chlorine, sulfur dioxide, oxygen, nitrogen, and hydrogen were washed in trains of towers containing glass pearls covered with suitable reagents. The hydrogen used in the final silver fusions was prepared by electrolysis of 20 per cent sodium hydroxide solution and purified by passage in succession through six 30 cm. × 2.5 cm. towers of 3-mm. pearls covered with concentrated sulfuric acid, a tube containing 50 cm. of No. 27 platinum wire carrying a current of 5.2 amperes, an 80 cm. × 2.5 cm. tube containing pieces of fused potassium hydroxide, and a 40 cm. × 2.5 cm. tube of glass pearls mixed with phosphorus pentoxide. The same train was later used in drying the purified nitrogen employed in the fusion of the potassium chloride. In analyses 3 to 7 inclusive, nitrogen was prepared by dropping a solution of sodium nitrite into a hot solution of ammonium chloride; in the other analyses the gas from a commercial tank was used. Both gases met the necessary requirements for purity and dryness when treated in succession with acid permanganate solution, hot copper gauze, potassium hydroxide solution, concentrated sulfuric acid, fused potassium hydroxide, and resublimed phosphorus pentoxide.

THE ANALYSES

Weighings were made at temperatures from 22°C. to 26°C. with relative humidities between 8 and 54. To eliminate a certain group of potential weighing errors the substitution method was extended to include a recheck of the first rest-point. The (true) mass values for the entire set of Class M weights were determined three times during the work, once at the U. S. Bureau of Standards. The greatest discrepancy in the three calibrations was one of 0.006 mg. in one of the platinum fractionals. For each weighing the air density was calculated from temperature, pressure, and psychrometric observations. Vacuum corrections were applied through the expression: $m = s + d(V_m - V_s)$, in which m is the mass of the object weighed, s the mass of the corresponding weights, with rider and rest-point corrections applied, d the air density, V_m the volume of the object, and V_s the sum of the volumes of the weights. The volumes of the gold-plated brass weights were determined by hydrostatic weighings; the other volumes were calculated with the aid of the densities: Pt, 21.45; Al, 2.70; KCl, 1.989; Ag, 10.49; KNO_3, 2.11. Counterpoises were used in weighing the fused salts in their platinum containers. A statistical examination of the rest-point data in relation to the sensitivity of the balance showed that the recorded weights are significant on the average to about 0.005 mg.

For each analysis a 7.1-g. sample of potassium chloride was fused in a 15-cc. platinum–rhodium boat in another quartz muffle of the same type used in the silver fusions, in a current of dry nitrogen. The muffle was lined with 0.001 in. sheet platinum.

The weighed salt was dissolved out of the boat and made to a volume of 500 cc. In analyses 7 to 15 the salt samples were first tested for alkali in a volume of 50 cc., by a modification of the method of Hönigschmid (1); the 0.05 cc. of 0.004 *M* chloride-free methyl red solution introduced in this procedure apparently had no effect in subsequent operations.

A weighed quantity of silver was next dissolved in a calculated excess of 7.68 *M* nitric acid in the 3-liter Pyrex analysis flask and the solution was warmed to remove nitrous fumes, except in analysis No. 15.[1] The solution was made up to 500 cc. and the salt solution was added drop by drop with constant rotation of the analysis flask, in the light of a Series OA Wratten Safelight. In analyses 3, 12, 13, 14, and 15, however, the silver chloride was precipitated by simultaneous drop by drop addition of the two 500-cc. solutions to 200 cc. of water, with constant rotation. In these five experiments the precipitation thus took place at concentrations which could scarcely have exceeded 0.0005 *M*, on the average.

In each case the analytical system was made up with water to contain 1520.7 g. of solution per 10.0000 g. of silver (9.3718 g. of potassium nitrate) and allowed to stand at room temperature for fifteen to fifty days, with occasional vigorous shaking. The acid concentration of the analytical solution was adjusted to 0.3025 molar after titration of a portion with standard alkali, and the system was brought to equilibrium by at least three days cooling at 0°C., with gradual reduction of the shaking to a minimum.

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[1] Nitrite, which would seriously affect the potentiometric analyses, is best removed at this stage. In analysis No. 15 it was found that nitrite is removed only very slowly by bubbling nitrogen or oxygen through the analytical solution.

The supernatant analytical liquid was analyzed both nephelometrically and potentiometrically for silver and chloride by comparison of filtered samples withdrawn at 0°C. with standard solutions having very nearly the same composition (2, 4). In the nephelometric analyses the standard and test solutions were at exactly the same temperature, i.e., room temperature; in the potentiometric analyses both solutions were at 0°C. The standards contained measured equivalent amounts of silver and chloride, 9.3718 g. of potassium nitrate per 1520.7 g. of solution, and were 0.3025 molar in nitric acid. Seven of these solutions were made up to cover the range of silver and chloride concentrations from 0.590 to 0.610 mg. (as silver) per liter. To make standard solutions 8 and 9 two 14-g. samples of silver chloride from completed analyses were rinsed and brought to equilibrium with solutions made up without chloride or silver to the same concentration as the other standards, from two different samples of potassium nitrate and nitric acid.

After preliminary analyses the supernatant analytical liquid was adjusted more closely to the end-point, the additions of chloride or silver being corrected to the original volume in the usual manner. The chloride and silver concentrations of the solution were finally determined by at least three nephelometric and three potentiometric analyses made over a period of at least five days with three different standard solutions. The analytical system was shaken once only after each set of withdrawals.

Measurements of the solubility of silver chloride in the analytical and standard solutions permitted an improvement in the manner of determining the chloride concentration from the potentiometric analyses. These measurements are summarized in table 1. The data show that the chloride concentration may be calculated precisely from the expression: $[\mathrm{Cl}] = 0.3697/[\mathrm{Ag}]$ or the corresponding approximation: $[\mathrm{Cl}] = 1.216 - [\mathrm{Ag}]$. The silver concentration was calculated from the E. M. F. of the cell Ag | analytical solution | standard solution | Ag by the expression: $\log [\mathrm{Ag}] = \pm E/0.0542 + \log S$, where S is the silver concentration of the standard solution. All concentrations are expressed in milligrams of silver per liter, and E is in volts. The data obtained from the corresponding cell with silver chloride electrodes were used only in analysis 3, but furnished valuable confirmatory information in the other analyses.

Equal-opalescence tests made in the usual manner, in connection with the standard solution analyses of various systems in equilibrium at 0°C., gave further evidence that there is an essential difference in the stability of the sols precipitated with excess silver and excess chloride upon which various factors may operate to produce marked differences in color and opalescence. Comparison of the equal-opalescence ratios with the accurately determined values of the silver and chloride concentrations showed that any estimate of the KCl:Ag ratio based on the assumption that the unit equal-opalescence ratio is characteristic of solutions at the correct end-point would be subject to corrections which would vary with the temperature, the acid concentration and volume of the analytical solutions,

TABLE 1

Solubility of silver chloride at 0°C.

NO. OF ANALYSES	TYPE OF ANALYSIS	SOLUTIONS ANALYZED	QUANTITY MEASURED	AVERAGE MG. OF Ag PER LITER
90	Nephelometric	15 Analytical	$\sqrt{[\mathrm{Ag}]\cdot[\mathrm{Cl}]}$	0.608
6	Nephelometric	Standard No. 8	[Ag] and [Cl]	0.608
6	Nephelometric	Standard No. 9	[Ag] and [Cl]	0.607
3	Potentiometric	Standard No. 8	[Ag] only	0.609
3	Potentiometric	Standard No. 9	[Ag] only	0.608

TABLE 2

Summary of end-point determinations

NO.	INITIAL VOLUME IN LITERS	Ag ADDED IN SOLN. TOTAL MG.	NEPHELOMETRIC ANALYSES MG. OF Ag PER LITER AS		POTENTIOMETRIC ANALYSES MG. OF Ag PER LITER AS		AVERAGE EXCESS Ag MG. PER LITER
			Chloride*	Silver	Chloride*	Silver	
1	1.56	−0.795	0.56	0.66	0.54	0.68	+0.12
		−1.057	0.612	0.600	0.621	0.595	−0.019
2	1.57	−0.704	0.605	0.616	0.584	0.632	+0.030
3	1.56	−0.748	0.628	0.613	0.626	0.590	−0.026
4	1.57	−0.475	0.56	0.64	0.57	0.64	+0.08
		−0.689	0.604	0.610	0.604	0.612	+0.007
5	1.57	−0.683	0.618	0.599	0.613	0.603	−0.015
6	1.57	−0.628	0.57	0.64	0.55	0.67	+0.10
		−0.729	0.59	0.61	0.60	0.61	+0.02
		−0.786	0.629	0.595	0.624	0.592	−0.033
7	1.57	−0.594			0.57	0.64	+0.07
		−0.712	0.61	0.61	0.604	0.612	+0.004
8	1.58	−0.733	0.605	0.615	0.608	0.608	+0.005
9	1.57	−0.208	0.603	0.606	0.598	0.618	+0.012
10	1.59	−0.307	0.605	0.611	0.597	0.619	+0.014
11	1.57	−0.208	0.602	0.595	0.623	0.593	−0.018
12	1.57	−0.139	0.62	0.59	0.63	0.58	−0.04
		−0.085	0.598	0.611	0.596	0.620	+0.019
13	1.56	0.000	0.603	0.606	0.608	0.608	+0.002
		−0.056	0.622	0.592	0.633	0.583	−0.040
14	1.59	0.000	0.625	0.601	0.632	0.584	−0.036
15	1.57	0.000	0.605	0.601			−0.004

* The values in this column are chloride concentrations in milligrams per liter, multiplied by the factor Ag/Cl.

the size of the analytical samples, and the method of forming the test suspensions. Equal-opalescence tests made upon solutions containing equivalent amounts of silver and chloride and saturated at 25°C. gave approximately unit ratios, but were insensitive to additions of excess silver nitrate or potassium chloride equivalent to 0.20 mg. of silver per liter.

DISCUSSION OF RESULTS

The amounts of silver "subtracted" from the analytical solutions and the results of the standard solution analyses made at the corresponding stages of adjustment to the end-point are given in table 2. From these data and the original weights of silver and potassium chloride added (table 3) the KCl:Ag ratio may be calculated. In table 3 the results of calculations based on the final sets of analyses are summarized. No corrections have been applied for hydrogen in the silver or nitrogen in the fused salt; they could hardly affect the final average by more than a few parts per million.

TABLE 3

Summary of analyses

NO.	KCl NO.	Ag NO.	KCl IN VACUUM	Ag IN VACUUM	TOTAL Ag ⇔ KCl	RATIO KCl:Ag
			grams	*grams*	*grams*	
4	1	1	7.174405	10.381709	10.38101	0.691109
15	2	1	7.159125	10.358857	10.35886	0.691111
6	3	1	7.139503	10.331248	10.33051	0.691108
7	4	1	7.110874	10.289814	10.28910	0.691107
3	5	1	7.119655	10.302444	10.30174	0.691112
13	1	2	7.113533	10.292932	10.29294	0.691108
9	2	2	7.124221	10.308618	10.30839	0.691109
10	3	2	7.241729	10.478735	10.47841	0.691110
12	4	2	7.128585	10.314855	10.31474	0.691107
2	5	2	7.163709	10.366249	10.36550	0.691111
5	1	3	7.132066	10.320468	10.31981	0.691104
11	2	3	7.151197	10.347646	10.34747	0.691106
14	3	3	7.230660	10.462442	10.46250	0.691103
8	4	3	7.212326	10.436676	10.43594	0.691105
1	5	3	7.102363	10.277835	10.27681	0.691106
Average						0.691108
Probable error						±0.0000005

While the analytical procedures were designed to reduce to a minimum all of the errors in the determination of the ratio, the plan of the research was calculated to reveal any sources of error in the procedures. The only factor whose effect upon the accuracy of the procedures could not be estimated in two different ways was the composition of the precipitated silver chloride. However, satisfactory evidence that silver chloride is a compound with an accurately reproducible composition was obtained in work on the atomic mass of sodium (2). The absence of effects due to greatly changed conditions of precipitation in five of the present determinations offered further evidence that silver chloride formed under the conditions of these experiments has a definite composition not measurably altered by adsorption effects.

The agreement of the independent and basically different nephelometric and potentiometric analyses of the solutions obtained by the analytical reaction and by the reverse method of synthesis (table 1) offers proof of the soundness of the end-point. The absence of variations in the final results shows the adequacy of the purifications and the precision of the method as a whole.

The fifteen determinations of the ratio have been made with sufficient independence to give general validity to the final average. It may thus be concluded that the value 0.691108 ±0.0000005 represents an accurate estimate of the KCl:Ag ratio. This value agrees well with the average of Stas's four series of determinations and is reassuringly close to the mean of the various results which have been obtained in recent times with the equal-opalescence method. The corresponding value of 39.100 for the atomic mass of potassium (Ag = 107.880; Cl = 35.457) is also close to the mean obtained in determinations of this constant through other ratios.

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HYDROLYSIS OF ALKALI CHLORIDES

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The work described herein offers information regarding the purity with which sodium chloride and potassium chloride may be obtained in weighable form. It also shows the extent to which samples of the latter material taken from different sources and purified by different methods may be depended upon to have the same composition. The experiments were undertaken primarily to supplement researches on the atomic masses of sodium and potassium, but they have a more general interest because of the many cases in which the alkali chlorides are used as reference standards in analytical and physical chemistry. The findings thus have a bearing on the preparation and handling of the compounds in conductance measurements, E. M. F. measurements, reaction velocity measurements, pH measurements, and other work in which weakly buffered solutions of the salts are used. Moreover, the method employed in the tests is a general one, applicable in the preparation of other compounds in weighable form of known composition.

By crystallization in platinum dishes sodium chloride and potassium chloride may be obtained free from all weighable impurities except water, platinum, and atmospheric gases. The platinum impurities are easily kept to negligible amounts, and the water and gases may be removed by fusion of the salts, but there is a limit set upon the purity of the fused material by the slight hydrolysis which occurs during fusion. The experiments supply quantitative evidence upon the magnitude of this limit when the pure well-dried salts are fused either in air of known humidity or in dry nitrogen.

REAGENTS

The potassium chloride, water, and nitrogen used in this work were prepared as set forth in the preceding article. The sodium chloride was taken from one 25-g. and two 26-g. fractions from a single source, the purification of which is described elsewhere (2).

EXPERIMENTAL

The experiments consisted in fusing portions of the salt samples under various conditions and determining the alkali in the fused material. In one set of experiments the gases evolved during the heating and fusion process were analyzed for acid, chloride, and total electrolyte. In this case the salts were fused in a 15-cc. platinum-rhodium boat in a closed platinum-lined quartz muffle (3), in a current of nitrogen. The gases from the muffle passed through a 200-cm. coil of dry 5-mm. Pyrex tubing into a conductance cell under conditions such that the absorption of electrolytes was practically 100 per cent complete.

The salts were weighed before and after fusion; the observed difference in weight includes loss by volatilization, loss of water, and mechanical loss. The platinum-rhodium boat lost about 0.01 mg. in each fusion; with pure platinum the losses were from 0.03 mg. to 0.06 mg. per fusion. The main part of these platinum losses did not take place from the salt–platinum system until the salt was dissolved out of the boat, i.e., the loss by volatilization of platinum was a minor effect.

The fused, partially cooled salts were transparent, colorless, and free from bubbles when removed from the muffle, but sometimes cracked on further cooling.

For each experiment 50 cc. of distilled water was placed in the cell and the conductance was determined after a slow current of nitrogen had removed most of the carbon dioxide. With the nitrogen still passing, the temperature of the furnace was gradually raised as follows: 3 amperes, 2 hours; 4 amperes, 30 minutes; 5 amperes, 30 minutes; 6 amperes, 10 to 15 minutes. The current was then raised to 7.7 amperes (8.1 amperes for the sodium chloride), whereupon the salt fused in about fifteen minutes. The current was shut off two to ten minutes after the salt had fused. In experiments 1 to 3 the nitrogen was passed continuously; in experiment 4 the gas current was stopped after the salt had fused; in experiments 5 to 12 it was stopped when the current was raised from 6 amperes; the furnace gases were passed into the conductance cell after the salt had ceased to volatilize.

Conductance measurements were made during the heating process and after the absorption of electrolytes was complete. The measurements were made at temperatures from 22°C. to 26°C. and have been corrected accordingly in calculating the electrolyte concentration, which is expressed arbitrarily as HCl.

Following the conductance measurements, two 10-cc. portions of solution from the cell were analyzed for acid (H^+) by titration with 0.001 *M* alkali in a nitrogen atmosphere. Another 20-cc. portion was analyzed nephelometrically for chloride by comparison with standard potassium chloride solutions.

In some cases the alkali content of the fused salt was determined by titration with 0.001 *M* nitric acid and methyl red indicator in the carbon dioxide-free atmosphere and solutions obtainable with cells of the type used by Kolthoff and Kameda (4). Freshly prepared solutions made from water, indicator, and the recrystallized neutral salts furnished the reference end-point. For the samples which were used in atomic weight analyses, the alkali was estimated by the method of Hönigschmid (1), using 50-cc. volumes of solution, 0.05-cc. portions of 0.004 M methyl red solution, and 0.001 M nitric acid. Microburettes were used throughout.

TABLE 1

Hydrolysis of salts fused in dry nitrogen

SALT	NO.	SAMPLE WEIGHT	LOSS ON FUSION	SPECIFIC CONDUCTIVITY × 10^6		TOTAL MOLES × 10^6 FROM				NITROGEN
				Initial	Final	Evolved gases			Salt	
						HCl	Cl^-	H^+	OH^-	
		grams	*mg.*							*cc. per minute*
KCl	4	7.1		0.47	$8.93^{22°}$	1.14	1.0	<1	0.05	18
KCl	2a	7.1		0.60	$6.78^{23°}$	0.75	0.42	<0.3		10
KCl	2b*	7.1	2.8	0.36	$9.99^{22°}$	1.19	1.4	<1	<0.02	25
KCl	3	7.2	3.5	0.58	$4.28^{26°}$	0.43	0.44	0.2	<0.02	45
KCl	2	7.2	3.6	0.38	$0.98^{25°}$	0.07	0.12	0.15	<0.05	32
KCl	4	7.1	7.5	0.31	$5.32^{24°}$	0.60	0.56	0.7	<0.09	27
KCl	1	7.1	9.0	0.31	$2.16^{23°}$	0.22	0.24	0.3	<0.08	37
KCl	3	7.2	4.8	0.33	$0.70^{25°}$	0.04	0.06	0.14	−0.09†	30
KCl	2	7.2	4.6	0.28	$1.04^{24°}$	0.09	0.09	<0.09	<0.09	35
KCl	5	6.9	3.8	0.63	$0.84^{22°}$	0.03	0.12	<0.05	−0.11†	30
NaCl	2	7.4	8.9	0.44	$1.09^{25°}$	0.08	0.10	<0.05	0.29	40
NaCl	4	6.6	10.5	0.61	$2.36^{26°}$	0.20	0.39	0.1	0.24	35

* Second fusion of same material.

† Solution of fused salt more acid than reference solution.

TABLE 2

Hydrolysis of salts fused in moist air

SALT	NO.	SAMPLE WEIGHT	LOSS ON FUSION	RELATIVE HUMIDITY	MOLES × 10^6 (AS OH^-)
		grams	*mg.*		
*NaCl	2 and 4	6.5	8.6	68	5.6
NaCl	1	6.3	13.3	67	5.8
*KCl	5	7.2	6.1	70	0.24
KCl	5	5.7	6.8	77	0.13
KCl	4	6.8	6.6	72	0.35
KCl	3	4.4	4.9	58	0.20
KCl	2	4.9	5.0	49	0.19
KCl	1	6.0	4.6	63	0.17

* Fused in 20-cc. crucible in porcelain beaker.

The results of the above-described experiments are summarized in table 1.

A second set of tests was made in which the salts were fused under exactly the same conditions as before, except that the cap of the muffle was removed and no nitrogen was passed. These experiments are summarized in table 2.

The muffle was washed out at intervals during the fusions. Table 3 gives the results of analyses made for alkali in the washings.

TABLE 3

Alkali recovered from muffle

SALT FUSED	TOTAL IN GRAMS	NO. OF FUSIONS	MUFFLE CAP	MOLES × 10^4 (AS OH^-)
KCl	84	11	On	1.0
KCl	57	8	On	<0.9
NaCl	14	2	On	1.08
NaCl	6	1	Off	
KCl	28	5	Off	0.76

TABLE 4

Observed mass of salts exposed to moist air

SALT	NO.	TIME EXPOSED	RELATIVE HUMIDITY	MASS IN GRAMS	SALT	NO.	TIME EXPOSED	RELATIVE HUMIDITY	MASS IN GRAMS
KCl	5	10 min.	8	7.102363			9 A.M.	65	5.470888
		7 hrs.		7.102360					5.470906
					NaCl	2	to		5.470908
KCl	4	10 min.	20	7.110874					5.470906
		8 hrs.		7.110863			2 P.M.		5.470899
KCl	3	10 min.	51	7.230660	NaCl	2	30 min.	85	Not found
		5 hrs.		7.230663					
KCl	2	10 min.	54	7.159125					
		15 hrs.	36	7.159124					

Tests were made to determine if the salts fused in nitrogen take up moisture when exposed to air during weighing. The salts were weighed without removing them from the boats or crucibles. The data obtained are summarized in table 4.

Eight of the identical fused potassium chloride samples listed in table 1 were used in the atomic mass determination described in the foregoing paper. Parts of the three sodium chloride fractions used in another atomic mass determination (2) gave values for the NaCl:Ag ratio from 0.541812 to 0.541821.

DISCUSSION OF RESULTS

The total loss of hydrogen chloride due to hydrolysis was extremely small when the salts were fused in dry nitrogen, but the amount of alkali left in the salt in the boat was even smaller. The larger part of the hydrolysis occurred either in the vapor phase or at the walls of the muffle.

When the nitrogen was passed continuously during the heating and fusion, the high values obtained from the conductance data were due to volatilized salt. The conductance measurements made at intervals as the temperature was raised showed that the hydrolysis took place mainly after the current was raised from 6 amperes.

Sodium chloride has a much greater tendency to hydrolyze than potassium chloride when fused in moist air. The corresponding difference observed for the samples fused in nitrogen is not significant, for the 107 g. of material from which the sodium chloride fractions were taken was cut from a 168 g. quantity which yielded 0.0011 g. of sodium bicarbonate to the rejected mother liquors.

SUMMARY

It has been shown that carefully purified sodium chloride and potassium chloride consistently hold less than one or two parts per million of alkali when fused in dry nitrogen under a specified set of conditions. It may be inferred that samples of the salts taken from different sources and purified by different methods may be prepared constant in composition to the same extent. The latter conclusion has been confirmed to the limit of the experimental precision, and independently, by analysis of various samples of the salts.

Sodium chloride and potassium chloride prepared, purified, and fused as described may be weighed in air of low and moderate humidity without taking up weighable amounts of moisture.

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THE STORAGE OF POLONIUM SOLUTIONS

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Polonium has been used but little as a radioactive indicator because, except in strong acid solution, it appears to be colloidally dispersed (18, 19). This behavior is unfortunate, because the radioelement possesses ideal properties which qualify it for use as an indicator. Polonium is a strong alpha-radiator, and therefore produces an intense and easily measurable ionization. Because it is the last active member of the uranium-radium series, there is no need for multiple measurements or for delay until establishment of radioactive equilibrium with succeeding products. In addition, it is sufficiently long-lived to obviate the necessity of making decay corrections in most cases. Since polonium in true solution would constitute a valuable tool for a proposed study of crystalline precipitates, it was believed advisable to determine, if possible, useful conditions under which radiocolloid (23) formation by polonium is minimized.

Elements like polonium, radium E, thorium B, etc., under suitable conditions of acidity, behave as though they were colloids. This conclusion is drawn from their dialyzability (18, 19), the small velocity with which they diffuse in solution (19, 20, 22), their centrifugability (2, 4, 24) and settling under gravity (16), their behavior in an electric field (8, 9, 10, 15, 19), and from the fact that radiograms (1, 11) of small quantities of their solutions apparently show the presence of large aggregates of radioactive atoms. Because it is uncertain whether true colloids are involved, the term "radiocolloid" (23) was coined.

Opinions as to the cause of the phenomenon are not in accord. One explanation (19) views the effect as true colloid formation, the sol consisting of extremely insoluble products of the hydrolysis of salts of radioelements. Actually, those radioactive elements which would be expected to yield, upon hydrolysis, insoluble hydroxides and basic salts, do show a pronounced radiocolloid effect (11). Since the solubility products of these compounds of lead and bismuth are never exceeded in solutions containing only the radioactive isotopes of these common elements, it is difficult to see how such precipitates can be formed. Hence others (15, 24, 26) hold that the phenomenon is really a pseudo-colloid formation resulting from the adsorption of radioelements by traces of colloidal impurities, such as dust, alumina, and silica particles, suspended in the liquid media employed. This view is supported by the fact that it is almost impossible to prepare and store in the laboratory, water which is truly optically void (13, 25).

Since the chief source of suspended silica is the walls of glass containers used for storage purposes, it occurred to the authors to study the behavior of polonium solutions kept in paraffined bottles. This procedure has the additional advantage of preventing adsorption of the polonium by the glass (5, 21) itself. Though by this simple expedient the radiocolloid effect could not be avoided entirely, it was found that polonium could be maintained in dilute acid solutions stored in paraffin for periods of time sufficiently convenient to permit its use as an indicator. The necessity of preparing fresh stock solutions for each set of experiments was thus eliminated.

EXPERIMENTAL

The centrifuging method (12) of demonstrating radiocolloid formation, was used in these experiments. Paraffined, cylindrical copper cups (2.5 cm. in diameter × 7 cm. in height), closed by paraffined stoppers, were used for centrifugation. Into each cup was placed 16 ml. of a given polonium solution, and the whole rotated for various times at a speed of 3000 R.P.M., with a radius of 22 cm. Then three 2.63-ml. samples of the supernatant liquid were carefully sucked off and evaporated in matched watchglasses on a water bath, prior to measurement in a Lind electroscope (17) equipped with an open door chamber. Samples of the uncentrifuged solution were taken as standards for comparison. All pipets used were paraffined. All experiments were done in duplicate. Electroscopic measurements were accurate to within ±1 per cent. In most cases, centrifuging was carried on for an hour.

Polonium was obtained from a number of old radon bulbs, after digesting the crushed glass in acid, by currentless electrochemical deposition (5, 6, 7) on silver. The silver was dissolved in concentrated nitric acid, hydrochloric acid was added to precipitate the silver, and, after removal of silver chloride by filtration, the filtrate was evaporated to dryness in a Pyrex beaker on a water bath. The polonium source, from which all other solutions were subsequently prepared, was obtained by taking up the residue in cold 1.015 *N* nitric acid. Boiling the acid solution to accelerate solution was found to yield a large amount of centrifugable polonium, and was therefore undesirable. In this fashion, 125 ml. of a stock solution containing 100 E.S.U. of polonium was prepared and stored in a paraffined bottle. The solutions used in the centrifuging experiments were formed by diluting this source with twice-distilled water, and then stored in large paraffined containers. This water was used shortly after the second distillation, to avoid long standing in glass receivers. More active solutions were made by evaporating a portion of the source, and taking up the residue in a solution of the proper acid concentration. The centrifugability of the polonium was measured at various times after the preparation of solutions. Results are expressed as per cent of polonium left in solution after centrifugation. Approximate polonium quantities are given in electrostatic units.

RESULTS

The acid concentration and polonium content of solutions studied, as well as the results of centrifugation experiments, are summarized in table 1.

TABLE 1

Centrifuging of polonium solutions

SOLUTION	COMPOSITION		AGE OF SOLUTION	DURATION OF CENTRIFUGING	POLONIUM LEFT
	Nitric acid concentration	Polonium content E.S.U./16.1 ml.			
	N		*days*	*hours*	*per cent*
1	1.09	0.06	45	1	98.8
2	0.114	0.06	45	1	97.3
3	0.0196	0.07	10	3	98.0
	0.0196	0.07	13	2	98.2
4	0.0108	0.48	22	1	95.2
5	0.00534	0.07	7	0.5	100
	0.00534	0.07	7	1	100
	0.00534	0.07	7	3	100
	0.00534	0.07	12	1	99.4
	0.00534	0.07	39	1	99.8
	0.00534	0.07	45	1	98.2
6	0.00534	0.59	9	1	96.2
7	0.00059	0.08	11	1	96.5
	0.00059	0.08	11	2	97.9
8	0.00059	0.80	8	1	96.3

From these data, it is evident that polonium solutions can remain practically uncentrifugable for long periods of time. Even the 0.00059 *N* acid solution shows little indication of radiocolloid formation after a week of standing. This is especially significant, because A. Korvezee (14) has recently reported a region of maximum centrifugability near this acid concentration.

That this is an improvement over storage in uncoated glass vessels can be illustrated simply by following the behavior of solution 5 kept in a common glass container for six days. After this period, the activities of the centrifuged and uncentrifuged solutions were measured in the usual fashion. By comparing these electroscope discharges with samples of the original solution kept in paraffin, both adsorption by glass walls and radiocolloid formation could be determined. Using 200 ml. in 250-ml. bottles, it was found that 8.4 per cent of the polonium had been removed from solution by the glass walls, and of the polonium remaining in solution, 20 per cent was removed by centrifuging for one hour. It seems definite that glass containers are undesirable as stock bottles for polonium solutions.

The disadvantage in using glass is further illustrated by preparing radioactive solutions with the use of inactive acid solutions which had been shaken gently for several days in common glass bottles. A 0.00059 *N* nitric acid solution was employed for this purpose. After the dilute acid had been transferred to paraffined flasks, portions were centrifuged for an hour and a half, and half of the supernatant liquid separated from the remaining liquid. Then three polonium solutions were made by diluting fresh solution 8 with measured volumes of uncentrifuged acid, the supernatant liquid, and the residual liquid. These solutions were shaken in paraffin for two days, and centrifuged for one hour in the usual manner. Table 2 shows the results of these experiments.

TABLE 2

Radiocolloid formation in solutions prepared from glass-stored acid

ACID SOLUTION EMPLOYED	COMPOSITION		AGE OF SOLUTION	POLONIUM LEFT
	HNO_3 concentration	Polonium content E.S.U / 16.1 ml.		
	N		*days*	*per cent*
Uncentrifuged acid	0.00059	0.077	2	81.9
	0.00059	0.077	8	72.5
Supernatant liquid	0.00059	0.18	2	93.0
Residual liquid	0.00059	0.11	2	39.5

The "uncentrifuged acid" solution clearly shows the radiocolloid formation, accompanied by its characteristic increasing centrifugability with age (3). On the other hand, the "supernatant acid" solution is practically free from the disturbing phenomenon. In accord with the last observation is the fact that the "residual acid" solution shows the greatest loss on centrifuging. Apparently the dilute acid, during its contact with glass, had become contaminated with impurities which promote the centrifugability of polonium.

DISCUSSION

Objections might be directed toward the use of such small amounts (0.06 to 0.8 E.S.U.) of polonium in studying the radiocolloid effect. These are unfounded, because the above experiments unquestionably point to the loss of polonium on centrifuging our weak solutions, unless paraffined containers are used. Furthermore C. Chamié and M. Haïssinsky (3) have demonstrated the phenomenon using 0.05 E.S.U. The stability of our solutions can be explained best by the care taken to avoid contact with uncoated glass walls. Even this precaution is insufficient to eliminate the effect in 0.00059 *N* acid after two weeks of storage.

Experiments of this type unfortunately are chiefly empirical, and do not explain the mechanism of radiocolloid formation. Probably glass alone is not responsible. Dust particles too will produce the effect, as was shown by I. E. Starik (21). We have found that as little as 25 mg. of laboratory dust, shaken in 16 ml. of solution 5 for ten minutes, will cause a separation of 87 per cent of the polonium after centrifuging for only ten minutes at 1600 R.P.M. This, together with colloid-producing impurities in the nitric acid used, probably accounts for the small losses found in table 1.

SUMMARY

1. The use of glass vessels for the storage of polonium solutions is undesirable.

2. Coating storage containers with paraffin eliminates, to a considerable extent, the disturbing radiocolloid effect in polonium solutions.

3. Polonium solutions which are as dilute as 0.00059 *N* in nitric acid may be used for more than a week if stored in paraffined vessels. More concentrated acid solutions may be kept for longer than a month and a half.

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THE THERMAL DECOMPOSITION OF DIETHYLAMINE[1]

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The study of the kinetics and mechanism of the decomposition of diethylamine was undertaken in order to continue the work in the amine series under investigation in this laboratory. The decompositions of the primary amines appeared at first sight to offer simple examples of homogeneous unimolecular reactions (8, 9, 11). This simplicity, however, was shown by Taylor (10) to be illusory in the decomposition of dimethylamine, owing to a mutual compensation of several concurrent reactions. It was hoped therefore that a fuller investigation, particularly of the mechanism, might yield a possible scheme of analysis of the complete results.

In a study of the catalytic influence of iodine on amines, Bairstow and Hinshelwood (1) assume the over-all change occurring with diethylamine to be

$$(C_2H_5)_2NH \rightarrow C_2H_6 + CH_4 + HCN$$

despite the fact that in the uncatalyzed reaction only from 15 to 30 per cent of the theoretical amount of hydrogen cyanide could be detected with silver nitrate and that this fell to from 5 to 10 per cent in the iodine-catalyzed decomposition. They conclude that the reaction is initially homogeneous and unimolecular. In view of the fact, as will be shown, that methane and nitrogen are the chief products and that no hydrogen cyanide was detected in any stage of the reaction, although a hydrazine which readily reacted with silver nitrate was always found, this mechanism appears untenable. Furthermore, there appears a distinct possibility that hydrogen cyanide, if formed, would add on to any unchanged amine and thus reduce still further the observed rate of pressure increase.

The rate of decomposition was studied statically in an apparatus identical with that used in the previous work already published. The diethylamine used was an Eastman sample, redistilled over lime, and boiling from 55.5 to 56.0°C. The capillaries connecting the amine reservoir, reaction vessel, and manometer were maintained at 60°C. to prevent any condensation occurring. Data were obtained over the temperature range

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[1] Abstract from a thesis presented by C. R. Herman in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

from 510 to 540°C., and at pressures from 40 to 400 mm. The pressure increase during reaction averaged around 160 per cent, although a perceptible effect of both temperature and pressure was observable. Thus at 510°C. the pressure increase varied from 182 to 166 per cent at pressures ranging from 44 to 419 mm., whilst at 540°C. the variation was from 176 to 134 per cent over the same pressure range. Such variations, however, may not be a true indication of the existence of an equilibrium but may be merely due to the fact that the end points taken are fictitious, owing to very slowly occurring secondary reactions.

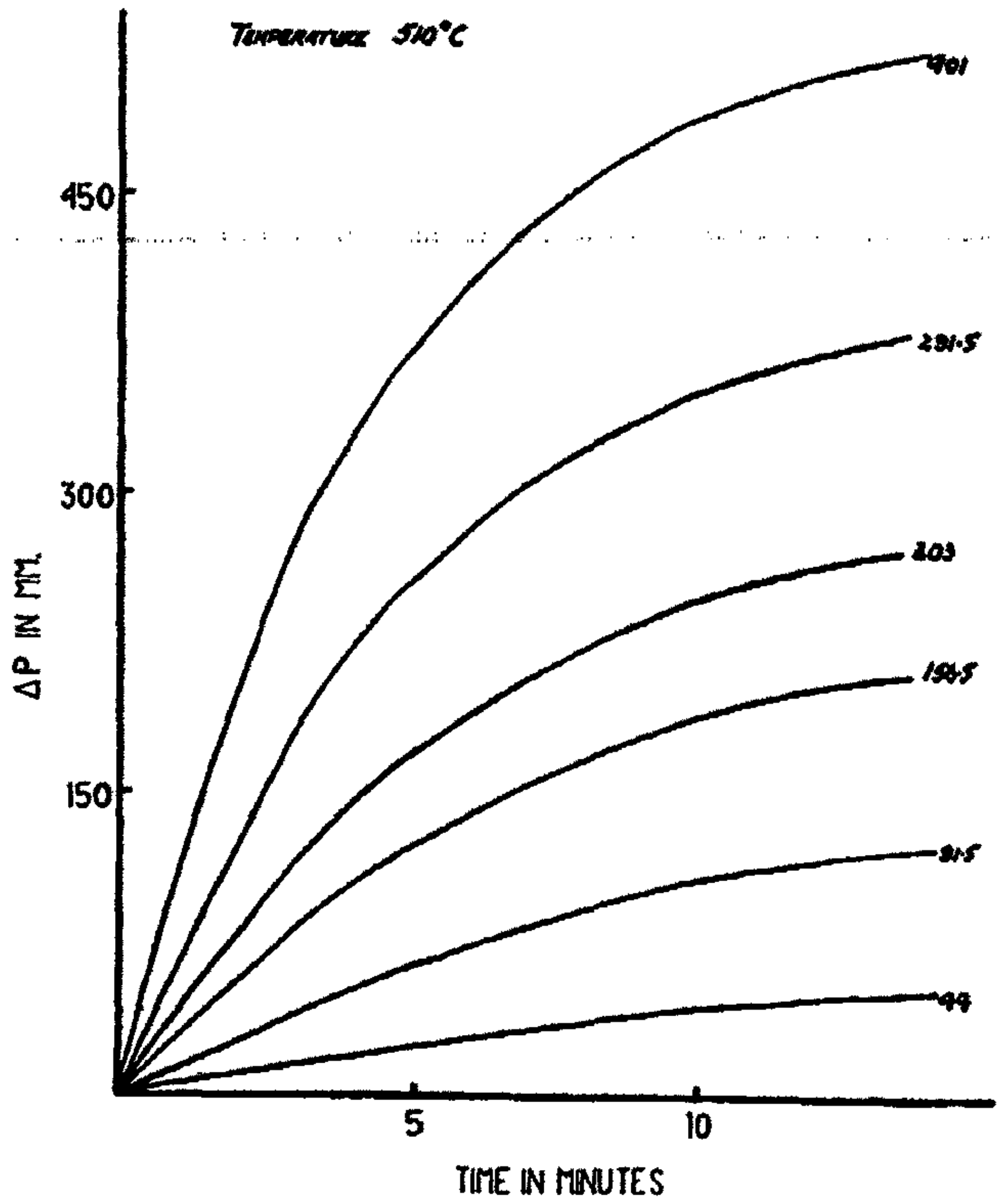

Fig. 1. Thermal Decomposition of Diethylamine

A typical diagram of the rate of pressure change with time is shown in figure 1 for initial pressures of 44, 91.5, 156.5, 203, 291.5, and 401 mm. at 510°C. Similar curves were obtained at the other temperatures.

In table 1 are given the values of the quarter-lives for the various temperatures and pressures studied, calculated as the time necessary for one quarter of the total pressure increase to occur.

The only obvious conclusion one can draw from these values is that the reaction has an order lying between one and two, more closely approaching the former however, but being in all probability complex. The variation in quarter-life with pressure is the more marked the lower the pressure, and the possibility therefore remains that at higher pressures a constant life might be found.

The reaction was shown to be homogeneous under the conditions studied by increasing the surface to volume ratio of the reaction vessel eleven times by packing with short lengths of Pyrex tubing. Table 2 shows a comparison of the actual pressure readings at various times for the same initial pressure in the packed and unpacked vessels.

TABLE 1

Values of the quarter-lives at different temperatures and pressures

INITIAL PRESSURE	t IN MINUTES	INITIAL PRESSURE	t IN MINUTES
Temperature = 510°C.		Temperature = 530°C.	
44.0	3.80	43	1.45
58.5	3.35	71	1.34
81.0	3.05	88	1.15
91.5	2.80	134	1.09
156.5	2.23	188	0.92
203	2.08	228	0.88
257.5	1.96	256	0.83
291.5	1.87	295	0.76
322.5	1.74	342	0.74
374.5	1.66	368	0.74
401.0	1.56	410	0.70
419.0	1.50	452	0.69
Temperature = 520°C.		Temperature = 540°C.	
37	2.30	41	1.20
85	1.87	91	0.85
127	1.65	129	0.77
142	1.48	152	0.68
185	1.35	209	0.63
204	1.30	252	0.60
245	1.21	275	0.57
282	1.15	315	0.56
385	1.03	358	0.54
432	0.96	439	0.50

The data in table 2 show that the reaction is in the main homogeneous, though there are indications of a speeding up over the later portion of the reaction, though the pressure increase for the unpacked vessel was 174 per cent whilst that for the packed vessel was 175 per cent.

The effects of added nitrogen, hydrogen, and ammonia were studied at the highest and lowest temperatures, namely, 540 and 510°C., and at initial pressures of amine of 40 and 200 mm., the pressure of added gas being 150 mm. These data are presented in table 3 in the form of percentage total pressure increase and the quarter-life.

It is readily seen that the effect of nitrogen is negligibly small at all temperatures and pressures. Ammonia, however, appears to retard the rate of pressure increase, and in all probability does so by specific chemical reaction. The effect of hydrogen is very marked. In the first place the end point is considerably reduced, showing again a probable chemical action. The quarter-life based on this end point is also largely reduced though, owing to the disproportionate end points, the effect is apparently larger than it actually is for the earlier portions of reaction. The actual pressure change for equivalent times is not however as great for the amine in presence of hydrogen as in its absence. There appears then to be an actual retardation by hydrogen.

TABLE 2

Changes in pressure observed when the reaction occurs in packed and in unpacked vessels

Temperature = 510°C.

TIME	PRESSURE CHANGE	
	Unpacked vessel. Initial pressure 233 mm.	Packed vessel. Initial pressure 230 mm.
minutes		
0.5	26	25
1.0	51	50
2.0	99	94
3.0	139	134
4.0	170	168
5.0	200	195
6.0	223	220
7.0	242	240
8.0	258	255
10.0	283	283
12.0	302	303
14.0	316	319
16.0	326	332

With the view of determining the end products of reaction a weighed amount of amine was sealed in a glass bomb and heated for three days at 500°C. to render reaction complete. The gaseous products were then analyzed,[2] yielding 2.1 per cent of ammonia as water-soluble, 3.2 per cent of unsaturated hydrocarbon absorbed by bromine, 0.2 per cent of hydrogen by preferential combustion over copper oxide, 70.1 per cent of methane,

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[2] Thanks are due to H. Tarnpoll of this laboratory for the gas analyses.

and 2.3 per cent of ethane. The remaining 23 per cent is nitrogen. The reaction in the main then appears to yield methane and nitrogen in the ratio of three to one. The difference between this value and their ratio in the original amine is to be accounted for by the large amount of black deposit obtained in such bomb experiments. Such results, though of little use in determining a mechanism, are necessary to the elucidation of the final goal of the reaction.

To obtain the details of the mechanism of the reaction in its earliest stages a small amount of liquid diethylamine was sealed in a tube and maintained at only 200°C. for twenty-four hours. Upon opening, a small pressure increase was noted, pointing to the accumulation of gaseous products. In other cases at 400°C. and for periods varying from one to eighteen hours similar gaseous products were found and analyzed. In no case was hydrogen found in other than mere traces. Nitrogen was always present. From the ratio of the carbon dioxide to the water formed on combustion the gas appeared to be a mixture of methane and butane. To test this specifically, a sample of the gas was kept in a solid carbon dioxide bath for some time, during which a decrease in volume was observed. The remaining uncondensed gas on combustion proved to be practically

TABLE 3

The effect of added gases

PRESSURE OF AMINE	GAS	PRESSURE OF GAS	PER CENT INCREASE	t
Temperature = 510°C.				
mm.		*mm.*		*minutes*
44			182	3.80
40	NH_3	153.5	179	4.20
43	N_2	151	182	3.75
46	H_2	152	170	3.55
203			175	2.08
201	NH_3	153	171	2.20
210	N_2	152	174	2.17
180	H_2	155	157	2.10
Temperature = 540°C.				
41			176	1.20
41	NH_3	154	177	1.30
48	N_2	148	175	1.17
38	H_2	151	166	1.10
210			156	0.63
207	NH_3	154	164	0.66
212	N_2	153	156	0.65
225	H_2	158	139	0.57

pure methane. The condensed portion upon vaporizing and combustion analyzed as more nearly pure butane. Analysis of the remaining liquid in these experiments showed a considerable amount of unchanged secondary amine with only traces of primary and tertiary amine. Specific tests for the cyanide group as, for example, by the Prussian blue test showed its complete absence. In like manner nitriles too were shown to be absent. Upon addition of silver nitrate a marked reduction occurred, yielding the characteristic silver mirror. It is probable that this reduction is caused by a hydrazine, and the initial reaction may tentatively be indicated as

$$2(C_2H_5)_2NH \rightarrow C_2H_5NH\text{—}NHC_2H_5 + C_4H_{10}$$

a bimolecular reaction involving no volume change. Subsequent reaction involving the liberation of nitrogen from the hydrazine and the decomposition of butane would account for the presence of nitrogen, methane, and ethane in the end products, the over-all volume increase, and for the observed slow secondary reactions yielding apparent equilibria in the final state. The absence of hydrogen in the high temperature bomb experiments is in line with the observations of rehydrogenation of unsaturated hydrocarbons in the butane decomposition (2, 3). The excess of methane over ethane is to be expected also because of decomposition of the ethane (4).

The decomposition, at least in its earlier stages, of butane, is admittedly a unimolecular reaction even if of a chain type (5), and it would appear reasonable from the complexity of the molecule that the diethylhydrazine would also decompose unimolecularly. This is under investigation in this laboratory at the present time. Assuming that this latter rate is faster than the observed rate of pressure increase of diethylamine itself, the rate actually being measured here would be that of the bimolecular split into butane and hydrazine, a reaction without a volume change, in terms of the volume increase of the unimolecular reactions. It does not seem advisable at present to speculate on these relative rates, but the observation that the rate of pressure increase found would indicate a reaction order between one and two is easily accounted for, other than by the assumption that it is due to a quasi-unimolecular reaction in the pressure range where the Maxwell-Boltzmann distribution of activated molecules is not maintained.

In view of the fact that all analyses of the reaction products, whether taken in the early stages or later on, show the presence of some primary amine, ammonia, and unsaturated hydrocarbon, the possibility is suggested of an initial split of the amine into ammonia and an unsaturated hydrocarbon. The quantities of the latter usually found are hardly more than traces, however. Such a rupture therefore must be much more difficult than the hydrazine formation and consequently occur only to a minor extent. The reverse reaction, between ammonia and the unsaturated hydrocarbon, will account for the repressing effect of the added ammonia previously mentioned, since in the butane decomposition some unsaturateds must certainly be formed, as may also be possible in the hydrazine decomposition. The effect of added hydrogen would be similar though more marked.

There remains one factor, following as a consequence of the suggested mechanism, to be discussed. If the major reaction is bimolecular and without a volume change, followed by unimolecular reactions, there should be expected a period of induction in the reaction. Depending on the relative rates this may be long or short. However, as was first pointed out by Schumacher and Wiig (7) in the case of ethylamine, the induction period only evidences itself on an extremely clean surface and at low initial pressures, and even then appears to show only very poor reproducibility. Under the present conditions the reproducibility is perfect even with an extended surface, though the argument might be advanced that the surfaces were all uniformly poisoned. Under such conditions it is legitimate nevertheless, to treat the reaction as homogeneous. There seems however no reason to doubt that if the decomposition of diethylamine were to be studied in a vessel which had been pumped out to less than 10^{-6} mm. for several days, an induction period would be observed, as is the frequent observation with ethylamine in this laboratory at present. Indications in this case seem to point however to the hydrazine formation reaction as the one which is so extremely sensitive to traces of foreign material.

An approximate idea of the energy of activation of the early reaction may be obtained from the observed quarter-lives. The average value yielded by the simple Arrhenius equation for the various pressures studied is 49,000 calories. This value, though somewhat higher than that found in a similar manner for the primary amines, namely 44,000 calories, is more nearly in agreement with the value of about 50,000 calories taken as indicative of the strength of the C—N bond by Rice and Johnson (6) from a study of the free radical formation by thermal decomposition.

SUMMARY

The rate of pressure increase in the diethylamine decomposition over a temperature range from 510 to 540°C. appears to indicate a homogeneous reaction with an energy of activation, in the early stages, of 49,000 calories. Analysis of intermediate products suggests the mechanism to involve the formation and subsequent decomposition of diethylhydrazine and butane.

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THE POLYMERIZATION AND HYDROGENATION OF ACETYLENE[1]

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The literature on the polymerization and hydrogenation of acetylene is voluminous (2), but practically all of it deals with the mechanism (3) and products (6) of reaction. The only work dealing in any detail with the kinetics of the reaction is due to Pease (8) and Schlaffer and Brunner (12). Pease concludes that the rate-determining process is the primary reaction involving two molecules of acetylene. No quantitative data on the velocity of the hydrogenation are available. It was deemed desirable therefore to study both reactions more thoroughly.

The majority of previous work has been carried out by the dynamic method and suffers consequently, for such a complex reaction, from definite uncertainties of the time of contact and the analysis of the products. Since Pease, by the dynamic method, has shown that the only reaction of importance in the early stages of the thermal treatment of acetylene is the polymerization, and since the static method is admirably fitted for a study under such conditions, particularly if a back extrapolation to zero time is advisable, the static method as used previously by Taylor and his coworkers (14) was adopted.

POLYMERIZATION

Acetylene was generated by dropping water on Baker's calcium carbide, the gas evolution being moderated by suspension of the carbide in alcohol. The gas was purified by passage through acid copper sulfate and dried over calcium chloride. Analysis by precipitation as copper acetylide gave, as a mean of several determinations, its purity as 98.7 per cent. As shown later, the only objectionable impurity in the acetylene is oxygen, and absorption in acetylene-saturated alkaline pyrogallol showed considerably less than 0.1 per cent of oxygen in the acetylene used.

It is repeatedly mentioned in the literature that acetylene decomposes more readily and smoothly in the presence of carbon formed in its pyrolysis. This became quickly appreciated during the work because of the diffi-

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[1] Abstract from a thesis presented by Andrew van Hook in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

culty of obtaining duplicate results if the reaction system was thoroughly cleaned after each experiment. It was found, however, that after one run had been completed, the reaction vessel was apparently seasoned in some manner, and subsequent experiments at a given temperature and pressure were almost ideally reproducible. A change in either of these factors, however, necessitated a new seasoning. After each run the apparatus was thoroughly evacuated for at least one hour with a mercury vapor pump backed by an oil pump. To illustrate this reproducibility, data are presented in table 1 of two runs, fortunately at exactly the same initial pressure, at 535°C., showing the rate of pressure decrease with time of 399 mm. of acetylene.

TABLE 1

Reproducibility of results after seasoning of the reaction vessel

Temperature, 535°C.; initial pressure, 399 mm. of C_2H_2

TIME	PRESSURE DECREASE		TIME	PRESSURE DECREASE	
	I	II		I	II
minutes	*mm.*	*mm.*	*minutes*	*mm.*	*mm.*
0.5	42	42	6	204	205
1.0	79	80	8	219.5	220
1.5	108	110	10	230	230
2	130.5	131	20	253	252.5
3	160	161	30	261	260
4	179.5	181	120	272	272

TABLE 2

Constancy of percentage pressure decrease with acetylene alone

TEMPERATURE	END-POINT
°C.	
495	0.671 (Average of 26 observations)
515	0.687 (Average of 10 observations)
535	0.669 (Average of 6 observations)
Mean	0.675

With acetylene alone the total percentage pressure decrease on completion of reaction was constant, independent of temperature and initial pressure. These facts are shown in table 2 as the ratios of the total pressure decrease to the initial pressure.

The end-point of the reactions occurring at temperatures from 495°C. to 535°C. may therefore be taken as approximately two-thirds. It is worth while to mention in this connection some observations made on a new reaction vessel which had not been seasoned. The first run is slower, as measured by the actual rate of pressure decrease, by an amount approximately equivalent to a 5°C. change in temperature. The end-point too is much lower, about 0.36 as against 0.66, and would seem to indicate the preference of the decomposition reaction on the clean surface and its progressive decrease with seasoning.

In order to test specifically the order of the polymerization reaction a comparison of the fractional lives for various initial pressures was made. As a result of the distillation of the liquid products formed during polymerization Pease (8) decided that the major reaction involved four molecules of acetylene, giving a tetrapolymer. This is not inconsistent with the end-points herein quoted, since admittedly these are composite of both polymerization and decomposition, despite the inherent suspicion of a trimer that the value of two-thirds would suggest. Assuming then with Pease the formation of the tetramer, the fractional life will be the time necessary for the pressure to fall by an amount $P/f - P/4f$, where P is the initial pressure of acetylene and $1/f$ the chosen fraction. In table 3 are listed the times necessary for $\frac{1}{10}$, $\frac{1}{4}$, and $\frac{1}{2}$ of the acetylene to react. The products of initial pressure and time are included as a test of the bimolecularity of the reaction. The velocity constants quoted are calculated from these times by the usual expression for a bimolecular reaction $k = 1/t \cdot x/a(a - x)$, the units used being seconds and atmospheres.

TABLE 3

Times necessary for one-tenth, one-fourth, and one-half of the acetylene to react

Temperature, 495°C.

INITIAL PRESSURE P	$t_{1/10}$	Pt	k	$t_{1/4}$	Pt	k	$t_{1/2}$	Pt	k
mm.	*minutes*			*minutes*			*minutes*		
748	0.50	374	0.0037	1.25	935	0.0045	3.35	2510	0.0050
729	0.51	372	0.0038	1.27	925	0.0046	3.67	2675	0.0047
558.5	0.68	380	0.0037	1.71	955	0.0044	4.69	2620	0.0048
380	1.15	436	0.0032	3.0	1140	0.0037	8.3	3160	0.0049
365	1.18	430	0.0033	3.1	1160	0.0036	8.8	3210	0.0040
103.5	7.0	725	0.0020	19.5	2020	0.0021	59.0	6100	0.0021
100	7.3	729	0.0019	20.6	2060	0.0021	67.2	6700	0.0019
92.5	8.0	738	0.0019	22.0	2150	0.0020	70.0	6460	0.0020
79	10.6	835	0.0017	29.0	2280	0.0019	89.0	7010	0.0018
70.5	11.4	800	0.0018	30.5	2145	0.0020	91.0	6400	0.0020
42	24.9	1042	0.0014	72.5	3020	0.0014	212	8860	0.0014
29.5	38	1150	0.0012	136	4000	0.0011	410	12050	0.0011
24	57	1370	0.0010	215	5150	0.0008	500	12000	0.0011

The figures indicate that in the early stages the reaction is bimolecular but deviates as the reaction proceeds, and furthermore, that the deviation is greater the smaller the initial acetylene pressure. Similar data at the other temperatures studied show that as the temperature increases the effect of the disturbing factor, which is undoubtedly decomposition, also increases. The values of the velocity constant obtained above from the one-tenth life were verified by a back extrapolation to zero time. Thus, by plotting the observed values of the pressure change in unit time against the time and extrapolating to zero time, the limiting rate of pressure change is found at the very start of reaction, and dividing this by the square of the initial pressure gives the velocity constant of the reaction at its inception. These values were slightly less than those found from the one-tenth life and are used in the subsequent calculation.

Since higher pressures favor polymerization the velocity constant calculated above is found to approach a limiting value at pressures which are only slightly above those actually studied. It is justifiable then to estimate this limiting value by plotting the velocity constants against the reciprocal of the pressure and extrapolating to infinite pressure. By this means the value of the velocity constant for the earliest reaction and under the ideal conditions of infinite pressure is obtained. In table 4 the values so found at the temperatures studied are given. For comparison there are included in the table also the values available in the literature already cited. In general the values found are almost double those reported by Pease. This is undoubtedly due to the approximate nature of the calculation in Pease's work, using a dynamic method, and to the devices used above to extrapolate to zero time and infinite pressure. Indeed, as Pease found, the value of k is usually the greater for those runs in which the least hydrogen and methane are found, that is, in which the pyrolysis was least.

TABLE 4

Values of the velocity constant

TEMPERATURE	VELOCITY CONSTANT	WORKER
°C.		
420	0.005–0.008	Schlaffer and Brunner
495	0.0039	Taylor and van Hook
500	0.0011–0.0015	Pease
515	0.0078	Taylor and van Hook
525	0.0030–0.0045	Pease
535	0.0145	Taylor and van Hook
550	0.0049–0.011	Pease

With the above values of the velocity constant an estimate of the energy of activation of polymerization can be obtained, using the simple Arrhenius equation. For the temperature interval 495°C. to 515°C. the value calculated is 41,700 calories; for the interval 515°C. to 535°C., it is 39,300 calories, giving as a mean 40,500 calories.

A comparison between the observed velocity constants and those calculated on the basis of the activated collision theory of bimolecular reaction is now possible. The total numbers of collisions occurring per cubic centimeter per second is given by $2n^2\sigma^2\sqrt{\pi kT/m}$, where n is the number of molecules per cubic centimeter, σ the diameter, and m the mass of the molecules. The diameter of the acetylene molecule is not given in the literature, though some scant data are available on the viscosity. Vogel (17) gives 93.5 micropoises as the value at 0°C. The temperature variation is not known, though for ethylene, which has an almost identical viscosity at 0°C., the variation with the temperature is given by the Sutherland constant of 226. Assuming the same value for acetylene, the molecular diameter at high temperatures evaluates to 3.64×10^{-8} cm. The number of effective collisions will be $e^{-E/RT}$ times the total number of collisions, and since two molecules take part in collision the rate of disappearance of acetylene will be twice this product. At 788°K. and a concentration of 1 mole per liter this product is equal to 1.33 in liters per mole per second. The value of k determined by experiment when expressed in these same units is 0.50.

TABLE 5

Ratio of observed to calculated velocity constants

REACTION	RATIO	REFERENCE
$C_2H_2 + C_2H_2$	1:3	
$C_2H_4 + H_2$	1:220	(10)
$C_2H_4 + C_2H_4$	1:370	(9)
$C_4H_6 + C_4H_6$	1:10,300	(15)
$C_5H_8 + C_5H_8$	1:530	(16)

The ratio of the observed to the calculated velocity constants, 1:3, may be compared with similar ratios found in other association reactions. Vaughan (16) has recalculated many of the available data and summarized the results on a comparable basis. In table 5 are listed the known examples.

The smallness of the ratio for acetylene is in harmony with the simplicity of the molecule, and though too much reliance may not legitimately be placed on the actual figure (the limits are probably 1 and 1:10) the position of the reaction in the series is significant.

HYDROGENATION

In the reactions with hydrogen measurements were made over the same temperature range, using different mixtures of acetylene and hydrogen.

Thus mixtures were made up which were approximately 1:1, 1:8, 1:16, and 1:24 acetylene to hydrogen, and each mixture was investigated over the whole temperature range and at partial pressures of the acetylene from about 20 to 70 mm. The observed end-point, that is, the ratio of the pressure decrease to the partial pressure of acetylene, varied with both temperature and composition, as is illustrated in table 6.

To discuss these figures as well as the subsequent treatment necessitates a consideration of the possible reactions which might occur. In the first place polymerization of acetylene will be proceeding, accompanied by the decomposition mentioned earlier. Since under the experimental conditions the partial pressures of acetylene used are rather small, a larger proportion of decomposition might be suspected as compared with that in the previous work with acetylene alone. In this connection Bone and Coward (1) and Pring and Fairlee (11) claim that decomposition is favored relative to polymerization by the presence of hydrogen. In the second place, hydrogenation of acetylene to ethylene should occur. The reaction is reversible, but the equilibrium constant at the temperatures in this study is of the order of 10^7 (5) and the reverse reaction may thus be neglected. Hydrogenation of ethylene to ethane might be expected, as well as the possible hydrogenation of the acetylene polymers. It would seem necessary to invoke all of these to account for the observed end-points. However, a study of the individual rates of pressure change showed there was a very gradual approach to the end-point, a pressure decrease approximately equal to the initial acetylene pressure occurring relatively rapidly, followed by a considerably slower decrease for many hours and even days before any semblance of an end-point was eventually reached. It is probable that the major reactions occurring in this early stage involve acetylene polymerization, decomposition, and hydrogenation almost exclusively, and since little is known of the decomposition it can only be grouped with the hydrogenation and allowance made for the known polymerization. The relative occurrence of these two tendencies may be roughly estimated.

TABLE 6

Variation in observed end-point with temperature and composition

TEMPERATURE	MIXTURE $C_2H_2:H_2$	END-POINT	TEMPERATURE	MIXTURE $C_2H_2:H_2$	END-POINT
°C.			°C.		
495	1:1	0.81	515	1:16	1.93
495	1:8	1.24	515	1:24	2.28
495	1:16	1.60	535	1:8	1.51
495	1:24	1.98	535	1:16	2.15
515	1:8	1.32	535	1:24	2.51

Assuming, in anticipation of later results, that the hydrogenation is bimolecular, the rate of disappearance of acetylene will be given by

$$-\frac{d[C_2H_2]}{dt} = k_1[C_2H_2]^2 + k_2[C_2H_2][H_2]$$

and the observed pressure change by

$$-\frac{dP}{dt} = k_1 p^2_{C_2H_2} + 2k_2 p_{C_2H_2} p_{H_2}$$

With mixtures high in hydrogen content it is apparent that the second term on the right will contribute predominatingly to the rate. Calculations, using as low a ratio as 1:10 for acetylene to hydrogen and arbitrary values of k_1/k_2, show the relative insignificance of the polymerization. The value of k_1/k_2 actually found is about 5, and it is legitimate therefore to neglect the polymerization at higher hydrogen ratios in order to approximate the value for k_2 for a more exact evaluation at the lower ratios. The method is virtually one of successive approximations. Thus, assuming only hydrogenation to ethylene to occur early in the reaction, for acetylene to hydrogen ratios of 1:32 or 1:24, the one-tenth or one-quarter lives will be the times necessary for the pressure to decrease by one-tenth or one-quarter of the initial pressure. Calculating an approximate velocity constant from these values gives a value of 5.0 for the 1:24 mixture and 5.5 for the 1:32 mixture for the ratio of the rates of polymerization and hydrogenation for the same acetylene pressure at temperatures from 495°C. to 535°C. Using this latter value and assuming the major reactions to be

$$4C_2H_2 \rightarrow (C_2H_2)_4$$
$$C_2H_2 + H_2 \rightarrow C_2H_4$$

the times taken for one-tenth of the acetylene to be hydrogenated for the various mixtures used may be evaluated. Thus for the 1:32 mixture the one-tenth life will be the time for the pressure to decrease an amount equal to 0.110 of the initial pressure, and similarly for other acetylene to hydrogen ratios. The times so found at one temperature as typical of the other temperatures are given in table 7, together with the velocity constants calculated from them by the usual bimolecular equation.

There can be no doubt that the previous assumption of bimolecularity is completely justified. Since, however, account has only been taken of the acetylene polymerization which is occurring simultaneously with the hydrogenation, and no account was taken in the above of the acetylene decomposition, more reliable estimates of the velocity constants of the hydrogenation would be obtained from data taken as early in the reaction as possible. To this end a procedure similar to that used for the polymerization was adopted, involving an extrapolation to zero time of the observed

TABLE 7

Velocity constants

Temperature, 515°C.

INITIAL C_2H_2 PRESSURE	$t_{1/10}$	k	$t_{1/4}$	k	$t_{1/2}$	k
			$C_2H_2:H_2 = 1:24$			
mm.						
27	3.78	0.00047	14.1	0.00040	31	0.00044
28.2	4.0	0.00043	14.3	0.00038	34	0.00039
			$C_2H_2:H_2 = 1:16$			
27.2	5.5	0.00049	19.5	0.00043	53	0.00039
37.9	5.1	0.00038	17.0	0.00036	39	0.00038
39.3	4.4	0.00043	15.5	0.00038	37	0.00038
			$C_2H_2:H_2 = 1:8$			
29.7	12.0	0.00040	35.5	0.00040	93	0.00037
41.9	9.5	0.00040	28.0	0.00039	73	0.00037
60.4	6.2	0.00042	17.5	0.00044		
665.	5.8	0.00041	16.5	0.00042	45.5	0.00037

TABLE 8

TEMPERATURE	$k_{\text{hydrogenation}}$	E
°*C.*		
495	0.00019	43540
505	0.00028	40410
515	0.00039	43010
525	0.00055	41470
535	0.00076	

rate of pressure change and calculation from this value of the velocity constant. Thus

$$-\frac{dP}{dt} = k_1 p^2_{C_2H_2} + 2k_2 p_{C_2H_2} p_{H_2}$$

Since k_1/k_2 is approximately 5.5

$$k_2 = \frac{-dP/dt}{5.5p^2_{C_2H_2} + 2p_{C_2H_2}p_{H_2}}$$

In this way the probability that the values of k_2 are vitiated by the occurrence of acetylene decomposition is reduced as far as would seem possible. The constants so obtained are presented in summary in table 8 for the five temperatures studied. The energies of activation for the succeeding temperature intervals are also included and give an average value of 42,000 calories. This value may be compared with that calculated by Sherman and Eyring (13) on the basis of quantum mechanics, namely 46,400 calories. This discrepancy is not unexpected in that the calculated value relates to 0°K. and depends on the choice of 10 per cent for the coulombic energy. Furthermore the value found is very close to that obtained by Pease for ethylene hydrogenation, 43,200 calories.

The comparison between the observed velocity constant at a particular temperature and that calculated on the basis of collision theory may again be made as in the previous case. Taking the total number of collisions occurring per cubic centimeter per second between unlike molecules as $2N_1N_2\sigma_{12}^2 \sqrt{2\pi kT(m_1+m_2)/m_1m_2}$, where N_1 and N_2 are the numbers of molecules per cubic centimeter of acetylene and hydrogen respectively, of masses m_1 and m_2, σ_{12} is the mean of their two diameters, so with 3.6×10^{-8} cm. as the diameter of acetylene and 1×10^{-8} cm. for hydrogen, using 42,000 calories as the energy of activation, it is calculated for the temperature 788°K. that the velocity constant should be 0.724 liter mole^{-1} sec.^{-1} The observed value in these same units is 0.252, whence the ratio is again found to be approximately 1:3, also in harmony with the values for other reactions previously quoted in view of the simplicity of the molecules partaking in the reaction.

SUMMARY

The homogeneous thermal polymerization of acetylene and its hydrogenation have been investigated in the temperature range 495°C. to 535°C. The principal processes are interpreted as bimolecular with energies of activation of 40,500 and 42,000 calories, respectively. The efficiency of the association is high, in that the ratio of the observed rates to those calculated on the basis of activated collisions is 1:3 in both cases.

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THE SYSTEM PYRIDINE-ACETIC ACID. IV

BOILING POINTS

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In earlier papers by one of the present authors and his collaborators (8, 9, 10), the viscosities, melting points, and electrical conductance of mixtures of pyridine and acetic acid have been reported. The object of these investigations was to determine the number and kind of complexes existing in this system. Of the methods of investigation used so far, all indicate the existence of a complex with a composition between 80 and 85 mole per cent acetic acid. The melting point–composition diagram shows some evidence of the existence of a second complex with a composition of 50 mole per cent acetic acid. This report deals with an extension of the work to include boiling point data for the system.

The presence of a stable complex should decrease the vapor pressure of a given mixture, at constant temperature, below the vapor pressure of the mixture if it were ideal or even only approximately so. This vapor pressure lowering should be most pronounced when the largest amount of the complex is present. This condition would manifest itself by the formation of a maximum boiling point mixture. Highly unstable complexes would probably have little or no effect in the production of a maximum boiling point, since such complexes would be very largely dissociated at the high temperatures at which the mixtures boil. It is also possible, in case the system does show a maximum boiling point, that the composition of the mixture having such maximum boiling point may change with pressure, owing to the variation in the extent of dissociation with the different boiling temperatures corresponding to the different pressures.

Gardner (5) concluded, from boiling point measurements on this system, that a compound of the composition $2C_5H_5N \cdot 3CH_3COOH$ was formed. He reports that a large part of this mixture distills at an approximately constant temperature of 139–140°C., with constant composition. André (1, 2), on the basis of boiling point measurements, reports a complex of the same composition. In the present paper, we have redetermined the boiling point–composition relations for the system, and have investigated the effect of pressure changes on the composition of the mixture showing the maximum boiling point.

MATERIALS

The pyridine and acetic acid used in these measurements were purified in the manner described in an earlier paper (9).

APPARATUS

The boiling point apparatus described by Nelson (6) was modified slightly and used for the boiling point measurements. A special glass distillation apparatus was built and used to obtain the composition and boiling point of the maximum boiling mixture at different pressures.

TABLE 1

Boiling points of pyridine-acetic acid mixtures

BOILING TEMPERATURE AT 760 MM. PRESSURE	COMPOSITION OF RESIDUE MOLE PER CENT ACID	COMPOSITION OF DISTILLATE MOLE PER CENT ACID
°C.		
117.85	100.0	100.0
122.30	92.3	99.2
126.80	86.7	97.0
130.15	81.4	92.0
134.00	74.4	86.1
136.95	66.8	76.0
137.25	65.1	72.2
138.05	62.0	66.5
138.40	57.6	57.3
138.35	56.2	54.4
138.00	53.7	47.0
137.20	49.3	37.6
135.05	43.0	26.8
130.70	32.2	14.0
125.5	23.4	6.2
120.55	13.8	2.5
115.00	0.0	0.0

Pressures were measured to 1 mm. mercury by means of a mercury manometer.

All thermometers used were carefully checked against thermometers calibrated by the Bureau of Standards.

METHOD

All solutions were made up by weight, and compositions are expressed in mole per cent acetic acid, accurate to 0.001 per cent.

The boiler and receiver of the Nelson apparatus (6) were filled with the same mixture and distillation then carried out (at 760 mm.) until equilibrium was established between the liquid in the two containers. Constancy of boiling point at 760 mm. pressure was taken as sufficient evidence that the equilibrium condition had been reached. About three hours were required for the attainment of equilibrium. The boiling temperatures were read to 0.05°C. When the equilibrium temperature was reached, samples of the residue and distillate were removed from the apparatus and analyzed. This procedure was repeated for mixtures over the entire range of composition, except for mixtures in the immediate vicinity of the maximum boiling point mixture (see table 1).

The boiling point and composition of the maximum boiling point mixture could not be obtained with the Nelson apparatus except by accident. A large volume of mixture of the approximate maximum boiling point composition was placed in the special all-glass still and the mixture boiled, at constant pressure (760 mm.), until a constant boiling point was reached. Samples of residue and distillate were taken as before (see table 2).

TABLE 2

Maximum boiling point mixtures of pyridine and acetic acid

PRESSURE	BOILING POINT		COMPOSITION, MOLE PER CENT ACETIC ACID	
	Initial	Final	Initial	Final
mm. Hg	*°C.*	*°C.*		
760	138.25	138.40	59.4	58.4
760	138.20	138.35	55.0	58.4
760	125.00	138.35	89.0	58.4
800	139.85	140.05	59.4	58.4
570	129.40	129.55	59.4	58.9
380	117.50	117.55	59.4	59.5
190	99.50	99.55	59.4	60.2
120	87.10	87.15	59.4	60.8

After the composition of the maximum boiling point mixture had been determined, the procedure was repeated at pressures of 800, 570, 380, 190, and 120 mm. of mercury.

The residue and distillate samples were analyzed by measuring their densities and comparing these values with the measured values of the densities of mixtures shown in table 3 and figure 3.

EXPERIMENTAL RESULTS

Figure 1 shows the pyridine–acetic acid system to exhibit a maximum boiling point of 138.35 ± 0.05°C. at 58.4 mole per cent acetic acid, under a pressure of 760 mm. The maximum boiling mixture contains slightly less acetic acid than the composition reported by Gardner (5) and André (1, 2). The maximum boiling temperature is also slightly less than the value reported by these workers. Figure 2 shows the manner in which the composition of the maximum boiling mixture changes with changes in pressure. At pressures less than 760 mm. the composition of the maximum boiling mixture shifts slightly in the direction of higher acetic acid content, approximating a mixture of 3 moles of acetic acid and 2 moles of pyridine

TABLE 3

Densities of pyridine-acetic acid mixtures at 32.38°C.

ACETIC ACID MOLE PER CENT	DENSITY	ACETIC ACID MOLE PER CENT	DENSITY
0.000	0.9720	77.722	1.0640
6.345	0.9769	78.698	1.0652
12.566	0.9818	79.734	1.0664
18.529	0.9870	80.771	1.0676
24.359	0.9923	81.543	1.0684
29.943	0.9976	82.221	1.0690
35.225	1.0032	82.669	1.0693
40.268	1.0089	83.720	1.0700
45.440	1.0149	84.773	1.0704
50.004	1.0209	85.234	1.0707
54.890	1.0273	85.894	1.0711
59.594	1.0345	86.470	1.0711
63.927	1.0415	86.790	1.0716
68.202	1.0487	88.568	1.0700
72.438	1.0558	90.710	1.0676
74.790	1.0595	94.834	1.0583
76.256		100.00	1.0380

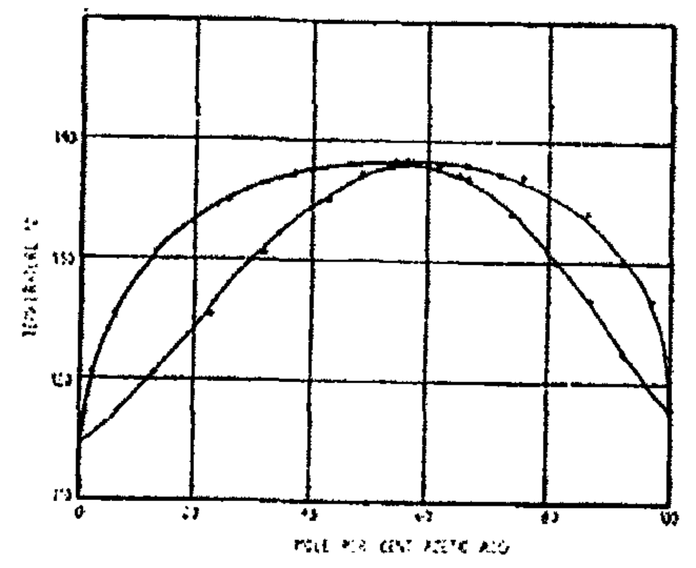

FIG. 1

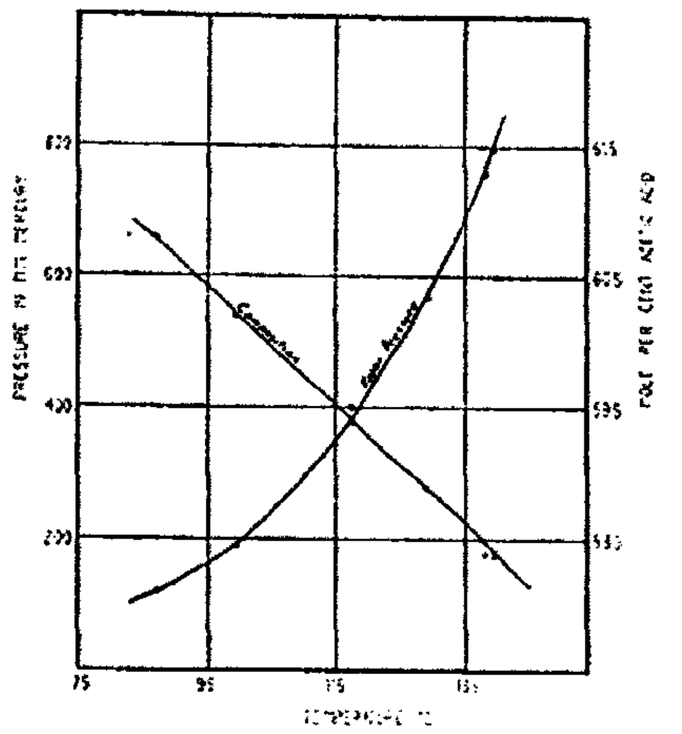

FIG. 2

FIG. 1. BOILING POINT CURVE FOR PYRIDINE AND ACETIC ACID MIXTURES

FIG. 2. MAXIMUM BOILING POINT MIXTURES OF PYRIDINE AND ACETIC ACID

at a pressure of 120 mm. This variation in composition of the maximum boiling mixture with changes in pressure precludes the existence of any very stable complex at this point.

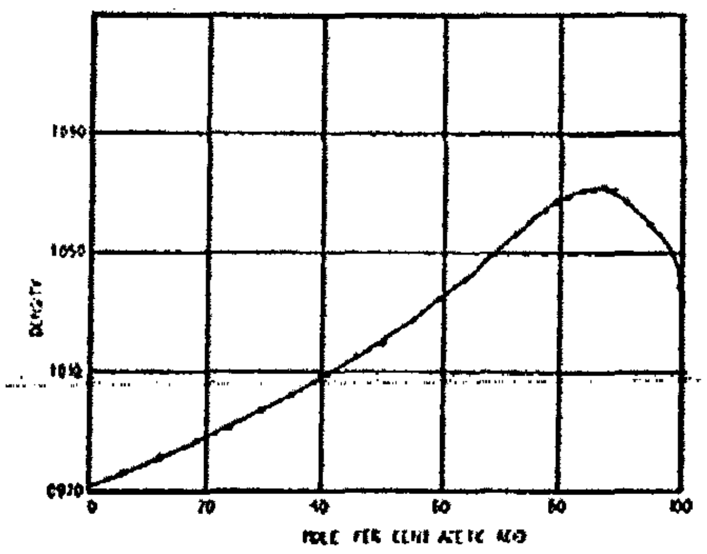

FIG. 3. DENSITIES FOR PYRIDINE AND ACETIC ACID MIXTURES AT 32.38°C.

TABLE 4

Complexes in the system pyridine–acetic acid

COMPLEX	METHOD OF IDENTIFICATION	INVESTIGATOR
1. Formula not given. Near 80 mole per cent acetic acid	Electrical conductance	Trifonov and Cherbov (12)
2. $3C_5H_5N \cdot rCH_3COOH$ (r unknown)	Electrical conductance	Sackhanov (7)
3. $2C_5H_5N \cdot 3CH_3COOH$	Boiling point Boiling point Boiling point	André (1, 2) Gardner (5) Swearingen and Ross
4. $C_5H_5N \cdot rCH_3COOH$ (r equals 4 or 5)	Viscosity	Tsakalotoes (11); Faust (4); Dunstan (3); Swearingen and Heck (8)
	Electrical conductance	Swearingen and Ross (10)
	Fusion point	Swearingen and Ross (9)
5. $C_5H_5N \cdot CH_3COOH$	Fusion point	Swearingen and Ross (9)

Table 4 facilitates a comparison of the complexes previously reported in the literature and those obtained in the current investigation.

The melting point–composition data, without doubt, furnish the most reliable basis for speculation and comment. These data point quite conclusively to the existence of the simple pyridonium acetate. While the flatness of the melting point–composition curve at the dystectic point indicates considerable dissociation of this complex, even at its melting point, there is yet the possibility that a sufficient amount of the complex persists, even at 138.35°C., to account for the maximum boiling point.

The second complex, indicated by the melting point–composition curve, has a composition between 80 and 85 mole per cent acetic acid, probably either at 80 or 83.3, since these compositions correspond to complexes $C_5H_5N\cdot 4CH_3COOH$ and $C_5H_5N\cdot 5CH_3COOH$, respectively. This complex is highly unstable, as shown by its incongruent melting point and high electrical conductivity in this region. The presence of this unstable complex is in no way revealed on the boiling point–composition diagram.

Thus, the boiling point data would seem to indicate dissociation of this complex into CH_3COOH and $C_5H_5N\cdot CH_3COOH$ molecules, while the conductance maximum would indicate dissociation into ions.

On the basis of all of the experimental evidence available, the behavior of this system might be formulated in the following equation:

$$\begin{array}{cl}
2C_5H_5N + 2rCH_3COOH & \\
\uparrow\downarrow & \\
2(C_5H_5N\cdot CH_3COOH) + (2r - 2)CH_3COOH & \text{(Indicated by freezing points)}\\
\uparrow\downarrow & \\
2C_5H_5N\cdot(2r - s)CH_3COOH + sCH_3COOH & \text{(Indicated by boiling points)}\\
\downarrow\uparrow & \\
2(C_5H_5N\cdot rCH_3COOH) & \text{(Indicated by conductance and viscosity)}\\
\downarrow\uparrow & \\
X^+ + Y^- &
\end{array}$$

where r equals 4 or 5, s equals 5 or 7 respectively, and X and Y are conducting ions.

SUMMARY

The boiling point–composition relations for pyridine and acetic acid mixtures have been determined over the entire range of composition.

A maximum boiling point mixture containing 58.4 mole per cent acetic acid was found to boil at 138.35°C., under a pressure of 760 mm.

No complexes indicated by viscosity, melting point, or conductance measurements are indicated on the boiling point–composition curve.

Data are presented to show that the composition of the maximum boiling mixture is influenced by pressure.

The densities of mixtures of pyridine and acetic acid have been determined at 32.38°C.

A résumé of all complexes reported for this system have been included.

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INFLUENCE OF CONCENTRATION AND AGE ON SOME COLLOIDAL PROPERTIES OF FERRIC CHLORIDE SOLUTIONS

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INTRODUCTION

The effect of dialysis and aging on particle size and constitution of colloidal ferric oxide sols prepared by a condensation method has been investigated by Nichols, Kraemer, and Bailey (4), who found that during aging the particle size distribution shifts slightly toward larger sizes, the formation of secondary aggregates being more pronounced in concentrated sols. The age of the stock solution of ferric chloride was observed to affect the particle size of the resulting ferric oxide. The particles gradually decreased in size with increasing age of the stock solution, and it was suggested tentatively that this was due to the formation of more and more nuclei therein.

Condensation methods for the preparation of colloidal suspensions depend upon creation of a supersaturation of the condensable phase, together with some starting points or nuclei to serve as centers for growth. The number of particles produced and the degree of dispersity depends upon the number of these starting points or centers. Further, the distribution of size of the condensed particles depends upon the rate of migration of material to the centers, taking into account the amount of dissolved material and the number of condensing centers. Nuclei are often produced by the condensation process itself, but in some cases artificial centers can be introduced. The rate at which the nuclei appear affects the distribution of the size of the particles, since those introduced or formed first are supplied with more material for building particles than are those formed later, and will consequently become larger. If it were possible to introduce all of the centers at the beginning, before the condensation process sets in, and to avoid spontaneous production of centers, one might expect to get much more uniformly sized particles. In fact, such principles have been used in Zsigmondy's nuclear method of preparing gold sols, with the result that fairly uniformly sized particles were obtained.

The object of the present investigation was to determine the effect of age and concentration of ferric chloride solutions on the pH values, the mobility, and the number of colloidal particles. The selection of ferric chloride systems for this work seemed desirable for two reasons: first, their property of spontaneous production of ultramicroscopically visible particles on standing at room temperature; and second, their frequent use in preparation of colloidal ferric oxide by high temperature hydrolysis.

TABLE 1

Measurements on ferric chloride solutions

AGE	NO. OF PARTICLES PER CC. × 10^{-9}	MOBILITY μ/SEC./V./CM.	pH
M/1000 ferric chloride			
0 hours	0.4	3.6	3.02
20 hours	0.6	3.1	2.70
2 days	0.7	3.0	2.66
7 days	38.	2.9	2.62
12 days	86.	2.7	2.49
21 days	107.	2.5	2.56
M/100 ferric chloride			
0 hours	4.7	4.2	2.37
20 hours	168.	3.7	2.10
2 days	655.	3.6	2.08
7 days	849	3.6	2.00
14 days	1090.	3.0	1.99
21 days	1155.	2.8	1.98
40 days	1336.		1.96
M/10 ferric chloride*			
0 hours	6.0	3.4	1.80
20 hours	56.	2.8	1.61
2 days	59.		1.65
7 days	69.		1.64
14 days†	93.		1.63
21 days	405.		1.58

* Mobility measurements for this concentration could not be accurately made because of a drift in the liquid due to electrolysis of the ferric chloride solution.

† Precipitation occurred.

EXPERIMENTAL

Ferric chloride solutions of three concentrations, *M*/1000, *M*/100, and *M*/10, were prepared, and immediately after preparation measurements of the number of particles (1), electrophoretic velocity (2), and pH (3) were made by methods previously described. Similar measurements were made at definite time intervals thereafter up to twenty-one days, the solutions being allowed to stand undisturbed at room temperature. The results of these measurements for the above concentrations are given in table 1.

Table 2 shows the results of measurements on ferric chloride solutions and the resulting high-temperature hydrolysis products. Solutions of *M*/1000 and *M*/100 ferric chloride were prepared as before and similar measurements made. Then definite quantities of these solutions (50 cc. of *M*/100 and 100 cc. of *M*/1000), were dropped slowly into 950 cc. and 900 cc. respectively of boiling water, following the usual method of preparing ferric oxide sols. Number of particles, migration velocity, and pH were then determined for these hydrolysis products.

TABLE 2

Measurements on ferric chloride solutions

AGE	NO. OF PARTICLES PER CC. × 10^{-10}		MOBILITY μ/SEC./V./CM.		pH	
	Original	Product	Original	Product	Original	Product
M/1000 solution						
0 hours	0.04	0.4	3.0	1.9	3.02	3.40
20 hours	0.06	0.9	2.9	2.3	2.70	3.46
2 days	0.07	1.0	2.8	1.8	2.68	3.47
7 days	2.2	18.8	3.0	2.2	2.63	3.41
14 days	3.4	37.7	2.8	2.4	2.58	3.34
21 days	10.1	117.0	2.5		2.56	3.30
M/100 solution						
0 hours	0.47	11.8	4.1	3.2	2.36	2.84
20 hours	3.5	85.	3.6	3.0	2.12	2.77
2 days	67.3	1151.	3.1	2.9	2.09	2.71
7 days	88.1	1640.	3.1	2.8	2.00	2.60
14 days	107.3	1992.	3.0	2.7	1.99	2.56
21 days	118.4	2302.	2.9	2.7	1.98	2.50

DISCUSSION

As was previously mentioned the rate of growth of colloidal particles is determined by the number of nuclei present and the degree of supersaturation of the system. In the system under consideration there are no nuclei present at the starting point, hence they must be produced by growth from the ferric chloride molecules in solution. The rate of nucleus formation is itself dependent upon the degree of supersaturation, so that ferric chloride solutions of different concentrations should exhibit initial growth stages of different lengths. When the particles have reached the minimum size necessary for nuclear action, i.e., when the initial growth stage is over, the particle growth is governed by the concentration of dissolved matter. If this concentration is sufficiently great a sudden appearance of particles will be evident.

If a solution contains C gram-equivalents of ferric chloride per liter and the degree of hydrolysis is denoted by x, the following expression may be written[1]

$$c_{\mathrm{Fe(OH)_3}} = xC$$

$$c_{\mathrm{H^+}} = 3xC \text{ (assuming complete dissociation)}$$

$$c_{\mathrm{Fe^{+++}}} = \alpha\,(1 - x)C$$

where α denotes the degree of dissociation of ferric chloride. Therefore,

$$x = \frac{c_{\mathrm{H^-}}}{3C} \text{ and } c_{\mathrm{Fe^{+++}}} = \alpha\left(1 - \frac{c_{\mathrm{H^+}}}{3C}\right)C = \alpha\left(C - \frac{c_{\mathrm{H^+}}}{3}\right)$$

The amount of ferric hydroxide formed is then directly proportional to the concentration of hydrogen ions. If the amount of ferric hydroxide in colloidal form is assumed to be directly proportional to the amount of ferric hydroxide in true solution, a linear relation should exist between the hydrogen-ion concentration and the number of particles observed under the ultramicroscope.[2] In figure 1 these quantities are plotted for $M/10$, $M/100$, and $M/1000$ solutions. Apparently the linear relationship is valid for certain stages of the process. It will be observed, however, that the initial points are in each case off the curve. Speculation regarding the reason for this behavior must be reserved until more experimental data can be obtained.

A consideration of the relationships between the age of the solution and the number of particles, graphically represented in figure 2, should lead to a more intimate understanding of the mechanism of particle formation. The abrupt changes in the courses of the curves indicate that the process may be considered as a summation of steps, rather than one step which

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[1] Making the simplifying assumption that no basic chlorides are formed.

[2] The observed number of particles may not exactly represent the amount of colloidal material, since obviously a number of amicrons may be present. The reaction is of course very complicated, notably because basic chlorides of varying composition are formed. The basicity of the latter possibly changes with aging of the solution, and this is accompanied by changes in the hydrogen-ion concentration. The rate of the reaction is opposed by increased hydrogen-ion concentration, and is favored by adsorption (which removes hydrogen ions from solution) and factors which tend to increase the adsorbing surface, such as particle formation. It is apparent from the data, however, that a consideration of the simple hydrolytic equilibrium given above cuts across these secondary phenomena and establishes a relation between the rate of particle formation and the hydrogen-ion concentration.

might be represented by a continuous function. It is well known that precipitation proceeds slowly until the nuclei have reached a size sufficient to function as condensation centers. In this connection Nordenson (5), during conductivity studies on the formation of gold sols, observed a similar stepwise character in the course of particle formation. He concluded that after the original precipitation the gold molecules slowly condense to colloidal gold particles until a great number of particles have reached the minimum size of nuclear action. After the nuclear limit is reached the reduction process proceeds rapidly, depositing the rest of the gold on the gold nuclei formed during the growth period. Nordenson demonstrated that the nuclear growth period could be arrested at will by the addition of colloidal gold particles, which then functioned as condensation nuclei causing a rapid particle growth. If it be assumed that a similar series of steps holds for the growth of colloidal particles from ferric chloride solutions, then the different stages for $M/100$ solution (figure 2) may be identified thus: (1) A to B—a slow nuclear growth stage; (2) B to C—a rapid condensation stage with large increase in the number of visible particles; (3) C to D—a slow growth stage similar to (1). Upon longer standing it might be expected that a fourth stage, similar to (2), would occur. Although no such stage was observed for the relatively short periods used in this investigation, a year-old sample of $M/100$ ferric chloride, originally clear, was found to have undergone marked precipitation, while still retaining a large number of colloidal particles in the supernatant liquid.

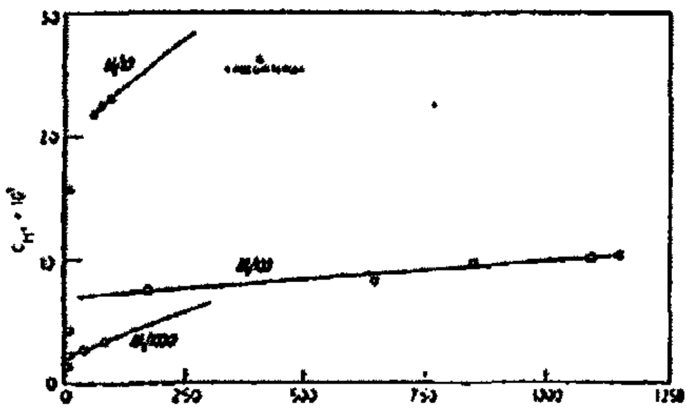

FIG. 1

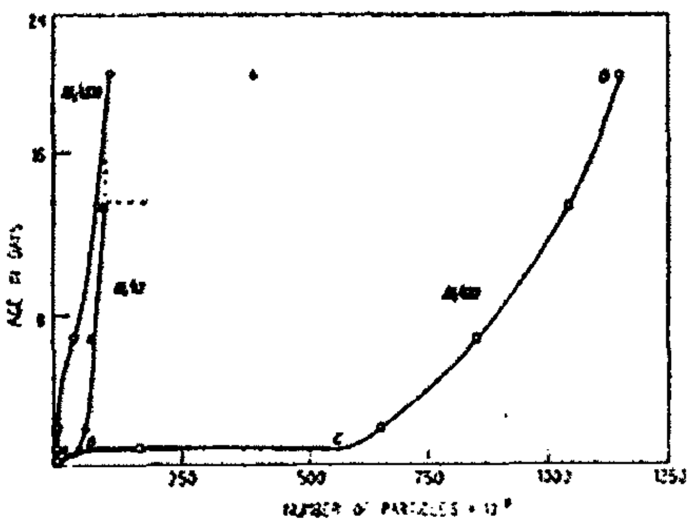

FIG. 2

It is a well-known fact that normal growth processes follow an exponential law. This behavior affords a means of differentiating more rigidly between successive stages in the curves of figure 2. If y denotes the number of particles and t denotes the time (age), the law of exponential growth is given by

$$y = y_0 e^{ct}$$

where y_0 represents the number of particles at the beginning of the growth stage and c is a constant.

Taking logarithms,

$$\ln \frac{y}{y_0} = ct$$

$$2.303 \log y = ct + 2.303 \log y_0$$

so that plotting $\log y$ against t should yield a straight line. This operation is carried out in figure 3. It will be observed that the linearity is quite good in all cases. The stepwise character of the process is clearly shown by the abrupt discontinuities in the curves. The fact that the number of particles in the $M/1000$ solution is smaller than the number in either of the other two solutions at any stage appears reasonable, as does the fact that the stepwise character of the curve (figure 2) is less pronounced. However, the position of the curve for the $M/10$ solution is anomalous.

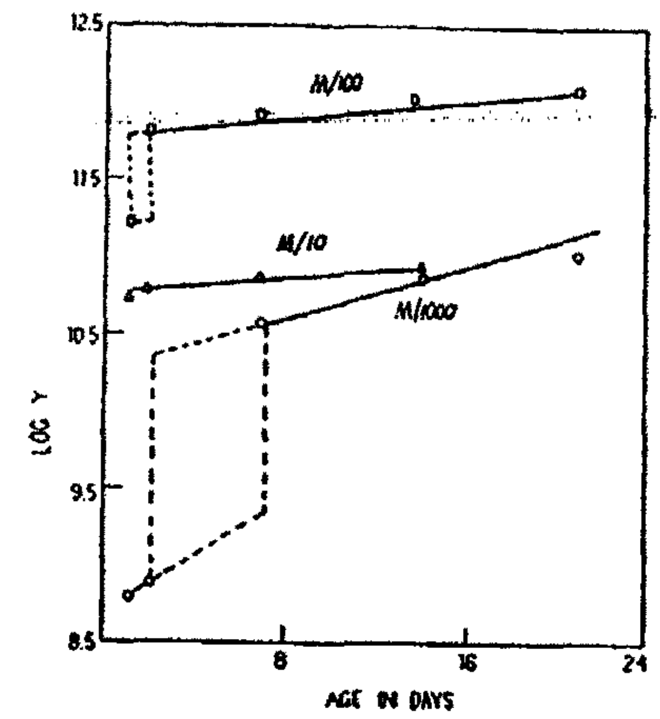

FIG. 3

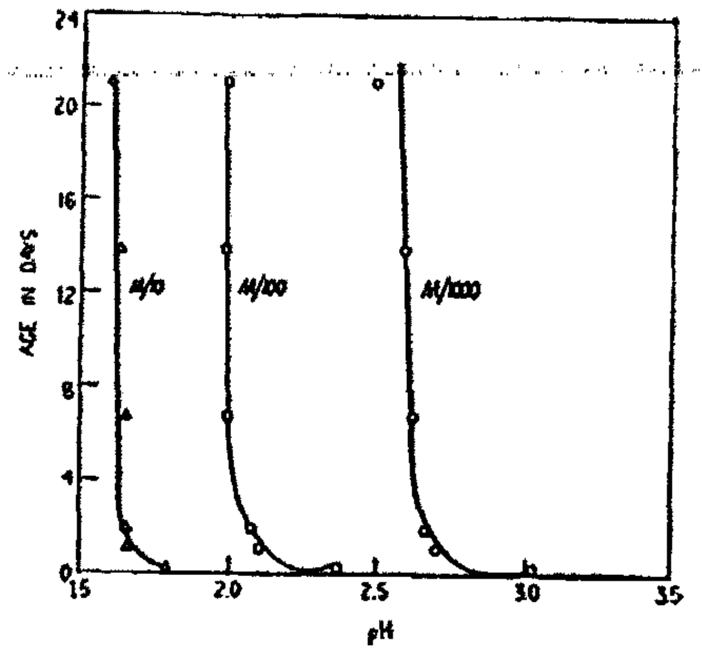

FIG. 4

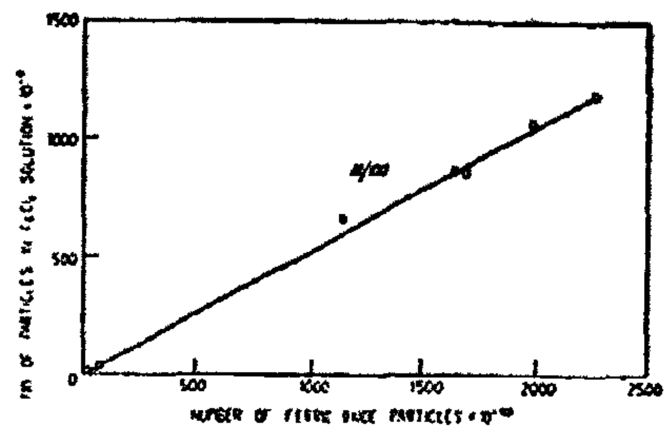

FIG. 5

The graphical representation of the relation between age and pH of the solutions is shown in figure 4. The relative positions of these curves for the different concentrations of solutions are quite normal, and the similarity of the curves is good. They are all typically logarithmic curves, the initial drop corresponding to a more rapid hydrolysis at the beginning of the process.

An examination of the tables reveals that with increasing age of the ferric chloride solutions a gradual decrease occurs in the migration velocity of the particles. At the start, when few particles are present, adsorption of positive ions (Fe^{+++} and H^+) is great, resulting in a high particle velocity. As more particles form, ferric ions are constantly used up, making less available for adsorption. At the same time the concentration of the solution gradually becomes less. With more particles and less available ions the charge on each particle is lowered, with a proportional drop in the migration velocity.

The results in table 2 show that the number of particles in the hydrolysis product of a ferric chloride solution is governed by the number of particles present in the original stock solution. This is shown graphically by the linear curve in figure 5.

SUMMARY

1. An investigation of the effect of age and concentration on some of the colloidal properties of ferric chloride solutions has been made. Ultramicroscopic methods were used to follow changes in particle number and particle velocity, while changes in pH were measured with a glass electrode.

2. Spontaneous formation of nuclei was found to take place in all concentrations of ferric chloride studied. The number of these nuclei present at the start was affected by the original concentration of the solution.

3. As the solutions of ferric chloride aged the number of colloidal particles increased in a stepwise manner.

4. The hydrogen-ion concentration of the solutions increased as hydrolysis proceeded. This increase when plotted against the increase in particle number gave an approximately linear relation.

5. Aging of the ferric chloride solutions resulted in a lowering of the electrophoretic velocity.

6. The number of particles in the ferric chloride solutions influenced the number of particles in the resulting high-temperature hydrolysis product.

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THE INTERMEDIATE STAGES OF ALDEHYDE OXIDATION. I

The Catalytic Action of Manganese Catalyst in the Various Stages of the Process of Acetaldehyde Oxidation

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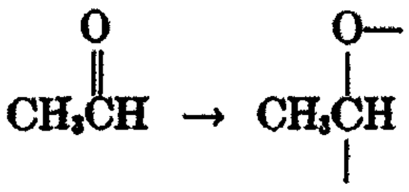
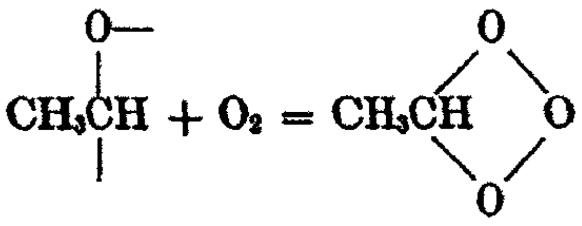
In the autoxidation of acetaldehyde we are concerned with the reaction of the formation of peracetic acid.

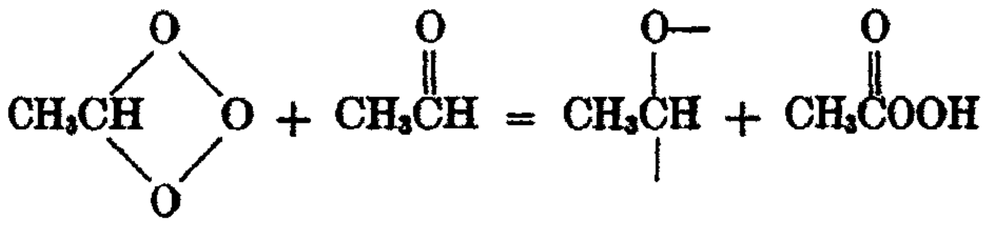
According to Bodenstein (2), the following chain mechanism takes place



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}H \rightarrow CH_3\overset{\overset{\displaystyle O—}{|}}{\underset{|}{C}}H \qquad (1)$$



(2)



(3)

Molecular oxygen adds to the active form of aldehyde (1), producing the active form of peracetic acid (2), in agreement with the theory of Bach (1) and Engler (4). The latter reacts with a normal molecule of acetaldehyde forming again an active aldehyde molecule and the final product (3). The peracetic acid obtained can in turn oxidize aldehyde further, forming acetic acid. The process of oxidizing acetaldehyde by oxygen directly to acetic acid in the presence of a catalyst is widely used in industry. For the investigation of the mechanism of this process, the study of the kinetics of not only the first stage of the formation of peracetic acid is important, but also the second stage, the interaction of peracetic acid with acetaldehyde.

We have made a special study of the second stage of this process (see the following article), and have found that the interaction between peracid and aldehyde proceeds also in two stages (a) and (b): (a) The addition of a molecule of aldehyde to the peracetic acid and the formation of an intermediate product of a peroxide character. The activation energy of this bimolecular reaction is 7000 calories, and its rate is higher than that of the second stage. (b) The decomposition of the intermediate product with the formation of two molecules of acetic acid. The activation energy of this monomolecular reaction is 15,000 to 16,000 calories.

The oxidation of acetaldehyde by oxygen to acetic acid at both low and room temperatures takes place at a slow rate, and in the absence of catalysts leads to the accumulation of peroxides. Hence it follows that the transformation of the peroxides to acetic acid proceeds more slowly than their formation. Bodenstein determined the activation energy of the first stage of acetaldehyde oxidation—the chain reaction of peracetic acid formation in the gaseous phase at about 10,000 calories.

In view of these facts we came to the conclusion that the study of the action of manganese catalyst, which is successfully applied for the oxidation of acetaldehyde to acetic acid, must follow the line of investigating the kinetics of the entire process of oxidation of acetaldehyde to acetic acid in the presence of a catalyst and of the influence of the catalyst on the kinetics of the separate stages of the process.

I. THE OXIDATION OF ACETALDEHYDE TO ACETIC ACID USING A MANGANESE CATALYST. ELIMINATION OF THE INDUCTION PERIOD OF THE REACTION

The experiments were carried out in the following manner: A known solution of acetaldehyde in acetic acid was sucked into a small vessel, provided with a stopcock and a small blank tube, where a small amount of the catalyst (a manganese salt) was placed. The vessel was previously evacuated and tared, and then connected by a piece of thin rubber tubing with a bomb of oxygen (2 liters), equipped with a manometer. Both the bomb and the reaction vessel were placed in a water thermostat. The vessel was then fastened to a vertical shaking machine (length of stroke, 5 cm.), and shaken in the thermostat at a rate of about 500 strokes per minute. The particles of the catalyst were washed down at the first stroke, and this moment was fixed as the beginning of the experiment. As the reaction proceeded, fresh portions of oxygen were automatically sucked from the bomb into the vessel, owing to the decrease in pressure above the liquid in the vessel. In the experiments which were carried out at constant pressure, the readings were taken on a buret with an automatic clamp connected with a levelling vessel (figure 1).

At the beginning of the experiment the stopcock in the right bend of the manometer (C) is closed. In proportion to the absorption of oxygen, the pressure of the system falls, making contact (K), and the electromagnet E weakens the clamp. Then a small amount of water runs from the buret (F) into the beaker (D), and the pressure in the system increases to the given level, after which the mercury in the left bend falls and the electromagnet breaks contact.

In spite of the large number of experiments which were carried out, it was not possible to determine exactly the reaction velocity constants, owing to the turbulent character of the reaction which took place highly exothermically in a short time so that the vessel had no time to cool down to the temperature of the thermostat. This accounts for the qualitative character of the results obtained, which nevertheless are of fundamental interest.

The commencement of the decrease of the oxygen pressure always coincided with the appearance of a dark brown coloration of the solution.[1] In some experiments the coloration did not appear at all, and the reaction did not take place; in others it appeared some time after the beginning of the shaking (3–75 minutes), and only after its appearance did the reaction and a sharp decrease of pressure in the system take place. Thus the added salts of bivalent manganese (acetate, nitrate[2]) do not appear to be catalysts. On the contrary the catalyst is formed in the aldehyde solution which is being oxidized, and only after its formation does the high reaction rate take place. The composition of the brown solution acting as catalyst

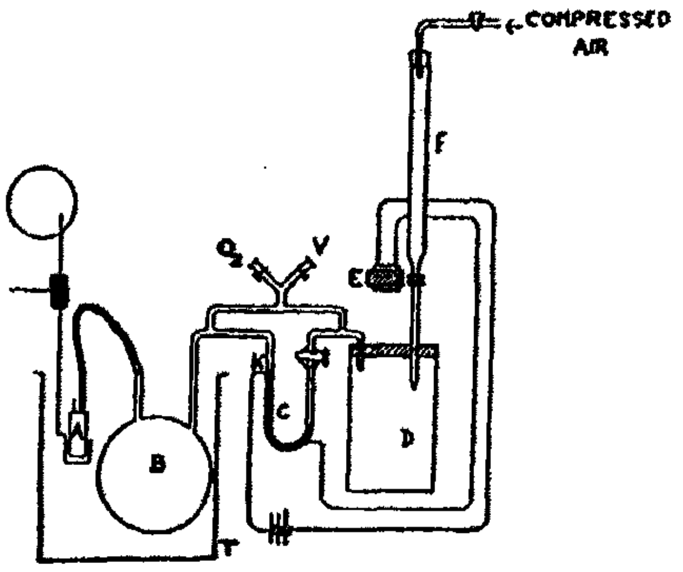


FIG. 1

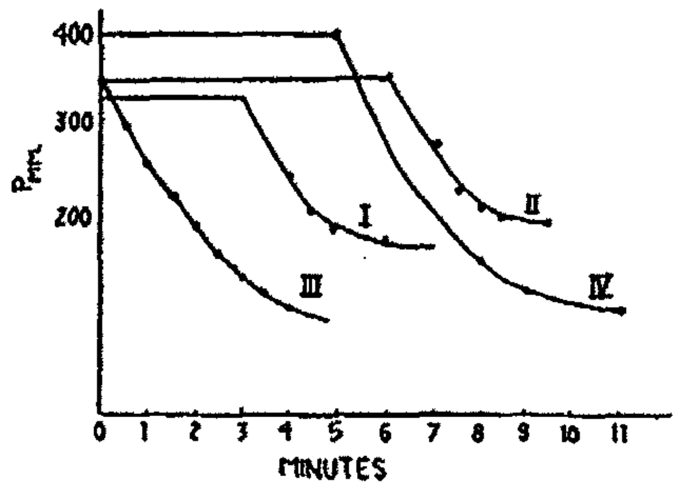


FIG. 2

FIG. 1. THE APPARATUS

V, to vacuum pump

FIG. 2. THE OXIDATION OF ACETALDEHYDE IN ACETIC ACID SOLUTION

I, catalyst $Mn(NO_3)_2$ at 25°C., induction period 43 minutes; II, catalyst $Mn(NO_3)_2$ at 25°C., induction period 73 minutes; III, catalyst $(CH_3COO)_2Mn$ at 15°C.; IV, catalyst $(CH_3COO)_2Mn$ at 15°C. in acetic acid and 10 per cent water solution, induction period 62 minutes.

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[1] The formation of the brown solution had been observed by Baeyer and Williger when introducing manganese acetate into a solution of perbenzoic acid.

[2] In a paper by M. J. Kagan and N. M. Morozov (6) it was shown that the activity of manganese nitrite as a catalyst of this process is 50 per cent greater than that of manganese acetate.

in this reaction was found to be an acetic acid salt of trivalent manganese. In the presence of this compound no induction period, which occurred in other experiments, was observed, as is shown by curves in figure 2. The accumulation of this compound evidently takes place during the induction period.

It is obvious that anything causing the decomposition of manganic acetate, $(CH_3COO)_3Mn$, must tend to lengthen the induction period. Thus, it was shown that the presence of water causes an induction period. Water decomposes maganic acetate, giving a precipitate of manganese hydroperoxide. When about 10 per cent of water was added to the solvent (acetic acid), a prolonged induction period was produced, even in the case when manganic acetate was used as catalyst (see figure 2, curve IV).

The oxidation of bivalent manganese to the trivalent form occurs under the action of peracetic acid, which is formed during the oxidation of acetaldehyde by oxygen. An acetic acid solution of manganic acetate may be readily prepared by the action of peracetic acid on manganous acetate, the peracetic acid being decomposed very turbulently. This fact cannot but influence the mechanism of the oxidation process (see below). The preparation of manganic acetate and its isolation in a pure state have been stated in detail by Christensen (3).

II. INFLUENCE OF THE CATALYST ON SEPARATE STAGES OF THE PROCESS

A. The influence of the catalyst on the rate of the interaction between peracetic acid and acetaldehyde

The determinations of the velocity of the summary reaction

$$CH_3COOOH + CH_3CHO \rightarrow 2\ CH_3COOH$$

with manganese catalyst are only of a qualitative character, owing to the poor reproducibility of the numerical values of the velocity constants in different experiments. However a sharp increase of the velocity with the addition of very small amounts of the catalyst has been positively determined (see figure 3). As shown above in the case of interaction between aldehyde and peracetic acid, the formation of the addition product is the faster, while the slower stage, limiting the reaction rates, is the decomposition of the intermediate product into two molecules of acetic acid. By studying the kinetics of the decomposition of this product in the presence of the manganese catalyst, we were able to obtain more reproducible quantitative results (shown in table 1). The experiments were carried out in the following manner: The mixture of peracetic acid and aldehyde dissolved in toluene was left standing for several hours at a temperature of $-30°C.$, as a result of which an addition product of a pêroxide character was formed. For the quantitative determination of this product in the presence of peracetic acid see paper II. The kinetics of the decomposition of this product at room temperature without a catalyst was studied. Then, at a definite moment, a solution of manganic acetate in chloroform was introduced. The reaction rate was estimated by the disappearance of the peroxide, the content of the latter being determined iodometrically.

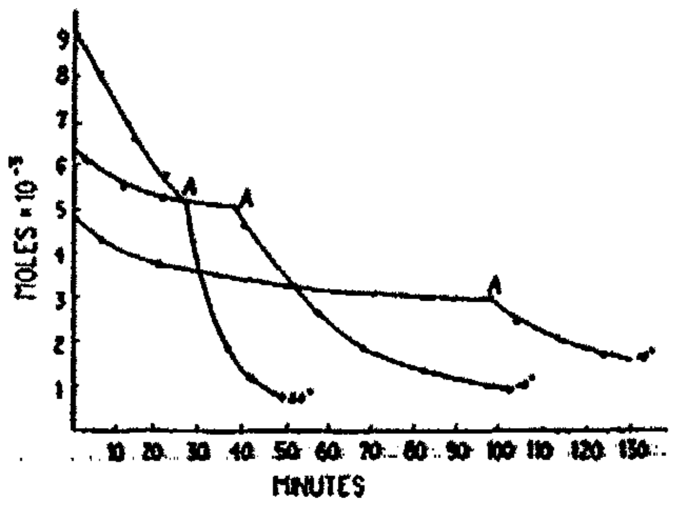


Fig. 3

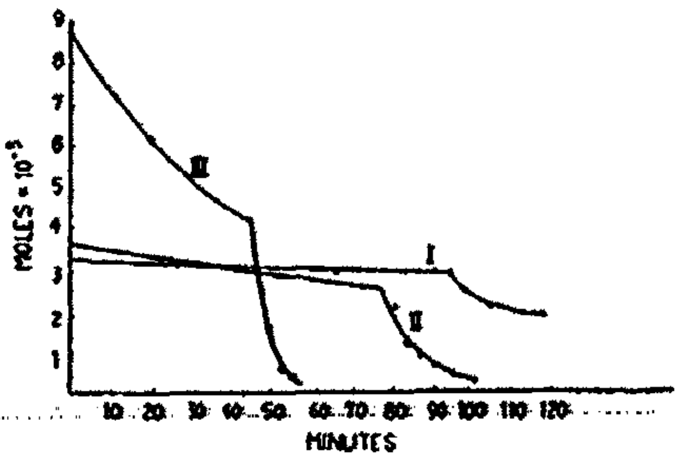


Fig. 4

Fig. 3. The Catalysis of Interaction between Peracetic Acid and Acetaldehyde

Points A correspond to the moments of pouring of the catalyst, 6×10^{-5} g.

Fig. 4. Catalytic Decomposition of the Addition Product (Peracetic Acid and Benzaldehyde) in Toluene Solution

I, experiment No. 119 at 10°C.; II, experiment No. 120 at 20°C.; III, experiment No. 121 at 30°C. (high concentration).

TABLE 1

Decomposition of the intermediate product (peroxide) obtained at −30°C. in a toluene solution

$t = +20$°C.			$t = +10$°C.		
Time from the beginning in minutes	Moles per liter	K (sec.$^{-1}$)	Time from the beginning in minutes	Moles per liter	K (sec.$^{-1}$)
(a) Without catalyst			(a) Without catalyst		
0	0.4015		0	0.2840	
13	0.3791	7.37×10^{-6}	21	0.2711	2.644×10^{-5}
73	0.2895	7.49×10^{-6}	51	0.2597	2.380×10^{-5}
123	0.2334	7.18×10^{-6}	86	0.2457	2.641×10^{-6}
			116	0.2351	2.436×10^{-6}
(b) With catalyst (manganic acetate = 0.0008 g.)			(b) With catalyst (manganic acetate = 0.0009 g.)		
0	0.2005		0	0.2130	
4	0.1504	1.2×10^{-3}	4	0.2004	2.545×10^{-4}
8	0.1169	1.05×10^{-3}	10	0.1830	2.825×10^{-4}
17	0.06466	1.1×10^{-3}	22	0.1548	2.325×10^{-4}

These data show a considerable increase in the reaction rate of this stage under the influence of the catalyst, and we are able to state quite definitely the catalytic effect of manganic acetate on the rate of this very slow reaction. Thus we have reason to suppose that the part played by the catalyst consists in accelerating the rate of decomposition of the intermediate peroxide product with the resulting speeding up of the whole oxidation process. On the other hand, a still greater catalytic effect is observed during the decomposition of the peracid, which points to the possibility of another mechanism of the catalysis.

The decomposition of peracetic acid under the action of manganous acetate

The study of the decomposition of peracetic acid in the presence of a manganese salt is of some interest in explaining the partial formation of carbon dioxide in the industrial oxidation of acetaldehyde. Moreover, as was pointed out, it may considerably influence our conception of the mechanism of the oxidizing action of peracetic acid. The decomposition was carried out at room temperature in acetic acid and water solutions in a small vessel of about 10-cc. capacity with a stopcock, connected by a piece of rubber tubing with a Hempel buret. A definite amount of the peracid solution was poured into the vessel, while manganese acetate particles were placed in the closed side-arm tube.

TABLE 2

Decomposition of peracetic acid

NO. OF EXPERIMENT	GAS CONTENT	
	CO_2	CO
	per cent	*per cent*
3	87.4	11.8
4	88.9	11.1
5	88.3	11.1
7	93.0	7.0

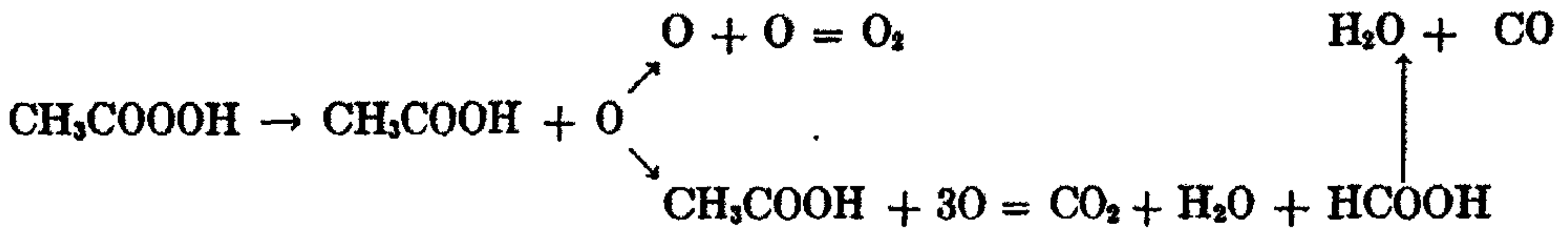
On shaking the vessel the particles of catalyst dropped into the solution, whereupon the evolution of gas began and the liquid became strongly heated. The gas was collected in the Hempel buret and afterwards analyzed for carbon dioxide, oxygen, and carbon monoxide. The results of the peracid decomposition in an acetic acid solution are very interesting. The gas evolved during the decomposition contained no oxygen, being composed chiefly of carbon dioxide and carbon monoxide, with a small percentage of hydrocarbons. The data given in table 2 are characteristic of such a process of decomposition. Immediately after coming into contact with manganous acetate, the solution acquired a dark brown color, due to the formation of manganic acetate. On diluting this solution with water, a brown-colored residue of manganese hydroperoxide is instantly formed.

A quite different process of peracetic acid decomposition was observed in a water solution; the process took place smoothly, slowly, and without any perceptible heating. When small quantities of manganous acetate were added, no manganese dioxide residue was formed, but the solution acquired the characteristic permanganate color. In case of an excess of manganous acetate the solution acquired an orange-red color, and after standing several hours or days (according to the quantity of manganous acetate) a precipitate formed. It must be noted that the decomposition of the peracid in the presence of potassium permanganate solution also proceeds very slowly. The titration of the peracid solution decomposed in the presence of potassium permanganate was as follows: 0.2 cc. of peracid solution = 4.5 cc. of thiosulfate solution (0.02 *N*); on the following day = 3.1 cc.; on the third day = 2.6 cc. The gas evolved during the reaction under these conditions was composed chiefly of oxygen, i.e., it had quite a different composition from the gas evolved during the decomposition in the acetic acid solution (see table 3). Therefore, we may conclude that oxygen forms the initial decomposition product of the peracid decomposition, which during its slow evolution is able to combine into molecules of oxygen, whereas during a turbulent evolution it oxidizes the molecules of organic compounds to carbon dioxide and carbon monoxide:

TABLE 3

Decomposition of peracetic acid

GAS CONTENT		
CO_2	CO	O_2
per cent	*per cent*	*per cent*
27.1	15.6	57.2
30.8	10.7	58.4
25.1	11.3	63.5



$$\begin{tikzcd} & O + O = O_2 & H_2O + CO \\ CH_3COOOH \rightarrow CH_3COOH + O \arrow[ur] \arrow[dr] & & \\ & CH_3COOH + 3O = CO_2 + H_2O + & HCOOH \arrow[uu] \end{tikzcd}$$

These data are in agreement with Hatcher and Tool (5), who observed that peracetic acid is decomposed when heated, forming carbon dioxide, formic acid, and glycolic acid.

The determination of the kinetics of the decomposition of peracetic acid in an aqueous solution in the presence of manganous acetate showed that this process proceeds as a reaction of the first order and at a very slow rate, the decomposition beginning at the moment of the appearance of a pink hue of the solution (apparently due to the formation of permanganic acid). Comparison of the kinetic data obtained may be seen from table 4.

The activation energy of this process is expressed by a value approximating 12 kg-cal.

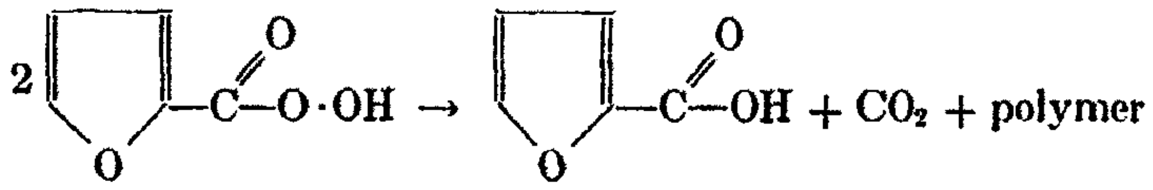
TABLE 4

Decomposition of peracid in aqueous solution in presence of manganous acetate (0.0048 g.)

Experiment 88

TIME FROM THE BEGINNING IN MINUTES	MOLES PER LITER	K (sec.$^{-1}$) × 10^5
	t = +40°C.	
0	0.3668	
19	0.3241	10 9
85	0.2273	8.96
98	0.2116	9.17
138	0.1673	9.8
	t = +20°C.	
0	0.1217	
35	0.1177	1.61
77	0.1111	2.28
113	0.1058	2 26

Observations analogous to ours were made by Milas (7) on investigating the decomposition of furo-peracid:



Solid furo-peracid was decomposed in a vacuum with the formation of a gas consisting only of carbon dioxide. In the residue was furo-acid and tarry polymer. In a weak solution of chloroform a monomolecular decomposition took place with the formation of oxygen and furo-acid. The energy of activation = 15,800 calories.

In comparing the above experimental data in the first as well as in the second version, the great influence exerted by the catalyst is observed.

In the first version, in the absence of the catalyst, we observe a high rate for the reaction of the addition of aldehyde to peracid, and a low rate of the decomposition of the addition product into 2 molecules of acetic acid. With manganese catalyst this slow process is accelerated about twenty times. It seems logical to infer that the action of the catalyst consists in the acceleration of the slowest stage, and that the scheme of the oxidation process remains the same whether it takes place in the presence or the absence of the catalyst.

$$A + O_2 = P; A + P = AP; AP = 2S^3$$

However, according to the above kinetics data, the decomposition of peracetic acid, using a manganese catalyst, proceeds with evolution of oxygen; only in the absence of aldehyde, which is the acceptor of oxygen, does the combustion of acetic acid take place. The decomposition of peracetic acid dissolved in glacial acetic acid occurs at an exceptionally high rate, and when aldehyde is present it may be oxidized very rapidly to acetic acid. It follows that the catalytic process may also proceed according to another scheme viz.:

$$A + O_2 = P; P = S + O; A + O = S$$

We showed above the scheme of Bodenstein for the chain mechanism of aldehyde autoxidation. The property of peracetic acid of decomposition under the action of manganese catalyst cannot but influence the chain process. At the same time the generation of the oxygen atoms may lead to a mechanism of a type differing from that proposed by Bodenstein.

The elimination of the induction period in presence of manganic acetate catalyst is of great interest. The induction period consists in the slowing down of the oxygen absorption, i.e., the delaying of the peracetic acid formation (which oxidizes Mn^{++} to Mn^{+++}). By introducing manganic acetate, the conditions are created for the reaction of the further transformation (decomposition) of peracetic acid, at the same time eliminating the induction period. It is hoped to resume this problem later in case of other oxidation reactions.

SUMMARY

1. The oxidation of acetaldehyde by oxygen in an acetic acid solution in the presence of manganese salts proceeds vigorously after the formation of a dark brown catalytic product.

2. In this process the catalytic product is trivalent manganese acetate obtained by action of peracetic acid on Mn^{++}.

3. One of the causes of the induction period of the reaction is the presence of water which decomposes the catalyst manganic acetate, forming

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[3] A = aldehyde; P = peracetic acid; S = acetic acid.

manganese hydroperoxide. In the absence of water the induction period is eliminated by the addition of a trivalent manganese salt as catalyst.

4. The rôles of the manganese catalyst may be two: on one hand it hastens the decomposition of the intermediate peroxide (product of addition of peracetic acid to aldehyde) leading to the formation of acetic acid; on the other hand it decomposes peracetic acid with the separation of active oxygen, which directly oxidizes aldehyde.

5. The formation of carbon dioxide during the oxidation of acetaldehyde by oxygen is due to the partial decomposition of peracetic acid under action of trivalent manganese. The gaseous products of peracetic acid decomposition consist chiefly of carbon dioxide (~ 90 per cent). The decomposition in the acetic acid solution takes place very turbulently and exothermically.

6. The decomposition of the peracid in the aqueous solution after the addition of manganese acetate takes place at a very slow rate. The gaseous decomposition products are chiefly oxygen (~ 60 per cent). The decomposition process is a first-order reaction and requires an activation energy approximating 12,000 calories.

7. Owing to the catalytic decomposition of peracid in the presence of aldehyde in the acetic acid solution no combustion product except acetic acid is formed, i.e., the oxygen atom oxidizes the aldehyde molecule. There seem to be good reasons for believing that such a scheme of the catalytic oxidation of aldehyde is very probable.

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THE INTERMEDIATE STAGES OF ALDEHYDE OXIDATION. II

KINETICS OF THE INTERACTION BETWEEN PERACETIC ACID AND THE ALDEHYDES

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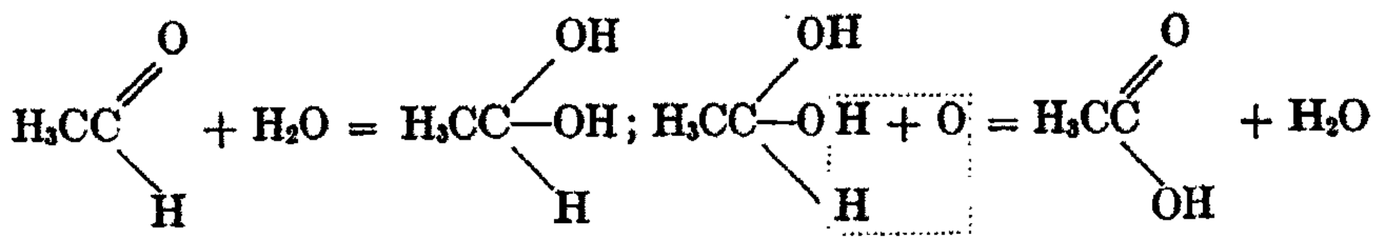
The study of the intermediate stages of aldehyde oxidation was limited chiefly to investigations of the first stage of oxidation, i.e., the formation of peracid from the aldehyde molecule and the oxygen molecule. The kinetics of the second stage of the process, the interaction between the peracid and aldehyde,

$$RCOOOH + RCHO \rightarrow 2RCOOH$$

remained unstudied.

In one of his recent papers Wieland (5) studied the process of interaction between the peracids and aldehyde. He came to the conclusion that in case of a reaction between peracetic acid and aldehyde, the reaction may be carried out with a marked velocity only in the presence of water, when aldehyde hydrate is formed. The latter is subsequently dehydrogenated by the oxygen of the peracetic acid.



In the present paper, the kinetics of interaction between peracetic acid and aldehyde is studied. It was found that the formation of two molecules of acid from a molecule of aldehyde and a molecule of peracetic acid involves an intermediate reaction, viz., the formation of an addition product of the reacting molecules having a peroxide character, and that water catalytically accelerates the decomposition of this product. At the same time the kinetics of each intermediate stage was studied.

I. EXPERIMENTAL PROCEDURE

Acetaldehyde was obtained by the oxidation of alcohol by air on the surface of a copper catalyst. The pure aldehyde, redistilled several times and boiling at 20.5°C., was sealed in tared thin-walled glass ampullae.

The ampullae were weighed with the capillary glass tips sealed off; thus the weight of the aldehyde was determined to the fourth decimal. The sealed ampulla was used for the reaction during the same day; in this manner freshly distilled aldehyde was always used. The peracetic acid was obtained by action of concentrated hydrogen peroxide on acetic anhydride (3) in presence of a few drops of sulfuric acid. At the beginning the reaction proceeds very rapidly, therefore it is necessary to cool the acetic anhydride to 0°C. and then gradually to add the hydrogen peroxide drop by drop especially at the beginning. The hydrogen peroxide (Kahlbaum, 27 per cent H_2O_2) was first concentrated by distillation. The residue in the distilling flask was generally found to be 80 per cent hydrogen peroxide, which was used in preparing peracetic acid. Peracetic acid was carefully distilled in vacuum (10–15 mm.) at 24–25°C., the middle fraction being collected; in this manner a 50 per cent solution of peracetic acid in acetic acid was generally obtained, which contained almost no diacetyl peroxide. When kept in the dark at room temperature such a solution decomposes very slowly, so that even after several months the concentration changes very little.

The glacial acetic acid (f. p., 16.4°C.) used as solvent was obtained by repeated crystallization of a distilled commercial glacial acetic acid. The other solvents—benzene, chloroform, nitrobenzene, toluene—were obtained chemically pure from Kahlbaum.

The investigation of the interaction between peracetic acid and aldehyde was carried out in a small closed cylindrical vessel about 120 mm. in height and 20 mm. in diameter. The vessel was placed into a thermostat, the temperature of which was regulated with an accuracy of 0.02°C. The small cross section of the reaction vessel facilitated the maintenance of a uniform temperature of the liquid. The vessel was filled with a definite amount of peracetic acid solution.

In the reaction vessel was placed a sealed ampulla with acetaldehyde, which was broken at a given moment taken as the beginning of the reaction. At the same time another vessel with a solution of peracid of the same concentration was placed in the thermostat and stability of the acid was periodically tested. The portions from the reaction and the test vessels were pipetted with a micropipet (generally 0.1 cc.) into a previously weighed beaker containing a 10 per cent solution of potassium iodide, and after weighing (which never exceeded three minutes) the iodine evolved was titrated with 0.02 *N* sodium thiosulfate solution (2). The small additional amount of iodine evolved in standing under action of an admixture of diacetyl peroxide was generally the same for all portions, and was disregarded.

When experimenting in neutral solutions (benzene, toluene, etc.) 2 cc. of 1 *N* sulfuric acid was added to the potassium iodide solution. The concentration of acetaldehyde in the solution generally did not exceed 2–3 per cent, which corresponds to a vapor pressure of 20–60 mm. in the temperature range used (10–30°C.). These results remained unchanged if the reaction was carried out in an atmosphere of nitrogen. The investigation was carried out under ordinary conditions in a closed vessel.

TABLE 1

Kinetics of interaction between acetaldehyde and the peracid in an acetic acid solution

Experiment No. 65. Peracid, 3.377 per cent. Aldehyde/peracid = 2.12

NO. OF PORTION	TIME INTERVAL IN MINUTES	MOLES PER LITER		K (mole^{-1} cm.^{3}sec.$^{-1}$)
		Peracid	Aldehyde	
t = 288°C.				
0		0.4266	0.9043	
1	1.5	0.3711	0.8488	1.77
2	30	0.2649	0.7426	0.236
3	57	0.1948	0.6725	0.127
4	54	0.1507	0.6284	0.122
5	31	0.1320	0.6097	0.115
t = 293°C.				
0		0.1235	0.6006	
1	21	0.1071	0.5848	0.192
2	20	0.09443	0.5722	0.181
3	20	0.08247	0.5612	0.202
4	15	0.07462	0.5533	0.200

II. KINETICS OF THE INTERACTION OF PERACTIC ACID WITH ACETALDEHYDE IN NON-AQUEOUS SOLVENTS

A. Reaction in acetic acid solutions

The interaction between peracetic acid and acetaldehyde was studied at a temperature of 10–30°C., the concentration of the solution of peracid and the ratio $\frac{\text{aldehyde}}{\text{peracid}}$ being varied from 0.5 to 3.3.

The results obtained can be described with a sufficient degree of accuracy by a second-order kinetic equation if we disregard the values obtained by calculation of the first portions taken two to ten minutes after the beginning of the reaction; as a rule these values are very high as compared with the following ones. We shall return to this point below.

Some typical experiments in acetic acid solution are given in table 1.

In table 2 the constants of the reaction rate in dependence on the temperature are given (the initial constants being disregarded).

The temperature effect is expressed by the Arrhenius equation (figure 1). The activation energy of the process is 15,400 ∓ 300 calories.

B. Reaction in other non-aqueous solutions

In order to determine the specific influence of the solvent on the reaction rate, a series of experiments was carried out using benzene, chloroform, and nitrobenzene solutions. Preliminary test experiments showed that in these solvents the peracetic acid is quite stable, and is not sensibly decomposed after standing a considerable time. Table 3 shows some of the results obtained. (Initial constants are disregarded.)

TABLE 2

Kinetics of interaction between acetaldehyde and peracid in an acetic acid solution

t	PER CENT OF PERACID	$\frac{\text{ALDEHYDE}}{\text{PERACID}}$	TIME OF EXPERIMENT	K (MEAN)
°C.			*minutes*	
10	2.96	1.8	120	0.0754
10	3.45	1.51	105	0.0756
15	4.91	1.35	180	0.123
15	3.38	2.12	174	0.122
20	3.12	2.2	200	0.196
20	3.38	2.1	76	0.195
25	4.8	1.45	230	0.290
25	4.77	1.61	300	0.288
30	2.5	2.43	312	0.475
30	4.32	1.39	215	0.483

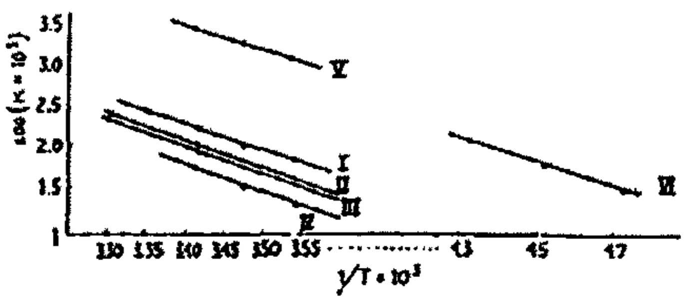


FIG. 1

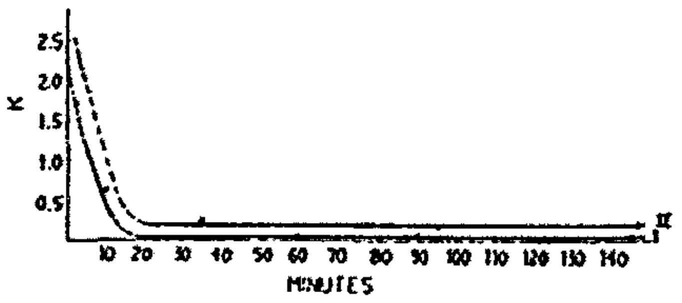


FIG. 2

FIG. 1. VALUES OF LN K PLOTTED AGAINST $1/T$

I, solvent, acetic acid; II, solvent, nitrobenzene; III, solvent, chloroform; IV, solvent, benzene; V, solvent, water (92 per cent); VI, solvent, toluene.

FIG. 2. THE REACTION VELOCITY CONSTANTS AS A FUNCTION OF TIME

I, solvent, benzene at 20°C.; II, solvent, chloroform at 30°C.

It will be noted from this table that the rate of the reaction in all the solvents is approximately equal, being lower than in the acetic acid solution. Curves obtained by plotting ln K against $1/T$ are straight lines (figure 1). The activation energy calculated from these data is approximately equal for this reaction in all solvents. Table 4 shows constants A and E of the Arrhenius equation, $K = Ae^{-E/RT}$, for various solvents.

It will be noted that in all non-aqueous solutions the velocity constants calculated from the data of the first portions (one to five minutes after commencement of the reaction) are always considerably higher than the following normal constants. When plotting the values of the velocity constants calculated according to the second-order equation, curves are obtained with a pronounced sharp inflection, after which the process goes on uniformly corresponding to the equation.

This phenomenon suggested that the sharp inflection of the reaction

TABLE 3

Kinetics of interaction between acetaldehyde and peracid in various non-aqueous solvents

t IN °C.	PERCENTAGE OF PERACID	$\frac{\text{ALDEHYDE}}{\text{PERACID}}$	K (mole^{-1} sec.$^{-1}$ cm.^{3})
		In benzene	
10	2.67	2.59	0.0220
15	2.88	2.48	0.0349
20	2.71	2.5	0.0610
		In chloroform	
20	1.73	2.09	0.0993
30	1.73	2.09	0.250
		In nitrobenzene	
20	1.76	3.09	0.1054
30	1.76	3.09	0.266
		In toluene	
20	2.58	3.1	0.0974

TABLE 4

The values of the constants of the Arrhenius equation for the reaction in various non-aqueous solvents

SOLVENT	A	E IN CALORIES PER GRAM-MOLE
Acetic acid	7×10^{10}	15,500
Benzene	8.5×10^{10}	16,260
Chloroform	6.6×10^{10}	16,200
Nitrobenzene	1.52×10^{11}	16,280
Water	4.56×10^{12}	16,230

velocity curve may be attributed to the presence of an intermediate stage, the first stage being carried out at a high rate but within the limits of the equilibrium, which is gradually shifted as the second slower stage of this reaction. This may be expressed schematically as follows:

$$\underset{\text{(rapid stage)}}{A + B \rightleftarrows AB} \rightarrow \underset{\text{(slow stage)}}{2C}$$

On this ground we might infer that if the temperature of the reaction is considerably lowered, the second stage will be slowed down in such a degree as to be almost imperceptible, while the rate of the first stage of the reaction will remain slow but quite perceptible. The reaction being obviously exothermic, the equilibrium concentration of the intermediate product will increase with cooling. Experiments absolutely confirmed this conclusion.

TABLE 5

Kinetics of interaction between aldehyde and peracid in a toluene solution

t IN °C.	PERCENTAGE OF PERACID	$\frac{\text{ALDEHYDE}}{\text{PERACID}}$	*K* (MOLE^{-1} CM.^{3} SEC.$^{-1}$) (MEAN)
−41	3.14	3.0	0.132
−51	3.95	2.79	0.066
−61	3.44	3.16	0.031

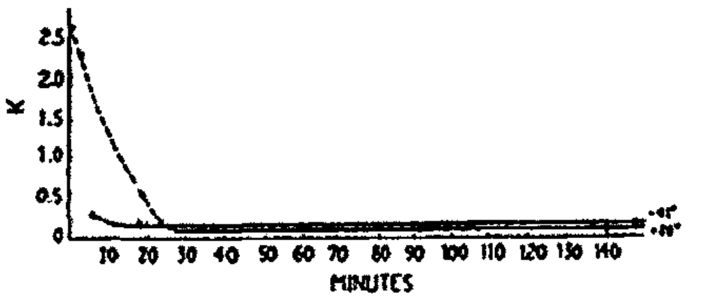


FIG. 3

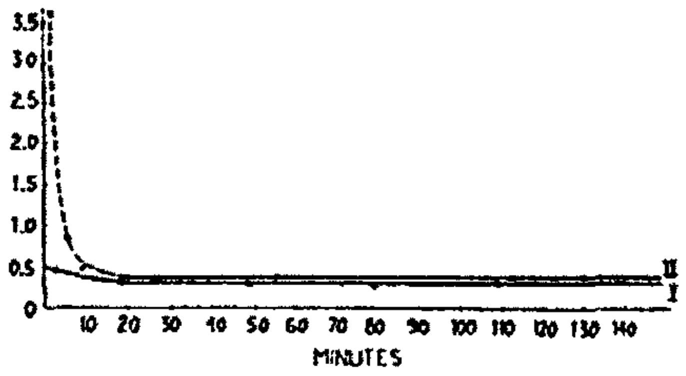


FIG. 4

FIG. 3. INTERACTION BETWEEN PERACID AND ALDEHYDE IN TOLUENE

FIG. 4. KINETICS OF INTERACTION BETWEEN VALERALDEHYDE AND PERACETIC ACID

C. *Kinetics of the reaction at low temperatures*

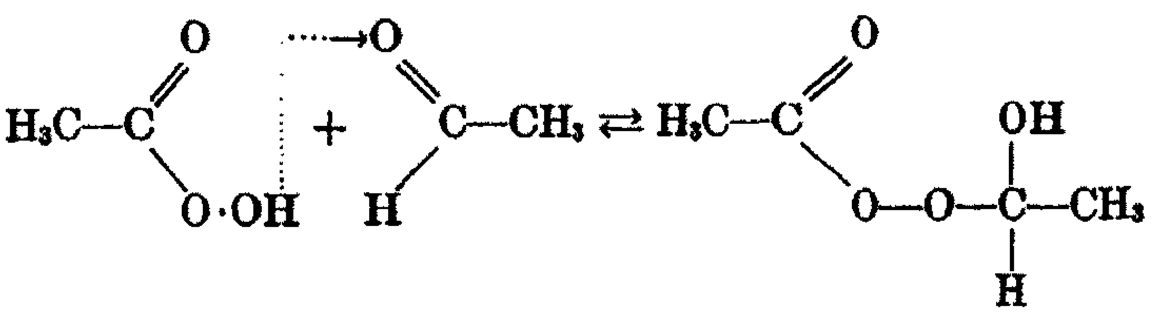
The series of experiments at low temperatures was carried out in a toluene solution, the reaction vessel being immersed in a mixture of acetone and solid carbon dioxide in a Dewar flask. The temperature was held at ±0.5°C. by means of the periodical addition of small bits of solid carbon dioxide. The test portions were taken out with a micropipet and added to a solution of potassium iodide acidified with 1 *N* sulfuric acid. Table 5 characterizes the most typical experiments.

Table 5 shows that the reaction rate at −41°C. is higher than the normal rate (corresponding to an established constant) at +20°C., i.e., at a low temperature we have quite another process. Curves on figure 3 give a graphical illustration of these reactions.

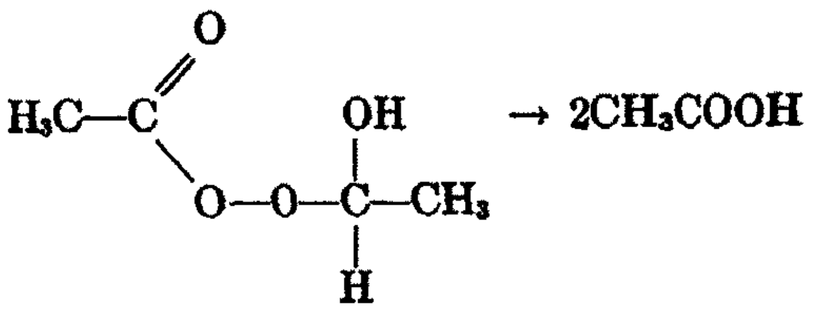
Plotting values of ln K against $1/T$ (figure 1) we obtain a straight line. The low activation energy, 7000 calories (notwithstanding the abnormally small value of the coefficient A of the Arrhenius equation, 5.2×10^6), indicates the facility with which the process takes place. This is also shown by the high values of the velocity constants: the calculation of the velocity constants at 20°C. using the values at these low temperatures gives the value 3.1. Thus the presence of two stages in the interaction between peracid and aldehyde cannot be doubted.

D. The mechanism of the reaction and the method for the quantitative determination of the intermediate stage

The intermediate product which is here formed might be thought of as a direct addition product of a molecule of peracid to a molecule of aldehyde according to the scheme:

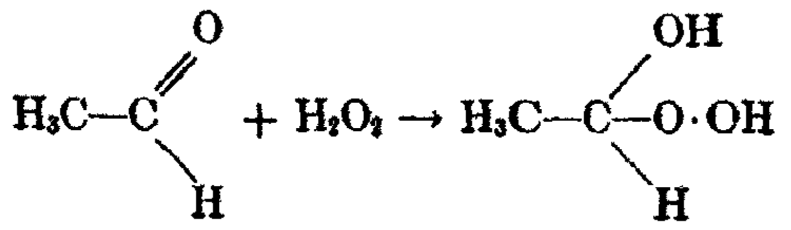

(a)

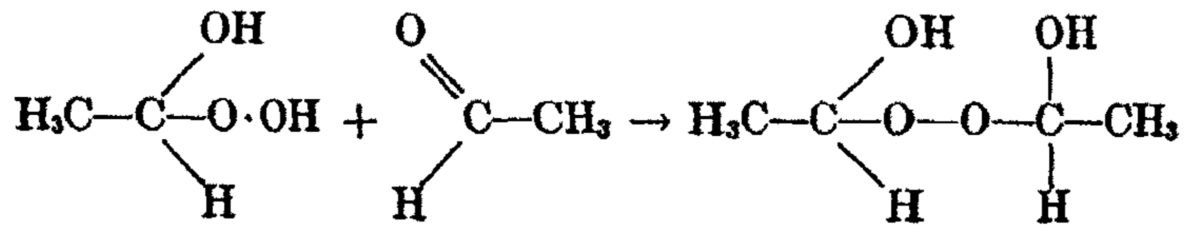
forming a new peroxide compound, hydroxyethylacetyl peroxide. The peroxide intermediate product shown in scheme a slowly decomposes, forming 2 molecules of acetic acid


(b)

In the course of the process b, the equilibrium in a is shifted to the right, and thus the reaction rate in a is determined by the reaction rate of the second stage (b).

The possibility of the formation of such a peroxide intermediate compound by the interaction of peracid with aldehyde was pointed out by Wieland (5). He was, however, not able to demonstrate by direct experiments the formation of the addition product of peracetic acid with acetaldehyde, and traced the disappearance of the peracetic acid only in the aqueous solution of aldehyde. Hence Wieland inferred that the oxidation of aldehyde by the peracid is due to dehydrogenation of aldehyde hydrate. Wieland and B. Wingler (6) obtained a compound like (a) by the action of hydrogen peroxide on acetaldehyde. Rieche (4) describes such a compound obtained by the action of ethyl-hydroperoxide on aldehyde:





We found the means of using the iodine evolved in the *neutral* potassium iodide solution (aqueous or methanol) for the determination of the whole amount of active oxygen contained in the peracetic acid and in the hydroxyethylacetyl peroxide. On the other hand, free peracetic acid may be determined in the acid solution of potassium iodide; under the action of the acid, the intermediate peroxide product is readily decomposed and the iodine evolved corresponds to the free peracetic acid only. Thus if the reaction is carried out at low temperatures and portions are introduced into a neutral potassium iodide solution, we are able to state that the amount of active oxygen remains practically unchanged throughout the experiment, so that it may seem that no process takes place at all. But when the same portions are brought into an acid solution of potassium iodide a gradual decrease of the amount of iodine evolved may be observed, which corresponds to the expenditure of peracetic acid for the formation of the intermediate peroxide product according to equation a.

The decomposition of the intermediate product according to equation b must be a monomolecular reaction, and this type of reaction is actually observed.

The data in table 6 may serve as an illustration for the above.

The experiments as well as other similar ones enable us to calculate the activation energy for the decomposition of the intermediate product. Thus, based on data of this experiment we find the latter to have a value of 18,800 calories, and from the data of another experiment 16,100. These values closely approach the values of the activation energy of the summary process of the reaction

$$CH_3COOOH + CH_3CHO \rightarrow 2CH_3COOH$$

at 10–30°C. shown in table 4 and amounting on the average to 16,000 calories.

Quite analogous data were also obtained in a chloroform solution. We were able also to demonstrate analytically the formation of the intermediate peroxide compound by preparing a highly concentrated solution of this compound. Owing to the interaction between acetaldehyde and peracetic acid in a toluene solution at −30°C., and the subsequent cooling of the solution down to −40°C., white crystals precipitated from the solution which could easily be separated from the mother liquor. These crystals readily melt at −20°C., forming a transparent liquid with a peroxide concentration 4.5 times higher than that of the solution decanted from the crystals.

TABLE 6

Formation of the intermediate product

$t = -40°C.$

TIME FROM THE BEGINNING IN MINUTES	PERACETIC ACID IN MOLES	
	Acid KI solution	Neutral KI solution
0	0.001946	0.001941
10	0.001305	0.001937
20	0.000903	0.001957
35	0.000601	0.001907

Decomposition of the intermediate product

TIME FROM THE BEGINNING IN MINUTES	INTERMEDIATE PRODUCT IN MOLES	K (sec.$^{-1}$) × 10^5
	$t = +10°C.$	
0	0.001881	
20	0.001821	2.70
46	0.001748	2.62
81	0.001653	2.66
	$t = +20°C.$	
0	0.001204	
30	0.001034	8.43
82	0.000795	8.42
107	0.000697	8.38

Thus an addition product of acetaldehyde and peracid of a peroxide character actually seems to exist. In this manner the proposed scheme of the mechanism of the process is fully supported kinetically and analytically. The proposed method enables us to study each stage of this process separately.

II. KINETICS OF INTERACTION BETWEEN PERACETIC ACID AND OTHER ALDEHYDES

It was interesting to determine whether the proposed scheme holds for reactions with other aldehydes or whether the behavior of the acetaldehyde is specific.

For this purpose a series of preliminary experiments was started with isovaleraldehyde and peracetic acid. The kinetics of this reaction is quite analogous to that of the acetaldehyde reaction.

The results obtained show the same characteristic features as the reactions with acetaldehyde, a sharp inflection of the reaction velocity curve near the beginning indicating the existence of an intermediate stage going on with a considerably high rate even at −30°C. Thus we have reason to infer that the proposed mechanism of interaction between peracetic acid and acetaldehyde is characteristic for all aliphatic aldehydes.

The effect of water on the reaction rate between peracetic acid and acetaldehyde was also studied. We have found that the accelerating effect of water is connected with the acceleration of the second stage of this process, i.e., the decomposition of the intermediate peroxide. These experiments confirmed the proposed mechanism. Details of this work will be given in another paper.

III. SUMMARY

1. The kinetics of interaction between peracetic acid and acetaldehyde were studied in acetic acid, benzene, nitrobenzene, chloroform and toluene solution at temperatures varying between 10–30°C. The activation energy varied between 15,400 and 16,300 calories in various solvents.

2. It was found that the reaction follows the second-order equation, but in the beginning there is a short period of high reaction velocity, due to the intermediate stage.

3. A mechanism of the process is proposed according to which a peroxide compound (hydroxyethylacetyl peroxide) is formed as intermediate product.

4. A method for the quantitative determination of the intermediate peroxide in presence of peracetic acid is given.

5. Experiments were carried out with the purpose of obtaining (chiefly) the intermediate peroxide as a product of the reaction at temperatures between −40° and −60°C. The activation energy of this reaction amounts to 7000 calories. The coefficient A of the Arrhenius equation $K = Ae^{-E/RT}$ has the abnormally low value of 5.2×10^5.

6. A series of experiments was carried out in order to determine the kinetics of the monomolecular decomposition of the intermediate product.

7. The mechanism proposed was extended to other aliphatic aldehydes

by testing its applicability to the interaction of peracetic acid with isovaleraldehyde.

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THE CHLORINATION OF PROPANE. I

THE HOMOGENEOUS REACTION[1]

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The chlorination of the paraffin hydrocarbons has been the subject of many investigations. Most of the chlorination studies have been concerned with methane and natural gas in the hope of obtaining important and useful products. The literature resulting from these investigations has been well summarized by Egloff, Schaad, and Lowry (2). Much of the work to date has been qualitative in nature and there are many patents which claim to be able to produce any one of the substitution products by a variation in the conditions of the reaction. A good deal of study has also been devoted to the effect of different catalysts.

Since the quantitative side of the chlorination problem has been largely neglected it was felt that such a study from the standpoint of kinetics was highly desirable. The results obtained would be of theoretical interest in addition to possible practical applications. The latter results would be of particular value in this country, where such large quantities of the lower paraffin hydrocarbons are available.

The following investigations give the results of quantitative studies on the chlorination of propane. The work was divided into studies on the homogeneous and the heterogeneous reaction. Propane was chosen as the chlorine acceptor because (1) it is the simplest hydrocarbon having a secondary carbon atom, (2) it is the simplest paraffin hydrocarbon all of whose chlorinated products are liquids at room temperature, and (3) it is readily available in a state of high purity.

APPARATUS AND MATERIALS

The reacting gases were passed through purification trains, drying tubes, flowmeter, and mixing chambers before being admitted to the electrically heated reaction zone. The products were condensed in a trap placed in a

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[1] The material here presented formed a part of thesis submitted to the Graduate Faculty of the University of Minnesota by Samuel Yuster in partial fulfillment of the requirements for the degree of Doctor of Philosophy, March, 1934.

[2] Shevlin Fellow, 1931-32.

salt-ice bath. The unused chlorine and the hydrogen chloride formed were absorbed in a solution of potassium iodide and the unused propane was collected in a gasometer. A by-pass system absorbed the chlorine and hydrogen chloride during the time the system was reaching a steady state.

Electrolytic chlorine was used throughout this investigation. It was found that chlorine from a fresh cylinder attacked the brass needle valve so that the rate of flow gradually decreased. The first chlorine was allowed to escape directly into a solution of sodium hydroxide for a short period of time. When this was done the rate of flow through the needle valve remained constant and no further trouble was experienced. Traces of water coming out with the first chlorine probably caused the difficulty.

Propane of a high grade was obtained in cylinders for use in this work. The purification train removed the unsaturated gases as well as those of an acidic character.

The Pyrex glass packing used in one of the runs was made by breaking scrap Pyrex and sieving. The 8 to 14 mesh fraction was used and cleaned with cleaning solution. It was washed with water, dried with alcohol and ether, and placed in the catalyst chamber.

METHOD OF OPERATION

At the beginning of a series of runs, the chamber was flamed while oxygen was slowly passed through it. The oxygen was then swept out with nitrogen.

The temperature of the furnace was set by means of the lamp bank and the rate of flow of the gases adjusted by means of the flowmeters. During this adjusting period the gases were passed through the by-pass system.

When a steady state had been reached, the necessary stopcock was turned so that the gases passed through the potassium iodide absorption train, where the unused chlorine and the hydrogen chloride formed were absorbed. The unused propane passed into a gas-collecting bottle, where it displaced an equal volume of water.

The flowmeter readings, chamber temperature, room temperature, duration of run, and the barometric pressure were recorded for a given run. The amount of water displaced by the unused propane was weighed and the volume of gas corrected to standard conditions. The potassium iodide solution was removed from the absorbers, and the iodine and hydrochloric acid content determined respectively with standard thiosulfate and alkali.

METHOD OF CALCULATION

In a normal chlorination, one molecule of hydrogen chloride is formed for each chlorine molecule used regardless of the mechanism of chlorination.

(cc. of sodium thiosulfate) × normality factor × 11.2 = cc. of chlorine unused. (cc. of potassium hydroxide) × normality factor × 22.4 = cc. of chlorine used. The sum of these two quantities will give the total chlorine admitted into the system. This should agree with the setting of the chlorine flowmeter if the reaction is behaving in a normal manner. The amount of chlorine used divided by the total chlorine input multiplied by 100 gives the per cent of chlorine used.

DISCUSSION OF RESULTS

Errors

The greatest difficulty encountered in this research was met in duplicating results. Since the slightest trace of oxygen inhibited the reaction even though the rate of flow and temperature were carefully controlled, check results were difficult to obtain. Despite the fact that the walls were flamed at the beginning of each series, the first measurements had to be discarded because of the extreme activity of the wall. After use, this catalytic effect reached a steady state and the results were more consistent.

The reaction was also diminished by the adsorption of chlorinated propanes by the wall. These adsorbed products were further acted upon by chlorine, became less volatile, and thus decreased their possibilities of escape. The rate of the reaction progressively decreased until the whole surface was covered with these poisoning agents. In these experiments, it was found that this autopoisoning was greatest at the higher temperatures and high chlorine to propane ratios.

In order to minimize these disturbing factors, the runs were made as rapidly as possible, but time was allowed for equilibrium to establish itself. The reactants were not allowed to remain in the reaction zone when the apparatus was not in use. They were swept out with nitrogen.

The rates of flow used in these series were 2, 10, 20, and 50 liters of reactants per hour. Since the volume of the reaction chamber was 100 ml., the space velocity, or the volume of gas passing through unit volume of the reaction zone in unit time, may be obtained by dividing the rate of flow in milliliters per minute by 100. For example, taking 10 liters per hour as the rate of flow:

$$\text{Space velocity} = \frac{\dfrac{10 \times 1000}{60}}{100} = 1.66$$

Then 1.66 of a volume of reactants pass through unit volume of reaction zone in one minute. Another way of stating it would be that on the average (disregarding adsorption, diffusion, convection currents, etc.) a given molecule would be in the reaction zone 0.6 of a minute.

Each rate of flow was divided into three series: runs in which the partial pressures of the reactants were equal, and runs in which the partial pressure of one of the reactants was twice that of the other. A series of runs was also made when the chamber was rinsed with a saturated solution of potassium chloride in an attempt to determine the effect of the wall.

Evidence from these experiments seemed to point to the fact that the so-called homogeneous gas phase chlorination of propane takes place by a chain mechanism. The reaction was inhibited by oxygen, an induction period was noticed when the reaction chamber walls were activated, explosions took place which are explained on the basis of branching chains, and a packed chamber cut down the extent of chlorination because of the decrease in the number of links in the chain.

The photochlorination of methane has been recently studied by Coehn and Cordes (1); they postulate a mechanism which is similar to that suggested in this problem. There are two possibilities to be considered, and the initial step in both cases would be the dissociation of a chlorine molecule into two chlorine atoms.

$$Cl_2 + \text{heat} \rightarrow Cl + Cl$$

This might take place in the gas phase owing to collisions, or on the wall because of some type of activated adsorption. The relative importance of the two processes is undoubtedly a function of the conditions.

The possible mechanisms for the chlorination of propane are given by the following equations:

Mechanism I.

$$\begin{array}{ll}
 & Cl + C_3H_8 \rightarrow C_3H_7Cl + H \\
 & H + Cl_2 \rightarrow HCl + Cl \\
\text{(a)} & Cl + C_3H_8 \rightarrow C_3H_7Cl + H \text{ etc.} \\
\text{(b)} & Cl + C_3H_7Cl \rightarrow C_3H_6Cl_2 + H \text{ etc.}
\end{array}$$

Mechanism II.

$$\begin{array}{ll}
 & C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\
 & C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl \\
\text{(a)} & Cl + C_3H_8 \rightarrow C_3H_7 + HCl \text{ etc.} \\
\text{(b)} & C_3H_7Cl + Cl \rightarrow C_3H_6Cl + HCl \text{ etc.}
\end{array}$$

Since no thermal data could be obtained on the chlorination of propane, the corresponding data given by Coehn and Cordes (1) on methane were used to decide on the most probable mechanism.

Mechanism I.

$$\begin{array}{lr}
CH_4 + Cl_2 \rightarrow C_4H_3Cl + HCl & +\ 22{,}000 \text{ cals.} \\
H + Cl \rightarrow HCl & +100{,}000 \text{ cals.} \\
Cl + Cl \rightarrow Cl_2 & +\ 58{,}000 \text{ cals.} \\
\hline
CH_4 + Cl \rightarrow CH_3Cl + H & -\ 20{,}000 \text{ cals.}
\end{array}$$

Mechanism II.

$$\begin{array}{lr} CH_4 + \Delta \rightarrow CH_3 + H & -90{,}000 \text{ cals.} \\ H + Cl \rightarrow HCl & +100{,}000 \text{ cals.} \\ \hline CH_4 + Cl \rightarrow CH_3 + HCl & +10{,}000 \text{ cals.} \end{array}$$

It may be seen, therefore, that mechanism II is the more probable from a thermal standpoint. In addition, the presence of free radicals is required to explain the evidence obtained for coupling reactions. Since mechanism I requires the formation of hydrogen atoms, it would be expected that some of these atoms would combine to form hydrogen molecules. To test this, the gases were condensed in a liquid air trap after passing through the reaction zone. All possible gases except hydrogen should be condensed. No hydrogen was detected.

We shall, therefore, take as our most probable mechanism the following:

$$\begin{array}{ll} \text{(a)} & Cl_2 + \text{heat} \rightarrow Cl + Cl \\ & C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\ & C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl \\ & C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\ & C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl \text{ etc.} \\ \text{(b)} & C_3H_7Cl + Cl \rightarrow C_3H_6Cl + HCl \\ & C_3H_6Cl + Cl_2 \rightarrow C_3H_6Cl_2 + Cl \text{ etc.} \end{array}$$

Chain-breaking reactions:

$$\begin{array}{c} Cl + Cl \rightarrow Cl_2 \\ C_3H_7 + Cl \rightarrow C_3H_7Cl \\ C_3H_6Cl + Cl \rightarrow C_3H_6Cl_2 \\ C_3H_5Cl_2 + Cl \rightarrow C_3H_5Cl_3 \text{ etc.} \\ C_3H_7 + C_3H_6Cl \rightarrow C_6H_{13}Cl \\ \text{Active group} + O_2 \rightarrow \text{Inactive group.} \end{array}$$

All of the chain-breaking reactions require three body collisions in order to take place. The reactions are so exothermic that the resulting molecule will not exist as such unless some third body (either a third molecule or the wall) removes enough energy to leave a stable group.

The complete picture is not given in the above equations, as the complete chlorination of propane (if possible) is an eight-stage process with an enormous number of combinations in the intermediate stages. The probability of reaching the higher stages of chlorination drops off very rapidly, but undoubtedly they are reached to a small extent.

Under some conditions, in the empty chamber runs, explosions took place with the deposition of carbon. This could not be explained on the basis of the reaction

$$C_3H_8 + 4Cl_2 \rightarrow 3C + 8HCl$$

as the probability of four chlorine molecules and one propane molecule colliding simultaneously is practically nil. We must therefore postulate a series of degradation reactions similar to that given by Coehn and Cordes (1) for the production of carbon in the chlorination of methane.

$$C_3H_7 + Cl \rightarrow C_3H_6 + HCl$$
$$C_3H_6 + Cl \rightarrow C_3H_5 + HCl$$
$$C_3H_5 + Cl \rightarrow C_3H_4 + HCl \text{ etc.}$$

In the case of propane there may be splitting of the C—C bond to give a more simple molecule.

On the basis of the mechanism postulated for a one-stage process, calculations were made to determine the theoretical rate of reaction. A cubic equation was obtained for the concentration of the chlorine atoms, which made the solution hopeless. It is believed that too many factors varied to make the results valid for comparison with theory. Since the wall can both initiate and break chains, it is to be expected that the adsorption of chlorinated propanes should complicate matters. The reaction is bimolecular, but what the order should be, considering all the stages, is unknown.

TABLE 1

Empty chamber runs

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
160	533	502	1	503	0.2
171	510	443	9	452	2.0
189	453	441	33	474	7.0
202	500	453	73	526	13.8
210	490	386	124	510	24.4
220	363	303	222	525	42.3
235	302	135	349	484	72.0
246	281	58	436	494	88.3
249	234	32	413	445	92.8
260	229	16	484	500	96.8
283	231		495	495	100.0

Figure 1, typical data of which is given in tables 1, 2, and 3, is a summary of the 2 liters per hour runs. Figure 2, a portion of which is shown in figure 1, shows the difficulty encountered in checking results. The points in this graph, a typical series of which is given in table 3, tend to diverge more and more from the average as the temperature rises. This series involved the use of a high partial pressure of chlorine. Both high temperatures and high chlorine content in the reactants favor the formation of higher chlorinated propanes. The poisoning of the wall under these conditions should also be greater. This was proved to be the case, since the chamber was found to be covered with a brownish substance after a series of runs. The curve in figure 2 represents one series of runs beginning with a clean chamber at low temperatures, followed by successive temperature increments.

TABLE 2

Empty chamber runs

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 2:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
126	638	264	6	270	2.2
166	695	310	30	340	8.8
182	680	278	62	340	18.2
190	656	254	86	340	25.3
194	660	226	124	350	35.4
208	521	111	214	325	65.8
217	505	61	282	343	82.3
230	469	25	313	338	92.6
251	465	6	323	329	98.1

TABLE 3

Empty chamber runs

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:2$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
171	345	675	2	677	0.3
185	368	658	11	669	1.6
197	352	554	35	589	5.9
212	280	574	107	681	15.7
222	231	425	215	640	33.6
231	163	262	415	677	61.3
238	173	184	505	689	73.2
245	126	170	415	628	72.9
258	140	203	451	654	69.0
266	141	181	457	638	71.6
275	97	51	596	647	92.1

An apparent negative temperature coefficient of reaction was found at the higher temperatures, which is not in harmony with chlorination reactions. It was thought that the phenomenon might be caused by a new type of reaction, but the effect was later proved to be due to poisoning. Poisoning at these higher temperatures was so rapid that there was apparently a negative temperature coefficient of reaction. After this poisoning reached a steady state a normal curve was obtained, but this was shifted along the temperature axis.

The ratio of chlorine to propane was varied in an attempt to determine the order of the reaction. It was realized that at least two effects would be involved in the determination of the extent of chlorination. The greater the partial pressure of chlorine in the reactants the more chlorine atoms are formed for the initiation of chains. However, a higher chlorine content would tend to produce higher chlorinated products which act as poisons. Because of these two effects, it should be expected that the extent of chlorination when plotted against the partial pressure of chlorine would go through a maximum. The type of curves represented in figure 1 should have the same relative position to one another no matter what the total rate of flow might be, providing the type of reaction taking place is not a function of the rate of passage of the reactants through the heated zone. A comparison of figures 1, 3, 4, and 5 shows that there was some change in the type of reaction with the rate of flow. This change was probably due to a change in the relative importance of chain initiation at the wall and in the gas phase. The complicating factor of explosions was introduced at the higher rates of flow. The decrease in reaction rate for an increase in the rate of flow, as shown by comparing figures 1 and 3, is to be expected.

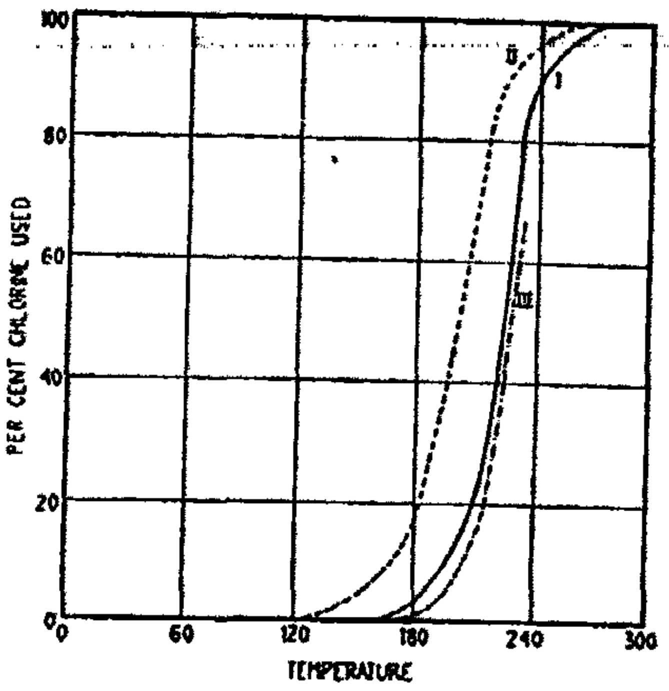

FIG. 1

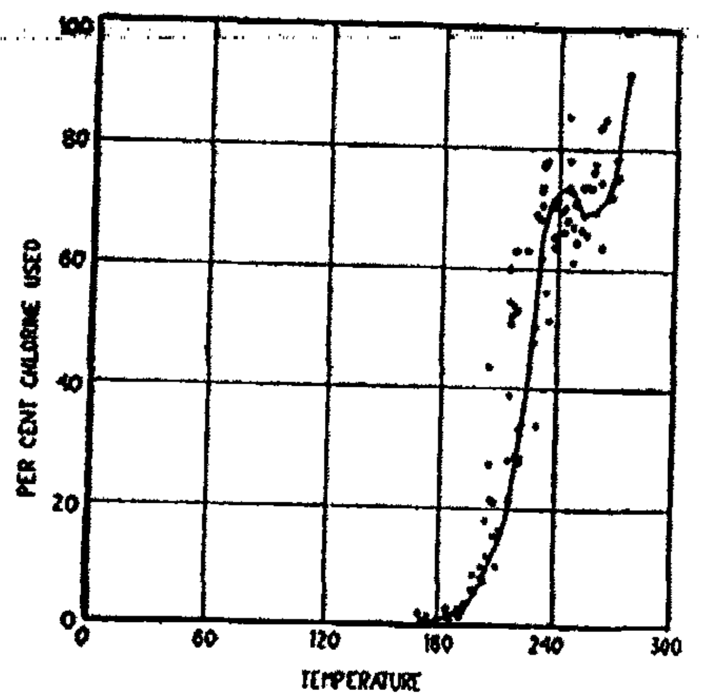

FIG. 2

FIG. 1. SUMMARY OF THE TWO LITERS PER HOUR RUNS
Curve I, $C_3H_8:Cl_2$ = 1:1; curve II, $C_3H_8:Cl_2$ = 2:1; curve III, $C_3H_8:Cl_2$ = 1:2

FIG. 2. EMPTY CHAMBER RUNS, SHOWING DIFFICULTY IN CHECKING RESULTS
Rate of flow, two liters per hour; $C_3H_8:Cl_2$ = 1:2

The large increase in rate of reaction in going from a 1:1 to a 1:2 ratio of propane to chlorine, using a total rate of flow of 2 liters per hour, does not compare very favorably with the corresponding result at 10 liters per hour, which only shows a small increase in rate.

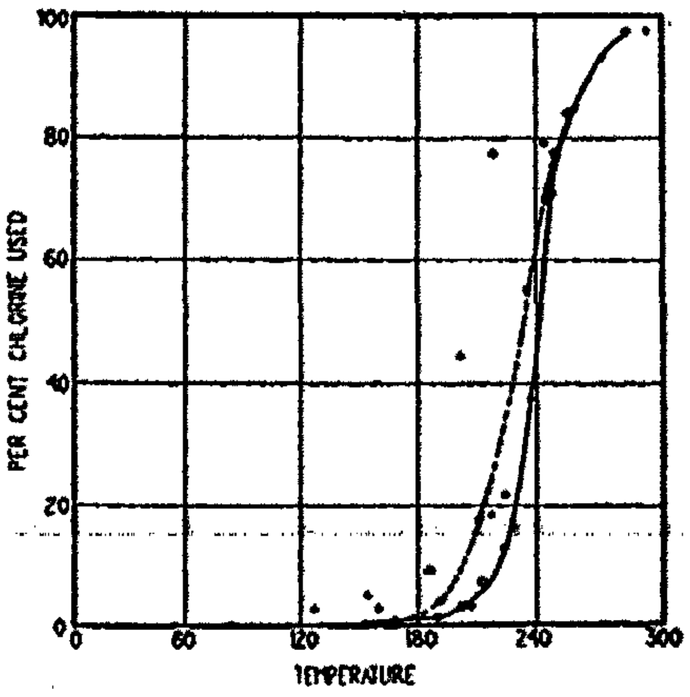

Fig. 3

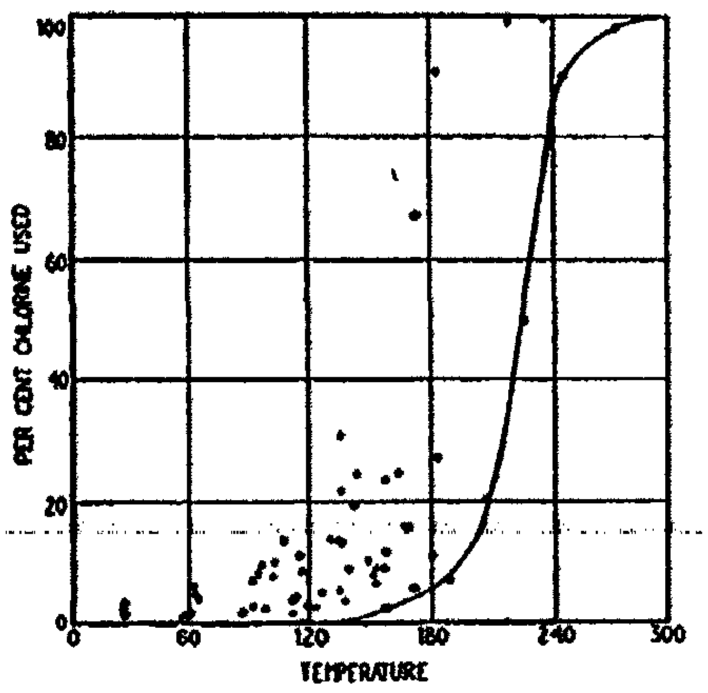

Fig. 4

Fig. 3. Results Obtained in Empty Chamber Runs with Rate of Flow Ten Liters per Hour

—⊙ $C_3H_8:Cl_2 = 1:1$
---⊡ $C_3H_8:Cl_2 = 2:1$
△ $C_3H_8:Cl_2 = 1:2$

Fig. 4. Results Obtained in Empty Chamber Runs with Rate of Flow Twenty Liters per Hour

⊙ $C_3H_8:Cl_2 = 1:1$; ⊡ $C_3H_8:Cl_2 = 2:1$; △ $C_3H_8:Cl_2 = 1:2$

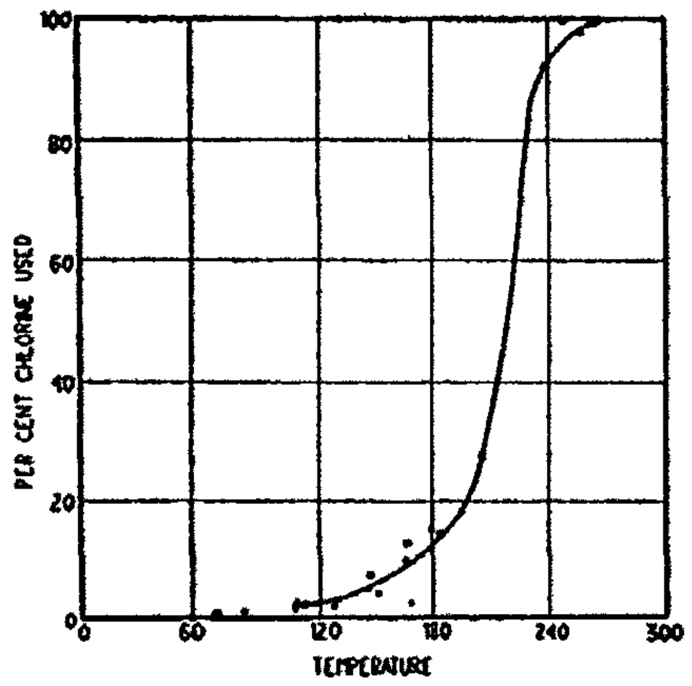

Fig. 5. Results Obtained in Empty Chamber Runs with Rate of Flow Fifty Liters per Hour

⊙ $C_3H_8:Cl_2 = 1:1$; △ $C_3H_8:Cl_2 = 2:1$; ⊡ $C_3H_8:Cl_2 = 1:2$; × $C_3H_8:Cl_2 = 1:2$ (Pyrex-packed chamber).

Pease (3) has shown that a solution of potassium chloride when placed on the walls of a reaction chamber will inhibit certain reactions initiated at the wall. Since the changing activity of the wall was especially troublesome in this reaction, it was thought desirable to test the effect of potassium chloride. The chamber was washed with a saturated solution of potassium chloride and then flamed. The reactions were carried out in the usual way. Comparing the results with the corresponding data from an untreated chamber showed very little difference. In fact, the results might lead one to conclude that there was a very slight catalytic effect in the potassium chloride experiments. This was not very definite.

TABLE 4

Empty chamber runs

4 minutes duration. Total rate of flow 10 liters per hour. $C_3H_6:Cl_2$ = 1:1

TEMPERATURE	C_3H_6 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°*C.*					
154	311	308	1	309	0.1
190	344	328	5	333	1.5
201	344	322	11	333	3.3
212	334	308	24	332	7.2
228	319	282	56	338	16.5
238	305	220	131	351	37.4
248	247	98	238	336	70.8
259	191	47	266	313	84.9
284	154	8	321	329	97.6

TABLE 5

Empty chamber runs

4 minutes duration. Total rate of flow 10 liters per hour. $C_3H_6:Cl_2$ = 2:1

TEMPERATURE	C_3H_6 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°*C.*					
169	455	219	2	221	0.9
190	446	208	9	217	4.2
211	440	179	38	217	17.5
236	396	97	119	216	55.1
250	382	50	172	222	77.5
272	384	16	210	226	92.9
294	389	6	215	221	97.2

Explosions

Figures 3, 4, and 5 show the results obtained at higher rates of flow. It will be noted that runs involving high chlorine partial pressures are the

TABLE 6

Empty chamber runs

4 minutes duration. Total rate of flow 10 liters per hour. $C_3H_8:Cl_2$ = 1:2

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
127	233	444	13	457	2.8
155	235	420	23	443	5.2
185	231	397	40	437	9.1
245	96	89	245	434	79.4
255	96	75	402	477	84.2
219	103	94	330	424	77.8
201	165	253	200	453	44.1

TABLE 7

Empty chamber runs

1 minute duration. Total rate of flow 50 liters per hour. $C_3H_8:Cl_2$ = 1:1

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
28	404	393		393	
70	422	400	1	401	0.3
83	420	390	3	393	0.8
108	420	396	5	401	1.3
127	420	392	7	399	1.8
150	447	368	15	383	3.9
184	411	338	55	393	14.0

TABLE 8

Empty chamber runs

1 minute duration. Total rate of flow 50 liters per hour. $C_3H_8:Cl_2$ = 2.1

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
108	542	269	7	276	2.5
128	546	264	9	273	3.3
144	544	258	13	271	4.8
165	536	244	26	270	9.6
179	535	230	40	270	14.7
196	518	232	49	281	17.4
207	522	195	74	269	27.5
239	426	23	253	276	91.5
258	415	7	268	275	97.4

least consistent. The two factors contributing to this are explosions and poisoning, which are favored by high chlorine partial pressures.

The explosions encountered in this research were never of the shattering type, as at no time were they strong enough to break the reaction chamber. The explosions were periodic and at 20 liters per hour total rate of flow, with a partial pressure of the chlorine of 0.5 atmosphere, they took place about every thirty seconds. At higher rates of flow, the explosions occurred more frequently.

The use of high partial pressures of propane seemed to eliminate the explosions. This would point to chlorine atoms as the initiators of the branching chains. With high partial pressures of chlorine, the explosions started at as low a temperature as 150°C. Using equal volumes of propane and chlorine, the temperature of initiation was about 190°C. In a few cases it was possible to "slip" past this temperature and proceed to higher temperatures without explosions. On dropping the temperature, explosions reappeared.

TABLE 9

Empty chamber runs

1 minute duration. Total rate of flow 50 liters per hour. $C_3H_8:Cl_2 = 2:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
112	287	519	15	534	2.8
145	281	493	34	527	6.5
167	270	472	66	538	12.3
Conditions same as above except chamber is packed with Pyrex					
168	283	517	11	528	2.1
250					100.0

Runs were also made when the chamber was packed with broken Pyrex glass of 8–14 mesh (see figure 5 and table 9). These experiments were made with a high chlorine partial pressure, a condition which greatly favors explosions. Comparing the values obtained with the corresponding results in the unpacked chamber, a sixfold decrease in the extent of chlorination is found at the lower temperatures. Even with ten times the surface exposed for the activation of the chlorine, the chain-breaking effect of the wall outweighed the initiation of chains. No explosions were encountered at any time while operating over the whole temperature range. It might be reasoned that explosions are not evidence for a chain mechanism, as any exothermic reaction taking place in a thermally insulated chamber may utilize the heat of reaction to activate other molecules.

This autoactivation could give explosions. Part of the explosion is undoubtedly due to this phenomenon, but the formation of branching chains is probably the chief factor. A packing having a good heat conductivity would both shorten chains and conduct away the heat of reaction. From the standpoint of its property of transferring heat, Pyrex glass is not so very different from a gas. Nevertheless, the glass packing very effectively suppressed the explosions. Consequently, the explosions must have been stopped by the breaking of the chains.

Using the Arrhenius equation the heat of activation can be calculated.

$$\ln \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{RT_2T_1}$$

k_2 and k_1 are the velocity constants at temperatures T_2 and T_1, E the heat of activation, and R, the gas constant, or

$$2.3 \log_{10} \frac{k_2}{k_1} = \frac{E}{R} \frac{T_2 - T_1}{T_2T_1}$$

Neither k_1 nor k_2 can be calculated, as the order of the reaction is not known. The rate equation for the single stage process is given by the equation

$$\frac{d(C_3H_7Cl)}{dt} = k(C_3H_8)^m(Cl_2)^n$$

Since m and n are not known, the above equation cannot be integrated to determine the velocity constant. The Arrhenius equation only requires a ratio of velocity constants at two temperatures and this can be obtained from the graphs.

Using the data from the experiments with a high partial pressure of propane, as given in figure 1, the following calculation was made. These data were chosen because a high partial pressure of propane minimized the poisoning of the walls.

The ratio k_2/k_1 is equal to 2 for the temperature range 184°C. to 199°C.

$$2.3 \log_{10} 2 = \frac{E}{2} \frac{472 - 457}{472 \times 457}$$

$$E = \frac{2 \times 2.3 \times 472 \times 457}{15} \log_{10} 2$$

$$E = 20{,}000 \text{ calories per mole of product formed}$$

If the data were to satisfy the Arrhenius equation over the whole temperature range, the curves would not be S-shaped but would become more and more vertical as the temperature increased.

It would be interesting to compare the energy of activation obtained from the temperature coefficient of reaction with the results from a calculation that assumes the chlorination to be of the simple bimolecular collision type. Since this reaction involves a chain mechanism, the energy of activation is undoubtedly composite, and it would be only fortuitous if any agreement was obtained by the two methods.

The equation for the collision theory is as follows:

$$N = N_0 e^{-\frac{E}{RT}}$$

where N = the number of effective collisions, N_0 = the total number of collisions, e = the natural logarithm base, R = the gas constant, T = the absolute temperature, and E = the energy of activation. N may be calculated from the data obtained from the extent of chlorination. The total number of collisions, N_0, is given by the formula:

$$\text{Collisions per cc. per sec.} = N_1 N_2 \sigma^2_{1,2} \sqrt{8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$$

N_1 and N_2 are the number of molecules of the two kinds per cubic centimeter, $\sigma_{1,2}$ is the mean of the molecular diameters, and M_1 and M_2 are the respective molecular weights.

According to figure 1 at 184°C. there was 20 per cent conversion of the chlorine to propyl chlorides. The partial pressures of the propane and chlorine were 0.667 atmosphere and 0.333 atmosphere, respectively. The number of molecules per cubic centimeter at the temperature T and partial pressure P would be given by the expression:

$$\frac{6.06 \times 10^{23} \times 273 \times P}{22{,}412 \times T}$$

Substituting our values:

$$\frac{6.06 \times 10^{22} \times 273 \times 0.667}{22{,}412\ (184 + 273)} = 1.085 \times 10^{19} \text{ molecules of } C_3H_8 \text{ per cc.}$$

$$\frac{6.06 \times 10^{23} \times 273 \times 0.333}{22{,}412\ (184 + 273)} = 0.543 \times 10^{19} \text{ molecules of } Cl_2 \text{ per cc.}$$

The diameter of the chlorine molecule as given by Rankine (8) is 3.2×10^{-8} cm. The diameter of the propane molecule given by Titani (9) is 4.16×10^{-8} cm. Substituting the proper values:

$$\text{Collisions per cc. per sec.} = 1.085 \times 10^{19} \times 0.543 \times 10^{19} \times$$

$$\left(\frac{3.2 \times 10^{-8} + 4.16 \times 10^{-8}}{2}\right)^2 \sqrt{8 \times 3.1416 \times 8.136 \times 10^7 \times 457\left(\frac{1}{71} + \frac{1}{44}\right)} \cdot$$

$$\text{collisions per cc. per sec.} = 4.68 \times 10^{28}$$

The chamber had a volume of 100 cc. and the rate of flow was 2000/3600 = 0.555 cc. per second (2 liters per hour). Therefore, the gas remained, on the average, 100/0.555 = 180 seconds in the heating zone.

The number of collisions taking place in the reaction zone per cubic centimeter during the 180 seconds of contact is $180 \times 4.68 \times 10^{28} = 8.42 \times 10^{30}$. Only 20 per cent of the chlorine was converted in the cubic centimeter or $\frac{0.543 \times 10^{19}}{5} = 1.08 \times 10^{18}$ collisions were effective. Substituting in our equation:

$$N = N_0\, e^{-\frac{E}{RT}}$$

$$1.08 \times 10^{18} = 8.42 \times 10^{30}\, e^{-\frac{E}{2 \times 457}}$$

$$E = 27{,}000 \text{ calories per mole}$$

This is in fair agreement with the value of 20,000 calories obtained from the Arrhenius equation. Whether this has any significance is not known. Pease and Walz (7) obtained a similar agreement in their calculation on the chlorination of methane.

Since the formation of atomic chlorine is essential to the reaction, it would be interesting to calculate the length of the chains, presupposing that all of the chlorine atoms were formed in the gas phase by thermal dissociation.

The affinity of the reaction

$$\frac{1}{2}\,\mathrm{Cl_2(g)} \rightarrow \mathrm{Cl(g)}$$

is given by the expression (5):

$$A = 3500 - 1.37T \ln T + 0.0025T^2 - 1.5T$$

At the temperature 457° absolute we have

$$A = 3500 - 1.37 \times 457 \ln 457 + 0.00025\,(457)^2 - 1.5 \times 457$$
$$A = 30{,}000 \text{ calories}$$
$$A = -RT \ln K = -RT \ln \frac{(\mathrm{Cl})}{(\mathrm{Cl_2})^{1/2}}$$

The partial pressure of the chlorine was 0.333 atmosphere and using this value the concentration of the chlorine atoms at 457° absolute may be calculated.

$$30{,}000 = -2 \times 457 \ln \frac{(\mathrm{Cl})}{(0.333)^{1/2}}$$

$$(\mathrm{Cl}) = 5.49 \times 10^{-14} \text{ atmospheres}$$

$$(\mathrm{Cl}) = \frac{6.06 \times 10^{23} \times 5.49 \times 10^{-14} \times 273}{22{,}412 \times 457} = 8.87 \times 10^{5} \text{ atoms per cc.}$$

The rate of combination of the chlorine atoms at the equilibrium concentration would be given by the expression

$$\text{Collisions per cc. per sec.} = N^2\sigma^2 \sqrt{\frac{4\pi RT}{M}}$$

where σ in this case is the diameter of the chlorine atom. Since the value of this is unknown, the diameter of argon, 2.46×10^{-8} cm., will be used as an approximation. The above calculation also presupposes that every time two chlorine atoms collide a chlorine molecule is formed.

$$Z = (8.87 \times 10^{5})^2(2.56 \times 10^{-8})^2 \sqrt{\frac{4 \times 3.1416 \times 8.136 \times 10^{7} \times 457}{35.5}}$$

$Z = 59$ chlorine molecules formed per second per cubic centimeter

Since, at equilibrium, the rate of combination equals the rate of formation, then 59 chlorine molecules decompose per second per cubic centimeter to form 118 chlorine atoms. The gas remains in the reaction zone for 180 seconds, therefore 21,200 chlorine atoms will form in that time.

From our previous calculation, 1.08×10^{18} chlorine atoms reacted in this same period of time. The 21,200 chlorine atoms initiated all of the reaction, which indicates that a chain has approximately 10^{14} links. This value seems beyond reason. The photochemical combination of hydrogen and chlorine only gives a chain length of 1.4×10^{5} molecules per quanta (3).

Two suppositions were involved in this calculation: first, that every collision between chlorine atoms results in a combination; and second, that no chlorine atoms are formed at the wall. The probability of the first taking place is not known, but the true situation would probably give a shorter chain. Any activated adsorption of chlorine on the walls would produce chlorine atoms which if included in the calculation would also shorten the chains. The magnitude of the result in the calculation would indicate that it is considerable.

Product

High partial pressures of chlorine favored the formation of the higher chloro derivatives. High rates of flow in which the chlorine conversion was high gave higher chlorinated propanes than did lower rates of flow under similar conditions. This was probably due to the problem of the greater amount of heat to be dissipated at the higher rates of flow. As high as 75 per cent of the product was monochloropropane when a high propane partial pressure was used coupled with a low space velocity. The conversion under these conditions was between 80 and 90 per cent of the chlorine input.

SUMMARY

1. The homogeneous reaction of propane with chlorine has been studied.

2. The reaction was shown to be of the chain type, as evidenced by an induction period, inhibitory effect of oxygen, reduction in rate by packing and explosions.

3. The type of reaction was shown to change with change in rate of flow.

4. A mechanism has been postulated which seems to satisfy the peculiarities of the reaction.

5. It was shown that chains were both initiated and stopped by the wall.

6. High partial pressures of chlorine cause the wall to be poisoned.

7. Explosions were favored by high rates of flow and high partial pressures of chlorine.

8. The heat of activation was calculated by means of the temperature coefficient and by collision efficiency; fair agreement was obtained between the two values, which were about 20,000 calories per mole.

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LIQUID AMMONIA AS A SOLVENT. IV

ACTIVITIES OF AMMONIUM NITRATE, IODIDE, BROMIDE, AND CHLORIDE AT 25°C.

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The activities of solid non-volatile solutes in liquid ammonia may be obtained by measuring the vapor pressures of their solutions at various concentrations. Vapor pressure data also furnish an excellent means of testing the theories of concentrated solutions, since the measurements can be made over a very wide range of concentration.

The vapor pressure data used in this paper have been reported in a previous article (3). The values used in calculating the activities were taken from a smooth mole ratio versus vapor pressure curve. Ammonia gas deviates considerably from the behavior of an ideal gas; therefore the fugacity rather than the vapor pressure must be used in calculating the activities and showing deviations from Raoult's law. The fugacity was calculated from the vapor pressure using the equation (5)

$$\ln f = \ln P - \int_0^P \frac{\alpha}{RT}\, dP \qquad (1)$$

f is the fugacity, P is the vapor pressure, and

$$\frac{\alpha}{RT} = \frac{1}{P}\left(1 - \frac{PV}{RT}\right) \qquad (2)$$

The last term in equation 1 was evaluated from the known data for ammonia gas at 25°C. (4), using the equation

$$PV = RT + aP + bP^2 \qquad (3)$$

a and b are constants. This equation becomes

$$\frac{1}{P}\left(1 - \frac{PV}{RT}\right) = -A - BP = \frac{\alpha}{RT} \qquad (4)$$

---

[1] This paper is a part of a thesis submitted by W. E. Larsen to the Faculty of Purdie University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

or

$$2.3026 \log \frac{f}{P} = AP + \frac{BP^2}{2} \tag{5}$$

A and B (P in cm.) were found to be -1.356×10^{-4} and -2.578×10^{-8}, respectively.

The relationship $a_1 = f/f_0$ gives the activities of the solvent, f_0 being the fugacity of liquid ammonia, and f the fugacity of the solution. Our value of the vapor pressure, although lower than that reported by Cragoe (1), was used in calculating the fugacity of liquid ammonia, because our manometer gives the same per cent lower value for the vapor pressures of the solutions.

The activity of the solute was calculated from that of the solvent by equations resulting from the Gibbs-Duhem equation, namely,

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

a_2 is the activity of the solute, and N_1 and N_2 the mole fraction of the solvent and solute, respectively. Upon integrating and changing to common logarithms

$$\log \frac{a_2}{a_2'} = -\int_{a_1'}^{a_1} \frac{N_1}{N_2}\, \mathrm{d} \ln a_1 \tag{7}$$

The value of the integral was obtained by a graphical method. Measurements could not be made for solutions dilute enough to allow extrapolation to infinite dilution; consequently this method gave only relative activities. This necessitated giving an arbitrary value to a_2' at some concentration used as a reference point. A concentration of 1 molal was chosen as the reference point. This arbitrary assumption amounts to placing $a \;= 1$ at 1 molal, and consequently $\log a_2' = 0$; then by measuring the area between this point and any other point we have

$$\log ka_2 = -\text{ area} \tag{8}$$

Using this equation a series of values was obtained proportional to the activity. Assuming that the ammonium salts dissociate into two ions, the relative mean ionic activity coefficient is given by

$$k'\gamma = \frac{ka_2^{1/2}}{M} \tag{9}$$

M is the molality.

This series of $k'\gamma$ values is plotted against the molality in figure 1, which brings out the differences between the ammonium halides.

TABLE 1

$k'\gamma$ for ammonium nitrate

M	P	f	a	$k'\gamma$
	cm. Hg			
48.9	86.3	85.3	0.1270	1.17
42.8	103.2	101.8	0.1512	1.20
34.5	138.5	135.9	0.2019	1.19
27.2	187.4	182.6	0.2713	1.14
22.8	235.8	228.2	0.3391	1.05
18.9	292.7	281.0	0.4175	0.930
15.2	373.8	354.7	0.5270	0.779
11.2	489.1	456.3	0.6779	0.601
8.63	572.0	527.1	0.7831	0.510
6.38	643.8	586.8	0.8719	0.452
4.19	692.0	626.1	0.9303	0.483
2.94	713.6	643.5	0.9562	0.550
1.97	726.5	653.9	0.9715	0.677
1.40	733.4	659.4	0.9797	0.825
1.14	736.6	661.9	0.9835	0.930
0.917	739.2	664.0	0.9866	1.05
0.683	742.0	666.2	0.9899	1.25
0.508	744.0	667.8	0.9923	1.49
0.411	745.1	668.7	0.9936	1.69
Pure NH_3	750.6	673.0	1.0000	

TABLE 2

$k'\gamma$ for ammonium iodide

M	P	f	a	$k'\gamma$
	cm. Hg			
25.4	73.8	73.1	0.1086	11.5
22.6	98.0	96.7	0.1437	9.14
18.0	160.0	156.5	0.2325	5.66
16.4	195.7	190.5	0.2830	4.45
14.3	263.0	253.6	0.3767	2.96
12.0	360.0	342.3	0.5086	1.81
9.32	475.8	444.8	0.6609	1.13
6.45	598.8	549.5	0.8165	0.743
5.21	640.4	584.0	0.8678	0.676
4.19	671.3	609.3	0.9054	0.645
3.19	697.5	630.6	0.9369	0.644
2.20	717.9	647.0	0.9613	0.706
1.33	732.1	658.3	0.9782	0.869
1.07	736.0	661.5	0.9828	0.966
0.883	738.8	663.7	0.9861	1.06
0.675	741.7	666.0	0.9895	1.21
0.521	743.5	667.4	0.9917	1.41
0.399	745.1	668.7	0.9936	1.63
0.309	746.3	669.6	0.9950	1.87

TABLE 3

$k'\gamma$ for ammonium bromide

M	P	f	a	$k'\gamma$
	cm. Hg			
24.8	162.0	158.4	0.2354	1.26
21.3	221.3	214.6	0.3189	0.993
17.3	319.7	305.7	0.4543	0.714
13.5	446.1	418.8	0.6223	0.500
10.5	550.4	508.8	0.7560	0.401
7.70	634.2	578.9	0.8602	0.360
5.23	688.2	623.1	0.9258	0.380
3.40	714.8	644.5	0.9576	0.464
2.39	725.4	653.0	0.9702	0.577
1.78	731.6	658.0	0.9776	0.696
1.28	736.9	662.2	0.9839	0.857
0.979	740.0	664.6	0.9875	1.01
0.766	742.1	666.3	0.9900	1.19
0.587	743.8	667.7	0.9920	1.42
0.455	745.1	668.7	0.9936	1.68
0.369	745.9	669.3	0.9945	1.93
0.280	747.3	670.4	0.9961	2.19

TABLE 4

$k'\gamma$ for ammonium chloride

M	P	f	a	$k'\gamma$
	cm. Hg			
24.4	314.0	300.5	0.4465	0.239
21.8	379.0	359.4	0.5339	0.213
18.9	453.0	424.9	0.6313	0.192
16.3	525.0	487.2	0.7239	0.177
13.7	591.8	543.7	0.8079	0.171
10.7	653.4	594.7	0.8836	0.176
8.76	684.3	619.9	0.9211	0.190
7.40	700.0	632.6	0.9399	0.209
5.49	717.3	646.5	0.9606	0.255
4.00	727.1	654.4	0.9723	0.324
2.61	733.9	659.8	0.9803	0.462
1.96	737.2	662.4	0.9842	0.585
1.47	739.7	664.4	0.9872	0.740
1.06	742.2	666.4	0.9901	0.958
0.850	743.4	667.4	0.9916	1.14
0.667	744.6	668.3	0.9930	1.38
0.506	745.9	669.3	0.9945	1.68
0.390	747.7	670.8	0.9966	1.89

The method of Randall and White, if it could be used, would give absolute activities. Although their method has been used successfully for aqueous solutions by Pearce and Nelson (6), the extrapolation involved in the case of liquid ammonia is much more difficult. Their method was used to give an approximate value of the activity coefficient. Using these activity coefficients the value of k' for each concentration of the more exact series was obtained. These values of k' vary within the maximum limits of 0.65 per cent, showing that the two methods run parallel to a reasonable extent. The fact that k' is constant does not mean that the extrapolation is necessarily correct, but only that the two methods run parallel. The average value of k' for ammonium nitrate is 37.7, ammonium iodide 31.8, ammonium bromide 50.6, and ammonium chloride 83.5. These values show that the activities of these salts are low in liquid ammonia.

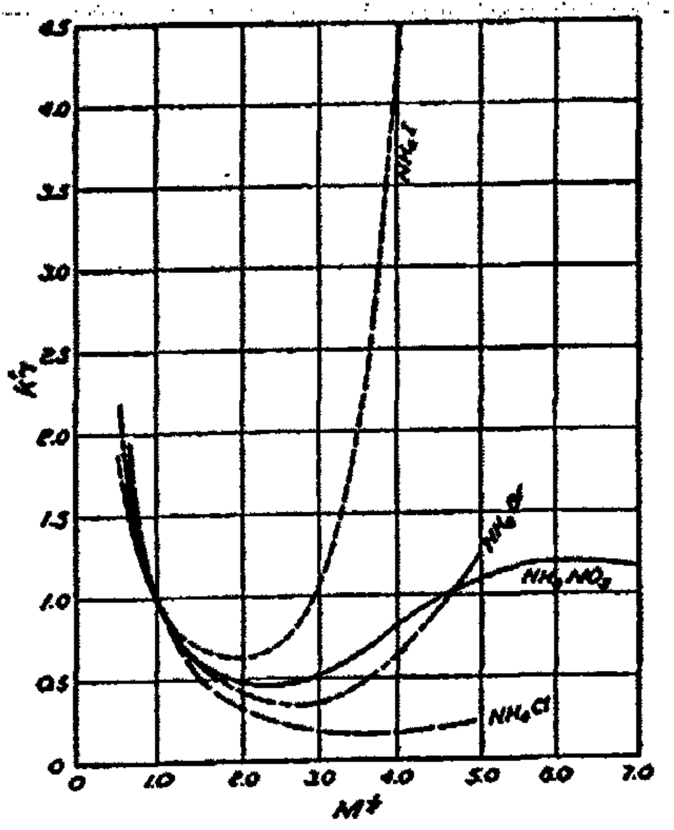

FIG. 1

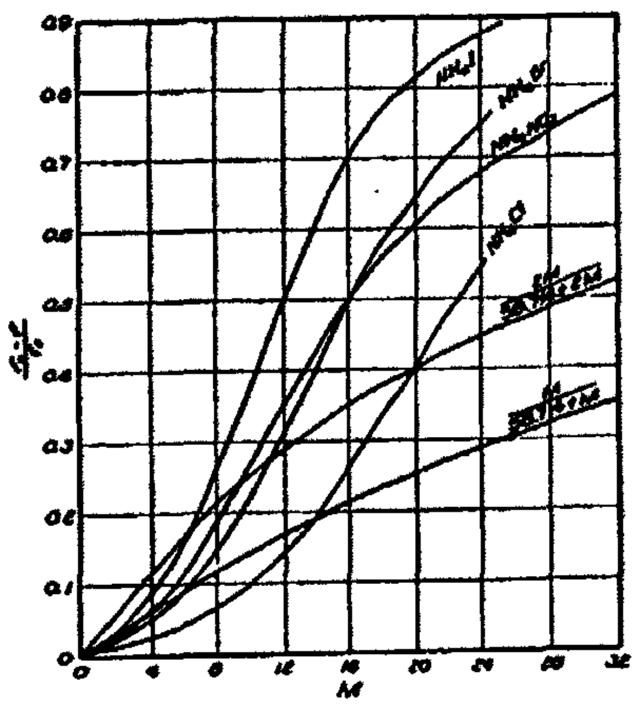

FIG. 2

FIG. 1. VALUES OF $k'\gamma$
FIG. 2. DEVIATIONS FROM RAOULT'S LAW

DEVIATIONS FROM RAOULT'S LAW

If the vapor is not ideal and the solute is a non-electrolyte, the fugacity depends on the concentration in the following manner;

$$f = f_0 N_1 \qquad (10)$$

or

$$\frac{f_0 - f}{f_0} = N_2 = \frac{M}{58.71 + M} \qquad (11)$$

The left side of equation 11 is really the fractional lowering of the fugacity.

If we consider that binary salts, such as the ammonium salts, are 100 per cent ionized, and that the ions resulting still behave as ideal solutes, then a relation similar to equation 11 is

$$\frac{f_0 - f}{f_0} = \frac{2M}{58.71 + 2M} \tag{12}$$

The deviations from the ideal are shown in figure 2, where two of the curves were made by plotting the right-hand side of equations 11 and 12 against the molality, and the others were made by plotting the fractional lowering of the fugacity against the molality. These solutions do not behave as ideal solutions either in the dilute or concentrated region. Such deviations in the concentrated region are not unexpected, but the trends of these curves in the dilute solutions are more unusual, since all but ammonium iodide show a smaller lowering of the fugacity than is predicted for a non-electrolyte. This effect is most marked for ammonium chloride, which does not cross the non-electrolyte curve until above 12 molal.

The interpretation of these results may be made from several viewpoints, as Hepburn (2) has shown. A possible explanation is that some form of association takes place, thus lowering the mole fraction of the solute. The relative positions of the curves for the different halides are what would be expected from this explanation.

The results in the concentrated region indicate that some of the solvent molecules have lost their fugacity, which may mean that they are attached to some of the solute ions. Although the solvation per ion is greater in the dilute solution, in the concentrated solution the number of solvent molecules that are bound up comprises a significant part of the total present, and the mole fraction of the solute increases faster than it otherwise would. The extent of solvation indicated makes it appear probable that both anion and cation are highly solvated.

SUMMARY

1. From the vapor pressures of solutions of ammonium nitrate, iodide, bromide, and chloride a quantity $k'\gamma$ has been calculated using the Gibbs-Duhem equation, and a plausible value of k' determined using the method of Randall and White.

2. The deviations from Raoult's law are shown, and it is suggested that these deviations can be explained if the solutes are partially associated, and there is considerable solvation between the ions resulting and the molecules of the solvent.

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THE RÔLE OF ORTHO SUBSTITUTION IN THE IONIZATION OF ORGANIC ACIDS AND BASES

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The conclusions of Smallwood (14) that the increase in acidity of ortho halogen-substituted acids over that of benzoic acid was due primarily to restricted rotation of the carboxyl group suggests that groups which have a depressing effect upon the ionization of aliphatic acids and meta and para substituted benzoic acids should produce an increased acidity in the corresponding ortho substituted benzoic acids.

Groups having low dipole moments and having little effect on the acidity of aliphatic acids are to be desired for a study of restricted rotation, in order to reduce internal electronic disturbances to a minimum. Methyl and ethyl groups fill these requirements. Table 1 shows the effect of ortho substitution on the dissociation constants of benzoic acids, based on the data of Scudder (13).

DISCUSSION

As predicted, the *m*- and *p*-toluic acids are weaker than benzoic acid. On the assumption that rotation is unrestricted, *o*-toluic acid should be weaker than benzoic acid; actually the ortho acid is stronger than the unsubstituted acid. *o*-Ethylbenzoic acid is also stronger than benzoic acid itself, and slightly more acidic than *o*-toluic acid. In the case of the dimethyl substituted benzoic acids, it is again evident that a methyl group in the ortho position is the primary cause for the increase in acidity, since the 3,5-dimethyl derivative is weaker and the 2,4- and the 2,5-dimethyl derivatives are stronger than benzoic acid. The trimethyl and tetramethyl derivatives also show that methyl groups in the ortho positions more than overcome the usual depressing effect of methyl groups in the meta and para positions. When both ortho positions are filled, the acidity of the resulting compound is greater than that in which but one ortho group is substituted.

It is known that the methoxyl and the ethoxyl groups have a slight acidifying effect upon substituted aliphatic acids. If the evidence presented by measurement of dipole moments is correct (6), substitution of these groups in the ortho position should cause no appreciable increase in acidity because they should not restrict rotation of the carboxyl group. The data for the methoxyl and ethoxyl derivatives shown in table 1 are in agreement with this assumption.

The evidence in favor of restricted rotation presented by the alkoxyl derivatives is less convincing because of the possibilities for molecular resonance (17), which would tend to have a decreasing effect upon acidity. However, if molecular resonance occurs in the toluic acids, the ortho acid would be weaker than the meta and para acids. Since *o*-toluic acid is stronger than either *m*- or *p*-toluic acid, the primary effect cannot be due to molecular resonance.

TABLE 1

Effect of ortho substituents on the dissociation constants of substituted benzoic acids

ACIDS	$K_{25°}$
Benzoic acid	6.6×10^{-5}
o-Toluic acid	1.37×10^{-4}
m-Toluic acid	5.8×10^{-5}
p-Toluic acid	4.3×10^{-5}
o-Ethylbenzoic acid	1.7×10^{-4}
3,5-Dimethylbenzoic acid	4.8×10^{-5}
2,4-Dimethylbenzoic acid	9.0×10^{-5}
2,5-Dimethylbenzoic acid	1.2×10^{-4}
2,4,6-Trimethylbenzoic acid	3.8×10^{-4}
2,3,5,6-Tetramethylbenzoic acid	3.0×10^{-4}
2,3,4,6-Tetramethylbenzoic acid	1.0×10^{-4}
2,3,4,5-Tetramethylbenzoic acid	6.5×10^{-5}
2-Methoxy-5-methylbenzoic acid	6.8×10^{-5}
2-Methoxy-4-methylbenzoic acid	4.1×10^{-5}
4-Methoxy-2-methylbenzoic acid	5.4×10^{-5}
2-Methoxybenzoic acid	8.2×10^{-5}
o-Ethoxybenzoic acid	7.2×10^{-5}
m-Ethoxybenzoic acid	9.2×10^{-5}
p-Ethoxybenzoic acid	5.1×10^{-5}

Pauling (12) has mentioned, in connection with molecular resonance, that bond energy is independent of orientation and that there will be free rotation about a single bond except in so far as rotation is hindered by steric effects arising from interactions of the substituent atoms or groups.

While both optical isomers of the free acid of the benzenesulfonyl derivative of 8-nitro-1-naphthylglycine, as well as their brucine salts, show mutarotation (11), it is not necessary that the di-ortho-substituted benzoic acids have the carboxyl group restricted to the extent necessary to produce optical isomerism. Several attempts to isolate optical isomers have resulted in failure: Lewkowitsch (9) failed to obtain optically active or mutarotatory 1-methyl-6-nitrobenzoic acid, and Adams and coworkers (7, 10) failed to isolate optically active di-ortho-substituted benzoic esters and diphenyl ketones. Following the usage of Betti (2), it would perhaps be better to use the term "diminished free rotation" in place of "restricted rotation," since the latter connotes optical activity. The diminished free rotation of the carboxyl group would be similar to the type occurring in 1,2-dichloroethane (15).

TABLE 2

The effect of ortho substituents on the dissociation constants of bases

BASE	$K_{25°}$
Aniline	3.8×10^{-10}
o-Toluidine	2.5×10^{-10}
m-Toluidine	4.9×10^{-10}
p-Toluidine	1.3×10^{-9}
N-Methylaniline	7.1×10^{-10}
N-Methyl-*o*-toluidine	3.9×10^{-10}
N-Methyl-*m*-toluidine	8.7×10^{-10}
N-Methyl-*p*-toluidine	2.1×10^{-9}
N-Ethylaniline	1.3×10^{-9}
N-Ethyl-*o*-toluidine	8.5×10^{-10}
N-Ethyl-*p*-toluidine	4.7×10^{-9}
N-Dimethylaniline	1.1×10^{-9}
N-Dimethyl-*o*-toluidine	7.3×10^{-9}
N-Dimethyl-*m*-toluidine	1.7×10^{-9}
N-Dimethyl-*p*-toluidine	3.2×10^{-9}
N-Diethylaniline	3.8×10^{-8}
N-Diethyl-*o*-toluidine	1.5×10^{-7}
N-Diethyl-*p*-toluidine	1.2×10^{-7}
Quinoline	6.3×10^{-10}
2-Methylquinoline	2.6×10^{-9}
Pyridine	2.3×10^{-9}
2-Methylpyridine	3.2×10^{-8}
2,6-Dimethylpyridine	1.0×10^{-7}
2,4,6-Trimethylpyridine	1.2×10^{-7}

Since substitution which causes increased acidity in organic acids usually leads to decreased basicity of organic bases, one would expect the *o*-toluidines to be less basic than aniline, which, in turn, should be less basic than the *m*- and *p*-toluidines. The expectation that ortho substitution leads to a decrease in the dissociation constants of organic bases (5) is borne out by the data presented in table 2.

The *N*-dimethyl and *N*-diethyl derivatives of aniline and substituted anilines fail to show the expected decrease in basicity. An explanation for this fact is that the introduction of two alkyl groups on the nitrogen causes a partial restriction of rotation such that further substitution in the ortho position has no further restricting effect. An instance similar to this, in the dimethyl and diethyl substituted malonic and glutaric acids, has been explained by Gane and Ingold (4), who suggest that an unexpected increase in acidity was caused by valency deflection, in addition to restricted rotation.

Within recent years a number of examples of retardation of chemical reactions by the presence of ortho substituents have been recorded (1). The question arises: Is the increase in acidity of acids or decrease in basicity of bases due merely to steric hindrance, or to diminished free rotation? It is possible that it may be due to both. In the quinolines, the nitrogen in the ring is not free to rotate. If substitution in the ortho position of quinolines causes steric hindrance, the resulting bases should be affected to about the same degree as are the *o*-toluidines. The data in table 2 show that ortho substituted quinoline and the ortho substituted pyridines are more basic than the parent substances, just the inverse of that noted for the *o*-toluidines. Therefore steric effect is excluded.

A similar case arises with the phenols, where the functional group contains only one atom attached to the oxygen. *o*-Cresol ($Ka = 6.3 \times 10^{-11}$) is weaker (8) than phenol ($Ka = 7.3 \times 10^{-11}$). This fact is also in accordance with the theory of restricted rotation and opposed to that of steric effect.

These results support the contention that diminished rotation of the functional group occurs in the ortho substituted benzoic acids and anilines. It must be borne in mind, however, that diminished free rotation cannot be measured quantitatively as yet, because there are very probably internal electronic disturbances accompanying diminished free rotation and incapable of being distinguished from it.

SUMMARY

Provisionally, the increase in acidity of ortho substituted benzoic acids and anilines has been attributed to the spacial proximity of the alphyl ortho substituent to the functional group to such an extent that there is diminished free rotation of the latter.

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THE CLASSICAL DISSOCIATION CONSTANT OF BENZOIC ACID IN VARIOUS SALT SOLUTIONS[1, 2]

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In the previous paper (10) the catalytic constant of the hydrogen ion ($k_{H_3O^+}$) in the hydrolysis of diethyl acetal was determined in aqueous solutions of nine solvent salts. With the determination of the temperature coefficient this reaction can now be employed to measure kinetically the hydrogen-ion concentration of suitable buffer solutions. This paper presents the determination of the dissociation constant of benzoic acid in the nine solvent salt solutions over a wide range of concentration.

EXPERIMENTAL PART

Suitable buffer solutions were made from benzoic acid and carbonate-free sodium hydroxide solution, and the purified salts were added. The experimental method was the same as that used in the previous paper. The hydrogen-ion concentration was calculated from the equation:

$$k_{\text{obsd.}}/k_{H_3O^+} = C_{H_3O^+}$$

where the value of $k_{H_3O^+}$ is that for the corresponding concentration of the electrolyte. The classical dissociation constant (K_c) was calculated from the $C_{H_3O^+}$ and the stoichiometric composition of the buffer solution.

Table 1 gives the results of the measurements with lithium chloride, and tables 2 and 3 summarize the results in the other salt solutions.

The results are presented graphically in figure 1. The wide variation in the dissociation constant of the acid in the different salt solutions is particularly striking. For example, at 1 molar electrolyte concentration the difference between the lowest and the highest values is over 100 per cent, the value in lithium chloride being 12.84 and that in sodium *p*-toluenesulfonate 5.47.

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[1] An abstract of this paper was presented at the Eighty-sixth Meeting of the American Chemical Society held at Chicago, September, 1933.

[2] Abstracted from the dissertation of Leonard C. Riesch presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[3] George Leib Harrison Fellow in Chemistry, 1933-34.

In order to analyze the differences further, the value of the ratio $f_H f_B/f_{HB}$ was calculated from the equation:

$$K_a = K_c f_H f_B/f_{HB} \tag{1}$$

where K_a represents the thermodynamic dissociation constant. The value of K_a used by Kilpatrick and Chase (4), 6.31×10^{-5}, has recently been confirmed by accurate measurements by Brockman and Kilpatrick (1).

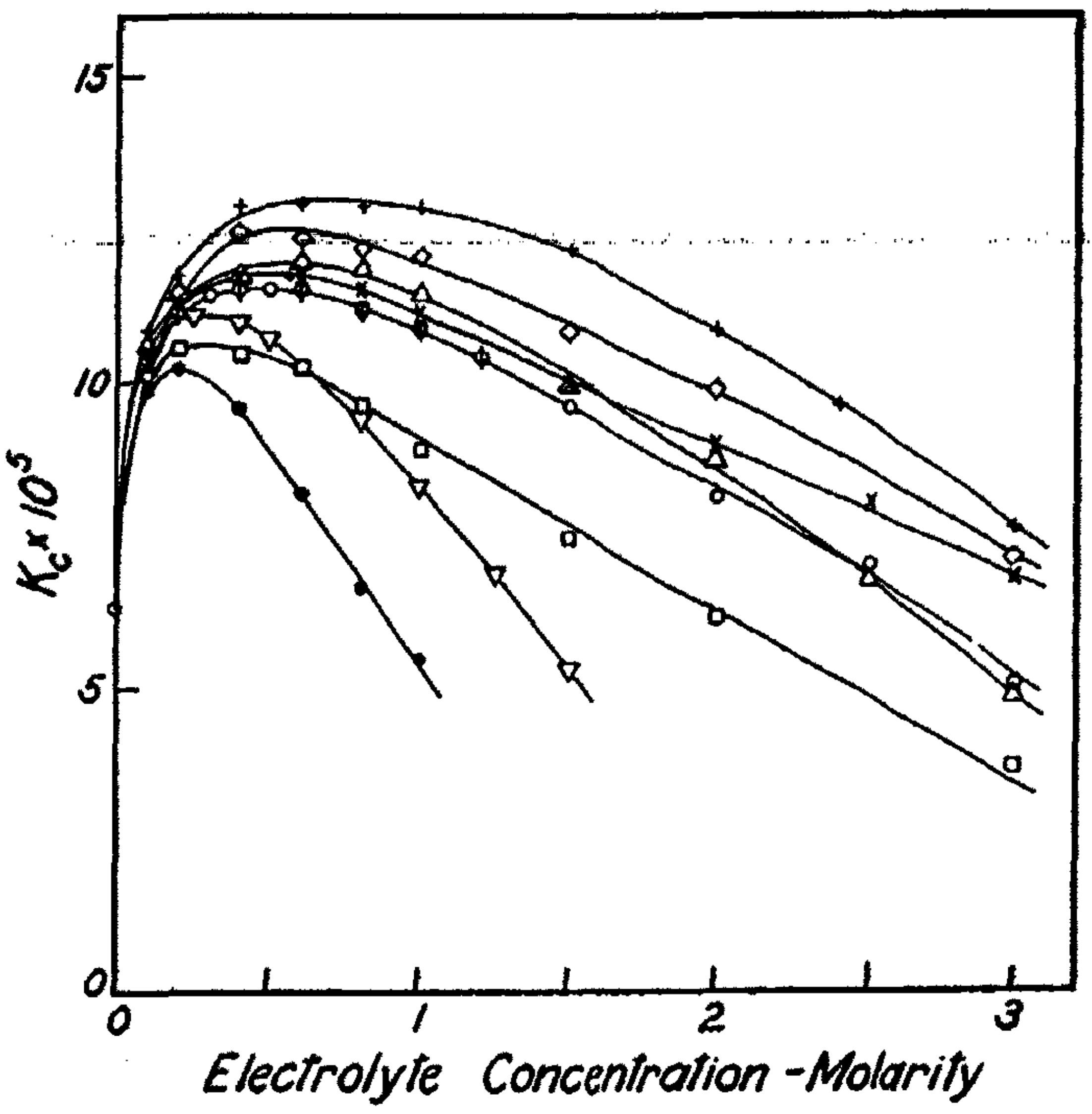

FIG. 1. ELECTROLYTE EFFECT ON THE DISSOCIATION CONSTANT OF BENZOIC ACID

○, KCl; △, NaCl; +, LiCl; □, $NaClO_4$; ◇, $LiNO_3$; ×, $NaNO_3$; ϕ, KNO_3; ▽, $C_6H_5SO_3Na$; ●, p-$C_6H_4(CH_3)SO_3Na$.

To obtain the mean activity coefficient of the ions of benzoic acid, $\sqrt{f_H f_B}$, f_{HB} was calculated from the equation

$$\log f_{HB} = \beta C \tag{2}$$

by using the experimental data in the literature. Table 4 gives the values of the "salting-out" constant.

In the case of the sulfonates the values were plotted from the data of Osol and Kilpatrick (9), and the activity coefficients were read from the plots. The values of $\sqrt{f_H f_B}$ are given in tables 5 and 6.

At 0.10 molar salt concentration the values of $\sqrt{f_H f_B}$ are the same within

2.5 per cent in the various salt solutions, while at 1, 2, and at 3 molar the maximum differences are 20, 25, and 40 per cent, respectively. The mean activity coefficient is greatest in sodium chloride solutions. The order for the chlorides and nitrates at high concentrations is Na > K > Li, and for the sodium salts the order for the anions is Cl > ClO_4 > NO_3 > sulfonates.

TABLE 1

The dissociation constant of benzoic acid in lithium chloride solutions at 25°C.

HB	LiCl + NaB	k OBSERVED	$c_{H_3O^+} \times 10^4$	$K_c \times 10^5$
moles per liter	*moles per liter*			
0.010	0.10	0.01794	2.040	10.83
0.010	0.20	0.02160	2.198	11.73
0.010	0.40	0.02828	2.402	12.90
0.010	0.60	0.03409	2.402	12.90
0.010	0.80	0.04030	2.398	12.87
0.010	1.00	0.04741	2.392	12.84
0.010	1.50	0.06770	2.277	12.18
0.005	2.00	0.04606	1.036	10.80
0.005	2.41	0.03025	0.4772	9.59
0.005	3.00	0.04025	0.3755	7.60

TABLE 2

The dissociation constant of benzoic acid in salt solutions at 25°C.

SALT + NaB	$K_c \times 10^5$			
	NaCl	KCl	$C_6H_5SO_3Na$	p-$C_6H_4(CH_3)SO_3Na$
moles per liter				
0.10	10.59	10.15	10.09	9.88
0.20	11.46	11.21	10.99	10.22
0.25			11.12	
0.30		11.41		
0.40	11.71		10.97	9.57
0.50		11.51	10.73	
0.60	11.94			8.18
0.80	11.85	11.20	9.39	6.63
1.00	11.40	10.88	8.27	5.47
1.25			6.84	
1.50	9.91	9.58	5.28	
2.00	8.71	8.11		
2.50	6.78	6.99		
3.00	4.85	5.04		

The other values for the dissociation constant of benzoic acid that are given in the literature are at 18°C. and 20°C., and it is probable that the change of the dissociation constant over this range of temperature is small.

This is borne out by the results of the determination of the temperature coefficient of the dissociation constant between 35°C. and 25°C. by the two-thermostat method. The results are summarized in table 7.

It is to be noted that, except for the values for 3 molar sodium chloride, the temperature coefficient in the various salt solutions is constant within approximately 3 per cent. From the average value 3.455, as compared with 3.395 for k_{35}/k_{25} for strong acids, it is evident that the temperature coefficient of the dissociation constant is small over this range.

TABLE 3

The dissociation constant of benzoic acid in salt solutions at 25°C.

SALT + NaB	$K_c \times 10^5$			
	$LiNO_3$	$NaNO_3$	KNO_3	$NaClO_4$
moles per liter				
0.10	10.21	10.43	10.35	10.43
0.20	11.28	11.31	11.10	10.87
0.40	12.46	11.71	11.48	10.47
0.60	12.32	11.73	11.49	10.24
0.80	12.16	11.52	11.14	9.63
1.00	12.02	11.15	10.83	8.88
1.20			10.41	
1.50	11.03	9.97		7.45
2.00	9.83	9.03		6.15
2.50		8.01		
3.00	7.16	6.81		3.73

TABLE 4

Values of the "salting-out" constant

SALT	"SALTING OUT" CONSTANT β	SOURCE
LiCl	0.192	Larsson (8)
NaCl	0.177	Larsson (7)
KCl	0.138	Chase and Kilpatrick (2)
$LiNO_3$	0.078	Larsson (8), Haessler (3) and Kolthoff and Bosch (6)
$NaNO_3$	0.080	Larsson (8)
KNO_3	0.040	Larsson (8)
$NaClO_4$	0.062	Kolthoff and Bosch (6)

A comparison of the values of the dissociation constant of benzoic acid in potassium chloride solutions as determined by the kinetic method with those determined by means of the quinhydrone electrode shows that the results are not in agreement at concentrations above 2 molar. Repeated determinations by the two methods in 3 molar potassium chloride solution consistently show this discrepancy. With 3 molar sodium chloride a similar discrepancy exists. In order to investigate this difference the assumptions of the kinetic method were tested further. The assumptions

TABLE 5

The mean activity coefficient of the ions of benzoic acid at 25°C.

ELECTROLYTE CONCENTRATION SALT + NaB	$\sqrt{f_H f_B}$			
	LiCl	NaCl	KCl	NaClO$_4$
moles per liter				
0.10	0.78	0.79	0.80	0.78
0.20	0.77	0.77	0.77	0.77
0.30			0.78	
0.40	0.76	0.80		0.80
0.50			0.80	
0.60	0.80	0.82		0.82
0.80	0.83	0.85	0.85	0.86
1.00	0.87	0.91	0.89	0.90
1.50	1.00	1.08	1.03	1.03
2.00	1.18	1.28	1.21	1.17
2.41	1.38			
2.50		1.60	1.41	
3.00	1.76	2.10	1.80	1.61

TABLE 6

The mean activity coefficient of the ions of benzoic acid at 25°C.

ELECTROLYTE CONCENTRATION SALT + NaB	$\sqrt{f_H f_B}$				
	LiNO$_3$	NaNO$_3$	KNO$_3$	$C_6H_5SO_3Na$	p-$C_6H_4(CH_3)SO_3Na$
moles per liter					
0.10	0.79	0.79	0.78	0.78	0.78
0.20	0.76	0.76	0.76	0.74	0.74
0.25				0.73	
0.40	0.74	0.76	0.75	0.72	0.71
0.50				0.72	
0.60	0.76	0.77	0.76		0.71
0.80	0.77	0.80	0.78	0.71	0.71
1.00	0.79	0.82	0.80	0.72	0.71
1.20			0.82		
1.25				0.74	
1.50	0.87	0.91		0.79	
2.00	0.95	1.00			
2.50		1.13			
3.00	1.23	1.26			

involved in the determination of $k_{H_3O^+}$ are as follows: (1) The hydrogen ion is the sole catalyst. (2) The energy of activation is constant within the experimental error of measurement from 0° to 35°C. (3) The energy of activation is independent of the salt concentration.

TABLE 7

The temperature coefficient in benzoate buffers

SALT	SALT + NaB	k_{35}/k_{15}	DEVIATION FROM 3.455
	moles per liter		
NaB	0.005	3.469	0.011
KCl	0.10	3.384	0.071
	0.50	3.505	0.050
	1.00	3.474	0.019
	1.50	3.457	0.002
	2.00	3.395	0.060
	3.00	3.519	0.064
NaCl	2.00	3.417	0.038
	3.00	3.168*	
	3.00	3.113*	
	3.00	3.148*	
$NaClO_4$	3.00	3.504	0.049
LiCl	3.00	3.379	0.076
$NaNO_3$	3.00	3.443	0.012
$C_6H_5SO_3Na$	1.00	3.423	0.032
p-$C_6H_4(CH_3)SO_3Na$	1.00	3.546	0.091
Average		3.455	±0.044

* Omitted from the average.

TABLE 8

The effect of reaction products upon the velocity constant

HB	KCl + NaB	k OBSERVED	$C_{H_3O^+} \times 10^4$	$K_c \times 10^5$
moles per liter	*moles per liter*			
0.005	3.00	0.01580	0.2590	5.22
0.005	3.00	0.01523	0.2497	5.03
0.005	3.00	0.01488	0.2440	4.91

To test these assumptions the dissociation constant of acetic acid in potassium chloride solutions was determined electrometrically. At the same time independent kinetic determinations were made on the same buffer solutions. Both methods gave results in agreement over the range from 0.10 to 3.0 molar potassium chloride concentration (5). Similar agreement was found for glycolic acid–glycolate buffers in potassium chloride solutions. Evidently the discrepancies at 3 molar salt concentration in the case of benzoic acid are not due to the invalidity of the assumptions. In fact, the results indicate that the high primary salt effect is not connected with any catalytic effect of the hydrochloric acid molecules. Any explanation of the difference in the results must therefore be related to the benzoic acid buffer itself or to some specific reaction with the acetal, or to the products of the reaction. Varying the buffer ratio has little effect on the calculated dissociation constant. It is not possible to vary the acetal

TABLE 9

Comparison with equation 5

ELECTROLYTE MOLES PER LITER	$\sqrt{f_H/f_B}$ OBSERVED	$\sqrt{f_H/f_B}$ CALCULATED	ELECTROLYTE MOLES PER LITER	$\sqrt{f_H/f_B}$ OBSERVED	$\sqrt{f_H/f_B}$ CALCULATED
$NaClO_4$ (B = −0.222)			KNO_3 (B = −0.176)		
0.10	0.78	0.80	0.10	0.78	0.79
0.20	0.77	0.78	0.20	0.76	0.76
0.40	0.80	0.79	0.40	0.75	0.75
0.60	0.82	0.82	0.60	0.76	0.77
NaCl (B = −0.218)			$LiNO_3$ (B = −0.166)		
0.10	0.79	0.80	0.10	0.79	0.79
0.20	0.77	0.77	0.20	0.76	0.76
0.40	0.80	0.78	0.40	0.74	0.75
0.60	0.82	0.82	0.60	0.76	0.76
KCl (B = −0.216)			$C_6H_5SO_3Na$ (B = −0.124)		
0.10	0.80	0.80	0.10	0.78	0.78
0.20	0.77	0.77	0.20	0.74	0.74
0.30	0.78	0.77	0.25	0.73	0.73
0.50	0.80	0.80	0.50	0.72	0.72
LiCl (B = −0.192)			p-$C_6H_4(CH_3)SO_3Na$ (B = −0.114)		
0.10	0.78	0.79	0.10	0.78	0.78
0.20	0.77	0.77	0.20	0.74	0.74
0.40	0.76	0.76	0.40	0.71	0.71
0.60	0.80	0.79	0.60	0.71	0.71
$NaNO_3$ (B = −0.178)					
0.10	0.79	0.79			
0.20	0.76	0.76			
0.40	0.76	0.75			
0 60	0.77	0.77			

concentration very greatly, but the effect of the products of hydrolysis was tested in the following manner. An experiment was carried out in the usual way; the buffer solution was then drawn back into the mixing chamber, another portion of acetal was added, and the experiment repeated. Upon completion of this experiment the process was repeated. The results are given in successive order in table 8. Although there is about 6 per cent change in the $k_{\text{obsd.}}$ and in the resultant dissociation constant, the magnitude of this effect cannot account for the 20 per cent difference between the results by the two methods in 3 molar potassium chloride solution. In no case did the velocity constants show a trend.

As pointed out by Chase and Kilpatrick (2) the mean activity coefficient of the ions of benzoic acid can be represented by an equation of the form

$$-\log\sqrt{f_H f_B} = \frac{0.5\sqrt{C}}{1+\kappa b} + \beta C \qquad (4)$$

where κ equals $0.33 \times 10^8 \sqrt{C}$ and b is the apparent average ionic diameter. The β is an empirical constant which should include salting-out and interaction effects. If we arbitrarily set b equal to 3.0×10^{-8} cm. the above equation becomes:

$$-\log\sqrt{f_H f_B} = \frac{0.5\sqrt{C}}{1+\sqrt{C}} + BC \qquad (5)$$

By plotting $\log\sqrt{f_H f_B} + \frac{0.5\sqrt{C}}{1+\sqrt{C}}$ against the concentration, B has been evaluated for each solvent salt. The observed and the calculated values up to 0.6 molar are given in table 9.

Over this range the order of decreasing activity coefficients is Na > K > Li. For the sodium salts one finds $ClO_4 > Cl > NO_3 > RSO_3$, but at higher concentrations the mean activity coefficients become greater in sodium chloride than in sodium perchlorate.

SUMMARY

1. The classical dissociation constant of benzoic acid has been determined kinetically in solutions of lithium chloride, sodium chloride, potassium chloride, lithium nitrate, sodium nitrate, potassium nitrate, sodium perchlorate, sodium benzenesulfonate, and sodium *p*-toluenesulfonate.
2. From the values of the activity coefficient of molecular benzoic acid and the thermodynamic dissociation constant, the mean activity coefficients of the ions of benzoic acid in the several salt solutions have been calculated.

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A STUDY OF THE BENZOIN REACTION. II

Negative Catalysis in the Benzoin Reaction

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INTRODUCTION

Having definitely established the fact that pure potassium cyanide and benzaldehyde in the absence of water do yield benzoin (2), attention was directed to the statement in the literature that water was necessary to induce the reaction. Preliminary experiments with various brands of potassium cyanide showed that certain commercial samples would not yield benzoin when shaken with pure benzaldehyde at 100°C. for 1 hour unless water were added. Further experiments showed that alkali halides and also hydrogen sulfide and sulfur can inhibit the benzoin reaction. The effect of increasing quantities of sodium and potassium chlorides (impurities likely to be present in commercial potassium cyanide), potassium iodide, and quinol on the benzoin reaction was examined (figures 1 and 2). The results show that these substances in sufficient quantity prevent the formation of benzoin in 1 hour, and that potassium iodide and quinol are particularly effective. The latter were tried because it is known that they are more effective than potassium and sodium chlorides in the inhibition of the oxidation of benzaldehyde.

TIME–YIELD CURVES IN PRESENCE OF INHIBITORS

Next, a series of experiments was made to obtain time–yield curves in the presence of various quantities of quinol, potassium iodide, and potassium chloride (figure 3). It will be seen that the curves thus obtained are of the same type as those yielded by pure potassium cyanide, with the difference, however, that a diminished quantity of potassium cyanide appears to be functioning in the heterogeneous reaction. (See figure 3, upper section, Curves IV and VI.) The homogeneous autocatalytic reaction is unaffected. Thus the curve obtained with 1 g. of potassium cyanide and 0.3 g. of quinol is almost identical, particularly in the earlier stage, with that given by 0.3 g. of pure potassium cyanide. In other words, 0.3 g. of quinol renders inactive 0.7 g. of potassium cyanide.

From the amount of benzoin obtained in 1 hour, we can determine how much cyanide is effective in producing it. This determination is facilitated

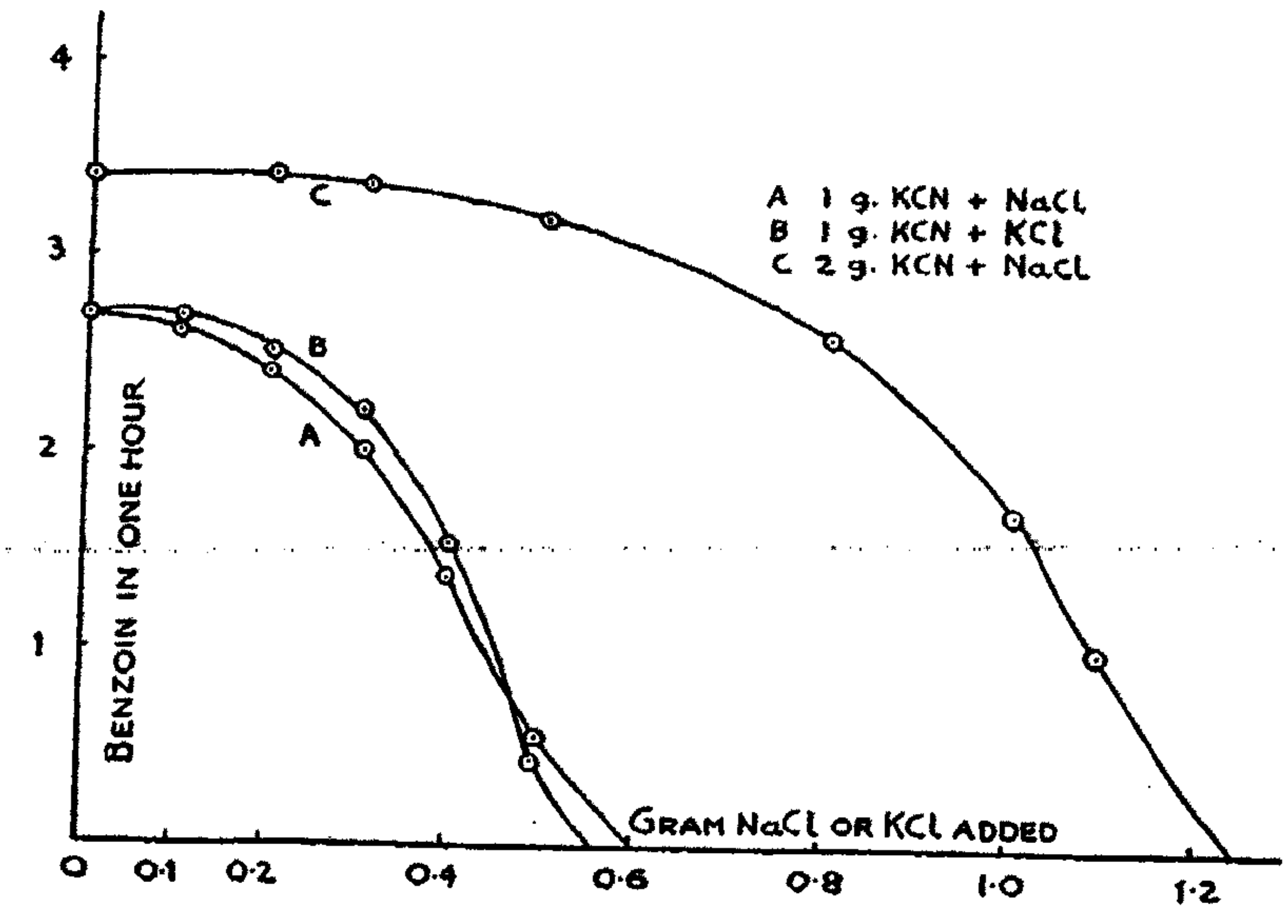

FIG. 1. EFFECT OF SODIUM CHLORIDE AND POTASSIUM CHLORIDE ON THE YIELD OF BENZOIN

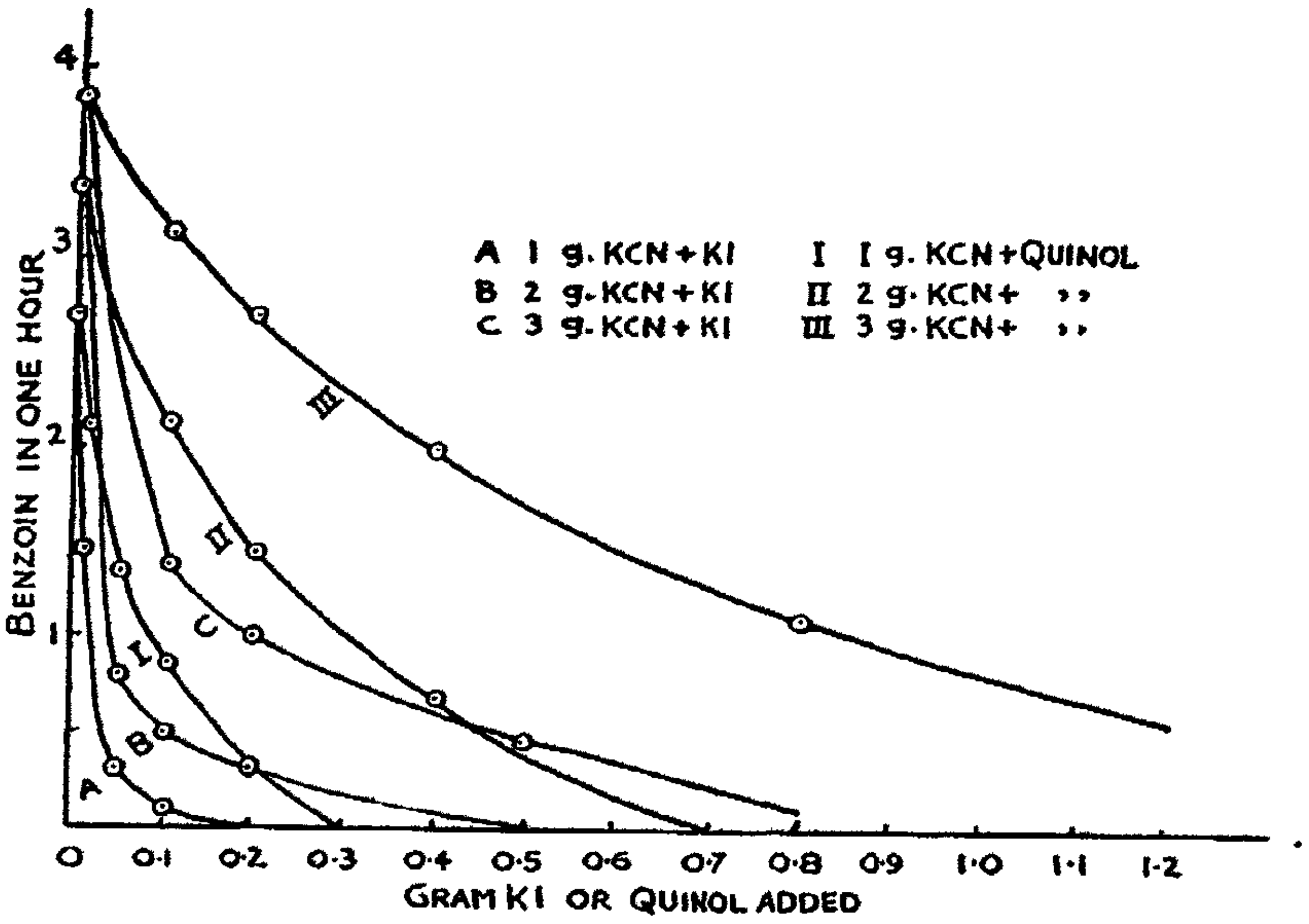

FIG. 2. EFFECT OF POTASSIUM IODIDE AND QUINOL ON THE YIELD OF BENZOIN

by plotting the quantity of benzoin obtained in 1 hour from 10 g. of benzaldehyde at 100°C., against the quantity of pure cyanide required to pro-

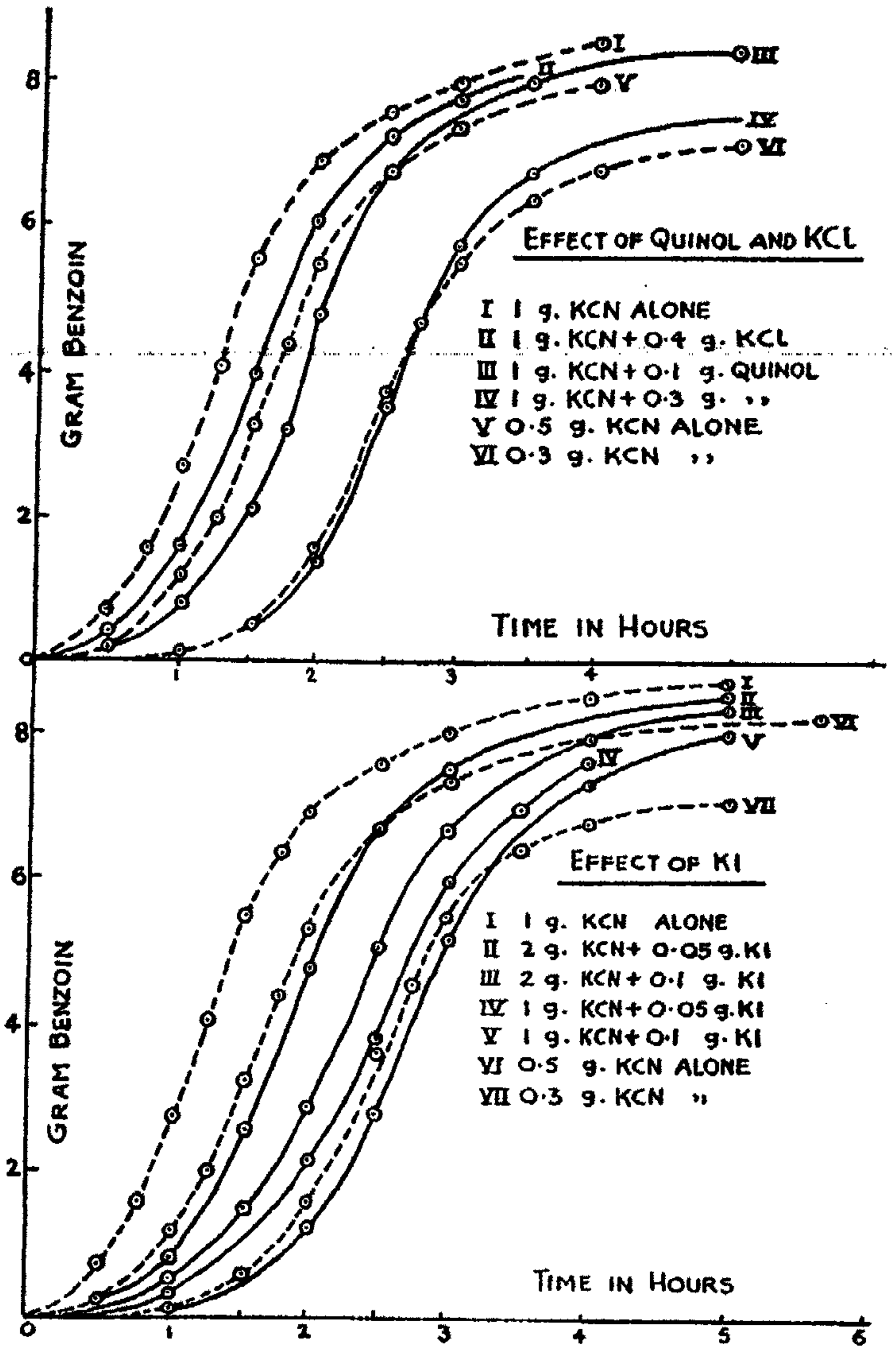

FIG. 3. EFFECT OF QUINOL AND POTASSIUM CHLORIDE ON THE YIELD OF BENZOIN; EFFECT OF POTASSIUM IODIDE ON THE YIELD OF BENZOIN

duce it, the correction of 0.17 g. (see Part I) being inserted. The yield of benzoin produced in 1 hour in any experiment with pure potassium cyanide and the added impurity is referred to this graph, from which the amount of

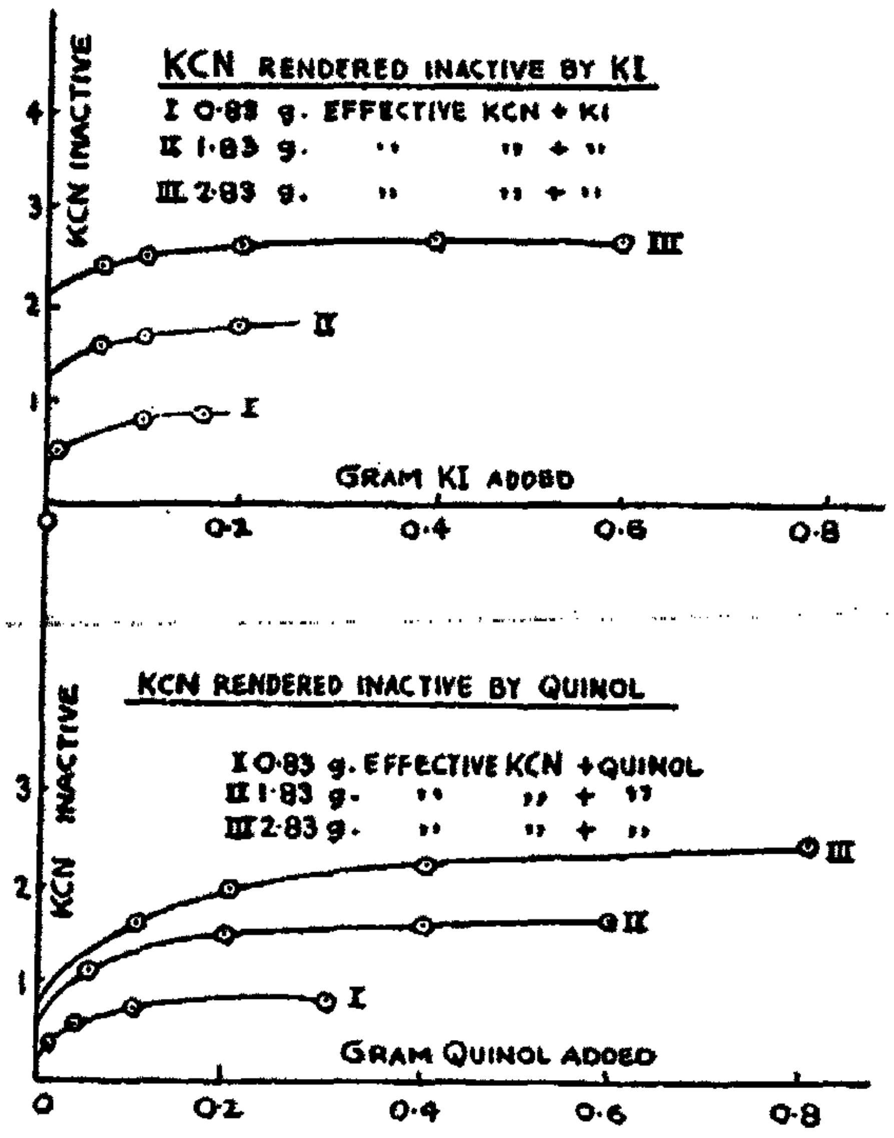

FIG. 4. POTASSIUM CYANIDE RENDERED INACTIVE BY POTASSIUM IODIDE AND BY QUINOL

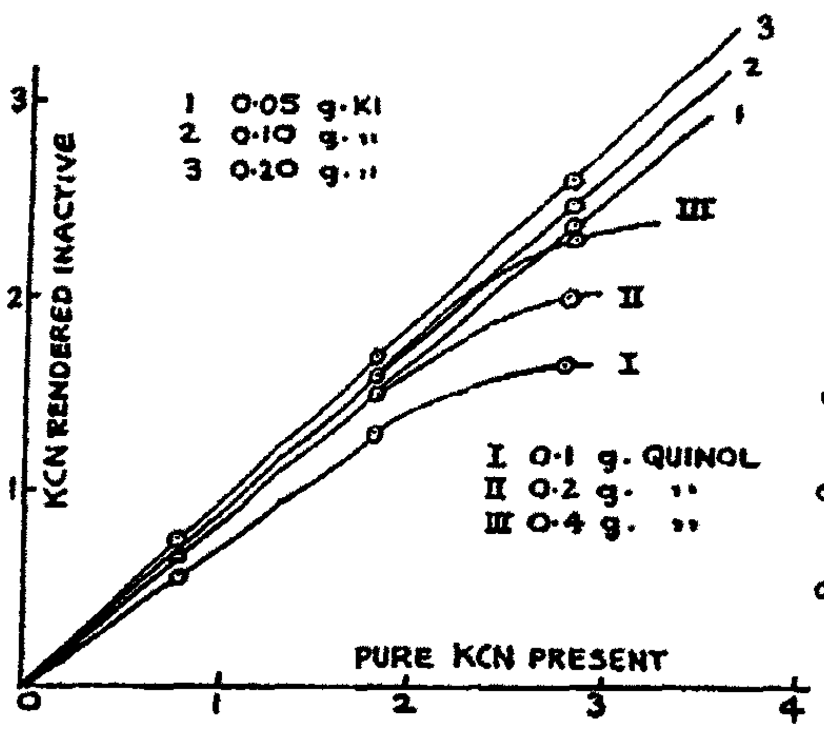

FIG. 5

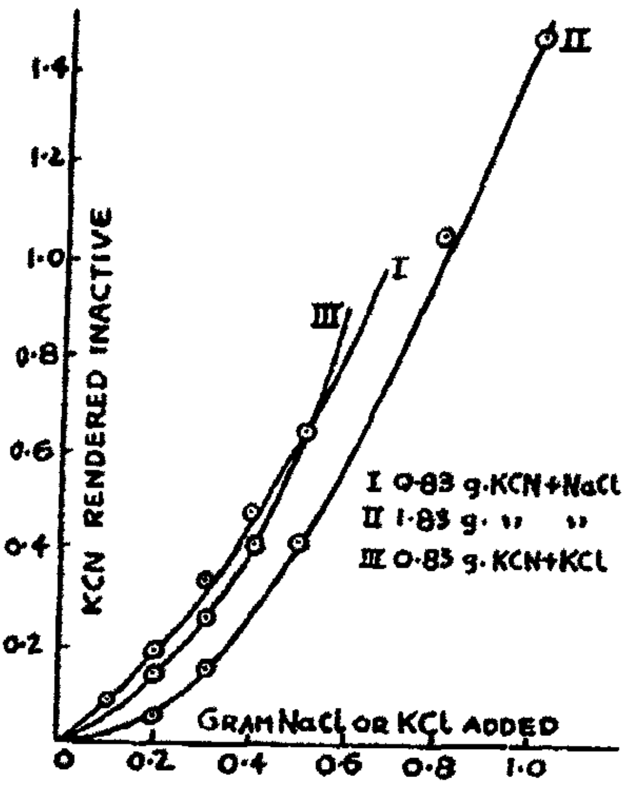

FIG. 6

FIG. 5. POTASSIUM CYANIDE RENDERED INACTIVE BY POTASSIUM IODIDE OR QUINOL, PLOTTED AGAINST PURE POTASSIUM CYANIDE

FIG. 6. POTASSIUM CYANIDE RENDERED INACTIVE BY SODIUM CHLORIDE OR POTASSIUM CHLORIDE

pure potassium cyanide required to produce the same yield of benzoin is found; the cyanide rendered inactive by the impurity added is obtained by subtraction.

THE DEACTIVATION OF POTASSIUM CYANIDE BY MEANS OF POTASSIUM IODIDE AND QUINOL

Figure 4 shows the quantities of potassium cyanide rendered inactive by various quantities of potassium iodide and quinol. With potassium iodide the quantity of cyanide rendered inactive increases very slowly with the potassium iodide added. Further, the amount rendered inactive by potassium iodide is proportional to the quantity of pure potassium cyanide present (figure 5, Curves 1, 2, 3).

These results can be interpreted to mean that potassium iodide is adsorbed *on the surface of the solid potassium cyanide, and thus inhibits* the reaction. The amount adsorbed is in equilibrium with the saturated solution of potassium iodide in benzaldehyde, and therefore is directly proportional to the amount of cyanide present. It is clear from the small quantities of potassium iodide required that little is adsorbed and little is required to saturate the benzaldehyde; about 90 per cent of the cyanide is rendered inactive by the potassium iodide.

Quinol behaves in much the same way as potassium iodide. Increase in the amount of quinol increases the inhibiting effect rapidly at first, and then more slowly. The quantities of quinol required to deactivate the potassium cyanide are larger than with potassium iodide.

It will be seen (figure 5) that up to a limit the quantity of potassium cyanide rendered inactive by a given quantity of quinol is proportional to the amount of potassium cyanide present.

DEACTIVATION OF POTASSIUM CYANIDE BY MEANS OF POTASSIUM AND SODIUM CHLORIDES

Potassium and sodium chlorides (figure 6) are less effective than potassium iodide and quinol and give results of a different type. The inhibiting effect increases with the quantity added. This may mean direct action between solid cyanide and solid chloride. The extent of the surface of the potassium cyanide rendered inactive will then increase with the quantity of the negative catalyst present, since it is more likely to be in contact with it. Presumably potassium and sodium chlorides are much less soluble in benzaldehyde than is potassium iodide.

DISCREPANCIES IN PREVIOUS RESULTS

These results explain the discrepancies in the results of previous workers, regarding the possibility of obtaining benzoin from benzaldehyde and potassium cyanide only. Where it was not obtained, impure cyanide had evidently been used. Lachmann's result (1) that benzoin can replace water in promoting the benzoin reaction can be referred to the fact that in the presence of benzoin the homogeneous autocatalytic reaction which is not affected by the inhibitor can proceed. The action of water in the presence of inhibitors is considered in Part III.

SUMMARY

1. It is shown that potassium and sodium chlorides, potassium iodide and quinol can inhibit the benzoin reaction.

2. They act by stopping the heterogeneous reaction, but they do not affect the homogeneous autocatalytic reaction.

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A STUDY OF THE BENZOIN REACTION. III

The Effect of Water on the Benzoin Reaction

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Received September 26, 1933

Having studied the reaction between potassium cyanide and benzaldehyde under anhydrous conditions (Parts I and II), it is of interest in view of the importance hitherto attributed to the cyano ion in the reaction to examine the effect of addition of water. Figure 1 gives the results of experiments at 100°C. with 10 g. of benzaldehyde and various quantities of potassium cyanide and water. No benzoin was obtained from 0.175 g. of potassium cyanide and 2.0 g. or more of water, nor from 0.17 g. of potassium cyanide even with as little as 0.1 g. of water.

It is clear from the curves that addition of water to a given quantity of potassium cyanide first increases and then reduces the rate of reaction.

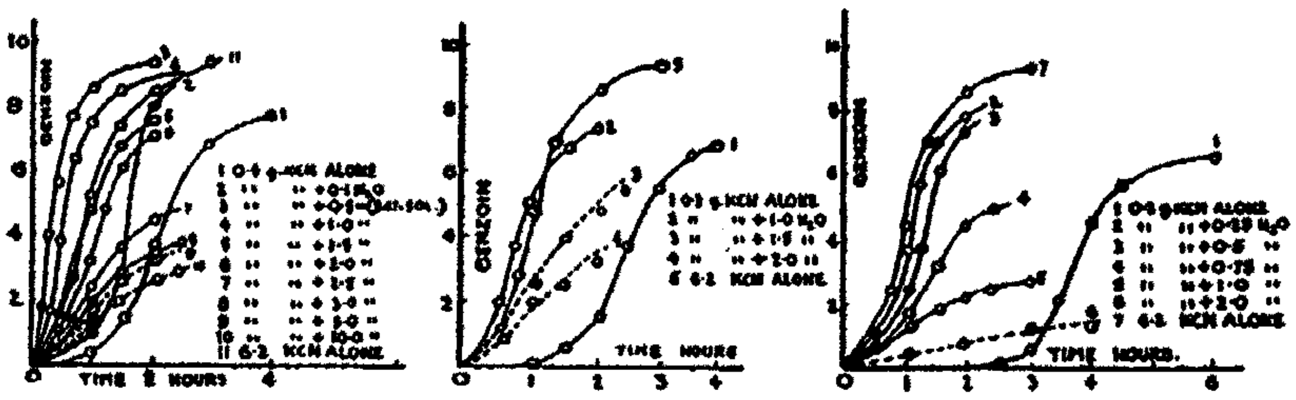


Fig. 1.

The dotted lines represent calculated curves, with experimental points thereon

Autocatalysis gradually disappears. While this persists the curves obtained are similar to those yielded by suitable quantities of potassium cyanide in the absence of water (see figure 2).

Table 1 gives the quantities of solid anhydrous potassium cyanide which correspond to certain strong solutions as regards the rate of production of benzoin in the heterogeneous reaction (see Part I, p. 733). The accelerating and subsequent decelerating effect of water is well brought out. Figure 3 shows that solutions of different strengths in suitable quantities can give similar results.

It is evident that with concentrated solutions of cyanide there are again two reactions involved. From the similarity of the curves obtained with anhydrous potassium cyanide and with strong solutions, the homogeneous autocatalytic reaction appears under these circumstances to be unaffected

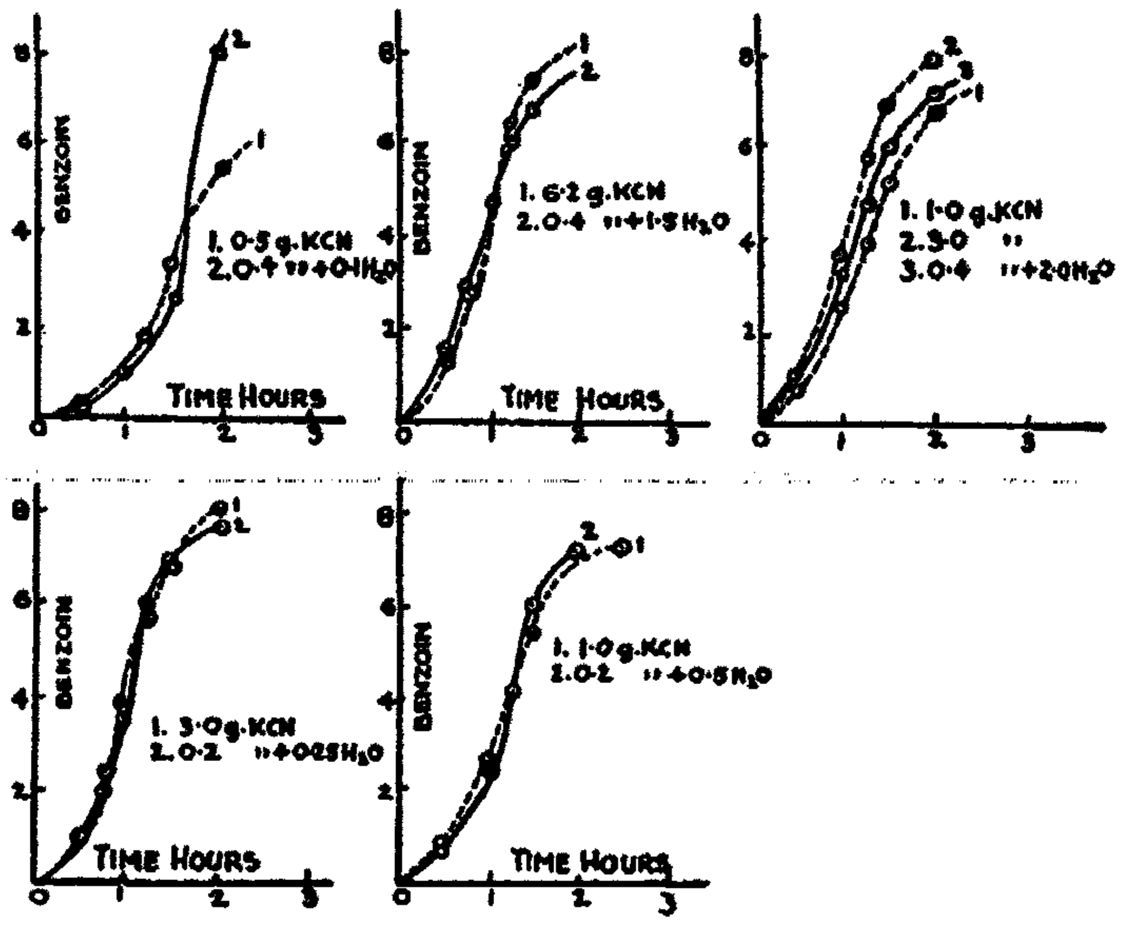


Fig. 2.

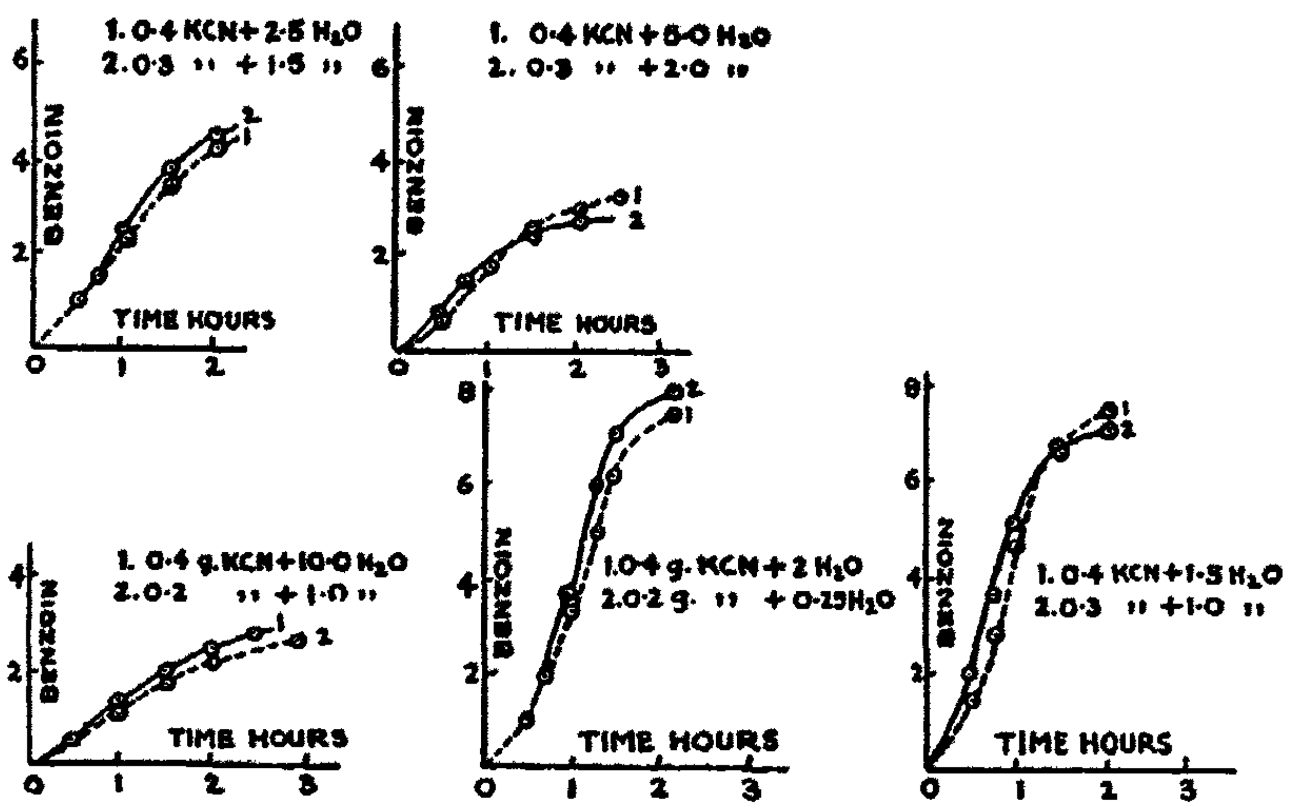


Fig. 3.

by the presence of water. The heterogeneous reaction between the strong solution and benzaldehyde is greatly accelerated.

The rapid fall in the rate of reaction with the addition of water beyond a certain limit may be referred to the fact that as the cyanide solution decreases in strength it extracts in increasing proportion the trace of cyanide dissolved in benzaldehyde which is producing the homogeneous reaction.

It is of interest to attempt to formulate mathematically the reaction occurring between the aqueous solution and benzaldehyde when sufficient water is present to stop the homogeneous reaction.

We may proceed as follows:

Let A = number of grams of benzaldehyde originally present.
y = number of grams of benzaldehyde present at time t.
$\frac{A - y}{2}$ = relative number of molecules of benzoin present.
$\frac{A + y}{2}$ = total number of molecules present.

TABLE 1

Quantities of solid anhydrous potassium cyanide corresponding to certain strong solutions

KCN TAKEN A	H_2O ADDED	EFFECTIVE KCN ($A - 0.17$)	YIELD OF BENZOIN IN ONE HOUR	EQUIVALENT EFFECTIVE ANHYDROUS KCN
grams	*grams*	*grams*	*grams*	*grams*
0.2	0.0	0.03	Nil	0.03
0.2	0.25	0.03	3.6	2.22
0.2	0.50	0.03	2.4	0.64
0.3	0.0	0.13	0.12	0.13
0.3	1.0	0.13	5.0	6.5
0.4	0.0	0.23	0.3	0.23
0.4	0.1	0.23	0.9	0.31
0.4	1.5	0.23	4.7	5.45
0.4	2.0	0.23	3.2	1.43

We assume that the rate of reaction is proportional to a constant depending upon the cyanide and water present and on the molecular concentration of benzaldehyde. The reason for this is that by a process of trial and error, it has been found that this assumption gives better results than that involving the square of the benzaldehyde concentration. We have therefore for a solution,

$$-\frac{dy}{dt} = k\frac{y}{\frac{A+y}{2}}$$

$$= \frac{2ky}{A+y}$$

and

$$-2k(t+c) = y + A \ln y$$

Therefore

$$t + c = \frac{y + 23.0 \log y}{-2k}$$

When $t = 0$, $y = 10$, so,

$$c = \frac{33}{-2k} = \frac{-16.5}{k}$$

$$-2k = 2\,\frac{16.5}{c} = \frac{33}{c}$$

Therefore,

$$t + c = \frac{c(y + 23.0 \log y)}{33}$$

TABLE 2

Values of k for various solutions

KCN TAKEN	EFFECTIVE KCN	WATER ADDED	c	$k = \frac{-16.5}{c}$
grams	*grams*	*grams*		
0.175	0.005	1.0	−34	0.49
0.2	0.03	2.0	−46	0.36
0.2	0.03	1.0	−12.3	1.34
0.2	0.03	0.75	−8.0	2.1
0.3	0.13	2.0	−8.8	1.9
0.3	0.13	1.5	−5.8	2.8
0.4	0.23	10.0	−13	1.3
0.4	0.23	5.0	−8.8	1.9
0.4	0.23	3.0	−7.2	2.3
0.4	0.23	2.5	−6.3	2.6

In figure 1 the curves indicated by dotted lines have been calculated by means of the above equation, with suitable values for c. While the agreement is not exact, the equations reproduce the general course of the experimental curves.

Table 2 gives the values of k for various solutions considered. In figure 4 these values are plotted against the quantities of water used. The curves for the same quantity of cyanide are regular.

THE EFFECT OF INHIBITORS IN THE PRESENCE OF WATER

It was shown by Lachmann (1) that potassium cyanide which did not yield benzoin with benzaldehyde alone, reacted when water was added. Water has thus the power of decreasing the inhibiting effect of the negative catalysts present in the cyanide. With a view to studying the effect of negative catalysts in the presence of water some experiments were carried out on the addition of potassium iodide to solutions of pure potassium cyanide in water (figure 5). It will be seen that 0.1 g. and 0.2 g. of potassium iodide with 0.2 g. of potassium cyanide and 0.25 g. of water do reduce the rate of reaction, but the effect is more marked in the absence of water; 0.1 g. of potassium iodide will prevent completely 0.2 g. of anhydrous potassium cyanide from reacting.

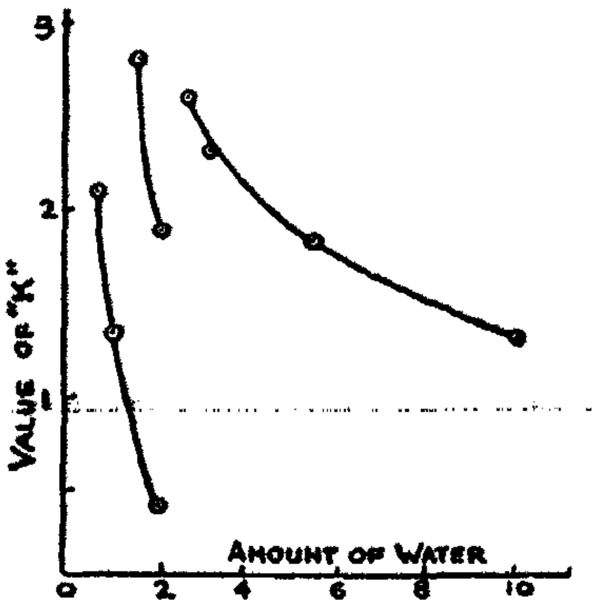


FIG. 4.

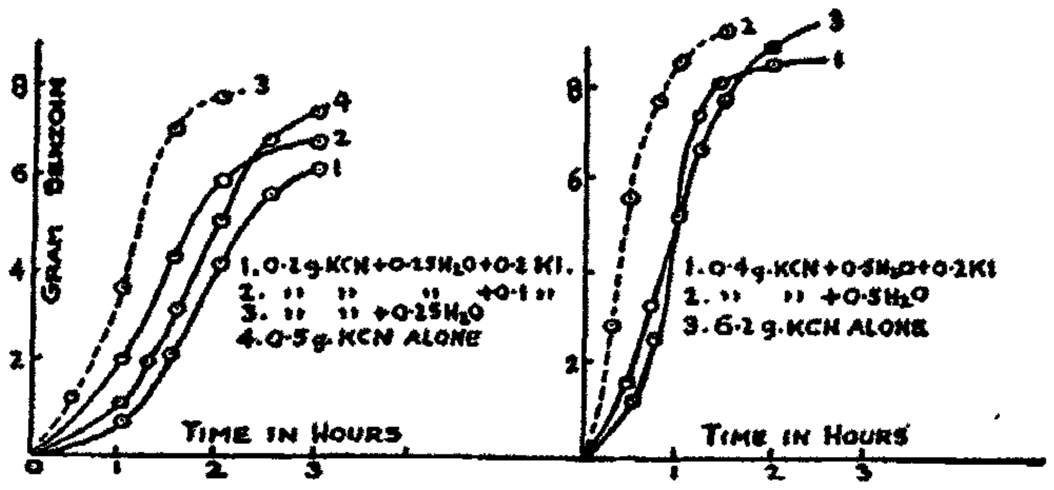


FIG. 5.

TABLE 3

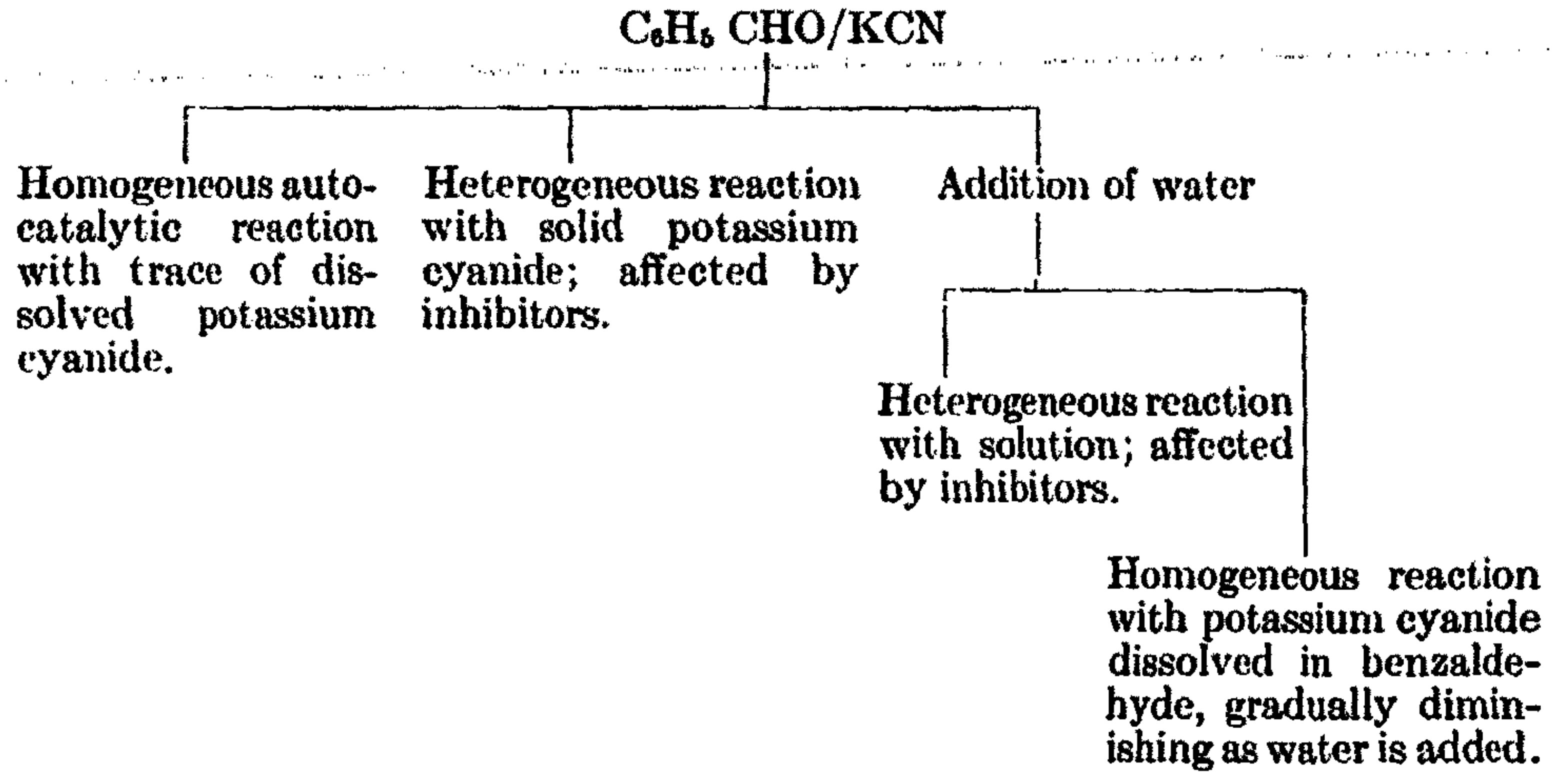
The equivalents in terms of anhydrous potassium cyanide of the solution containing potassium iodide

KCN TAKEN	WATER ADDED	IMPURITY ADDED	EFFECTIVE KCN A − 0.17	BENZOIN IN ONE HOUR	EQUIVALENT EFFECTIVE ANHYDROUS KCN
grams	*grams*		*grams*	*grams*	*grams*
0.2	0.25	Nil	0.03	3.6	2.22
0.2	0.25	0.1 KI	0.03	2.01	0.48
0.2	0.25	0.2 KI	0.03	0.72	0 23
0.4	0.5	0.2 KI	0.23	5.2	7 1

Figure 5 also compares the results with curves obtained in the absence of water. It will be seen that the curves with potassium iodide in the presence of strong solutions of potassium cyanide are of the same type as those obtained with anhydrous potassium cyanide, so that we can deduce the equivalents in terms of anhydrous potassium cyanide of the solution containing potassium iodide (see table 3).

Lachmann's result quoted above was thus due to the capacity of water to reduce the effect of the negative catalysts.

The results obtained in the investigations described in Parts I, II, and III of this study of the benzoin reaction may be summarized as follows:



REFERENCE

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COMMUNICATION TO THE EDITOR

ON THE $(\mathrm{C—C})_{\mathrm{diam}}$ BOND ENERGY

The most probable experimental value for the heat of sublimation of carbon is 154 ± 10 Cal. W. E. Vaughan and G. B. Kistiakowsky (Phys. Rev. **40**, 457 (1932)) calculate 161 to 176 Cal., with the assumption of a considerable amount of C_2 in equilibrium in the saturated carbon vapor.

Theoretically, the heat of sublimation S_C corresponding to the process

$$C(^5S)_{\mathrm{diam}} \rightarrow C(^3P)_{\mathrm{gas}} - S_C$$

is given by

$$S_C = 2E_{CC} - E^* \qquad (1)$$

where E_{CC} is the energy of the $[C(^5S) - C(^5S)]_{\mathrm{diam}}$ bond and E^* the energy difference between the ^5S and ^3P states of carbon (according to the Heitler-London valency theory, C_{diam} is in the ^5S state).

Recently R. F. Bacher and S. Goudsmit (Phys. Rev. **46**, 948 (1934)) have found from B. Edlén's measurements (Z. Physik **84**, 746 (1933)) the value $E^* \sim 4$ v.e. $= 92$ Cal., instead of the former value $E^* \sim 1.6$ v.e. $= 37$ Cal. (Heitler, W., and Herzberg, G.: Z. Physik **53**, 52 (1929)).

Equation 1 must therefore be written

$$154 \pm 10 \text{ Cal.} = 2E_{CC} - 92 \text{ Cal.}$$

Consequently

$$E_{CC} = 123 \pm 5 \text{ Cal.}$$

and not 70 to 80 Cal. as is generally accepted.

The usual value $E_{CC} \sim 75$ Cal. would give, according to equation 1, $S_C \sim 60$ Cal., which is very improbable since, for example, the heat of sublimation of copper is 70 Cal.

A cycle starting from C_2N_2 ($\frac{1}{2}\, C_2N_2 \rightarrow CN - 38$ Cal. (Kistiakowsky, G. B., and Gershinowitz, H.: J. Chem. Physics **1**, 432 (1933); Mooney, R. B., and Reid, H. G.: Proc. Roy. Soc. Edinburgh **52**, 152 (1932)), with the new value of E^* and with the exact value of $D_{N_2} = 169.47 \pm 0.11$ Cal. recently obtained by G. Büttenbender and G. Herzberg (Ann. Physik **21**, 577 (1935)) ($D_{N_2} \sim 208$ Cal. was the value used formerly for thermochemical calculations), gives for the dissociation energy of CN:

$$CN(X^2\Sigma) \rightarrow C(^3P) + N(^4S) - 165 \pm 3 \text{ Cal. } [7.2 \text{ v.e.}] \qquad (2)$$

or

$$CN(X^2\Sigma) \rightarrow C(^5S) + N(^4S) - 257 \pm 3 \text{ Cal.} \qquad (3)$$

The value $D_{CN} = 7.2$ v.e. corresponding to equation 2, which gives a carbon atom in the ^3P state, is in good agreement with $D_{CN} = 7.09$ v.e. obtained by R. S. Mulliken (Rev. Modern Physics **4**, 1 (1932)) from spectroscopical data on the lower $X^2\Sigma$ state of CN.

It is clear that the new values of E^*, D_{N_2}, and especially E_{CC} lead to important consequences for many problems of molecular structure and chemical calculations (cf. Norrish, R. G. W.: Free Radicals. General Discussion of the Faraday Society September, 1933, p. 103).

W. Lasareff.

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March 28, 1935.

NEW BOOKS

Neuere massanalytische Methoden. By E. BRENNECKE, K. FAJANS, N. H. FURMAN, AND R. LANG. 25 x 16 cm.; xi + 211 pp., with 15 diagrams. Stuttgart: Ferdinand Enke, 1935. Price: unbound, 18.00 RM; bound, 19.80 RM.

This work is divided into six sections: Section I, dealing principally with a standardized method of determining indicator corrections in acid-alkali titrations; Section II, giving full details of the use of ceric sulfate in volumetric analysis; Section III, describing titrations by means of standard iodate or bromate solutions, as developed chiefly by Andrews, Lang, Berg and Manchot and Oberhauser; Section IV, setting out the advantages of chromous salts as standard reducing agents, and giving full details of the necessary indicator electrode and of many useful applications; Section V, a discussion of the principles and uses of oxidation-reduction indicators; Section VI, an account of the theory and practice of the use of adsorption indicators.

The names of the collaborators are a sufficient guarantee that the treatment of the sections associated with their work is authoritative; and in the last section, particularly, much useful and, in some cases, hitherto unpublished information is discussed in a concise and clear manner.

The references testify to a careful search of the literature. The inclusion of an author from the U. S. A. may be partly responsible for an impartial treatment of the literature from that country, but British chemists, too, receive justice in this respect, although some of them suffer from incorrectly spelt names and one of them is given a wrong initial. Apart from this there are very few typographical errors.

The work can confidently be recommended as being a comprehensive and careful survey of the vast mass of recent material which falls within its purview. Its price, however, as with so many new German books, is high even in terms of currencies on a gold standard, and is almost prohibitive in terms of depreciated pounds and dollars. This is unfortunate, for the book merits a wide circulation, particularly because it shows that there is a fruitful field in which analysts and physical chemists can coöperate with mutual advantage.

A. D. MITCHELL.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 26 x 17 cm. Berlin: Verlag Chemie, 1934. (1) System Nummer 35: Aluminium. Teil B, Lieferung 2; pp. xvi + 309—13. Price: 49 RM. (2) System Nummer 4: Stickstoff. Lieferung 1; pp. v + 292. Price: 43 RM. *Subscription price:* 38 RM.

(1) The section on aluminium deals with the silicates and double silicates, and contains a long and interesting section on ultramarine, in which the recent literature is very fully covered. The alums and the aluminates are also included. The text is fully illustrated by phase rule diagrams and the results of physical and physicochemical methods are considered in detail. This section of the work is of special interest from the point of view of physical chemistry and constitutes an invaluable source of information on many subjects of considerable technical interest.

(2) The volume on nitrogen deals with the general chemistry of the element, including natural ammonia fixation and nitrification, with the physical and physico-

chemical properties of nitrogen (a very full account of the spectra being included), and with active nitrogen. The account of the technical production of nitrogen includes patent literature. There is a good discussion of the atomic weight of nitrogen in which analyses of a large number of researches are set out in a very clear and instructive form. This first section of the volumes on nitrogen is very complete and of high standard, and covers a very extensive field of literature.

J. R. Partington.

Free Radicals. A general discussion held by the Faraday Society. 25 x 15.5 cm.; 2 + 248 pp. London: Gurney and Jackson, 1934. Price: bound, limp cloth, 12/6.

Once more the Faraday Society has placed physical chemists under a debt of gratitude. The reports of the discussions which they organize at frequent intervals are now well-known and highly appreciated, alike by those who are, and those who would be, up-to-date in their knowledge of the latest developments. By bringing together distinguished workers in a special field, hearing and answering questions, they not merely present the subject but present it alive.

This volume is most timely and will be most welcome. It indicates how much preparatory work has already been achieved—work on the existence and preparation of free radicals—and these results are discussed by the men who have attained them. It also shows how the application of exact physiochemical methods to the available material may now be expected to lead to important conclusions.

The first part (12 papers) deals with free radicals of relatively long life; the second with those of short life, and this is subdivided into chemical aspects (A) general and inorganic (5 papers), B, hydrocarbons (7 papers). The third part deals with the physical aspects of radicals of short life (5 papers).

Part I opens with an account of prevalent carbon radicals, followed by a short paper by Schönberg on a new class of radicals having a free sulfur bond. Sugden gives an account of magnetism in free radicals due to an odd number of electrons. Sulfur monoxide and oxygen are discussed; theoretical papers are contributed by Hückel, Lennard Jones, and Ingold; electronic levels are dealt with by Snow and Allsopp and the C=C double bond is specially considered.

Part II opens with an account by Norrish of the photochemical production of free radicals, followed by a theoretical paper by Franck and Rabinowitsch. Part IIB contains important contributions by Bone, Rice, Paneth, Hartel, Polanyi, and others.

Part III has an introductory paper by Mecke on free radicals and spectroscopy, and an account of the positive ray method of investigating the decomposition of hexane by Conrad (with some excellent photographs). There are papers by Harkins and by Willey on free radicals produced in the electric discharge, and one by Semenoff on the transference of energy in collisions.

Taken together, the papers and discussions give an admirable idea of the state of knowledge and opinion on a subject which has only recently begun to attract much attention; they are very suggestive of developments in the near future. Much light is being thrown on the problems of molecular stability and molecular change.

E. B. Ludlam.

Gasentladungstabellen. Tabellen, Formeln und Kurven zur Physik und Technik der Elektronen und Ionen. By M. Knoll, F. Ollendorff, and R. Rompe (with the collaboration of A. Roggendorf). 25 x 17 cm.; x + 171 pp. Berlin: Springer, 1935. Price: 29RM (in cloth).

The authors have attempted to give in this volume, in as convenient a form as possible, all the data likely to be required by workers with the discharge of ions and electrons through gases at moderate down to very low pressures. These are by no means the least coy or elusive of the more out-of-the-way data of physics, and their tracing down, even in relatively simple special cases, taxes or overtaxes the resources even of a large library. In many sections of the subject, sufficiently precise and extended numerical data were practically nonexistent a few years ago, and all workers—even those favored ones who have enjoyed the help of a more experienced hand in the same laboratory—must have felt acutely the need for tables of the kind now under review.

The book therefore undoubtedly fills a serious gap in the literature. The completeness of the filling can only properly be judged after prolonged use of the book in the laboratory. The less stringent test of a fairly close inspection reveals no serious omissions or errors in the work, which contains not only a comprehensive summary of the relevant properties of atoms, molecules, electrons, ions, and photons, but also the equivalent of "workshop hints" on the materials in common use in discharge tubes, and on high vacuum technique, together with a useful collection of mathematical formulæ and tables.

Some minor criticisms may be offered, mainly on matters of form; for instance, the unjustifiable piling up of unsignificant figures on some of the data, and the habit of referring the more inquisitive reader to the *Handbuch der Physik* or similar works, and not to the original papers. These points do not however affect the general utility of the book.

The price is somewhat high, especially in sterling, but the book, with its elaborate tables and large number of specially drawn curves, cannot have been a cheap one to produce.

H. R. Robinson.

Röntgenoskopie und Elektronoskopie von dispersen Systemen, Faden, Filmen, und Grenzschichten. Sonderheft der Kolloid-Zeitschrift, Bd. 69, H. 3. Edited by Wo. Ostwald (12 contributors). 27 x 19.5 cm.; 138 pp. Dresden and Leipzig: Steinkopff, 1935. Price: 9 RM (stiff paper cover).

This volume presents the contributions of Ostwald, Schiebold, Brill, Fricke, Halle, Astbury, Hofmann, Saupe, Wever, Rupp, Trillat, and Brüche to the General Meeting of the Kolloid-Gesellschaft in Hanover in September, 1934. It provides a useful and authoritative general sketch for those wishing to acquire some familiarity with these comparatively new applications of x-ray and electron optics, with some hundreds of references to original papers which will be invaluable to those whose interests are more specialized.

H. R. Robinson.

Dizionario di Chimica generale e industriale. Volume II. F-Z. By Michele Giua and Clara Giua Lollini. 29 x 20 cm.; iii, 71 + 1137 pp. Turin: Unione Tipografico-Editrice Torinese, 1934. Price: 175 lire.

This second, and final, volume of the Dictionary of Chemistry, containing 54 more pages of text than the first volume, covers the headings F–Z. Thus it is evident that, even when allowance has been made for the difference in the Italian alphabet, the matter in this volume has been more condensed than in the previous one. The second volume contains 23 full page plates and 521 illustrations in the text, as against 28, and 565, respectively, in the first. In addition, the second volume includes 71 pages of comprehensive index to the whole, 2 pages of corrections, and a list of journals with their quoted abbreviated titles.

The dictionary is comprehensive, dealing not only with pure chemistry, but also its application and connection with agriculture, biology, medicine, geology, etc.; it includes also biography. The biographies number altogether some 722 (living chemists have not been included); in many cases these are very brief, e.g., only 4 lines are devoted to Volta and rather more to Faraday, although fairly full references are appended to each from which fuller information may be sought. Further, in the case of the former, more information is found in the text under such headings as galvanic pile, electrochemistry, methane, and eudiometry, the cross references to which are not quoted in the biography. Among the biographies one notices names like Marsh, Kipp, and Selmi, but the absence of others, e.g., Hooke, Mayow, Watson, Hales, Rayleigh, and LeChatelier.

A special feature has been made of phase rule diagrams, especially in the case of metals; this is to be expected as the authors had previously published a book on chemical combination among metals, which was translated into English by Robinson in 1918. Branches of chemistry especially important to Italy are detailed with much valuable information, e.g., vegetable and essential oils, mercury and its medicinal preparations, marbles etc.

The high standard of production of the previous volume has been fully maintained in the present one, and the whole constitutes a mine of interesting and accurate information.

W. H. PATTERSON.

Arsenical and Argentiferous Copper. By J. L. GREGG, with a foreword by H. Foster Bain. American Chemical Society Monograph. 189 pp. New York: The Chemical Catalog Co., Inc., 1934. Price: $4.00.

This monograph was prepared at the Battelle Memorial Institute under the sponsorship of the Calumet and Hecla Consolidated Copper Co. The author has made a thorough survey of the existing literature on the properties of arsenic- and silver-bearing copper and copper alloys, and in this monograph gives a detailed and critical discussion of the literature. He has not been satisfied with simply quoting the literature; he discusses it at length and attempts to explain the discrepancies and to bring out the correct facts and figures. In this he was considerably aided by use of hitherto unpublished data of research work done at Battelle and at the laboratories of the Calumet and Hecla company.

Not only has the author made an admirable review and summary of the literature, but he has added to it valuable new material. It is unfortunate that some of the curves have been reduced too much in printing, making it rather difficult to read them correctly. The reviewer is in agreement with the foreword that "The monograph constitutes one of the most authentic and complete, as it is certainly the most up-to-date, of compendiums on the properties and uses of the metals. Nowhere else will so much modern knowledge of this ancient metal be found in so few pages."

S. SKROWRONSKI.

Étude thermodynamique de la tension superficielle. By RAYMOND DEFAY. xi + 372 pp. Paris: Gauthier-Villars & Cie., 1934.

This book offers a detailed study of the thermodynamic treatment of capillary phenomena and of adsorption, applied not only to systems in equilibrium but also to irreversible transformations. Reaction velocity, catalysis, and velocity of adsorption are included in the topics treated by the author. The thermodynamic methods of Th. de Donder furnish a basis for much of the discussion.

This book can be commended to the attention of all serious students of the matters treated by the author.

F. H. MACDOUGALL.

The Aliphatic Free Radicals. By F. O. and K. K. Rice, with a foreword by F. A. Paneth. 204 pp. Baltimore: The Johns Hopkins Press, 1935. Price: $4.50.

Professor Rice and his wife have presented in this volume a problem for solution in the field of reaction mechanism which is of fundamental importance not only in the theoretical realm but also in many fields of industrial activity. That problem is the determination of the extent to which the path from an initial to a final state in a number of processes involving organic chemical molecules and their decompositions occurs through a series of steps involving the production of free radicals followed by a radical chain or chains. The authors show that, prior to Gomberg's isolation of free radicals in 1900, the quadrivalence of carbon was the practical basis of organic chemistry in the preceding period. It was, however, not the Gomberg work but the *development of the photochemistry of atom reactions involving hydrogen, chlorine,* bromine, etc., which in the interval from 1912 to 1925 laid the foundations for the examination of the rôle of organic radicals in reaction mechanism. Paneth and Hofeditz, in 1929, by demonstrating the existence of free methyl in the decomposition of metal methyls by heat at low pressures, carried the problem into the field of thermal reactions. Since 1929, the mental attitude of those interested has undergone a great change from frank derision, through scepticism to reluctant admission of the possibility of radical participation in organic mechanisms. Professor Rice and his associates are largely responsible for this change by their continued insistence on the supporting evidence and finally, with Herzfeld, by the demonstration that reactions kinetically simple as to reaction order can actually have a chain mechanism.

This book will be of great assistance in the research work which will be done in the next few years to provide a decisive answer, affirmative or negative, to the issue raised. It details methods of preparation and identification of free radicals, aliphatic in nature. It sets forth their properties, their lifetimes, their stabilities. A further chapter deals with bond energies and the effect of substitution and structure on bond strengths. It formulates the problem that must be solved,—that of the activation energies of reactions involving free radicals. At first sight such a problem may seem hopeless, but one can take courage from the progress that has been made with the corresponding atom reactions. There follow half a dozen chapters dealing with the various types of organic molecules that may give rise to free radicals by bond breakage, and a formulation and discussion in each case of hypothetical free radical mechanisms. A final chapter deals with the evidence for such mechanisms in organic liquid systems. The whole subject of radicals in reaction mechanism has been gathering momentum in recent years. Professor and Mrs. Rice have provided us with an excellent résumé of our knowledge as it now exists and a challenge to our judgment in these matters for the future.

Hugh S. Taylor.

Schwebstoffe in Gasen. Aerosole. By A. Winkel and G. Jander. 25 x 16 cm. 116 pp. Sammlung chemischer und chemisch-technischer Vorträge. Stuttgart: Ferdinand Enke, 1934. Price: 7.50 RM.

This monograph appears in the well known *Sammlung chemischer und chemisch-technischer Vorträge,* and deals with suspensions of fine particles of fog (mist or cloud), dust, and smoke in air or other gases. The subject is fairly well treated, both from a scientific and practical standpoint, and the book will be of value to colloid chemists, physicists, meteorologists, and military tacticians. The authors are familiar with the notable work of R. Whytlaw-Gray and his collaborators in this field, and devote a considerable amount of space to it. It is a pity, however, that they do not appear to know of the pioneer books of W. E. Gibbs (*Clouds and Smokes,* Churchill, London, 1924; and *The Dust Hazard in Industry,* Ernest Benn, London, (1925). These two books, together with the present one and the book by R. Whytlaw-Gray and H. S. Patterson (*Smoke, a Study of Aerial Disperse Systems*, Edward Arnold, London, 1932), give a comprehensive account of practically all aspects of the subject.

There is an interesting chapter in the present book on the electrical properties of aerosols—a subject of importance to aircraft pilots and meteorologists. The authors refer to the pioneer investigations of J. J. Thomson on the formation and stability of electrically charged droplets and of droplets whose surface tension is a function of the radius. These are both important subjects. It could not be expected that the authors would be familiar with that famous (or infamous) n-component system, the "London particular," i.e., the yellow smoky fog that used to occur so frequently in the winter months. This "meteoric" monster has now, however, practically vanished, owing to the increasing use of gas and electrical energy for heating and cooking, and of central heating systems employing oil or coke.

The reviewer can recommend the following simple lecture experiment on the electrical coagulation of an aerosol. Take an old-fashioned bell jar (one fitted with a tubulure and cork at the top). Stick a metal wire well through the cork, and connect it with the secondary of an induction coil. Lift the bell jar from its glass plate, burn a piece of magnesium wire under it, replace it on the plate, and start the coil. In a few seconds the magnesium oxide aerosol will come down as a beautiful "snow" storm (*verb. sap.*).

Although the specialist may detect certain *lacunae* in the book of Winkel and Jander, the authors have succeeded in compressing a great deal of highly interesting material into 111 pages, and their book may be recommended to a wide circle of readers.

F. G. Donnan.

From Galileo to Cosmic Rays. By Harvey Brace Lemon. 450 pp. Chicago: University of Chicago Press, 1934. Price: $5.00 (including stereoscope).

The title of this work might lead one to suppose it to be another popular treatment of certain aspects of modern physics addressed to the adult reading public. While the author states that he had the latter somewhat in mind, it is essentially a pandemic textbook of elementary physics designed for the undergraduates in the "Chicago System." The writer's statement in the preface that the need has been felt of such a text under one cover in preference to allowing the student to browse among selected passages from miscellaneous sources is interesting.

Since visual instruction is the watchword of the newer educational methods, the author has spared no trouble not only in illustrating the principles under discussion, but in providing marginal pen sketches on almost every page intended to enliven the subject and to catch and hold the reader's interest.

It is perhaps a matter for a psychologist to predict, or of experience to show, whether the desired end is to be attained in this way; whether, for example, comprehension of the principles of the components of force will be facilitated if accompanied by a sketch of a canal boat with all details including not only the mule and driver but the family laundry being dried en route; whether an Alaskan dog team, an Alpine climber, an East Indian student (or is it merely the proverbial wet towel) are all essential on one page to illustrate *work*. Will the imagination be stimulated by that which leaves nothing to the imagination? Or is the imagination which is so dull as to need stimulation worth the effort and expense?

The usual principles of physics are set forth, mainly following classical methods except in the matter of illustrations which undeniably are artistic and attractive. Although neutrons and positrons are described, one is surprised to find deuterium and deuterons neglected.

Those who are interested in a pandemic presentation of the principles of physics will find this work of undoubted value. It is not intended for a more serious or fundamental approach to the subject.

S. C. LIND.

The Science of Rubber. Handbuch der Kautschukwissenschaft. By K. MEMMLER, translated by R. F. Dunbrook and V. N. Morris. 770 pp. New York: Reinhold Publishing Corporation, 1934. Price: $15.00.

The editor has been assisted in the preparation of this treatise by seven collaborators, who join him in writing the various chapters into which the book is divided. The editors of the English edition have been assisted by a group of ten translators, all members of the Research Staff of the Firestone Rubber Company.

The author wisely chose to ignore plant practice in the fabrication of rubber products and the factory technology of rubber, so as to devote his efforts exclusively to the science of rubber production, treatment, and testing. In carrying out this object, he has given a thorough presentation of the botany, cultivation, collection, and properties of rubber, the treatment of the latex to convert it to crude rubber, the chemistry of rubber and its derivatives, including artificial rubber, the theory of vulcanization, the analytical methods of testing, the physics of rubber, and the physical methods of testing.

The work is replete with statistics, scientific data, and descriptions of methods which are of great value to all of those interested in any aspect of rubber production or treatment. The theories of the structure of rubber, of its polymerization, of vulcanization, of rubber as a disbursing medium, are all of great interest to the physical chemists as well as to organic chemists and chemical engineers. In fact any scientist not already familiar with the science and properties of rubber is sure to find new ideas extending into many different fields of physics and physical chemistry.

In preparing this translation for the English reading public, a valuable service has been rendered in a very acceptable manner. The translators have made such additions and corrections in the way of footnotes as were necessary to make the work clear and to bring it up to date. They have checked the literature references and added an unusually well arranged and classified bibliography covering the entire subject. The work appears indispensable to all those interested in any of the scientific phases of rubber.

S. C. LIND.

Physical Chemistry. By A. J. MEE. 14 x 22 cm.; xix + 780 pp. London: William Heinemann, Ltd., 1934. Price: 15s.

"This book," the author states, "sets out to give an up-to-date outline of the results and methods of Physical Chemistry. . . . The book is suitable for students who are preparing for the Higher School Certificate and Intermediate Science Examinations of the various Universities, for University Scholarships, and for University degrees up to Pass standard." In achieving the end which he had in view, the author has been very successful. In the book under review, we have a well-written and clear discussion of a wide range of topics, "all the topics usually dealt with under the heading of Physical Chemistry," as the author assures us, including photochemistry and the methods used in determining the structure of the simpler molecules; and any student who masters this work will have a knowledge of physical chemistry which should carry him well beyond the standard for a Pass degree. Mr. Mee has given, on the whole, a remarkably clear and comprehensive survey of the whole range of physical chemistry, and he has taken pains to keep the mathematical treatment and the explanation of physical concepts as simple as is consistent with an exact treatment of the subject. Sometimes, it is true, one feels that rather too great a comprehensiveness has been attempted and that the book may too easily lead to "cramming" on the part of the student. Useful summaries are given at the end of each chapter, together with a list of books and memoirs for further reading and a large number of questions and problems by which the student can test his mastery of the subject. The book is a readable and trustworthy introduction to physical chemistry and should serve very well the purpose for which it was written.

ALEX. FINDLAY.

The Nitrogen System of Compounds. By EDWARD CURTIS FRANKLIN. American Chemical Society Monograph No. 68. 23 x 15 cm.; 339 pp.; 26 figs.; 12 tables. New York: Reinhold Publishing Corp., 1935. Price: $7.50.

Nitrogen is unique among the elements in the multiplicity of types of chemical combinations into which it enters and in the diverse reactions which it exhibits. Nitrogen compounds have long been the object of many excellent and painstaking researches, and numerous volumes have been written on the subject of nitrogen chemistry. Yet withal no single point of view has been set forth so far which is sufficiently broad and simple to realize a systematic classification of their reactions. The simplest and most powerful tool which has been proposed for the accomplishment of the above ends is that of the "nitrogen" system of compounds formulated by E. C. Franklin and developed by him and his students. The present monograph embraces the life-long work of Professor Franklin and summarizes a unique American development of chemical thought.

Professor Franklin states that "the object of this monograph is to outline what we have chosen to call the nitrogen system of compounds and to bring to the attention of chemists the remarkable extent to which the compounds of nitrogen simulate in their properties and behavior the analogous compounds of oxygen." This purpose is kept paramount throughout the work. So also are the general objectives set for the A. C. S. monograph series.

The essential idea of the "nitrogen" system (more frequently referred to as the "ammonia" system) is a simple one. Granting the dominating rôle played by oxygen in a majority of the more familiar types of chemical compounds (a relationship clearly expressed by Laviosier), the contention is that nitrogen similarly conditions the behavior of an equally large number of compounds. We are less familiar with the latter because of the natural abundance of water on this planet and of the chemist's long enslavement to the use of water as a solvent and reaction medium. Impressed by the marked similarity between the physical and chemical properties of liquid ammonia and water, Franklin early sought to show that this resemblance extends to the derivatives of these two substances. In this manner he established two systems of compounds, an oxygen (or water) system and a nitrogen (or ammonia) system, and showed experimentally that the corresponding members of both systems possessed similar physical properties and took part in essentially the same kind of chemical reactions. For the sake of clarity and emphasis, Franklin found it necessary to devise a nomenclature which would portray the behavior of nitrogen in the reactions of its compounds as the existent nomenclature so well portrayed the similar behavior of oxygen in the reactions of its compounds. Hence the use of the terms ammonation, deammonation, nitridation, ammonolysis, ammolytic, etc.

With no thought of describing the behavior of the various representatives of the nitrogen system, it is well to note that one finds ammonates, ammono acids, bases and salts, acid anammonides, basic nitrides, ammonobasic salts, and salts of amphoteric amides whose chemical behavior closely parallels that of the oxygen compounds of the corresponding type. Further there are many substances which belong at the same time to the nitrogen and oxygen systems, the nitrogen and sulfur systems, etc. A unique and significant contribution of the concept of a nitrogen system of compounds is the classification and correlation which it provides for the so-called mercuriammonia compounds. The same concept is of tremendous value among organic compounds in its systematization of the chemistry of such a wide variety of materials as the amines (ammono alcohols and ethers), aldimines (ammono aldehyde-alcohols), ketimines (ammono ketone-alcohols), and hydramides (ammono aldehyde-acetals), Schiff's bases (ammono aldehyde-ethers and ammono ketone-ethers), amidines (ammono carboxylic acids), nitriles (carboxylic acid anammonides), isocyanides (esters of ammonocarbonous acid), cyanamide and guanidine (ammonocarbonic acids), nitrosoamines and diazo compounds (derivatives of ammono- or aquo-ammononitrous acids), and the nitrogen heterocycles such as pyridine (cyclic ammono aldehyde-ether). It might be argued that any concept based on analogy carries with it certain elements of weakness. Yet when this argument is applied to the concept of systems of compounds it loses much of its significance because the extreme fruitfulness of the concept is sufficient evidence of its strength.

As a presentation of exciting knowledge in its field, the book is remarkably complete and contains considerable material not otherwise readily available. There can be no question that this book will greatly stimulate research in the field of nitrogen chemistry. Already the chemical literature gives ample evidence of the influence of Franklin's ideas. Not only are investigators following his lead in interpreting reactions of nitrogen compounds according to the nitrogen system, but they are also proposing other systems of compounds to correlate behavior for substances other than those containing ammonia nitrogen.

There seems to be only one factor which is likely to hinder the great usefulness of this monograph—the price asked for it prevents many students from realizing their desire to own it.

A very desirable feature of the book is the appendix on the experimental manipulation of liquid ammonia solutions. It is to be hoped that we may soon have available a compilation of existing data relative to liquid ammonia solutions to supplement Professor Franklin's monograph on the nitrogen system.

W. CONARD FERNELIUS.

Colloidal Electrolytes. A general discussion held by the Faraday Society. 16 x 25 cm.: 421 pp. London: Gurney and Jackson, 1935. Price: 18s. 6d.

The volume contains thirty-six main contributions to the subject, originating from twenty different universities and research institutes distributed throughout ten European countries and the United States, and a considerable amount of critical discussion in which other schools of research are represented. Such variety and number has naturally necessitated a very wide meaning being attached to the title. In consequence this, the largest of the Faraday discussion volumes yet published, will probably be less easily comprehensible as a whole to individual workers in the field than its forerunners. It should all the more prove extremely useful to them, since at least half the matter in it will be immediately relevant to any one interested, and the remainder may prove more relevant than might at first appear. The book will therefore be a stimulus as well as a work of reference to recent progress.

The subject is divided broadly into a general part and a special and technical part. The former comes mainly under the heading of theory, but includes also a short section on experimental methods. The latter is divided into five headings: (a) soaps and other long-chain electrolytes, (b) dyes, (c) silicates, (d) proteins, and (e) other substances. In the theoretical section thermodynamic and electrical properties are discussed from the points of view of electrolyte and surface theory, and under the special headings biological and industrial applications, as well as the special properties of the substances concerned, are described. The absence of any general summary of the work of McBain and collaborators, who contribute, however, two special papers, will disappoint those interested in soap-like substances, but on the whole the book is very well balanced and the society and its editor are certainly to be congratulated on their achievement.

The binding in boards is an improvement on the old paper covers but is still insufficiently strong for a book which should find so much use.

G. S. Hartley.

Reports on Progress in Physics. Published by the Physical Society. 25 x 18 cm.; iv + 371 pp. Cambridge: Cambridge University Press, 1934. Price: 12s. 6d. net to non-fellows.

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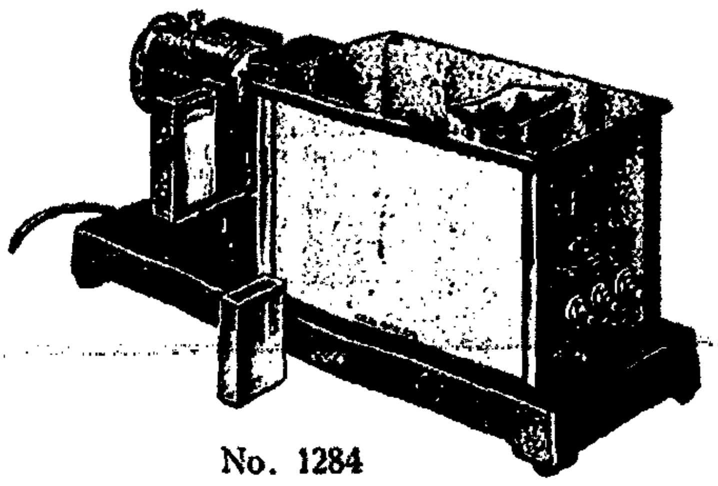

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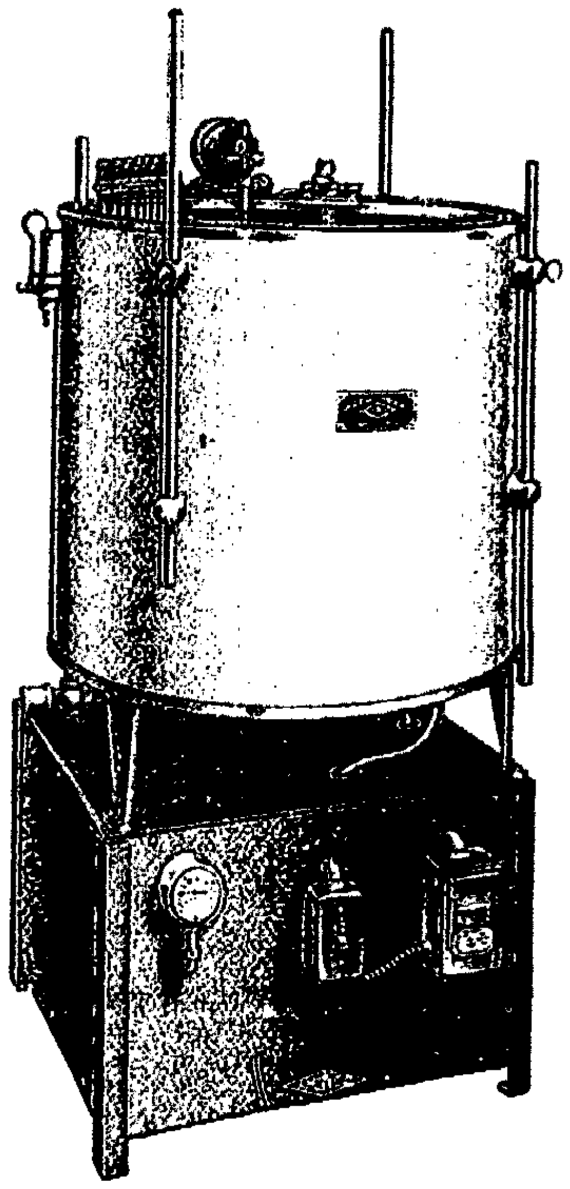

FACTORS INFLUENCING ELECTROPHORETIC MOBILITIES AND APPARENT CRITICAL POTENTIALS

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Various observers have reported that electrophoretic mobility is increased above the water value by the addition of uni-univalent salts. Powis (16) found the mobility of oil droplets to increase with added potassium chloride up to 2.5×10^{-3} *M* and then to fall off. He also found (17), according to his table 1, that clouding of an oil emulsion after two days begins in 5×10^{-3} *M* potassium chloride, where the zeta potential is 52 mv. or electrophoretic velocity is 3.7μ per second per volt per centimeter, the zeta potential in water being 46 mv. With barium chloride, clouding after two days begins in 5×10^{-4} *M*, with a zeta potential of about 37 mv.; with aluminum chloride in 1×10^{-5} *M* with a zeta potential of 38 mv.; and with thorium chloride between 5×10^{-6} and 1×10^{-5} *M* with a zeta potential between 40 and 7 mv. However, Powis rather arbitrarily takes a break in the clouding–concentration curve as the criterion of the critical condition, this occurring in all cases at a higher concentration than that required to initiate clouding. At these critical concentrations so defined, the zeta potential is about the same with all the salts investigated, that is, close to 30 mv., which is taken as the critical potential.

Powis (18), working with arsenic trisulfide sol, took the conditions obtaining in 5×10^{-4} *M* barium chloride as critical. Here coagulation is rapid and the zeta potential is 26 mv. The same degree of coagulation was first obtained in aluminum chloride at 5×10^{-5} *M* with a zeta potential of 25 mv. and in 7×10^{-6} *M* thorium nitrate with a zeta potential of 26 mv. The zeta potential with the "pure" colloid was not determined, but he concludes that it would be less than 100 and probably less than 60 mv. With potassium chloride, however, the critical concentration was 4×10^{-2} *M* and the zeta potential 44 mv. Powis ascribes the higher critical potential in potassium chloride to a salting-out effect due to the higher concentration required with univalent salts, i.e., the sol would still have been stable at a zeta potential of 44 mv., but for the salting-out effect.

Kruyt and van der Willigen (9), working with arsenic trisulfide, selenium, and mercuric sulfide sols, do not carry the mobility–concentration curves quite out to the flocking concentrations, but it is evident that with all the sols mobility at flocking concentration of uni-univalent salts is greater than for salts with bivalent cations. With the former salts the mobility usually increases continuously almost up to the flocking concentration. They conclude that electrophoretic mobility is not a true measure of zeta. They ascribe the increasing mobility with increasing concentration of univalent salts up to nearly the flocking concentration and the fact that mobility at flocking concentration is higher with univalent than with multivalent cations to (1) variations in dielectric constant produced by the relatively high univalent salt concentration required for flocking (3 to 8 × 10^{-2} M) and to (2) the probable incorrectness of the assumption that the mean distance between the electrical double layers equals the distance from the wall at which fluid velocity becomes constant. As to the first of these points, considerable difference of opinion exists regarding the effect of added electrolytes on the dielectric constant of water; the effect postulated by Kruyt may exist but cannot at present be evaluated quantitatively (10). As to the second point, Koenig (6) has pointed out that this assumption is not essential to the derivation of the electrokinetic equations. The above results were obtained with an ultramicroscopic method. Kruyt and Tendeloo (8) also find the mobility of lyophilic sols increased on addition of electrolytes, using a moving boundary method. However, in a later paper Bungenberg de Jong, Kruyt, and Lens (2) question the earlier results, showing increased mobility in presence of electrolytes, and state that unpublished results of Kruyt and de Haan with a microscopic method show no such increase, the implication of this last paper apparently being that electrophoretic determinations properly carried out are a true index of zeta.

Pennycuick (14) found the mobility of platinum sols to increase slightly in low sodium chloride concentrations and then to fall off slowly, being at the coagulating concentration about 80 per cent as great as in water. The critical mobility, i.e., that at the coagulating concentration, was about the same for barium chloride, barium hydroxide, and hydrochloric acid and was about half as great as the critical mobility in sodium chloride; the critical concentrations for barium chloride were much lower than for sodium chloride, the latter being about 3 × 10^{-3} M.[1]

Similar results with various sols have been reported by Ivanitzkaja and Proskurvin (5),[2] by Briggs (1), and by various other workers. Freundlich and Zeh (3), however, find only a decrease of mobility of arsenic trisulfide

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[1] The concentration figures of figure 2 of this paper are apparently all too low by tenfold, evidently a typographical error; compare Pennycuick (Z. physik. Chem. 148, 419, 424 (1930)).

[2] The results in their very dilute solutions, as with 1 × 10^{-11} M potassium chloride added, can hardly be of any significance.

sol on adding potassium chloride or other univalent salts; they used the moving boundary method. Rabinowitsch and Fodimann (19) find that addition of potassium chloride decreases mobility of arsenic trisulfide sols if the acid content of the sol is low and increases it if the acid content is high; their results seem surprising in that after adding 7 × 10^{-4} *M* hydrochloric acid, additional 2 × 10^{-5} *M* potassium chloride exerts a significant effect.

Various explanations for the increasing electrophoretic mobility on addition of uni-univalent electrolytes have been proposed. Powis (18) believes that it is due to an actual increase in zeta, effected presumably by an increase in the charge density by adsorption of added anions. The later fall in mobility in the higher concentrations would then be ascribed to a lessened diffuseness of the positive layer with a resultant lowering of zeta. That the higher critical mobility with univalent inorganic salts is dependent on the high concentrations required for coagulation is shown by the results of Briggs (1) with highly adsorbed univalent organic cations. With these coagulation is produced in low concentrations, and the critical mobility is that common to all polyvalent cations. With the monovalent inorganic potassium cation Briggs agrees with other workers in finding an initial increase in mobility which may be back to normal in 5 × 10^{-3} *M*. Briggs accepts the view of Kruyt and van der Willigen (7) that the maintained or increasing mobility in relatively concentrated uni-univalent inorganic electrolyte solutions is due to an increase in dielectric constant rather than in zeta. Rabinowitsch and Fodimann could not consistently verify Freundlich and Zeh's prediction, which was based upon a concept developed by Hevesy (4) that if the original zeta potential is greater than 70 mv., addition of electrolytes will lower it to 70, while if the original value is less than 70, electrolytes will raise it to 70. Rabinowitsch and Fodimann's explanation of the salt effect appears to be self-contradictory. They first say that the chief factor lowering zeta is the replacement of hydrogen ions in the electrical layer by potassium ions; this occurs in their non-acidified sols with a resultant lowering of mobility. This replacement is inhibited by an increased acidity of the medium, and therefore with an acidified sol the addition of potassium chloride does not lower the zeta potential or mobility. In the next paragraph, however, to explain the actual increase in mobility often seen in acidified sols on addition of potassium chloride, they assume that potassium ions form a more diffuse layer than hydrogen ions with a resultant increase in zeta.

Pennycuick (14, 15) assumes that the strong affinity of the platinum surface for hydroxyl groups causes a hydrolytic cleavage of the salt, the basic cleavage product then reacting at the surface to form new ionogenic spots. It is difficult to accept this explanation, however, since the addition of a neutral salt to water does not increase the hydroxide-ion activity.

In any case Pennycuick makes no attempt to explain the finding that the critical mobility with bases and neutral monovalent salts is higher than with salts of polyvalent cations.

In a previous publication (White, Monaghan, and Urban (22)) it was shown that in water and dilute solutions the ratio of electrosmotic velocity on a plane Pyrex surface to electrophoretic velocity of Pyrex particles 1 to 3μ in diameter was always greater than unity. The ratio decreased as the concentration of added salt increased, becoming unity at a concentration between 10^{-3} and 10^{-2} M potassium chloride and at all higher concentrations. Although values for the absolute magnitude of electrokinetic velocity were not obtained at that time, it was pointed out that the discrepancy in the ratio was undoubtedly to be ascribed to retardation of the particles in dilute solutions. Several factors were assumed to be responsible for this retardation. Two of these, the decrease of (1) double layer thickness and (2) charge density, with decreasing particle radius, retard the particle by lowering the zeta potential. This effect is present whether or not an external voltage is applied; it will therefore contribute to the instability of the particle. A third factor, the distortion of the electric field by the particle, is of doubtful significance in the case of the conducting particles of metallic sols. The fourth factor, however, the polarization of the diffuse double layer by the external field, which was considered most important in causing deviation of the ratio from unity, applies to all particles in dilute solutions. Zeta, calculated from electrophoretic velocity, will therefore be considerably lower than the electrosmotic zeta, lower also than the true zeta of the particle. Furthermore, it will appear to go through a maximum on the addition of salt when no maximum exists in the electrosmotic or true zeta-concentration curves.

The bearing of these findings on the problem of critical potentials of lyophobic sols is obvious. Those salts which coagulate at low concentrations will appear to have a lower critical potential (measured by electrophoresis) than the monovalent salts and bases which require much higher concentrations to precipitate. This apparently lower critical potential is, however, an artifact inherent in the electrophoretic method.

It is difficult to obtain electrosmotic measurements on surfaces identical with the colloidal sols used in coagulation studies. On the other hand, both electrosmotic and electrophoretic data may easily be obtained on glass and protein-coated glass surfaces. The present paper is concerned with the absolute magnitude of electrosmotic and electrophoretic velocities on glass and protein-coated surfaces as a function of electrolyte concentration.

EXPERIMENTAL

Both electrophoretic and electrosmotic velocities were obtained by observing microscopically the movement of particles at stated levels in a

Pyrex electrophoresis cell of the type described by Mattson (11). It follows from the formula expressing electrosmotic flow of the liquid at different levels in a cylindrical cell (Mattson (12)) that true electrophoretic velocity in such a cell is the observed velocity of the particles at 0.147 of the diameter from the wall. True electrosmotic velocity is the velocity of the water immediately adjacent to the wall, or (with reverse sign) that of the water in the center of the cell. It may be obtained by subtracting algebraically the true electrophoretic velocity from the observed velocity of the particles either at the wall or in the center of the tube. Both methods were used in the present experiments and gave good agreement.

TABLE 1

Potassium chloride–Pyrex at 37°C.

CONCENTRATION OF KCl	µ/SEC. TOP	µ/SEC. MIDDLE	V_p = µ/SEC. AT 0.147	V_w µ/SEC. ($V_p + V_{top}$)	V_w µ/SEC. ($V_{middle} - V_p$)	V_w µ/SEC. AVERAGE	$\frac{V_p}{V./\text{cm.}}$	$\frac{-V_w}{V./\text{cm.}}$	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar											
H_2O	−44.6	+78.8	+15.9	60.5	62.9	61.7	3.49	13.6	35	134	3.8
10^{-5}	−41.7	+73.3	+15.5	57.2	57.8	57.5	3.41	12.6	34	124	3.7
10^{-4}	−29.8	+66.7	+18.6	48.4	48.1	48.3	4.09	10.6	40	105	2.6
10^{-3}	−13.7	+59.9	+22.7	36.4	37.2	36.8	4.99	8.09	49	80	1.6
10^{-2}	0	+46.1	+23.5	23.5	22.6	23.0	5.16	5.05	51	50	0.98

TABLE 2

Potassium chloride–Pyrex

CONCENTRATION OF KCl	AT 25°C.					AT 32°C.				
	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*µ/sec./v./cm.*	*µ/sec./v./cm.*				*µ/sec./v./cm.*	*µ/sec./v./cm.*			
H_2O	3.49	11.8	38	130	3.4	3.65	11.2	46	141	3.1
1×10^{-5}	3.14	9.59	35	105	3.0	3.45	10.8	43	136	3.2
1×10^{-4}	3.54	9.12	39	100	2.6	3.54	9.74	45	123	2.7
5×10^{-4}	4.04	8.15	44	90	2.0	4.26	8.33	54	105	1.9
1×10^{-3}	4.39	7.10	47	78	1.7	4.62	7.61	59	96	1.6
1×10^{-2}	4.77	3.89	52	43	0.83	4.13	4.13	52	52	1.0
1×10^{-1}						2.24	2.24	28	28	1.0

Table 1 contains the results of a typical experiment showing the effect of varying concentrations of potassium chloride on the electrophoretic mobility of Pyrex particles and the electrosmotic velocity at a Pyrex surface. Glass-distilled water with a conductivity of 1 to 1.5 × 10^{-6} mhos was used throughout. The particles were obtained by pulverizing Pyrex tubing in a porcelain mortar. A fairly uniform stock suspension of particles about 1µ in diameter was obtained by fractional sedimentation. The

TABLE 3

Hydrochloric acid-Pyrex at 30°C.

CONCENTRATION OF HCl	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec./v./cm.*	*μ/sec./v./cm.*			
H_2O	2.64	10.1	26	101	3.9
10^{-5}	3.34	12.1	33	121	3.7
10^{-4}	3.63	6.02	36	60	1.7
10^{-3}	3.58	4.11	36	41	1.1
10^{-2}	2.31	2.20	23	22	0.96

TABLE 4

Potassium ferrocyanide-Pyrex at 27°C.

CONCENTRATION OF $K_4Fe(CN)_6$	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec./v./cm.*	*μ/sec./v./cm.*			
H_2O	2.97	10.1	36	121	3.4
10^{-6}	3.01	7.50	36	90	2.5
10^{-5}	3.43	7.30	41	88	2.1
10^{-4}	4.33	6.68	52	80	1.5
10^{-3}	4.68	4.68	56	56	1.0

TABLE 5

Sodium hydroxide-Pyrex at 25°C.

CONCENTRATION OF NaOH	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec./v./cm.*	*μ/sec./v./cm.*			
H_2O	2.44	8.18	31	103	3.3
10^{-5}	3.01	9.30	38	117	3.1
10^{-4}	3.56	12.3	45	155	3.4
10^{-3}	4.44	10.3	56	130	2.3
10^{-2}	5.95	6.83	75	86	1.1

TABLE 6

Potassium sulfate-Pyrex at 25°C.

CONCENTRATION OF K_2SO_4	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
molar	*μ/sec./v./cm.*	*μ/sec./v./cm.*			
H_2O	3.38	9.80	43	123	2.9
10^{-5}	3.58	9.43	45	119	2.6
10^{-4}	4.46	8.48	56	107	1.9
10^{-3}	5.45	7.00	69	88	1.3
10^{-2}	3.12	2.84	39	36	0.92

cell was allowed to stand in chromic acid cleaning solution between experiments. The voltage across the cell was 116 volts, giving a field strength of 4.55 volts per centimeter. V_p represents true electrophoretic velocity; V_w the true electrosmotic velocity. The sign refers to the electrode toward which the particles were observed to move at the levels indicated. The zeta values were calculated from the well-known formula:

$$\zeta = \frac{4\pi V\eta}{ED}$$

where V = velocity, η = viscosity, E = field strength, and D = dielectric constant. The room temperature at which the experiments were performed is given for each experiment.

TABLE 7

Potassium chloride-gelatin at 38°C.

CELL	CONCENTRATION OF KCl	V_p	V_w	APPARENT ζ_p	ζ_w	$\frac{\zeta_w}{\zeta_p}$
	molar	*μ/sec./v./cm.*	*μ/sec./v./cm.*			
Flat cell	H_2O	1.94	3.34	19	32	1.7
	10^{-5}	2.07	3.64	20	32	1.6
	10^{-4}	1.90	2.78	18	25	1.4
	10^{-3}	1.75	1.84	17	19	1.1
	10^{-2}	0.94	0.98	9.1	9.5	1.04
Cylindrical cell	H_2O	1.58	3.54	15	34	2.3
	10^{-5}	1.69	3.43	16	33	2.1
	10^{-4}	1.80	3.38	18	33	1.8
	10^{-3}	1.56	2.22	15	22	1.5
	10^{-2}	1.01	1.01	9.8	9.8	1.0

In tables 2 to 7 only the velocities and the calculated zeta values are given. Table 2 contains the results of two additional experiments on potassium chloride. Some variations in velocity at a given concentration, especially in water and the more dilute solutions, are perhaps to be expected, considering the great effect which small amounts of contaminating substances may exert on the surface potential of glass. Tables 3 to 6 show the effect of various other electrolytes on glass.

Table 7 gives the results of two experiments on gelatin-coated glass surfaces in varying concentrations of potassium chloride. Each solution contained $\frac{1}{10}$ g. per liter of gelatin, a concentration sufficient to coat the glass completely with a protein film. No attempt was made to regulate the pH. The first set of readings was obtained with a flat electrophoresis cell of the Northrop-Kunitz type. The field strength was determined in each solution from measurements of the current and the conductivity of the solution. The experiment was then repeated, using the cylindrical Mattson cell. Since the gelatin itself contained a considerable amount of electrolyte (the specific conductivity of the gelatin solution in distilled water was 5.4 × 10^{-6} mhos, corresponding roughly to that of a 2 × 10^{-5} *M* potassium chloride solution) the addition of small amounts of potassium chloride had little effect on either electrophoretic or electrosmotic velocities.

DISCUSSION

It will be seen from the tables that, with the exception of sodium hydroxide, all the electrolytes investigated, including the tetravalent $Fe(CN)_6$ anion, reduce the electrosmotic velocity at the glass-water interface. Similar results were obtained by Powis (16) with electrosmosis and by Kruyt and van der Willigen (9), using the stream potential method on glass capillaries. *In spite of the fact that zeta is decreasing, the electrophoretic* velocity increases continuously up to concentrations of about *M*/100 for the uni-univalent electrolytes. Since the main factor (polarization of the double layer by the impressed field) discussed in our previous paper (22), which is responsible for the retardation of the electrophoretic mobility of glass particles, applies equally well to all particles in dilute solutions, it may be inferred that the metallic sols studied by Pennycuick, Briggs, Kruyt, and others have a higher potential in dilute solutions than that calculated from their electrophoretic mobility. The true zeta potential can be measured by the electrophoretic method only in relatively concentrated solutions, about *M*/100 or more. When large concentrations of electrolyte are required for precipitation, as is the case with inorganic uni-univalent salts and bases, the electrophoretically measured critical potential probably represents approximately the true zeta potential of the particle at the coagulation point. This is not the case, however, for the acids and polyvalent cations which precipitate in concentrations so small that polarization of the double layer may occur; here the electrophoretically measured critical potential is lower than the true zeta potential of the particle at that concentration.

The explanation of Powis (18) for the higher critical mobility (which he considers as evidence for higher critical potential) with inorganic uni-univalent salts than with multivalent salts is that of a salting-out effect which lowers the stability of the particles without lowering zeta. It seems improbable to us, however, that such a low concentration as 5 × 10^{-3} *M* potassium chloride could exert any significant effect of this type. The same statement applies, as pointed out by Weiser (21), to Kruyt's postulated changes in dielectric constant. The changes in dielectric constant with added potassium chloride are about 2 to 3 per cent as the salt concentration is increased from 0 to *M*/100 (Pechold (13); Walden and Werner (20)), whereas the variations in electrophoretic mobility are of the order of

50 per cent. It is, of course, possible to postulate greater deviations in the dielectric constant within the double layer itself, but such assumptions cannot be investigated experimentally. The point to be emphasized in the present paper is that no such assumptions are necessary to account for the facts that electrophoretic mobility (1) increases with increasing salt concentration, and (2) is lower at the critical concentration of the salts of polyvalent cations than it is at the much greater critical concentration of potassium chloride; an adequate explanation is to be found in the retardation of electrophoretic mobility in dilute solutions, which has here been experimentally demonstrated.

SUMMARY

The electrophoretic mobility of small glass particles is found to be much less than the electrosmotic mobility at a glass surface in dilute electrolyte solutions, whereas the mobilities are identical in solutions of concentration $M/100$; the same holds for gelatin surfaces. This is believed to be due to a retardation of the particles in dilute solutions, chiefly because of the polarization of the double layer by the applied field. On this basis the increase in electrophoretic mobility (with increasing concentrations of neutral univalent salts) while electrosmotic mobility is decreasing is explained. Also, the apparently lower critical potential obtained with electrolytes which coagulate in low concentrations as compared with those which require higher concentrations is considered to be an artifact, due to the impossibility of calculating the zeta potential from electrophoretic mobility in dilute solutions. It is thus concluded that the mobilities of particles in critical concentrations of polyvalent salts are abnormally low, rather than, as has usually been assumed, that the critical potentials with inorganic monovalent salts are abnormally high. According to this concept the critical mobility in inorganic monovalent salt solutions is a true measure, while the true zeta potential in the critical concentrations of polyvalent salts is higher than that indicated by mobility and may be the same as that with inorganic monovalent salts. The often reported finding that the apparent zeta, as measured by electrophoresis, is higher in the critically flocking concentration of uni-univalent salts than it is in lower concentrations or in water, where the sol is stable, is given an explanation.

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A COMPARISON OF THE ELECTROKINETIC POTENTIALS AT FUSED AND UNFUSED GLASS SURFACES

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It has recently been shown (White, Monaghan, and Urban (6)) that the electrophoretic mobility of microscopic Pyrex particles is much less in dilute solutions than electrosmotic mobility in Pyrex cells. Since, however, the particles (prepared by pulverizing Pyrex tubing in a mortar) had broken surfaces, while the surface of the cell was fused Pyrex, the possibility remained that the observed discrepancies in electrophoretic and electrosmotic mobilities were due to differences in the adsorptive properties of fused and unfused surfaces rather than to differences in the phenomenon of electrophoresis as compared with electrosmosis. The object of the present paper is (1) to prepare fused Pyrex spheres 3μ or less in diameter and (2) to compare the electrophoretic mobility of such spheres with (a) the electrophoretic mobility of broken Pyrex particles and (b) electrosmotic mobility at fused Pyrex surfaces.

A method for the preparation of microscopic glass spheres has been described by Sklarew (4). A simpler and much less bulky apparatus for the preparation of small quantities of fused powder was designed with the help of J. H. Zimmer.[1]

The apparatus consists of a glass chamber, A, which holds the powder. A stirrer shaft, B, bearing a stirrer, C, which is beneath the powder, and wings, D, which agitate the air above the powder, is driven by an air turbine, E. The fine mist of glass powder is carried up through the alundum heating tube, F, and settles in the glass collecting chamber, G, which is covered loosely enough to allow escape of the air. The upward velocity of the particles depends upon the height of the heating tube, the extent to which it is heated, and the size of the air inlet, H. The collecting chamber is supported by a rod, I. A narrow section of the alundum tube is heated to white heat with an oxygen flame, the tube being heated and cooled gradually in order to prevent cracking. When the air intake is so adjusted that the particles move upward with a slow and uniform velocity, all of the particles up to 10μ in diameter are fused in passing through the heated

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[1] Departmental mechanic.

portion of the tube and on microscopic examination are seen to be perfect spheres.

Both electrophoretic and electrosmotic measurements were carried out in a Pyrex electrophoresis cell of the type described by Mattson (1). In such cylindrical cells the water is at rest at a depth of 0.147 diameter from the wall (Mattson (2)); consequently the observed velocity of the particles at this depth is true electrophoretic velocity. Electrosmotic velocity of the water in the cell may be obtained by subtracting electrophoretic velocity from the observed velocity of the particles at the center of the cell. Both particles and cell were previously cleaned in chromic acid cleaning solution, the acid being removed by repeated washings in distilled water. The electrokinetic potential, ζ, was calculated from the well-known formula:

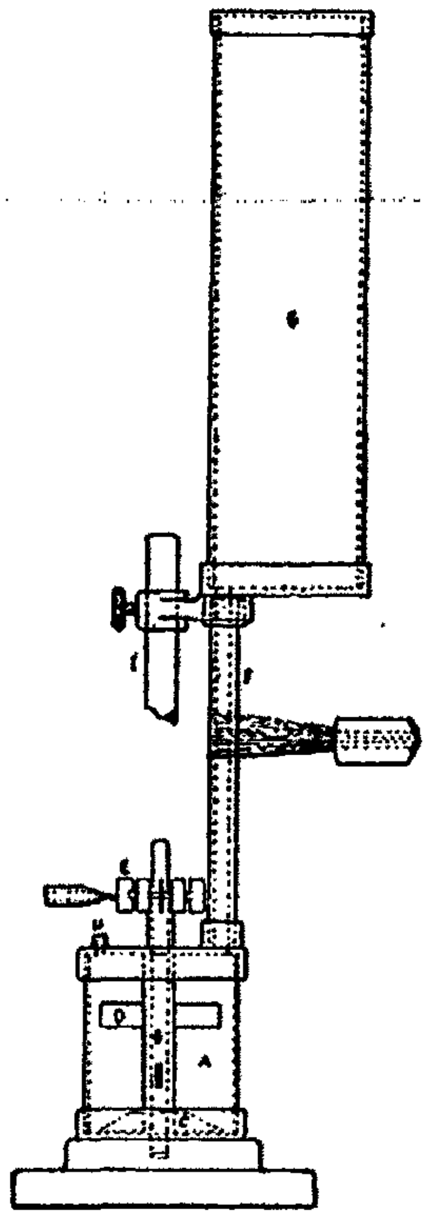

FIG. 1. APPARATUS FOR PREPARATION OF MICROSCOPIC GLASS SPHERES (× $\frac{1}{4}$)

$$\zeta = \frac{4\pi V\eta}{ED}$$

where V represents either electrosmotic or electrophoretic velocity, η the viscosity of the medium, E the applied field strength, and D the dielectric constant of the medium.

As a further check, electrosmotic experiments were also carried out on several Pyrex capillaries by the method described by Quincke (3). This consists in the measurement of the head of pressure developed by electrosmosis in a capillary of known radius under an applied E.M.F. A diagram of the apparatus is shown in figure 2. The Pyrex capillary, C, is connected by transparent rubber tubing to the open reservoir, R, and the closed vessel, V. Platinum discs, P, are sealed into the two arms of the apparatus close to the rubber connections so that practically all of the potential drop is across the capillary. Platinization of the electrodes permitted large currents to be used.[2] A larger capillary, the climbing tube T (about 1 mm. in diameter), is connected with the closed arm of the apparatus with rubber tubing. When a voltage is applied across the capillary C, the meniscus rises or falls in the climbing tube T according to the direction of the current. Since the cross section of T is very small with respect to that of R, the level of the liquid in R may be considered to be constant and the entire change in level takes place in T. The horizontal projection of the movement of the meniscus is measured by means of a microscope fitted with a calibrated scale in the eyepiece. The vertical height through which the liquid rises or falls for a given applied E.M.F. is the product of the tangent of the angle, a, which the climbing tube makes with the horizontal and the horizontal projection. The capillary C and the climbing tube T are thoroughly cleaned by heating in chromic acid before each determination. The electrokinetic potential is calculated from the formula:

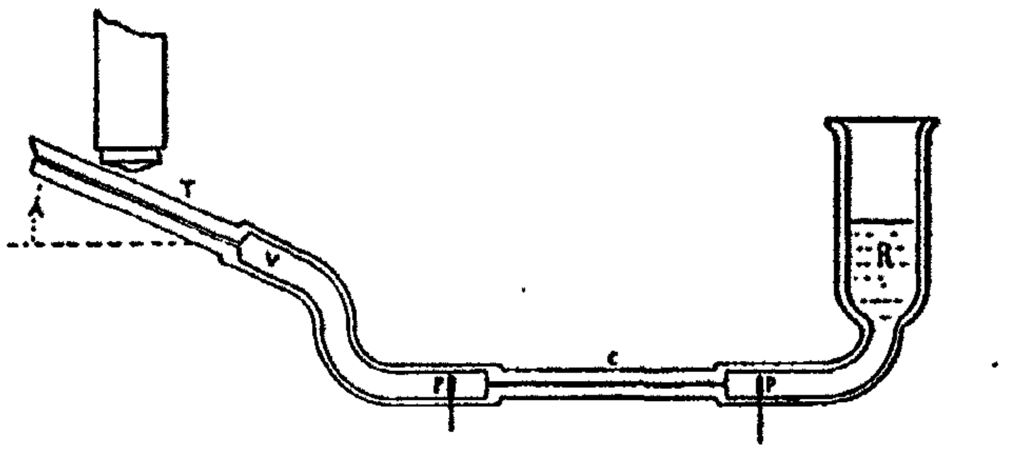

FIG. 2. APPARATUS FOR ELECTROSMOTIC MEASUREMENTS IN SINGLE GLASS CAPILLARIES

$$\zeta = \frac{P\pi r^2}{2HD}$$

where P is the pressure change, r the radius of the capillary C, H the total E.M.F. between electrodes, and D the dielectric constant.

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[2] In all experiments 350 volts were applied to the cell. This was conveniently supplied by a constant voltage "power pack," the output D.C. voltage showing fluctuations not greater than 0.01 volt. We are indebted to Dr. H. B. Peugnet of this department for the loan of this apparatus.

The results of electrophoresis and electrosmosis experiments in the closed cell are given in tables 1 and 2. V_p and V_w represent the velocity of the particles and the liquid, respectively, for an applied field of 1 volt per centimeter. The results show that, within the limits of experimental error, the fused Pyrex spheres move with the same velocity as the broken particles, and that the velocity of all the particles is less than electrosmotic velocity in solutions less concentrated than $M/100$. As previously stated (White, Monaghan, and Urban (6)) the discrepancy between electro-

TABLE 1

Electrophoresis of unfused Pyrex particles and electrosmosis at a fused Pyrex surface at 24°C.

CONCENTRATION OF KCl	V_p	V_w	ζ_p	ζ_w	$R = \frac{\zeta_w}{\zeta_p}$
moles per liter					
H_2O	3.4	10.0	44	130	2.9
H_2O	3.3	9.7	43	126	3.0
10^{-4}	3.4	7.6	44	99	2.2
10^{-3}	4.0	5.6	52	73	1.4
10^{-2}	3.1	3.0	40	39	0.98

TABLE 2

Electrophoresis of Pyrex spheres and electrosmosis at a fused Pyrex surface at 24°C.

CONCENTRATION OF KCl	V_p	V_w	ζ_p	ζ_w	$R = \frac{\zeta_w}{\zeta_p}$
moles per liter					
H_2O	3.1	8.6	40	112	2.8
H_2O	2.9	8.7	38	113	3.0
10^{-4}	3.2	7.3	42	95	2.3
10^{-3}	3.7	5.1	48	66	1.4
10^{-2}	3.0	3.1	39	40	1.02

TABLE 3

Electrosmotic zeta potentials of Pyrex capillaries

Quincke method

CONCENTRATION OF KCl	ZETA POTENTIAL						
	Capillary radius = 2.68×10^{-2} cm.			Capillary radius = 1.60×10^{-2} cm.			Mean
moles per liter							
H_2O	102	109	114	103	112	123	111
10^{-4}	103	101	93	96	103	93	98
10^{-3}	92	78	85	86	80	80	83
10^{-2}	50			53	59	52	53

phoretic and electrosmotic velocities is believed to be due to a retardation of the particles because of several factors, chiefly the polarization of the diffuse double layer by the applied field.

Table 3 contains the electrokinetic potentials calculated from electrosmotic measurements by the Quincke method. Two capillaries of different radii were used. Three sets of determinations were made on each capillary, the determinations being made on different days with different samples of water. Each figure in the table represents the average of three determinations for each direction of current flow, these determinations agreeing among themselves within 10 per cent. It will be seen that the zeta potentials calculated from the Quincke method show satisfactory agreement with those obtained from electrosmosis in the closed cell, and are very much greater in dilute solutions than electrophoretic "zeta potentials." The rather wide discrepancy between the mean of the Quincke values in $M/100$ potassium chloride and the two values obtained for electrosmotic zetas in the closed cell is probably to be ascribed to experimental error rather than to any fundamental difference in the two methods. The means of several determinations of electrosmotic zetas in the closed cell reported elsewhere (White and Monaghan (5)) agree quite well with the values obtained here with the Quincke cell.

SUMMARY

1. A method is described for the preparation of microscopic glass spheres.

2. The electrophoretic velocity of Pyrex spheres is found to be the same as that of unfused Pyrex particles.

3. The electrophoretic velocity of Pyrex particles (fused or unfused) is much less in dilute solutions than electrosmotic velocity at a fused Pyrex surface, the latter being measured by two independent methods.

The work reported in this paper was aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

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JUNCTION POTENTIALS BETWEEN SOLUTIONS OF SUGARS AND POTASSIUM CHLORIDE

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The measurement of electrode potentials in sugar solutions has been frequently and advantageously employed by many workers to determine the pH of such solutions and to gain further insight into the oxidation-reduction behavior of the sugars. In making such measurements, potassium chloride salt bridges are almost universally used to connect the electrode in the sugar solution with the reference electrode,—a calomel half-cell, for instance.

Such procedure is not invariably safe. That is, if the sugar solution is too alkaline, or has been heated too much, or both, the solution may have present in it so high an ionic concentration that even a saturated potassium chloride salt bridge can not completely "smother out" the liquid junction potential. Urban and Shaffer have fully demonstrated that the junction potential between a saturated solution of potassium chloride and an even moderately alkaline solution of glucose is not a negligible quantity.

The purpose of this note is to present evidence that if the pH of the sugar solution does not greatly exceed 10, a saturated potassium chloride salt bridge may be relied upon to eliminate effectually all significant liquid junction potentials, no matter how concentrated the sugar solution may be. No attempt is made to explain the ionic mechanism involved in liquid junction potentials in general.

For the purposes of comparison, platinized platinum electrodes were immersed in two kinds of solutions, namely, normal hydrochloric acid and concentrated glucose. Both kinds of these solutions were connected to saturated calomel electrodes by potassium chloride salt bridges. Readings are given in table 1.

Columns 3 and 5 give the differences between the readings of the cells which included the stronger potassium chloride bridges and the reading of the cell with a 0.05 *N* bridge.

In the case of the solutions of *N* hydrochloric acid, there is seen to be a

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difference of 0.0167 volt between the readings of the cells with salt bridges of *N* and of 5 *N* potassium chloride. Such a difference may possibly be construed to mean that a greater concentration of potassium chloride than 5 *N*, if it could be prepared, would eliminate still more junction potential; namely, that even a saturated potassium chloride salt bridge fails appreciably to eliminate all the junction potential. Fales and Mudge, however, have expressed the belief that saturated potassium chloride bridges actually eliminate all but negligible junction potentials under these conditions.

In considering column 5 in table 1, it is seen that the junction potentials involved in even concentrated glucose solutions of pH as high as 10 are much less than those for *N* hydrochloric acid. The reading for the saturated bridge is but little different from that of a *N* potassium chloride bridge. Since a fivefold increase in the concentration of potassium chloride produces only a small difference in the over-all reading of the cell, it seems reasonable to suppose that even a *N* potassium chloride bridge eliminates most of the junction potential and that a saturated bridge eliminates practically all of it.

TABLE 1

Over-all readings, in volts, of the various cells at 30°C.

(1) NORMALITY OF KCl IN BRIDGE	APPROXIMATELY NORMAL HCl		SOLUTIONS OF 60 G. GLUCOSE IN 100 CC. BUFFER pH 10	
	(2) Readings	(3) Differences	(4) Readings	(5) Differences
0.05	0.3102	0	0.8527	0
0.10	0.3000	0.0102	0.8506	0.0021
0.50	0.2742	0.0360	0.8464	0.0063
1.00	0.2633	0.0469	0.8459	0.0068
5 (saturated)	0.2466	0.0636	0.8456	0.0071

Likewise we may assume that a solution of an infinite concentration of potassium chloride, if such were possible, could eliminate absolutely all such potential difference. In considering these data in the light of this assumption, we noticed that the values in column 5 fulfilled, within the limit of experimental error, the relationship demanded by the following equation:

$$Y = Y'10^{\frac{-K}{x-0.05}}$$

where Y = junction potential eliminated in excess of whatever is eliminated by a 0.05 *N* potassium chloride bridge. $Y = Y'$ when x, the concentration of potassium chloride, becomes infinitely large. K = a constant.

Since the above formula holds quite accurately throughout the range of all concentrations of potassium chloride that can be prepared, it is interesting to note that, according to this formula, the difference between the reading for a saturated bridge and the reading for a bridge of a concentration of potassium chloride of infinity is only 0.00016 volt. We therefore conclude that for the purposes for which most potential measurements are made on glucose solutions, the solution junction potential may be ignored when saturated potassium chloride salt bridges are used and the pH of the glucose solution does not greatly exceed 10, provided also that the sugar solution has not been heated or treated in any way that produces a large amount of ionized decomposition products.

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THE OXIDATION POTENTIAL OF THE SYSTEM POTASSIUM FERROCYANIDE-POTASSIUM FERRICYANIDE AT VARIOUS IONIC STRENGTHS[1]

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The oxidation potential of the ferrocyanide–ferricyanide system has been determined by a number of investigators (1, 3, 8, 9, 10, 11, 12, 13). After the introduction of the Debye-Hückel theory of strong electrolytes, this system becomes of special interest, since we are dealing here with highly unsymmetrical salts of high valence type. If potassium ferrocyanide and potassium ferricyanide behave like strong electrolytes, the oxidation potential should be greatly affected by a change of the ionic strength of the solution. In the first place, the purpose of this study was to determine the potential of the potassium ferrocyanide–potassium ferricyanide system at varying ionic strengths and to extrapolate the value to an ionic strength of zero; in other words, to determine the normal potential of the system. In addition, the potential of a very dilute ferro–ferricyanide solution was determined in the presence of different neutral salts at varying ionic strengths, in order to test the applicability of the Debye-Hückel equations.

At extremely small ionic strengths, the relation between the activity coefficient of an ion and the ionic strength of the solution is given by the expression:

$$-\log f = 0.5z^2\sqrt{\mu} \tag{1}$$

at 25°C. in water, in which z is the valence of the ion, and μ the ionic strength. The oxidation potential E of the system ferrocyanide–ferricyanide at 25°C. then is given by:

$$\begin{aligned} E &= \epsilon_0 + 0.0591 \log \frac{a_{\mathrm{Fe_{ic}}^{---}}}{a_{\mathrm{Fe_{oc}}^{----}}} \\ &= \epsilon_0 + 0.0591 \log \frac{c_{\mathrm{Fe_{ic}}^{---}}}{c_{\mathrm{Fe_{oc}}^{----}}} \cdot \frac{f_3}{f_4} \end{aligned} \tag{2}$$

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[1] From the experimental part of a thesis submitted by William J. Tomsicek to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

The normal potential ϵ_0 denotes the potential referred to the normal hydrogen electrode in a system in which the activity of the ferricyanide $a_{FeCy_6^{---}}$ is equal to that of ferrocyanide $a_{FeCy_6^{----}}$. $c_{FeCy_6^{---}}$ and $c_{FeCy_6^{----}}$ represent the corresponding concentrations, whereas f_3 and f_4 represent the activity coefficients of the ferricyanide and the ferrocyanide ions. If the limiting Debye-Hückel expression (equation 1) holds at extremely small ionic strengths and the system contains equimolecular amounts of potassium ferricyanide and potassium ferrocyanide, it is found from equations 1 and 2 that:

$$E = \epsilon_0 + 0.0591 \log \frac{f_3}{f_4} = \epsilon_0 + 0.0591 \times 3.5 \sqrt{\mu} \qquad (3)$$

Therefore if the limiting Debye-Hückel expression holds, the measured potential E should change by 0.2068 volt for one unit change in the square root of the ionic strength.

The practical work in this study involves the use of a cell with liquid junction, the ferro–ferricyanide half-cell being measured against the quinhydrone electrode in a mixture containing 0.01 of an equivalent of hydrochloric acid and 0.09 of an equivalent of potassium chloride per liter, the saturated potassium chloride–agar salt bridge being used for making electrolytic contact between the two half-cells. No correction has been applied for the liquid junction potential, which is very small in dilute solutions containing potassium ferrocyanide and potassium ferricyanide, but may be greater in the presence of larger amounts of neutral salts. The introduction of the liquid junction potential, however, does not invalidate the conclusions arrived at in this paper.

EXPERIMENTAL PART

Materials used

$K_4Fe(CN)_6 \cdot 3H_2O$. A C.P. product of potassium ferrocyanide was recrystallized twice from conductivity water and kept over deliquescent sodium bromide hydrate. An analysis of the salt showed that it had the theoretical composition.

$K_3Fe(CN)_6$: A C.P. product of potassium ferricyanide was recrystallized twice from conductivity water and dried over anhydrous calcium chloride.

The various salts used in this work had been analyzed by W. Bosch and had been used in a previous study (4). Conductivity water was used throughout this work.

Apparatus and method for the measurement of the potential

The potential of the ferro–ferricyanide system was measured in a Pyrex cell as shown in figure 1, a piece of bright platinum gauze serving as electrode. One terminal of the potassium chloride–agar salt bridge was placed in the side well b, thus preventing diffusion of potassium chloride from the bridge into the main body of the solution. Nitrogen gas from a tank was introduced through c. Oxygen gas was removed from the nitrogen by passing the gas through electrically heated copper gauze at 500°C. The solution in the standard reference half-cell (0.01 *N* hydrochloric acid, 0.09 *N* potassium chloride saturated with quinhydrone) was prepared fresh every day. The normal potential of the quinhydrone electrode is 0.6990 volt at 25°C. Assuming that the paH of the acid mixture in the quinhydrone half-cell is equal to 2.075[5], we find that the potential of the latter against the normal hydrogen electrode is equal to 0.5764 volt at 25°C.[2]

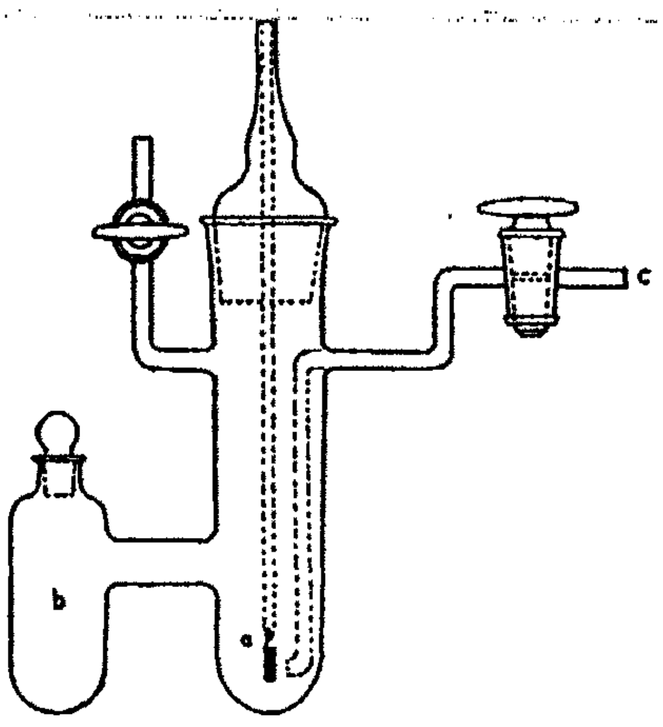

FIG. 1

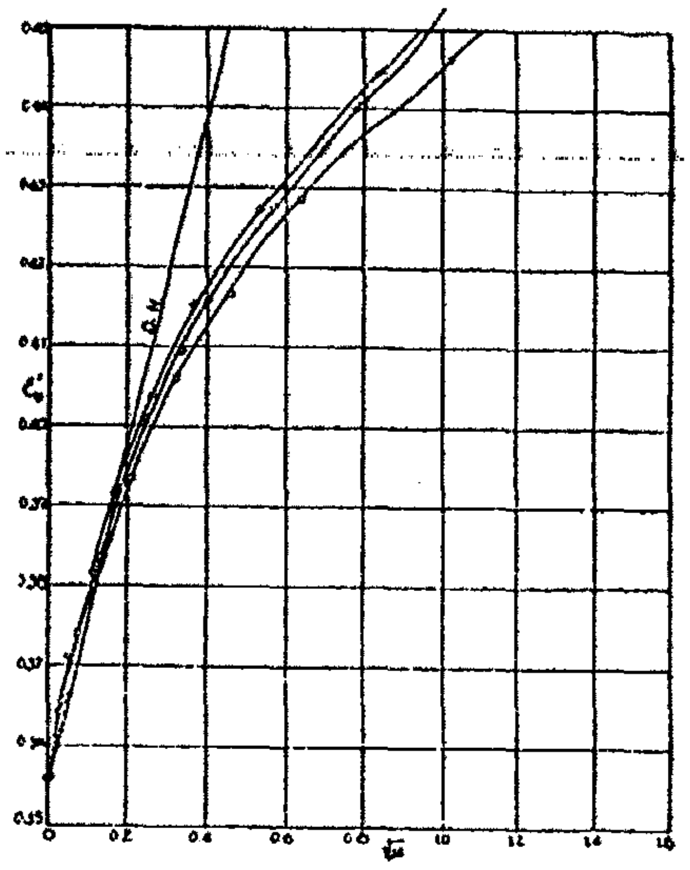

FIG. 2

FIG. 1. THE CELL

FIG. 2.

Ratio of $K_3Fe(CN)_6$ to $K_4Fe(CN)_6$: ○, ratio 1:1; △, ratio 10:1; □, ratio 1:10. D. H., calculated from simple Debye-Hückel expression.

All the measurements were made in a thermostat at 25°C. ± 0.05°. Various salt bridges were used, all yielding the same values. The measurements were made with a Leeds and Northrup student potentiometer. For the dilution experiments a stock solution containing 0.1 *M* potassium ferrocyanide and 0.1 *M* potassium ferricyanide was carefully prepared by weight from the pure salts. This stock solution was kept in the dark and

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[2] Recently Guggenheim and Schindler (J. Phys. Chem. 38, 533 (1934)) gave evidence that the paH of the standard acid mixture used in the quinhydrone electrode is equal to 2.10.

prepared fresh each day. The solutions from 0.1 to 0.004 molar were found to give the same potential in air as in a nitrogen atmosphere. The potential of the 0.004 molar solution in air referred to the normal hydrogen electrode was 0.4009 volt after 5 minutes and 0.4011 volt after 60 minutes. The same solution in a nitrogen atmosphere gave readings of 0.4011 and 0.4012 volts after 5 and 60 minutes respectively. More dilute solutions gave higher readings in air than in nitrogen. The potential of the 0.0004 molar solution was measured at least ten times during the course of the investigation. In a nitrogen atmosphere, the values found after 5 minutes remained unchanged for periods of twelve hours and more. The various readings agreed within ±0.0003 volt, the average being 0.3754 volt. The reproducibility of measurements with solutions from 0.0004 to 0.00006 molar was within 0.0005 volt. Each of the solutions was prepared fresh and measured at least four times.

TABLE 1

Oxidation potential of equimolecular mixtures of potassium ferrocyanide and potassium ferricyanide

M	μ	$\sqrt{\mu}$	E (AGAINST STANDARD QUINHYDRONE)	E (AGAINST NORMAL HYDROGEN ELECTRODE)
0.1*	1.6	1.265	0.1178	0.4586
0.04	0.64	0.8	0.1362	0.4402
0.02	0.32	0.5657	0.1490	0.4276
0.01	0.16	0.4	0.1610	0.4154
0.007	0.112	0.334	0.1670	0.4094
0.004	0.064	0.253	0.1753	0.4011
0.002	0.032	0.173	0.1856	0.3908
0.001	0.016	0.1265	0.1930	0.3834
0.0008	0.0128	0.1131	0.1950	0.3814
0.0004	0.0064	0.08	0.2010	0.3754
0.0002	0.0032	0.0566	0.2050	0.3714
0.0001	0.0016	0.04	0.2100	0.3664
0.00008	0.00128	0.0358	0.2112	0.3652
0.00006	0.00096	0.031	0.2122	0.3642
0.00004	0.00064	0.0253	0.2145	0.3619

* M = 0.1 designates that the concentrations of both potassium ferrocyanide and potassium ferricyanide are equal to 0.1 mole per liter.

Light was found to have a distinct effect on solutions whose concentrations were 0.0004 M or less, the E.M.F. tending to increase in light. All measurements were therefore made in a darkened room. Under these conditions, the potentials of even the most dilute mixtures remained constant for at least one hour.

Experimental results

Table 1 gives the average of the results of measurements with equimolecular mixtures of potassium ferrocyanide and potassium ferricyanide, μ representing the ionic strength. The value of ϵ_0 was found by plotting the measured values of E against $\sqrt{\mu}$ on large cross section paper and extrapolating to an ionic strength of zero. It was found to be equal to 0.3560 volt. The data are plotted in figure 2. The straight line represents the change of E, assuming that the limiting Debye-Hückel expression holds (equation 3).

TABLE 2

Oxidation potentials measured in a mixture containing $K_3Fe(CN)_6$ *and* $K_4Fe(CN)_6$ *in the ratio 10:1*

$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	TOTAL μ	$\sqrt{\mu}$	E (AGAINST STANDARD QUINHYDRONE)	E (AGAINST NORMAL HYDROGEN ELECTRODE)	ϵ_0' CALCULATED
M	*M*					
0.1	0.01	0.7	0.8366	0.0723	0.5041	0.4450
0.04	0.004	0.28	0.529	0.0898	0.4866	0.4275
0.02	0.002	0.14	0.3742	0.1020	0.4744	0.4153
0.01	0.001	0.07	0.2646	0.1130	0.4634	0.4043
0.004	0.0004	0.028	0.1673	0.1258	0.4506	0.3915
0.002	0.0002	0.014	0.1183	0.1337	0.4427	0.3836
0.001	0.001	0.007	0.0837	0.1398	0.4366	0.3775
0.004	0.00004	0.0028	0.0530	0.1462	0.4302	0.3711

TABLE 3

Oxidation potentials measured in a mixture containing $K_3Fe(CN)_6$ *and* $K_4Fe(CN)_6$ *in the ratio 1:10*

$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	TOTAL μ	$\sqrt{\mu}$	E (AGAINST STANDARD QUINHYDRONE)	E (AGAINST NORMAL HYDROGEN ELECTRODE)	ϵ_0' CALCULATED
M	*M*					
0.01	0.1	1.06	1.0295	0.1895	0.3869	0.4460
0.004	0.04	0.424	0.6511	0.2068	0.3696	0.4287
0.002	0.02	0.212	0.4604	0.2188	0.3576	0.4167
0.001	0.01	0.106	0.3256	0.2295	0.3469	0.4060
0.0004	0.004	0.0424	0.2083	0.2420	0.3344	0.3935
0.0002	0.002	0.0212	0.1456	0.2495	0.3269	0.3860
0.0001	0.001	0.0106	0.1029	0.2555	0.3209	0.3800
0.00004	0.0004	0.00424	0.0651	0.2615	0.3149	0.3740

In addition, the oxidation potentials were measured in mixtures containing ratios of potassium ferrocyanide and potassium ferricyanide of 10:1 and 1:10. The data are given in tables 2 and 3. They were recalcu-

TABLE 4

E.M.F. measurements in 0.0004 molar ferrocyanide-ferricyanide mixture in the presence of salts

SALT CONCENTRATION	TOTAL μ	SALT											
		KCl	NaCl	KNO_3	KBr	$NaC_2H_3O_2$	$NaNO_3$	$NaClO_4$	NH_4Cl	LiCl	$LiNO_3$	RbCl	CsCl
M													
0.5	0.5064	0.4581	0.4476	0.4560	0.4584		0.4482	0.4478	0.4588	0.4479	0.4482	0.4689	
0.25	0.2564	0.4422	0.4326	0.4416	0.4429		0.4334	0.4334	0.4428	0.4326	0.4324	0.4524	
0.10	0.1064	0.4244	0.4161	0.4242	0.4248	0.4154	0.4167	0.4164	0.4248	0.4161	0.4154	0.4334	
0.05	0.0564	0.4121	0.4054	0.4121	0.4124	0.4054	0.4059	0.4057	0.4123	0.4054	0.4046	0.4217	0.4324
0.025	0.0314	0.4014	0.3964	0.4014	0.4019	0.3957	0.3967	0.3964	0.4016	0.3964	0.3953	0.4079	0.4169
0.01	0.0164	0.3900	0.3872	0.3902	0.3906	0.3867	0.3874	0.3874	0.3902	0.3872	0.3869	0.3947	

TABLE 5

Influence of salts on the oxidation potential

CONCENTRATION OF SALT	TOTAL μ	SALT									
		K_2SO_4	Na_2SO_4	$Na_2C_2O_4$	$BaCl_2$	$Ba(NO_3)_2$	$SrCl_2$	$Ca(NO_3)_2$	$Mg(NO_3)_2$	Na_2CO_3	Na_2HPO_4
M											
0.1667	0.5064	0.4439	0.4354	0.4338	0.4717	0.4683	0.4684	0.4706	0.4762	0.4355	0.4354
0.0833	0.2564	0.4311	0.4231	0.4224	0.4588	0.4559	0.4557	0.4572	0.4614	0.4231	0.4231
0.0333	0.1064	0.4158	0.4090	0.4086	0.4444	0.4420	0.4414	0.4424	0.4454	0.4089	0.4090
0.0166	0.0564	0.4054	0.4000	0.3996	0.4342	0.4324	0.4314	0.4322	0.4347	0.4000	0.3998
0.00833	0.0314	0.3960	0.3920	0.3920	0.4237	0.4224	0.4209	0.4216	0.4237	0.3919	0.3920
0.00333	0.0164	0.3867	0.3844	0.3844	0.4009	0.4086	0.4076	0.4080	0.4094	0.3844	0.3844

lated on the basis of a ratio of the concentrations of 1:1 and correspond to the ϵ_0' values plotted in figure 2. These ϵ_0' values are identical with the values of the potential E measured in the equimolecular mixtures of ferrocyanide and ferricyanide. The reproducibility of the measurements in the very dilute solutions containing unequal molecular ratios of ferrocyanide and ferricyanide is not as good as of those reported in table 1; therefore, the extrapolated value of ϵ_0' at an ionic strength of zero is less reliable in the former cases.

The effect of neutral salts upon the potential

In all of the following determinations a solution containing 0.0004 molar potassium ferrocyanide and 0.0004 molar potassium ferricyanide, freshly prepared by dilution of a 0.01 molar mixture, was used. Ten ml. of the latter was diluted with conductivity water in a 250-ml. volumetric flask, a weighed amount of pure salt added, and the flask filled up to the mark. The results are given in tables 4, 5, and 6. "Total μ" refers to the sum of the ionic strengths of the added salt and of the 0.0004 molar ferrocyanide–ferricyanide mixture (μ = 0.0064). From equation 3 it is found that

$$\log \frac{f_3}{f_4} = \frac{E - \epsilon_0}{0.0591}$$

TABLE 6

Influence of salts on the oxidation potential

TOTAL μ	CONCENTRATION OF $Na_4P_2O_7$	E (AGAINST NORMAL HYDROGEN ELECTRODE)	CONCENTRATION OF Na_3 CITRATE	E (AGAINST NORMAL HYDROGEN ELECTRODE)	CONCENTRATION OF $MgSO_4$	E (AGAINST NORMAL HYDROGEN ELECTRODE)
	M		M		M	
0.5064	0.05	0.4187	0.0833	0.4262	0.125	0.4584
0.2564	0.025	0.4097	0.0416	0.4154	0.0625	0.4474
0.1064	0.01	0.3987	0.0166	0.4034	0.025	0.4344
0.0564	0.005	0.3918	0.0083	0.3953	0.0125	0.4246
0.0314	0.025	0.3864	0.00416	0.3889	0.00625	0.4152
0.0164	0.001	0.3809	0.00166	0.3826	0.0025	0.4028

The values of $\log f_3/f_4$ thus derived in various salt solutions are plotted in figure 3 against $\sqrt{\mu}$. The straight line again gives the values calculated with the assumption that the limiting Debye and Hückel expression holds at extreme dilutions.

DISCUSSION OF RESULTS

1. The generally accepted value of the normal potential of the ferro–ferricyanide electrode of 0.44 volt is much too high. At an ionic strength

of zero, a value of 0.356 volt was derived in this paper. From a practical viewpoint it is of interest to mention that the oxidation potential increases very rapidly with the increasing ionic strength and that it even can exceed the value of 0.44 in equimolecular mixtures of ferricyanide and ferrocyanide.

2. Even at infinite dilutions, the behavior of the system is not in harmony with the postulates of the simple Debye-Hückel expression. The slope of the curve giving the change of the oxidation potential or of log f_3/f_4 plotted against the square root of the ionic strength is greater than that calculated on the basis of the Debye-Hückel limiting equation. It is impossible to account for this anomaly on the basis of ionic size, using the present form of the Debye-Hückel theory, for, as V. K. La Mer (6) states, "absurd negative values of '*a*' would be demanded at very high dilutions followed by positive values in more concentrated solutions." Deviations of experimental data from the theoretically predicted curves have been described by various authors, a discussion of which is given in a paper by La Mer, Gronwall, and Greiff (7). Gronwall, La Mer, and Sandved (2) have shown that these discrepancies disappear if the influence of higher

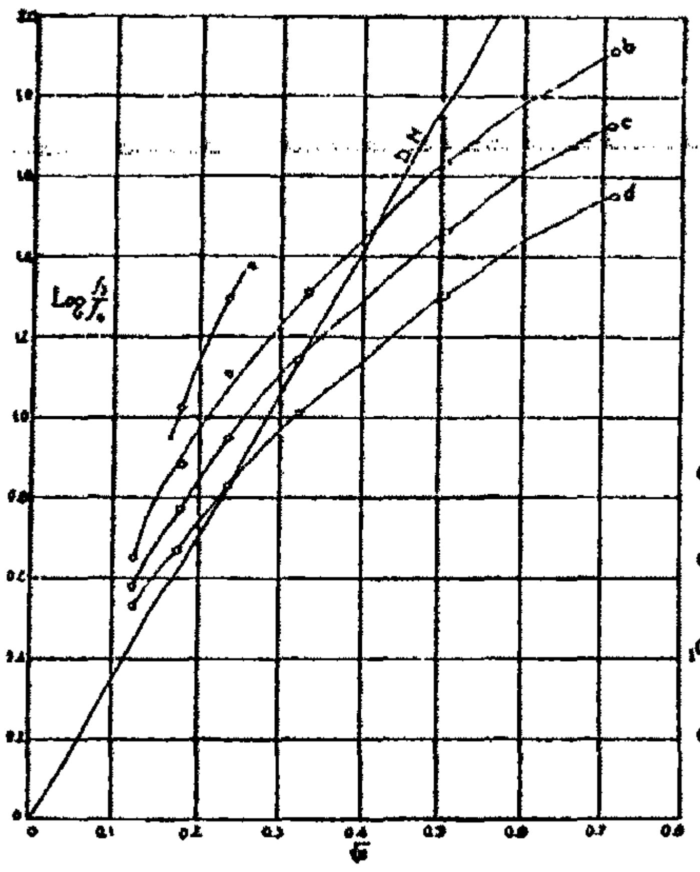

FIG. 3

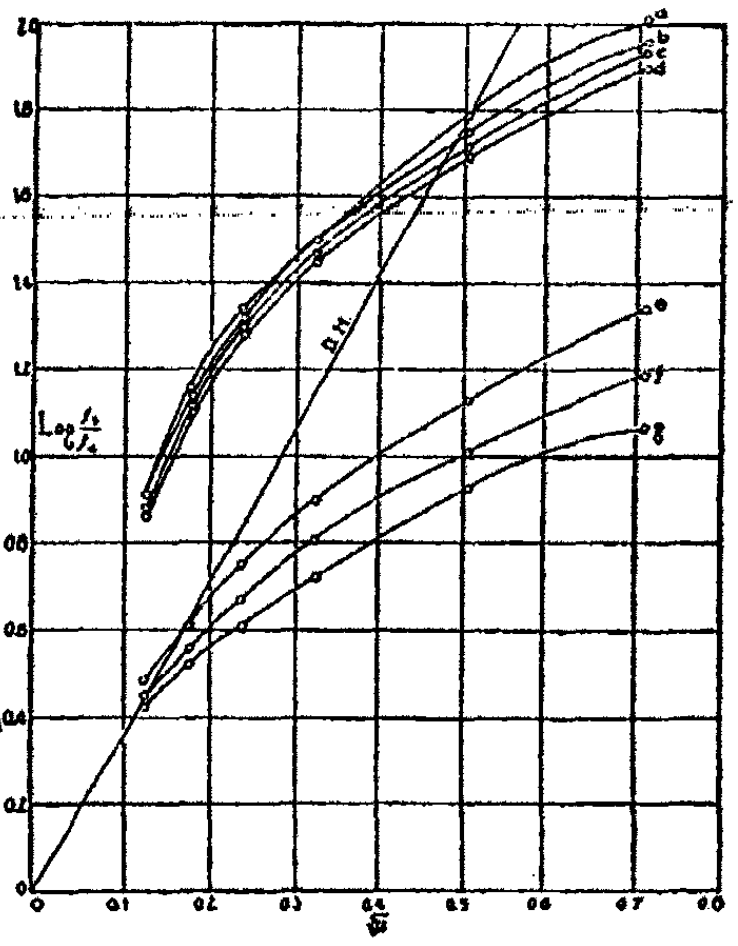

FIG. 4

FIG. 3.

a, CsCl; b, RbCl; c, KCl and NH_4Cl; d, LiCl. D. H., calculated from simple Debye-Hückel expression.

FIG. 4.

a, $Mg(NO_3)_2$; b, $BaCl_2$; c, $Ca(NO_3)_2$; d, $SrCl_2$; e, Na_2SO_4; f, Na_3 citrate; g, $Na_4P_2O_7$. D. H., calculated from simple Debye-Hückel expression.

terms of the Debye-Hückel theory in the case of unsymmetrical valence type electrolytes is taken into account. On the basis of the extended Debye-Hückel equation, values are found which fit the experimental data without assuming ion association or incomplete dissociation of the strong electrolytes. Undoubtedly, in a quantitative interpretation of the data found in this study, the extended equation of Gronwall, La Mer, and Sandved should be applied, since we are dealing with highly unsymmetric valence type electrolytes. Still, we have evidence to believe that even the extended equation does not account quantitatively for the results obtained, and that potassium ferrocyanide has to be considered as an incompletely dissociated electrolyte. In a subsequent paper, it will be shown that the curve obtained in a study of the potential of the potassium molybdo-molybdicyanide electrode, a system very similar to that of ferro-ferricyanide, does not intersect with the straight line calculated from the simple Debye-Hückel expression, but is found below this line even at extreme dilutions. In addition it was found that the fourth dissociation of molybdocyanic acid

$$HMo(CN)_8^{---} \rightarrow H^+ + Mo(CN)_8^{----}$$

is complete whereas that of ferrocyanic acid

$$HFe(CN)_6^{---} \rightleftarrows H^+ + Fe(CN)_6^{----}$$

is incomplete. This means that the proton combines with the ferrocyanide ion to form $HFe(CN)_6^{---}$, and it is quite plausible that other cations behave similarly. In the study of the influence of salts upon the potential of a very dilute potassium ferrocyanide-potassium ferricyanide mixture described in this paper it was found that the effect is virtually independent of the type of the anions. Potassium bromide, chloride, and nitrate have an identical effect at the same ionic strength; the same is true for sodium chloride, nitrate, and perchlorate on the one hand and sodium sulfate, oxalate, carbonate, and phosphate on the other.

The type of cation, however, has a very pronounced effect. With the alkali cations it decreased in the order Cs, Rb, K = NH_4, Na = Li, and we conclude that the degree of dissociation of the corresponding ferrocyanides decreased in the same order. The dissociation becomes more incomplete with the increasing valence of the cations, the effect of the various alkaline earths being of about the same order. This larger effect of the divalent ions is especially pronounced at the smaller ionic strengths.

Since the concentration of the cation is of primary importance, it is easily understood why the oxidation potentials found in potassium ferrocyanide-potassium ferricyanide mixtures of various ratios and recalculated on the basis of a ratio of 1:1 are not the same at the same ionic strength (figure 2). The potentials found increase from the mixture with a ratio of 10 ferrocyanide to 1 ferricyanide to that with a ratio of 1 to 10. In the former, the potassium-ion concentration is much smaller than in the latter at the same ionic strength. In a similar way, it is explained why the 1-2 valence types of electrolytes (sodium sulfate, carbonate, etc.) have a smaller effect than the 1-1 valence type of salts (sodium chloride, etc.).

SUMMARY

1. The normal potential of the ferrocyanide-ferricyanide electrode is equal to 0.3560 volt at 25°C.

2. The change of the potential of a very dilute ferrocyanide-ferricyanide solution with increasing ionic strength is greater than calculated on the basis of the simple Debye-Hückel expression. This is partly explained by incomplete dissociation of alkali and alkaline earth ferrocyanides.

3. For the same valence type of salts the anion effect upon the potential is the same for different anions at the same ionic strength. A pronounced cation effect was observed, the effect decreasing in the order Cs, Rb, K = NH_4, Na = Li for the alkali ions and being of about the same order for the alkaline earth ions. The latter, especially at the smaller ionic strengths, have a much greater effect than the univalent cations.

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THE FOURTH IONIZATION CONSTANT OF FERROCYANIC ACID[1]

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Strong acids increase the oxidation potential of a ferrocyanide-ferricyanide mixture much more than neutral salts at the same ionic strength. This effect was attributed by Kolthoff (1) to the pronounced basic properties of the ferrocyanide ion:

$$Fe(CN)_6^{----} + H^+ \rightleftarrows HFe(CN)_6^{---}$$

Since hydrogen ions remove ferrocyanide ions from the system they must increase the oxidation potential. From colorimetric measurements Kolthoff estimated the fourth ionization constant of ferrocyanic acid as being equal to 5×10^{-4}. He did not consider activities, and the value reported is very uncertain. In the present study the fourth ionization constant of ferrocyanic acid was derived from the effect of hydrogen ions upon the oxidation potential of a mixture of potassium ferrocyanide and potassium ferricyanide at known ionic strengths.

$$K_4 = \frac{a_{H^+} \cdot a_{Fe(CN)_6^{----}}}{a_{HFe(CN)_6^{---}}} = \frac{a_{H^+} \cdot c_{Fe(CN)_6^{----}}}{c_{HFe(CN)_6^{---}}} \cdot \frac{f_4}{f_3} \qquad (1)$$

$c_{Fe(CN)_6^{----}}$ denotes the concentration of the ferrocyanide ions, $c_{HFe(CN)_6^{---}}$ that of the hydroferrocyanide ions, and f_4/f_3 the ratio of their activity coefficients.

The oxidation potential of mixtures containing 0.0004 mole of potassium ferrocyanide and ferricyanide in a liter of a buffer solution of known paH was determined in the way described in the preceding paper (2). From the data reported before and the new measurements it was possible to evaluate K_4. It is assumed that the value of f_4/f_3 (equation 1) is the same as that of the activity coefficients of ferrocyanide and ferricyanide ions at the same ionic strength in the same electrolyte solution. Considering the similarity in structure and size of $Fe(CN)_6^{---}$ and $HFe(CN)_6^{---}$, the assumption of these trivalent ions having the same activity coefficients at

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[1] From the experimental part of a thesis submitted by William J. Tomsicek to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1934.

the same ionic strength seems justified. The paH of the buffer solutions used was measured with a quinhydrone electrode using a similar electrode in a mixture of 0.01 *N* hydrochloric acid and 0.09 *N* potassium chloride as a standard half-cell. The paH of this mixture was taken to be equal to 2.075.

The method of calculating the various data needed in solving equation 1 is demonstrated by the following example. The first measurement reported in table 1 gives an oxidation potential of 0.4156 volt against the normal hydrogen electrode in a mixture containing 0.0004 mole of potassium ferrocyanide and ferricyanide, 0.01 mole of sodium acetate, and 0.2 mole of acetic acid per liter. The paH of the buffer solution alone is 3.392, and the effect of the hydrogen ions upon the ionic strength is negligibly small. In table 4 of the previous paper (2) it was reported that the oxidation potential of an identical mixture without acetic acid was equal to 0.3867 volt. In each mixture the oxidation potential is given by the expression:

TABLE 1

Measurements in acetate buffers at 25°C.

CONCENTRATION OF ACETIC ACID	CONCENTRATION OF $NaC_2H_3O_2$	paH	$E_{Q.H.}$	$E_{N.H.E.}$	$K_4 \times 10^{-5}$
M	*M*				
0.2	0.01	3.392	0.1608	0.4156	5.8
0.1	0.01	3.683	0.1704	0.4060	5.6
0.05	0.01	3.983	0.1787	0.3977	5.7
Average					5.7

TABLE 2

Measurements in biphthalate-hydrochloric acid buffers

paH	$E_{Q.H.}$	$E_{N.H.E.}$	$K_4 \times 10^{-5}$
3.997	0.1607	0.4157	7.4
3.437	0.1500	0.4263	5.5
3.037	0.1363	0.4401	5.5
2.637	0.1163	0.4601	4.7
2.222	0.0893	0.4371	3.8
Average			5.4

TABLE 3

Measurements in dilute hydrochloric acid solutions

Molar concentration of HCl	0.0029	0.0058	0.0145	0.0291	0.0581
$E_{N.H.E.}$	0.4577	0.4825	0.5173	0.5447	0.5735

$$E = \epsilon_0 + 0.0591 \log \frac{c_{\mathrm{Fe(CN)_6^{---}}}}{c_{\mathrm{Fe(CN)_6^{----}}}} + 0.0591 \log \frac{f_3}{f_4}$$

In the mixture without acetic acid $c_{\mathrm{Fe(CN)_6^{----}}} = 0.0004$; in the mixture with acetic acid (table 1) $c_{\mathrm{Fe(CN)_6^{----}}} = x = 0.0004 - \mathrm{HFe(CN)_6^{---}}$. From the difference in oxidation potential between the two mixtures, being $0.4156 - 0.3867 = 0.0289$ volt, it is easily found that:

$$0.0289 = 0.0591 \log \frac{0.0004}{x}$$

$$x = 1.29 \times 10^{-4}$$

and

$$c_{\mathrm{HFe(CN)_6^{---}}} = 4 \times 10^{-4} - 1.29 \times 10^{-4} = 2.71 \times 10^{-4}$$

From the known normal potential ϵ_0 and the value of the oxidation potential of 0.3867 volt in the mixture being 0.01 molar in sodium acetate a value for f_4/f_3 of 0.30 is derived.

Therefore

$$K_4 = \frac{4.06 \times 10^{-4} \times 1.29 \times 10^{-4}}{2.71 \times 10^{-4}} \times 0.30 = 5.8 \times 10^{-5}$$

In table 1 the results of the measurements and calculated values of K_4 are reported in mixtures containing 0.01 mole of sodium acetate and varying concentrations of acetic acid. The measurements were repeated using a series of potassium acid phthalate buffers with hydrochloric acid. The analytical concentration of the potassium salt was 0.05 molar. In the calculation of f_4/f_3 it is assumed that potassium biphthalate (not considering the pH effect) has the same effect upon the oxidation potential of the ferrocyanide-ferricyanide mixture as potassium chloride has at the same ionic strength. This assumption is justified by the fact found in the previous paper, that the "salt effect" upon the oxidation potential is virtually independent of the kind of anion in dilute solutions. The values of K_4 reported in table 2 decrease with increasing hydrogen-ion concentration of the mixture. This is to be attributed to a specific effect of the hydrogen ions upon the potential of the ferro-ferricyanide electrode. No correction has been applied, since this effect is not quantitatively known. Still there is a very good agreement between the average values of K_4 found in tables 1 and 2, the total average being 5.6×10^{-5} at 25°C. Measurements were also made in mixtures containing various concentrations of hydrochloric acid. In this case insufficient data were available for the computation of K_4, and only the values of the oxidation potentials found are reported in table 3. Comparison of these figures with those given in table 4 of the previous paper shows the very large effect of the acid upon the oxidation potential of the ferri–ferrocyanide system.

SUMMARY

The fourth ionization constant of ferrocyanic acid was found to be equal to 5.6×10^{-5} at 25°C.

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A SIMPLE MASS SPECTROMETER

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It had long been thought desirable to use a mass spectrograph (particularly the type that allowed the direct measurement of intensities of the ions produced by electrons of known energy) for the analyses of substances having a small vapor pressure (0.001 mm. of mercury or higher). These analyses would be of value from a purely chemical point of view as well as from the physicochemical aspects involved in the determination of bond energies, the energetics of certain reactions, etc. The labor and cost of setting up the usual more refined types of spectrographs[1] makes one feel that the general applicability of this apparatus has been somewhat restricted on that account. An outstanding situation has arisen, due to the discovery of deuterium, which impressed many chemists that numerous problems in that field could be more easily solved by the use of such an instrument. It is proposed that a simple mass spectrometer can be constructed, based on a principle first discussed by W. R. Smythe (4) and later made use of by him and Mattauch in the development of an efficient velocity filter for ions (1, 2, 5, 6).[2]

The experimental arrangement here suggested differs from the above in that the oscillating field is directly made to be the mass analyzer, it being assumed in this discussion that a condenser can be treated as ideal, i.e., one which produces a uniform field ending sharply at its geometrical boundaries, that the wave-form of the oscillating field is a definitely known odd function, and that the ions to be analyzed are uniformly accelerated (homogeneous in voltage drop).

For the simplified arrangement suggested, these assumptions can be justified. (1) The condenser plates are to be placed close together, so that the inhomogeneous region (equal approximately to three times the distance between the plates) will be limited to a small fraction of the total distance traveled. (2) The ions will travel in a path deviating but slightly from the plane half way between the plates. (3) The technic in designing

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[1] An excellent summary of the methods of mass spectroscopy describing various arrangements of fields which will produce the desired focusing in directions and velocities of the ions is given by Mattauch (Physik. Z. 35, 567 (1934)).

[2] Such an application was indicated by him; see reference 4, p. 1285.

oscillating circuits has reached such a stage of development that it is not difficult to obtain an almost pure sine wave in the frequency range desired. (4) Work done with mass spectrographs as of the Dempster type, in which homogeneity in accelerating voltage of the ions is assumed, has apparently been quite successful (3). (5) Since deviations from the simple equations derived here will only distort the mass scale slightly, calibrations with a series of known gases will circumvent the difficulty.

Consider the arrangement shown in figure 1.

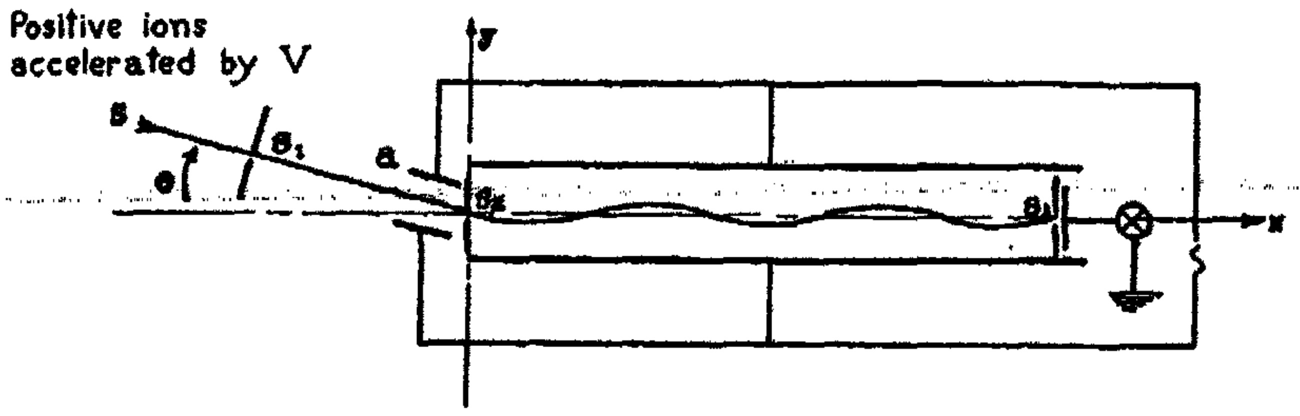

FIG. 1. ARRANGEMENT OF THE MASS SPECTROMETER

The equations to be solved are:

$$\ddot{x} = \ddot{z} = 0$$

$$\ddot{y} = E_y e/m$$

where

$$E_y = \sum_{n=1}^{\infty} a_n \sin 2\pi n f t$$

with the initial conditions:

$$\left.\begin{aligned} \dot{x}_0 &= \sqrt{2eV/m}\cos\Theta \\ \dot{y}_0 &= -\sqrt{2eV/m}\sin\Theta \\ \dot{z}_0 &= 0 \end{aligned}\right\} \quad \begin{gathered} \text{at} \\ x = y = z = 0 \\ \text{and} \\ t = 0 \end{gathered}$$

i.e., the ions enter the field when the argument of the sine terms is a whole multiple of π (hence the necessity of the small condenser, a, which is to act as a valve). The solutions obviously are

$$x = (\sqrt{2eV/m}\cos\Theta)t$$

and

$$y = \frac{e}{m}\left(\sqrt{\frac{m}{2eV}}\,\frac{x}{\pi f\cos\Theta}\sum_{n=1}^{\infty}\frac{a_n}{2n} - \frac{1}{\pi^2 f^2}\sum_{n=1}^{\infty}\frac{a_n}{(2n)^2}\sin\left(\frac{2\pi f n x}{\cos\Theta}\sqrt{\frac{m}{2eV}}\right)\right) - x\tan\Theta$$

As indicated in the diagram, Θ is so chosen as to make $y = 0$ at a given x. Thus is the condition stated in assumption (2) assured.

It is to be noticed that the value of y depends on linear terms in x upon which are superposed small oscillatory terms whose maximum values are between 0.1 and 0.05 of the values of the corresponding linear ones for the frequencies used. The effect of the oscillating part diminishes very rapidly for the higher harmonics, since their amplitudes are proportional to $1/n^2$. Were we to neglect these smaller terms, we would obtain the relation

$$e/m = 8\pi^2 f^2 V \sin^2 \Theta / a^2$$

where

$$a = \sum_{n=1}^{\infty} \frac{a_n}{n}$$

and

$$\frac{\Delta m}{m} = \frac{2\Delta a}{a} = -\frac{2\Delta f}{f} = -\frac{\Delta V}{V} = \frac{2\Delta\Theta}{\tan\Theta}$$

from which it is obvious that: (a) the presence of harmonics serves only to affect the value of Θ initially chosen to make $y = 0$. (b) For large angles there will be slight directional focusing due to the fact that $\cot\Theta$ does not change rapidly then. (c) e/m is independent of x. (d) There are enough variables in this arrangement so that one can adjust any mass range to come in a convenient range of experimentation.

That the effects of neglecting the oscillating terms are small in certain cases, can readily be seen from the following calculations made with the last expression:

Atomic weight	100	30	1
e/m (in E.M.U.)	95.7	319	9570
V, accelerating voltage (E.M.U.)	8×10^{10}	8×10^{10}	4×10^{11}
f, frequency of fundamental	5×10^5	1×10^6	5×10^6
a (in E.M.U.)	8×10^{10}	8×10^{10}	8×10^{10}
x (in cm.)	20.0	20.0	20.0
$\sin\Theta$	0.6231	0.5679	0.2784
Θ	38° 32.5′	34° 36.5′	16° 10.0′
$\frac{\text{linear term}}{\text{amplitude of oscillating term}}$	20.5	21.4	7.48

On the other hand, when the amplitudes of the harmonics become negligibly small, one can retain the sine term obtaining the relationship.

$$\frac{m}{e} x \tan\Theta - \frac{a_1 x}{2f\cos\Theta}\sqrt{\frac{m}{2eV}} + \frac{a_1}{(2\pi f)^2}\sin\left(\frac{2\pi f x}{\cos\Theta}\sqrt{\frac{m}{2eV}}\right) = 0 \qquad (1)$$

Below are two curves of this equation where m/e is plotted versus one of the variables (a_1, figure 2; V, figure 3), while the others are kept at the arbitrary values

$f = 5 \times 10^6$
$x = 25.21$ cm.
$\Theta = 16° 10.0'$
$V = 4 \times 10^{11}$ E.M.U. when a_1 was taken as the variable.
$a_1 = 8 \times 10^{10}$ E.M.U. when V was taken as the variable.

In order to plot the second curve, one is obliged to make the substitutions

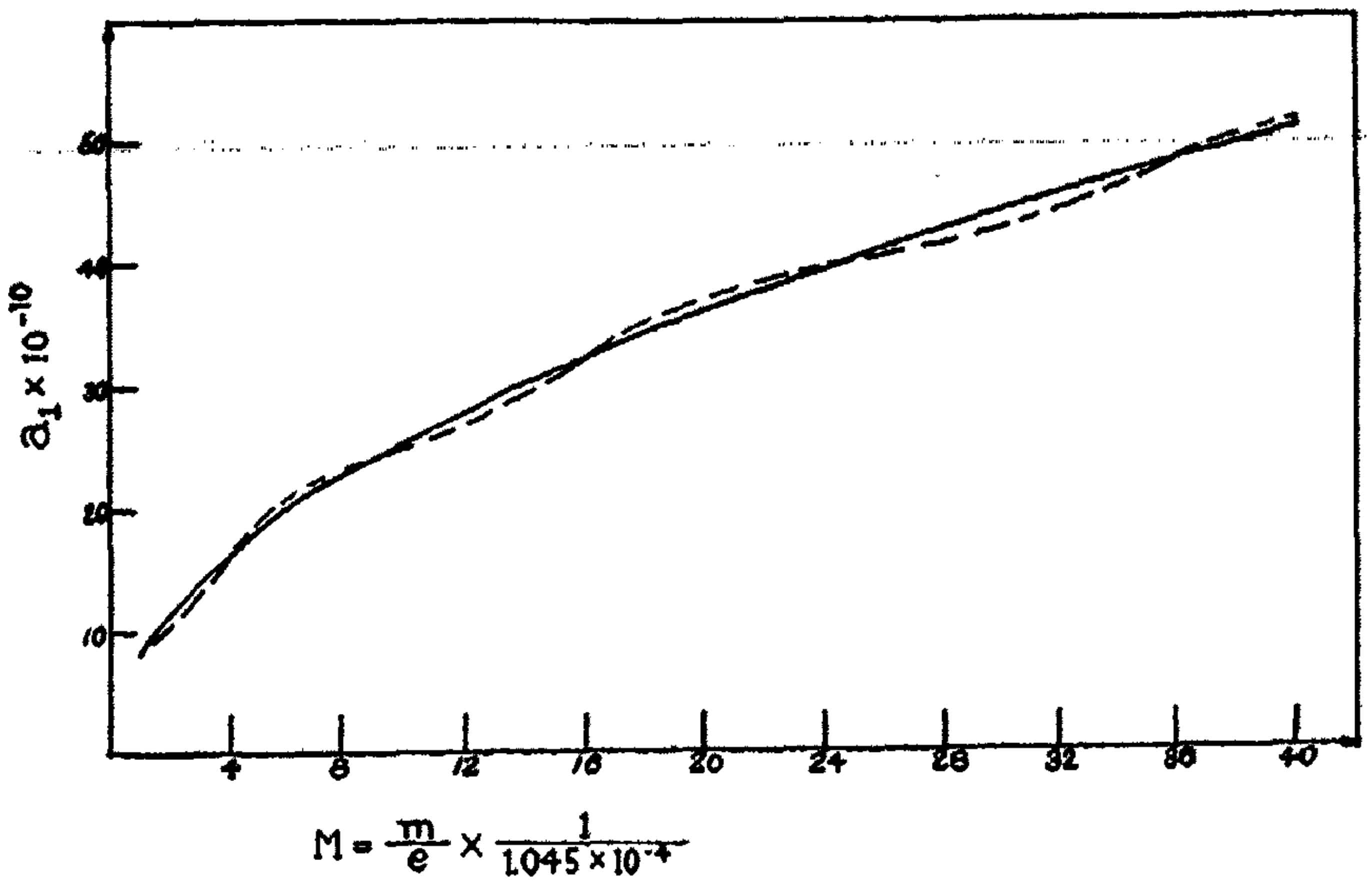

FIG. 2. M/e AS A FUNCTION OF a_1

Solid curve, neglecting sine term, equation $a_1 = \sqrt{8\pi^2 f^2 V \sin^2\Theta\, m/e}$
Broken curve, considering sine term, equation 1.

$\sqrt{m/e} = 1.022 \times 10^{-2}\alpha$ and $\sqrt{1/2V} = 1.118 \times 10^{-6}\beta$ and set $\alpha\beta = k$. He can then solve for $1/\beta^2$ in terms of k, i.e.,

$$\frac{1}{\beta^2} = \frac{V}{4 \times 10^{11}} = \frac{7.638 \times 10^{-4}k - 81.04 \times 10^{-6} \sin 3\pi k}{7.638 \times 10^{-4}k^2}$$

and on assigning definite values to k, can obtain the corresponding $V(\beta)$, whence he can calculate the necessary m/e. In similar manner one can find m/e as a function of Θ, f, or x.

These curves permit us to make the important conclusion that, owing to the small amplitude of the oscillating term, m/e will be a monotonic function of each of the variables so that there is no danger of obtaining ghost peaks or the possibility of several peaks coming at the same point. Furthermore, it is obvious that harmonics will only distort the mass scale. It is interesting indeed, to find in the second curve the linear relationship $\Delta M/M = \Delta V/V$ for all integral values of M. Here the oscillating terms of the harmonics as well as that of the fundamental will have no effect whatever. This will be true whenever conditions are so chosen to make the oscillating term disappear for some integral value of M as has been done in the calculation of this plot. When there will not be at least one integral value of M for which the arguments of the sine terms are whole multiples of π, the linear relation will no longer hold and the curve of m/e versus V will have the general aspect of the curve presented for the entire mass range including the non-integral M's.

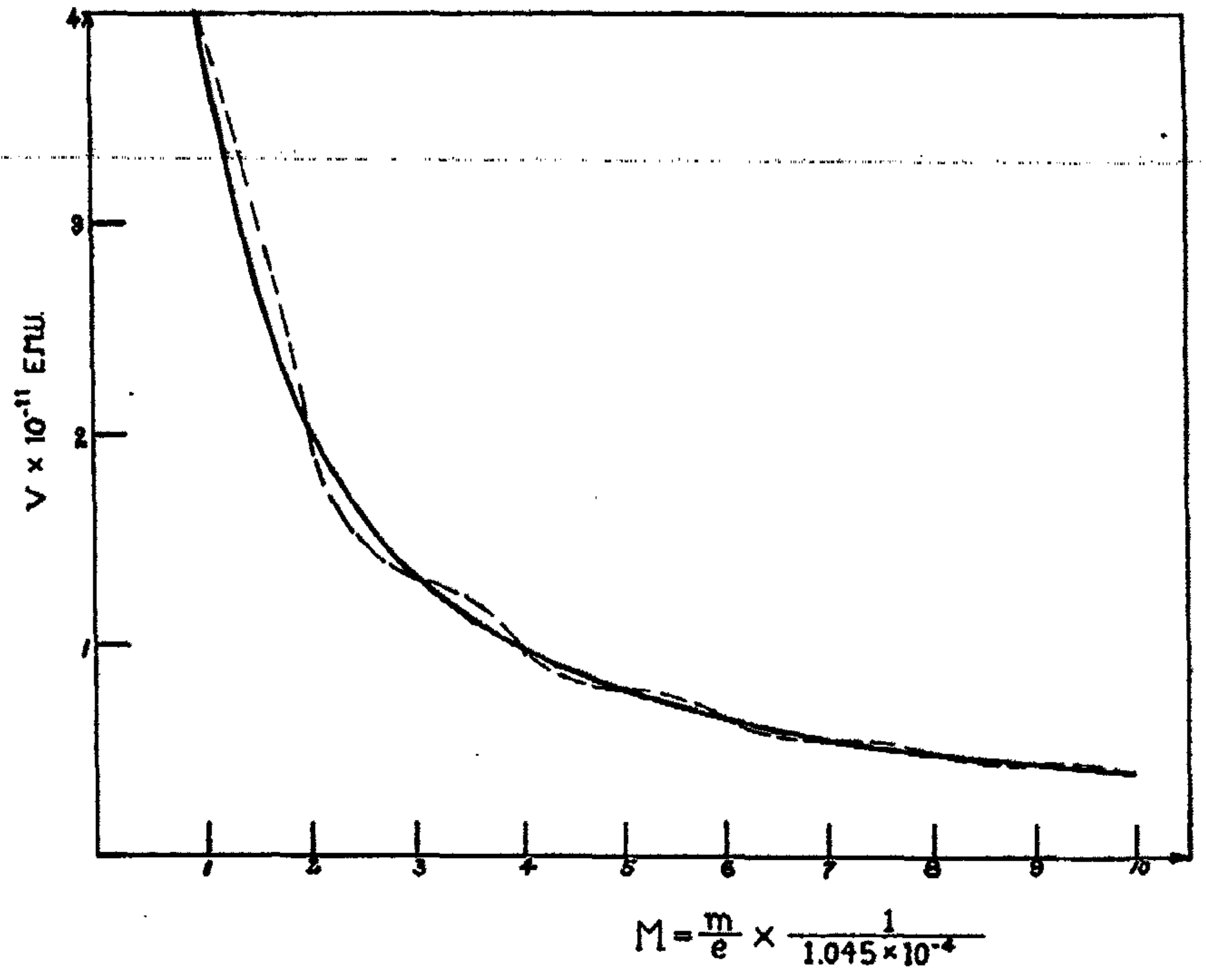

FIG. 3. M/e AS A FUNCTION OF V

Solid curve, considering only integral M's, $V = \dfrac{a^2}{8\pi^2 f^2 \sin^2\Theta} \quad \dfrac{1}{m/e}$

Broken curve, considering all values of M, equation 1.

It is evident that a broadening of the peak will result from the fact that even though $\sin 2\pi nft \neq 0$ but differs very little from it, ions will still enter the analyzing condenser with a definite y component of velocity due to the finite width of the slit S_2. In order to make even a rough estimate, it is necessary to assume a definite form for the field in the small condenser along the line SS_2. The arbitrariness of this type of procedure made the author feel that this as well as other limitations of the proposed arrangement[3] could best be appreciated after an experimental attempt has been made. It is to be noted that this type of condenser valve is inherent in the apparatus of Smythe and Mattauch and thus has been proved quite successful. Hence, its effects on the width of the mass and velocity peaks as well as those due to the bending of the lines of force at the entrance of the analyzing field, the influence of other perturbing fields, etc., can be calculated in a general way similar to the one used by Herzog and Mattauch, to which the reader is referred.

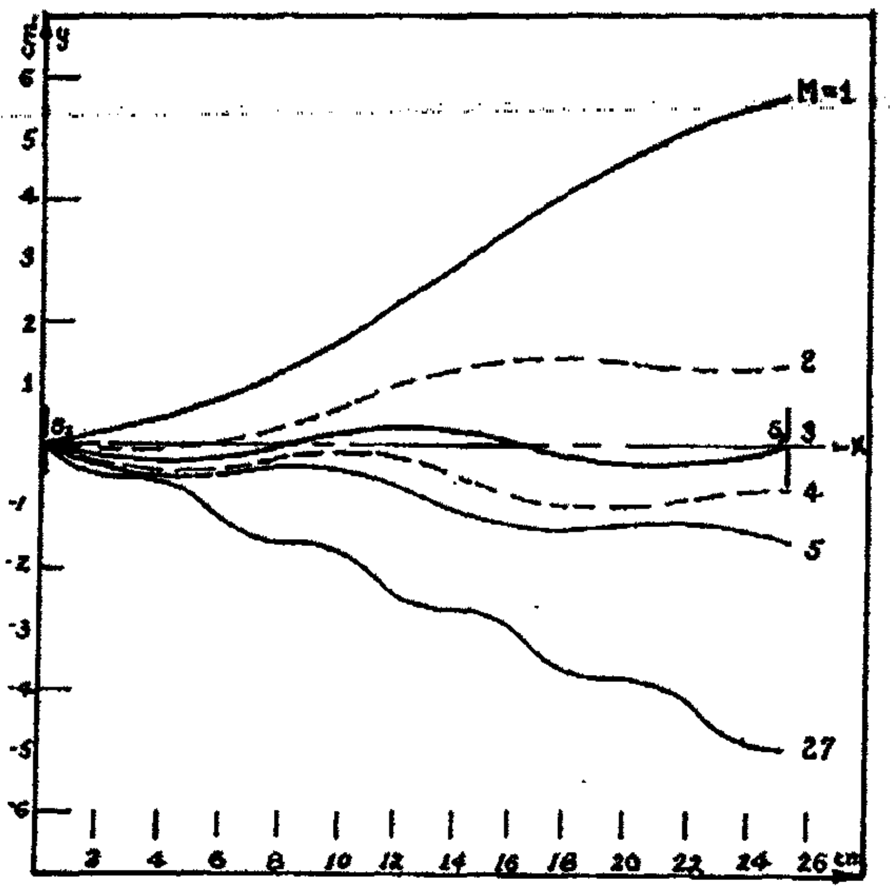

FIG. 4. CONDITIONS CHOSEN SO THAT IONS WITH $M = 3$ FOCUS ON RECEIVING SLIT

The study of the trajectories of the ions in this type of apparatus is instructive. Under the conditions given below, the curves in figure 4 were traced for the masses 1, 2, 3, 4, 5, and 27, using the expression·

$$y = \frac{e}{m}\frac{a_1}{2\pi f}\left(\sqrt{\frac{m}{2eV}}\frac{x}{\cos\Theta} - \frac{\sin\left[(2\pi f\sqrt{m/2eV}\;x)/\cos\Theta\right]}{2\pi f}\right) - x\tan\Theta$$

where $V = 1.333 \times 10^{11}$ E.M.U.
$f = 5 \times 10^6$
$\Theta = 16° 10.1'$
$a_1 = 8 \times 10^{10}$ E.M.U.
$x_{\max} = 25.21$ cm.

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[3] For instance, the necessity for the correct displacement of S_1 from the plane half way between the condenser plates of a, so that the ions will enter the analyzing condenser just when $E_y = 0$, will cause some difficulty, no doubt.

The writer wishes to thank Dr. T. R. Hogness for the helpful discussions regarding this paper.

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THE TERNARY SYSTEM ISOAMYL ALCOHOL-PROPYL ALCOHOL-WATER

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INTRODUCTION

In the course of investigating the solubilities of the alkali chlorides in mixtures of isoamyl alcohol, propyl alcohol, and water, it was found necessary to determine the limits of the solubility of these three liquids. Although a large number of alcohol-water systems have been investigated, we were unable to find solubility data for the above system.

MATERIALS

The isoamyl alcohol was Baker's A.C.S. reagent grade, which boiled over a range of 128–132.5°C. and was therefore subjected to fractional distillation, the fraction coming over at a constant boiling point of 130.5°C. being collected. This agrees with the accepted value (2). The normal propyl alcohol was redistilled and the fraction boiling at 97.8 ±0.1°C. was taken (3).

APPARATUS

A Zeiss Pulfrich refractometer was used in determining the indices of refraction. The values could be read to 0.00005 and were rounded off to the nearest 0.0001. The temperature of the liquid in the prism cup was held at 25 ±0.1°C. by means of a circulating stream of water as described by Hoyt (1). The Westphal balance used in the density determinations was checked against a 25-cc. pyknometer. It was found that using a 10-cc. float the error involved was ±0.0001. The solutions were prepared by mixing known volumes of the three liquids at 25°C., and were correct to ±0.1 per cent.

PROCEDURE AND DISCUSSION

The solubility curve, figure 1, was determined by placing a series of constant isoamyl-propyl alcohol mixtures, each of 200 cc., in a thermostat at 25 ±0.01°C. Each sample was thoroughly agitated while water was being added until the first appearance of turbidity was noted. The agitation was continued over a period of six to eight hours to ensure equilibrium.

Certain portions of the curve were determined by using mixtures of water and propyl alcohol, to which isoamyl alcohol was added. These results are shown in table 1. The densities were determined in the usual manner, care being taken to keep the solutions at 25°C. In making the index of refraction measurements, trouble was experienced in getting a suitable cement on which the isoamyl alcohol had little solvent action. Picene was unsatisfactory for this reason. Fish glue could not be used because of its solubility in water. If, however, the cleaned surfaces were treated with a thin layer of Canada balsam and were allowed to stand from two to three days, no trouble was experienced.

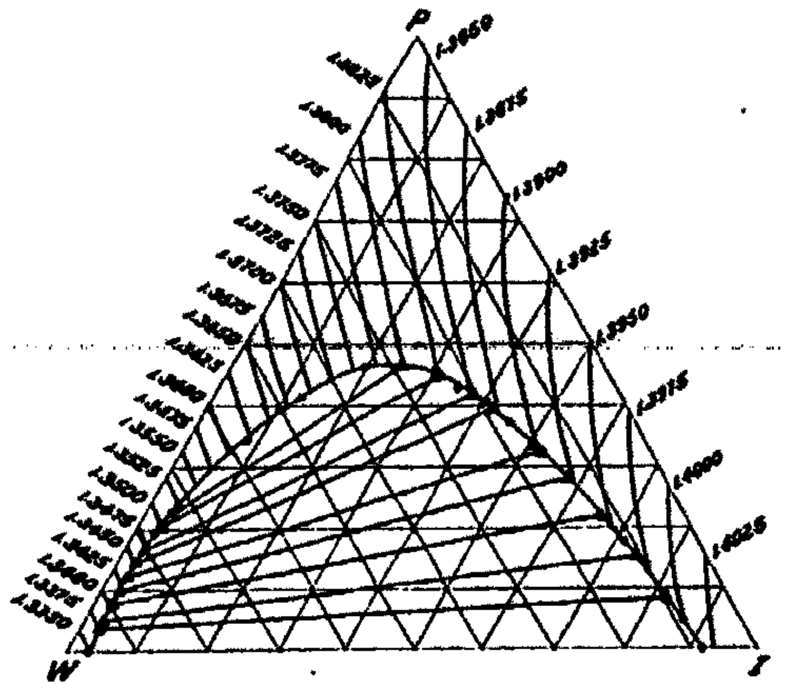

FIG. 1. THE SOLUBILITY CURVE

TABLE I

Solubility of isoamyl and propyl alcohols in water at 25°C.

VOLUME PER CENT ISOAMYL ALCOHOL	VOLUME PER CENT *n*-PROPYL ALCOHOL	VOLUME PER CENT WATER	VOLUME PER CENT ISOAMYL ALCOHOL	VOLUME PER CENT *n*-PROPYL ALCOHOL	VOLUME PER CENT WATER
40.40	40.40	19.20	19.80	46.21	33.99
45.47	37.21	17.32	13.77	41.32	44.91
50.63	33.76	15.61	8.60	34.40	57.00
60.84	26.08	13.08	2.53	19.50	77.97
71.10	17.78	11.12	4.08	23.98	71.94
81.37	9.04	9.59	2.44	4.88	92.68
86.83	4.57	8.60	2.29	9.77	87.94
89.90	2.30	9.22	2.25	14.66	83.09
93.32		6.68	2.53	19.49	77.98
35.02	42.81	22.17	4.03	23.99	71.98
30.17	45.26	24.57	3.10		96.90
25.10	46.59	28.31			

In addition to the solubility curve, equilibrium compositions were

TABLE 2

Values of the refractive index at different alcohol ratios

ALCOHOL RATIO I/P	VOLUME PER CENT ISOAMYL ALCOHOL	VOLUME PER CENT n-PROPYL ALCOHOL	VOLUME PER CENT WATER	REFRACTIVE INDEX AT 25°C.	SPECIFIC GRAVITY AT 25°C.
0/10		100.0		1.3841	0.8016
		80.0	20.0	1.3788	0.8527
		50.0	50.0	1.3648	0.9163
		25.0	75.0	1.3501	0.9652
		10.0	90.0	1.3398	0.9852
		5.0	95.0	1.3368	0.9911
1/9	9.6	85.4	5.0	1.3859	0.8158
	9.1	80.9	10.0	1.3842	0.8286
	8.1	71.9	20.0	1.3800	0.8522
	7.8	67.2	25.0	1.3781	0.8634
	7.1	62.9	30.0	1.3760	0.8742
	6.1	53.9	40.0	1.3709	0.8955
	5.1	44.9	50.0	1.3655	0.9164
	4.2	35.8	60.0	1.3607	0.9359
	3.1	26.9	70.0	1.3545	0.9548
	10.0	90.0		1.3867	0.8025
2/8	20.0	80.0		1.3888	0.8028
	19.2	75.8	5.0	1.3875	0.8159
	18.2	71.8	10.0	1.3860	0.8286
	16.2	63.8	20.0	1.3817	0.8154
	15.1	59.9	25.0	1.3797	0.8633
	14.2	55.8	30.0	1.3771	0.8741
	12.2	47.8	40.0	1.3719	0.8948
2/3	40.0	60.0		1.3929	0.8043
	38.0	57.0	5.0	1.3915	0.8166
	36.0	54.0	10.0	1.3898	0.8293
	32.0	48.0	20.0	1.3846	0.8156
3/2	60.0	40.0		1.3973	0.8051
	57.0	38.0	5.0	1.3952	0.8181
	54.0	36.0	10.0	1.3930	0.8291
	51.0	34.0	15.0	1.3904	0.8402
8/2	80.0	20.0		1.4011	0.8082
	76.0	19.0	5.0	1.3988	0.8174
	72.0	18.0	10.0	1.3964	0.8291
10/0	100.0			1.4058	0.8061
	95.0		5.0	1.4033	0.8177
	93.0		7.0	1.4018	0.8220
	2.0		98.0	1.3346	0.9949

determined for a series of nine different mixtures having a total composition inside the solubility curve (i.e., the heterogeneous area). These compositions are shown in table 3. It was thought that the compositions of the equilibrium layers could be obtained by using the method of Smith (4), who investigated the system methyl alcohol–isobutyl alcohol–water.

TABLE 3

Composition of layers in equilibrium at 25°C.

UPPER LAYER				LOWER LAYER			
Index of refraction	Volume per cent isoamyl alcohol	Volume per cent *n*-propyl alcohol	Volume per cent water	Index of refraction	Volume per cent isoamyl alcohol	Volume per cent *n*-propyl alcohol	Volume per cent water
1.3987	81.8	8.7	9.5	1.3375	2.6	3.9	93.5
1.3965	74.1	15.2	10.7	1.3383	2.8	5.0	92.2
1.3943	65.8	22.2	12.0	1.3404	2.8	7.8	89.4
1.3921	57.9	28.1	14.0	1.3422	3.0	10.0	87.0
1.3903	52.1	32.9	15.0	1.3434	2.7	12.3	85.0
1.3871	41.9	39.6	18.5	1.3449	2.5	14.5	83.0
1.3851	37.5	42.0	20.5	1.3461	2.9	16.2	80.9
1.3828	31.3	45.0	23.7	1.3480	3.0	20.8	76.2
1.3802	25.1	46.8	28.1	1.3506	3.0	22.2	74.8

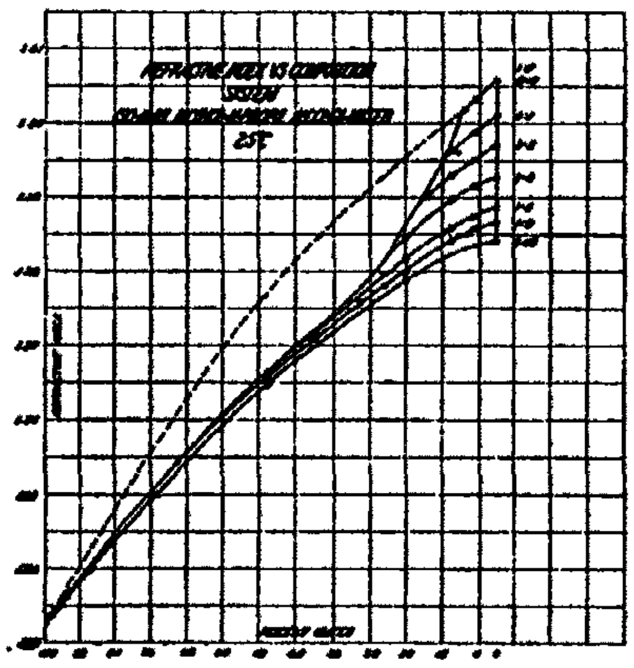

FIG. 2. REFRACTIVE INDEX VERSUS COMPOSITION FOR THE SYSTEM ISOAMYL ALCOHOL–*n*-PROPYL ALCOHOL–WATER AT 25°C.

Because of the relatively large portion of the ternary diagram over which the liquids are insoluble, as compared with the system investigated by Smith, it becomes a matter of the utmost difficulty to draw the lines for refractive index vs. alcohol ratio, at constant water content. This difficulty arises from the fact that large extrapolations have to be made from one or two experimental points in regions where the percentage of water is high. It was found, however, that the experimental values of the refractive index at different alcohol ratios (table 2) when plotted on a large scale as in figure 2 enabled lines of constant refractive index to be drawn on the ternary as shown in figure 1. From the index of refraction of the equilibrium layers, the compositions of the solutions as indicated by the tie lines were correct to within ±0.2 per cent.

SUMMARY

The solubilities, densities, and indices of refraction have been determined for the system isoamyl alcohol–propyl alcohol–water at 25°C. Tie lines were determined for nine pairs of solutions.

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THE INFLUENCE OF THE PROXIMITY OF A SOLID WALL ON THE CONSISTENCY OF VISCOUS AND PLASTIC MATERIALS. IV

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INTRODUCTION

In the first paper (7) of this series experiments were described in which aqueous pastes of soils, clays, and finely divided minerals were forced through narrow glass tubes. The instrument used was the modified Bingham plastometer described in an earlier paper (13), in which two bulbs are connected by a tube of known length L and radius R. The material can be made to flow in either direction under a measured air pressure P. The volume V of flow per second was measured indirectly by the small back-pressure set up by the air in escaping through one of a series of standardized capillary leaks.

The data so obtained presented a problem, for on plotting $V/\pi R^3$ against $PR/2L$ ($=W$, the shearing stress per unit area on the wall of the tube) the points for tubes of different radii did not fall on the same curve, those for a narrower tube lying above those for a wider one. It was already known from the work of Bingham (2) and others, that such materials do not conform to Poiseuille's law, which means that the velocity gradient is not directly proportional to the shearing stress as it is for true fluids; but it was shown that no equation of dependence of velocity gradient on shearing stress, however complicated, would account for the phenomenon. The discrepancy is far too large to be put down to experimental error, and the only possible conclusion is that somewhere in the tube the velocity gradient depends on *something else besides the shearing stress.* So much seems certain.

An examination of the data obtained with a series of different radii led us to put forward the hypothesis that the *proximity of a solid wall* is the disturbing factor. It was suggested that, where the $V/\pi R^3$–W curves for different radii were not coincident, a shearing stress operating near the wall of the tube gives rise to a greater velocity gradient than does the same stress operating in the bulk of the material. In the subsequent papers of this series (8, 10) it was shown that although the data are not sufficiently exact to enable a precise estimate to be made of the thickness of the modified layer, in the case of a certain soil paste, it could not be greater than 8×10^{-3} cm. or less than 1×10^{-3} cm.

A different hypothesis has recently been put forward by Ambrose and Loomis (1) to account for the anomalous behavior of bentonite pastes. They point out that bentonite is known to be thixotropic, and suggest that the velocity gradient depends not only on the magnitude of the shearing stress, but also on the time it is applied. They conclude that this material appears to have a lower consistency the narrower the tube used, because "for constant shearing stress at the wall, the material flows at higher linear velocity in the larger tubes, thus being subjected to the same distribution of shearing stresses for a shorter time than in the smaller tubes."

While it is possible that, with the material used by these authors and under the conditions of their experiments, thixotropy may have been of importance, we do not think it can have had any measurable influence on our published data. Before any measurements were made, the whole of the material was driven through the tube from one bulb into the other, and although the direction of flow had to be reversed several times to get a complete set of points for a curve, the experimental figures give no indication that time of shear influences the rate of flow.[1] Feeling, nevertheless, that the matter should be further investigated, we have made new measurements on several of the materials studied before, using tubes which differ considerably in length as well as in radius. It is clear that, if the material flows more readily under a given stress the longer it is applied, the rate of extrusion under a given pressure gradient will increase with the length of a tube of given radius. Comparatively little work has been done on the effect of length of tube on consistency. Our own earlier experiments (13) were confined to a comparatively small difference of length. Ambrose and Loomis (1) quote Peek and Erickson (5) as having "learned that the apparent viscosity of agar solutions and starch pastes at constant shearing stress is lower in the longer tubes," though these authors themselves say that they "do not consider the data conclusive evidence of a difference of the type observed." On the contrary Staudinger and Heuer (17) state that "the solution of a high polymer (polystyrol) flowing through a long tube appears more viscous than in a short tube of the same diameter, since here, owing to the long fiber molecules, the hindrance to a normal flow is more marked" (our translation).

The point which we have set out to settle is, therefore, this: Is the variation of $V/\pi R^3$ for a given value of W, which we have observed in aqueous pastes of certain soils, clays, and minerals, directly associated with the

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[1] When materials showing marked thixotropy are investigated in our instrument, the flowmeter readings for a given pressure do not remain steady, but tend to increase so long as the shearing is continued. In consequence of this, we have not published any data for such materials.

radius of the tube, or is the association indirect, the governing factor being in reality the proportions of the tube, i.e. the ratio of some function of the radius to the length?

GENERAL BEHAVIOR OF THE MATERIALS INVESTIGATED

Before giving detailed consideration to the new data, it will be as well to recapitulate very briefly the flow characteristics of the aqueous paste, which are fully set out in the paper already referred to. Four stages may be distinguished as the pressure gradient is increased from zero.

Stage I. No movement.

Stage II.[2] Slow movement as a solid plug, flow increasing linearly with pressure.

Stage III. A very rapid increase of flow with pressure, the plug being separated from the wall by a sheath of material in laminar flow.

Stage IV. Rapid flow increasing almost linearly with pressure, the central plug occupying only a small part of the cross section and having little influence.

According to the mathematical treatments of Buckingham (3) and Reiner (6) stage III is reached when the shearing stress W at the wall of the tube surpasses the critical shearing stress (S_0) of the material, and the sheath of material in laminar flow should have a thickness $R(W - S_0)/W$ which is proportional to the radius of the tube. The mean velocity of flow $V/\pi R^2$ for a given value of W greater than S_0 should therefore be proportional to R, which is another way of saying that the curve of $V/\pi R^3$ against W should be independent of R. The fact that the $V/\pi R^3$-W curve is not independent of R is interpreted by us as indicating that mean velocity of $V/\pi R^2$ may be resolved into two parts, one proportional to R, and the other independent of it. The part that is independent of R is mathematically similar to the term introduced by Buckingham to cover stage II. But whereas the velocity of sliding of the plug in stage II is so low that the lubricating sheath, assumed to consist of water, has a mean thickness of only 10^{-5} cm., the additional term needed to account for the flow in stages III and IV is about one hundred times as great.

In order to get a quantitative measure of the anomaly in stage IV, it was found convenient to plot the mean velocity $V/\pi R^2$ against W. The best straight lines making a common intercept on the W-axis were drawn, and their slopes σ plotted against R. The extent of the anomaly is indicated by the intercept σ_0 of this derived graph on the σ-axis; hence the name σ-phenomenon.

The need for a reiteration of the distinction between the "plug flow" of stage II and the anomalous flow near the wall of the tube which sometimes occurs in stages III and IV, is evident from a paper by Lawrence (4), who

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[2] For work on stage II, see references 11, 12, and 16.

quotes our work and suggests that ammonium oleate sols show a "plug flow." This is demonstrably not so in the sense in which we use the words, and in any case it seems more likely that the disturbance he observes is due to the elasticity of the sol than to anomalous flow.

EXPERIMENTAL PART

As already recorded, the phenomenon under consideration was first observed in pastes of soils and clays. The composition of these materials is, however, highly variable, and the extent of the phenomenon depends on factors not all of which are understood. Since the question at issue is a fundamental one, it seemed wisest to use, for the present tests, a material of simple and known composition which is easily procurable by others who may wish to repeat the experiments. Barium sulfate (pure) as supplied by British Drug Houses was therefore selected. Microscopic examination showed that the material was reasonably homogeneous and consisted mainly of cubes with sides 2 to 3μ in length.

TABLE 1

(a)			(b)		
TUBE NO.	*R*	*L*	TUBE NO.	*R*	*L*
	cm.	*cm.*		*cm.*	*cm.*
h	0.131	4.7	III	0.073	12.10
j	0.126	7.5	IV	0.048	12.25
a	0.126	11.8	V	0.0407	12.30
b	0.129	22.5			

In preparing this paste, the barium sulfate was triturated with distilled water with a rubber pestle, then gently pressed through a 100 mesh per inch sieve, thoroughly stirred, sieved again, bottled, brought to temperature (25°C.) in the thermostat, well shaken and then tested in the plastometer (A). Another portion of the same sample was kept overnight, and tested the next day (B). The concentration of the two samples differed slightly, but a moisture test at the end of the second experiment showed that 100 g. of paste had contained about 55 g. of dry barium sulfate.

Owing to the tendency for the barium sulfate paste not to leave a clean surface on the walls of the plastometer tubes, the insides of the bulbs were coated with a thin layer of vaseline. This worked excellently until the material had been sheared a considerable number of times, when small spots of the vaseline surface rubbed off, and got into the capillary, readings then becoming erratic. This happening was well defined, all readings up to a certain time being steady and reproducible, but this difficulty precluded a comparison of a very great number of tubes in a single experiment.

Preliminary measurements made without the use of vaseline gave essentially similar results, but the accuracy was less, owing to the difficulty of observing the level of the material in the bulbs.

Moreover, slight losses of material during the changing of the tubes and the advisability of continuing a given experiment over too long a period of time also precluded the use of a very great number of tubes for each experiment, and introduced an element of haste into the experiments which prevented their accuracy from equalling that of the earlier and more leisurely experiments. They were, nevertheless, amply accurate for the purpose in hand.

TABLE 2

Results of experiment A

Capillaries are given in the order in which the experiments were done

CAPILLARY	RESISTANCE USED IN FLOWMETER	P_m	a	V	P	$W/100$	$V/100\,\pi R^3$
a	(2)	7.0	0.6	0.167	5.2	3.65	0.266
		8.0	1.2	0.333	6.15	4.35	0.535
		9.0	2.2	0.61	7.0	4.94	0.985
		10.0	4.1	1.14	7.8	5.50	1.84
		11.0	7.1	1.97	8.6	6.05	3.18
		12.0	9.1 (?)	2.52 (?)	9.5	6.70	4.07 (?)
b	(2)	13.0	2.0	0.555	11.0	4.17	0.825
		15.0	3.1	0.86	12.9	4.90	1.28
		17.0	5.5	1.53	14.85	5.65	2.27
		19.0	9.0	2.50	16.5	6.25	3.72
		21.0	14.0 (?)	3.90 (?)	18.3	6.95	5.80 (?)
j	(2)	5.0	0.6	0.167	3.2	3.59	0.265
		6.0	1.4	0.388	4.1	4.6	0.619
		7.0	3.9	1.08	4.85	5.45	1.71
		8.0	6.9	1.91	5.6	6.3	3.02
		9.0	10.5	2.90	6.4	7.2	4.60
V	(6)	10.0	0.3	0.009	8.4	1.85	0.425
		12.0	0.6	0.017	10.4	2.28	0.800
		14.0	1.0	0.029	12.4	2.72	1.38
		16.0	1.3	0.038	14.4	3.17	1.80
		18.0	1.8	0.052	16.3	3.59	2.45
		20.0	2.3	0.067	18.3	4.02	3.15

The plastometer bulbs were connected to the capillary by means of rubber sleeves. In earlier papers (14, 15) it was shown that such a procedure was liable to cause unexpected errors in the case of saturated solutions of very soluble salts, but that no such errors occur in the case of pastes of soils or clays. There is no reason to suspect any such trouble with pastes of insoluble barium sulfate, and in any case the effect would be small compared with the very gross phenomena being investigated in these experiments. A series of tubes having the dimensions shown in table 1(a), was prepared. The radii were determined by a viscometric comparison with our previously carefully standardized tubes (table 1(b)) by measuring the flow/stress ratio for a glycerol-water solution for each tube, and so calculating *R*. Corrections for resistance in plastometer bulbs were made throughout by connecting the bulbs directly together as described in the first paper of this series (7).

TABLE 3

Results of experiment B

CAPILLARY	RESISTANCE USED IN FLOW-METER	P_m	a	V	P	$W/100$	$V/100\,\pi R^3$
V	(6)	8.0	0.2	0.006	6.5	1.43	0.280
		12.0	0.4	0.012	10.5	2.30	0.569
		16.0	0.8	0.023	14.5	3.18	1.09
		20.0	1.5	0.044	18.5	4.07	2.07
		22.0	2.0	0.058	20.4	4.50	2.75
		24.0	2.7	0.078	22.4	4.92	3.70
		26.0	3.2	0.093	24.4	5.39	4.40
III	(6)	8.0	0.7	0.020	6.5	2.60	0.165
		10.0	1.5	0.044	8.5	3.40	0.365
		12.0	3.3	0.096	10.4	4.15	0.795
		14.0	5.6	0.162	12.2	4.88	1.34
		16.0	9.2	0.267	14.1	5.62	2.22
		18.0	13.8	0.400	16.0	6.40	3.30
IV	(6)	15.0	0.8	0.023	13.5	3.50	0.665
		17.0	1.4	0.041	15.3	4.03	1.19
		20.0	2.4	0.070	18.4	4.73	2.04
		22.0	3.5	0.102	20.3	5.25	2.95
		25.0	4.3	0.125	23.2	6.02	3.62
		27.0	5.2	0.151	25.2	6.55	4.38
a (incomplete)	(2)	8.0	1.0	0.277	6.15	4.33	0.448
		11.0	4.0	1.11	8.8	6.18	1.80

Tube h showed slightly anomalous behavior, but, since its *L/R* ratio is only 36, this was disregarded.

Since the presence of a small metal disk drilled with a hole of 0.14 cm. radius in place of a capillary made no serious difference to the plastometer resistance, end-effect corrections were neglected. (Cv. Ambrose and Loomis' criticisms of capillary tube methods.)

Table 2 gives the results of experiment A, and table 3 of experiment B. The data are also plotted in figures 1 and 2, plotting $V/100\pi R^3$ against $\frac{W}{100}$, where $W = PR\Delta g/2L$. V is flow in cubic centimeters per second and equals flowmeter reading "a" × appropriate constant. P is pressure (cm. Hg) corrected for bulb resistance, and P_m the uncorrected pressure as read on the manometer.

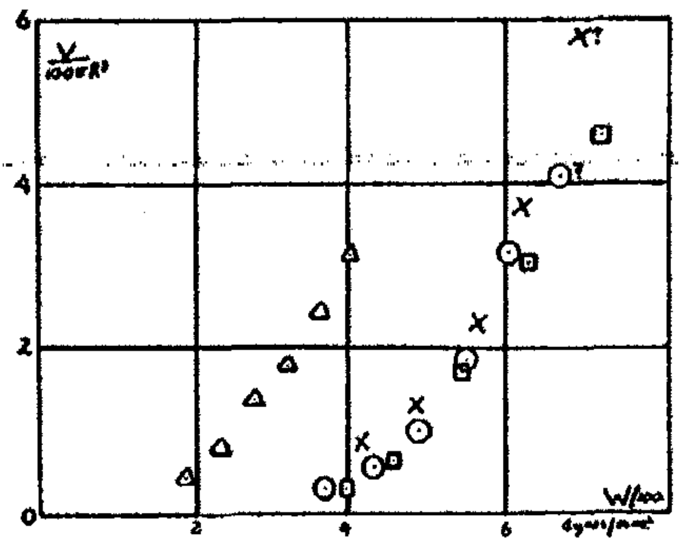

Fig. 1

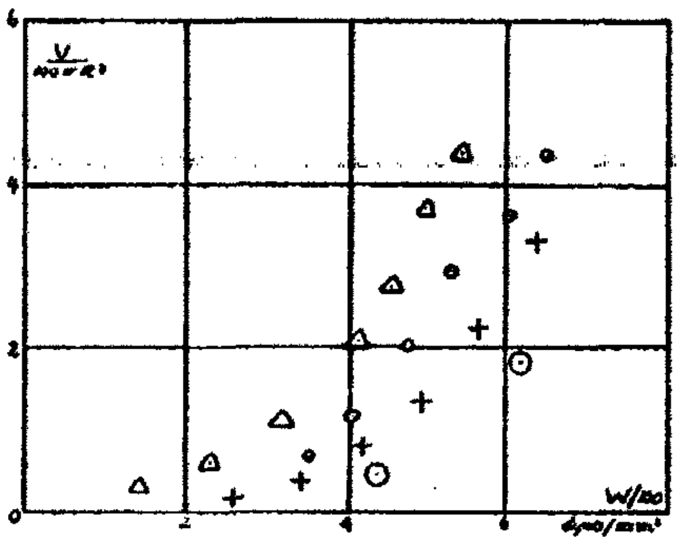

Fig. 2

Fig. 1

⊙ Capillary a, $R = 0.126$ cm., $L = 11.8$ cm.
△ Capillary V, $R = 0.0407$ cm., $L = 12.3$ cm.
× Capillary b, $R = 0.129$ cm., $L = 22.5$ cm.
⊡ Capillary j, $R = 0.126$ cm., $L = 7.5$ cm.

Fig. 2

⊙ Capillary a, $R = 0.126$ cm., $L = 11.8$ cm.
△ Capillary V, $R = 0.0407$ cm., $L = 12.3$ cm.
+ Capillary III, $R = 0.073$ cm., $L = 12.1$ cm.
⊙ Capillary IV, $R = 0.048$ cm., $L = 12.25$ cm.

The figures in the second column of each table refer to the resistance used in the flowmeter. For (2) flowmeter readings (a) are multiplied by 0.277. For (6) flowmeter readings (a) are multiplied by 0.029.

Figure 1 shows that length of tube has no effect on consistency, within the limits investigated, whereas the tube having a different radius shows an entirely different curve. The σ-effect (effect of radius) is shown more definitely in experiment B (figure 2).

The maximum length of tube used was 40 cm., as compared with 10 cm. in the earlier experiments, and with the apparatus in its present form stage IV could only be reached at the highest pressures. Most of the points therefore, are in stage III. This makes the data unsuitable for evaluating σ_0, but does not prevent their being used to decide whether an anomaly exists in connection with variations in length at constant radius.

Essentially similar results were obtained in some preliminary tests with soils, but for the reasons already stated, we have given the details of the experiments only in the case of barium sulfate.

CONCLUSIONS

These measurements show quite conclusively that for barium sulfate paste the rate of flow in tubes of a given radius and under a given pressure gradient (within the limits used) is independent of the length of the tube. The data thus lend no support to the idea that this material suffers a progressive breakdown with time under shear.

The effect of changing the radius upon the position of the $V/\pi R^3$–$PR/2L$ curves is as marked as in the earlier experiments on this material. From a calculation made from the curves published in an earlier paper (7), it may be concluded that the thickness of the layer which is modified by its proximity to the wall of the tube cannot be less than 20μ (the thickness, if this layer had the viscosity of pure water). This is very remarkable, since we now know that the individual particles are only 2 to 3μ in linear diameter. The thickness of the modified layer seems to be more comparable with the size of the flocculated aggregates as shown by sedimentation.

SUMMARY

Measurements have been made of the rate of flow of an aqueous paste of barium sulfate through tubes differing considerably both in radius and length under a series of pressure heads. The results show that for tubes of the same radius and under the same pressure gradient, the rate of flow is independent of the length of the tube; from which it is concluded that under the conditions of these experiments, this material shows no progressive breakdown with time under shear, as suggested by Ambrose and Loomis (1) for bentonite.

For different radii, however, curves for $V/\pi R^3$ against $PR/2L$ were obtained which, as previously recorded, do not coincide as they should if at every point in the tube the velocity gradient depends only on the shearing stress.

The hypothesis previously advanced that the proximity of the wall of the tube causes a sheath of material to shear more easily than does the bulk of the material, appears therefore to be the only one so far advanced that accounts for the facts.

The case of this barium sulfate paste is particularly interesting, as the particles are roughly cubical in form, and the thickness of the modified layer is many times the average particle diameter.

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APPLICATION OF AN EMPIRICAL CORRECTION TO THE DONNAN EFFECT IN THE ESTIMATION OF MOLECULAR WEIGHTS OF PROTEINS BY OSMOTIC PRESSURE MEASUREMENTS

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Osmotic pressure determinations of the molecular weights of proteins have hitherto been made at the isoelectric points, or within a pH range very close to the isoelectric points, of the proteins, and in the presence of high concentrations of salts. This procedure has been necessary in order to eliminate the osmotic effects of ions other than the colloid, resulting from the setting up of a Donnan equilibrium in which there exists an unequal distribution of diffusible ions on the two sides of the membrane. According to the Donnan theory of membrane equilibria, a knowledge of the active concentrations of these diffusible ions in the inner, colloid-containing solution, and in the outer solution with which it is in equilibrium, would make possible the estimation of the fraction of the observed osmotic pressure due to these ions, which, when corrected for, would give the osmotic pressure due to the colloid even at points distant from the isoelectric point and in dilute solutions. Attempts to make such corrections have repeatedly been unsatisfactory, however, and the results have been taken to indicate, among other things, variations in size of molecule of the colloid (2, 5), change in the osmotic activity of the colloidal molecule (1), and absence of, or modified osmotic activity of the diffusible ions derived from the colloid electrolyte (Gegenionen) (6, 7, 8).

In a series of experiments (3) in which the osmotic pressure of purified gum arabic was studied throughout a range of variation in the concentration of colloid, pH, and concentration of foreign salt, an empirical relationship has been found to exist between certain determinable variables in the system and the deviation of the observed osmotic pressure from that calculated upon the basis of differences in concentration of the diffusible ions across the membrane at equilibrium. This relationship was arrived at by assuming that the colloid micelle itself showed no appreciable osmotic pressure, in that the molecular weight of the arabate ion was so high that osmotic pressure due to the micelle was negligible in comparison with that derived from the unequally distributed diffusible ions. Such an assumption, of course, cannot be made with such proteins as egg and serum albumin, whose molecular weight is known to be low enough to give an osmotic pressure which would be of the same order of magnitude as that derived from the unequal distribution of the diffusible ions alone. However, if it can be assumed that the relationships found to exist for gum arabic solutions will also define the fraction of the osmotic pressure derived from the diffusible ions in solutions of such proteins, it should be possible to apply this correction and arrive at a value for the molecular weights of the proteins in the dilute salt solutions and at pH values other than the isoelectric point of the proteins. Conversely, if the accepted values of molecular weights and osmotic activity of the proteins can be assumed to hold for regions of pH distant from the isoelectric points and in dilute solutions, it becomes possible to correct the observed values of osmotic pressure in such protein solutions for the pressure due to the colloid and find whether or not the relationships found to exist for the gum arabic solutions are of general application in defining the osmotic pressure resulting from the unequal distribution of diffusible ions.

Where only monovalent diffusible ions are present, the empirical relationship found to exist in the experiments with gum arabic is given by the equation

$$\frac{E\alpha'[-]_i^{0.211}}{P_c - P_o} = \text{constant}$$

where P_o = the observed osmotic pressure at equilibrium, E = the membrane potential as obtained from electrometric hydrogen-ion measurements made upon the two solutions (inside and outside the membrane) after equilibrium had been reached, α' = the calculated equivalents of diffusible ions derived from unit weight of the colloid electrolyte, $[-]_i$ = the calculated concentration of diffusible ions of the same charge as that of the colloid present inside the membrane at equilibrium and is a measure of the foreign salt concentration in the solution containing the colloid, and P_c = the osmotic pressure to be expected from the difference in total diffusible ion concentrations across the membrane at equilibrium. When $\log \frac{E\alpha'}{P_c - P_o}$ is plotted against the $\log [-]_i$ a straight line is obtained with a slope equal to 0.211. The slope of the curve is not the same for all colloids, but does not show any lyotropic effect between ions of equal valence (i.e., H^+, Na^+, Li^+, etc.).

Since the proteins on the acid side of their isoelectric points are positively charged colloids, it should be possible to obtain a straight line when the $\log \frac{E\alpha'}{P_c - (P_o - P_p)}$ is plotted against $\log [+]_i$ if the correct molecular weight of the protein is used in calculating P_p, the osmotic pressure due to the protein. Here $[+]_i$ is a measure of the foreign salt concentration in the colloid-containing solution and will be equal to $[H^+]_i + [Na]_i$, since these are the only ions present, other than the protein, bearing this charge. The osmotic pressure due to the colloid, P_p, is assumed to be directly proportional to the molar concentration of the colloid.

EXPERIMENTAL

Crystalline ovalbumin was prepared by the method of Cole (4) and was recrystallized three times. Crystalline horse serum albumin was prepared and was not recrystallized. Serum albumin from cow serum was not obtained crystalline but was dissolved and reprecipitated. Each of these proteins was dialyzed against water saturated with toluene until nearly free of sulfate ion, and then electrodialyzed until entirely free of salt ions. From the cow serum albumin there was always a fairly large percentage of the protein which precipitated during electrodialysis. This was removed from the supernatant solution before the latter was dried. The two crystalline proteins gave no precipitate during electrodialysis, although the salt-free solution of horse serum had the appearance of a definitely colloidal solution (Tyndall cone, etc.) in contrast to the clear solutions of the egg and serum albumins. These proteins were dried at room temperature and solutions of them were prepared as needed.

The method used for measuring osmotic pressure was the same as that employed in the gum arabic experiments (3). Small collodion sacs (about 15-cc. capacity) were used for membranes. In order to prevent the proteins from passing through the membranes it was necessary to dry them for a longer time in air before placing them in water than had been necessary with gum arabic. This in itself indicated that the molecular dimensions of the proteins were smaller than were those of the gum arabic. Known amounts (*A* in the tables) of the salt-free, isoelectric protein, in solution, were placed in the collodion sacs and these were connected with a source of constant pressure (P_o) and placed in contact with an external solution containing known amounts of hydrochloric acid and sodium chloride. The total water content of the system was known. A few drops of toluene were added to the external solution to act as a preservative for the protein. Equilibrium was attained in forty-eight to sixty hours, after which time the contents of the membranes were weighed (*F*) and the hydrogen-ion activity of the inner and outer solutions was determined electrometrically by means of a hydrogen electrode. From these measurements were obtained *R*, the ratio of distribution of each ionic species across the membrane, and *E*, the electrical potential existing across the membrane. All experiments were made on the acid side of the isoelectric point of the proteins, and for each protein a series of experiments was made in which the total salt concentration present was varied sufficiently to give the desired curve. The temperature was 25°C. In some cases the chloride-ion concentration was measured in the external solution by means of the silver–silver chloride electrode. The chloride-ion concentration (rather than activity) was arrived at as follows: Voltage readings for a silver–silver chloride electrode, plus a saturated calomel half-cell, were made for solutions of hydrochloric acid and potassium chloride of known concentrations. The chloride-ion concentrations of these solutions were plotted against the voltage readings for the cell, and when voltage readings were obtained similarly for the external solutions of the above experiments (containing only hydrogen, sodium, and chloride ions), these were placed on this curve and the corresponding chloride-ion concentration read off.

It has been assumed that, in the concentration range studied in these experiments, the concentration ratio of distribution across the membrane for the various diffusible monovalent ionic species present does not vary more than a few per cent from the activity ratio as obtained from hydrogen-ion measurements. The concentrations of sodium ions on the two sides of the membrane can then be calculated by the equations

$$(\mathrm{Na}^+)_i = \frac{\text{Total Na present (equivalents)}}{(R \cdot V_o/1000) + V_i/1000}$$

and

$$(\mathrm{Na}^+)_o = R \cdot (\mathrm{Na}^+)_i$$

where

$$R = \frac{[\mathrm{H}^+]_o}{[\mathrm{H}^+]_i}$$

and V_o and V_i are the equilibrium volumes of solvent in cubic centimeters on the outside and inside of the membrane, respectively. Similarly the chloride-ion concentration could be calculated by the equations

$$(\mathrm{Cl}^-)_o = \frac{\text{Total Cl present (equivalents)}}{(R \cdot V_i/1000) + V_o/1000}$$

and

$$(\mathrm{Cl}^-)_i = R \cdot (\mathrm{Cl}^-)_o$$

If the above assumptions can be safely made, the results of the calculations must satisfy the requirement of electrical neutrality on each side of the membrane. Inside, the concentration of colloidal ions is unknown, but outside the membrane, where only monovalent diffusible ions are present, it is necessary that $(\mathrm{Na}^+)_o + (\mathrm{H}^+)_o = (\mathrm{Cl}^-)_o$. In the experiments with gum arabic this requirement was satisfied after calculations were made similar to those given above, so that it would seem that the assumptions were justified. In the case of the proteins, however, such calculations consistently led to the result that $(\mathrm{Cl}^-)_o > (\mathrm{Na}^+)_o + (\mathrm{H}^+)_o$, which was taken to indicate that the protein chloride formed when hydrochloric acid came in contact with the isoelectric protein could not be assumed to be completely ionized. Therefore, instead of calculating the chloride-ion concentrations by the above equations, it was necessary to measure them, as described, with the silver-silver chloride electrode. This was done in the case of cow serum albumin. It was found that $(\mathrm{Cl}^-)_o$ obtained in this manner closely agreed with the sum of $[\mathrm{H}^+]_o$, obtained by measurement, and $(\mathrm{Na}^+)_o$, obtained by calculation. With the other two proteins, then, this relationship was assumed to hold and the $(\mathrm{Cl}^-)_o$ was taken to be equal to $(\mathrm{H}^+)_o + (\mathrm{Na}^+)_o$ without actually making the measurement with the silver-silver chloride electrode. From the $(\mathrm{Cl}^-)_o$ value the $(\mathrm{Cl}^-)_i$ value was obtained from the equation $(\mathrm{Cl}^-)_i = R\cdot(\mathrm{Cl}^-)_o$. (Electrode measurements of (Cl^-) in the presence of the colloid were never quite satisfactory, for some reason not yet determined. The voltage readings so obtained would indicate chloride-ion concentrations higher than those known to be present.) It is to be noted that hydrogen-ion activities are added to sodium-ion concentration outside. This is, of course, not strictly correct but apparently causes no great error, owing to the fact that at low ionic strengths the hydrogen-ion activity is very nearly equal to its concentration, while at those ionic strengths at which there would be an appreciable deviation of hydrogen-ion activity from hydrogen-ion concentrations, the amount of hydrogen ion present, as compared to sodium ion, has become so low as to make such a deviation (never more than 8 per cent) of minor importance in the totals.

In the tables, then, are given the calculated or measured values of the concentration per liter of each of the diffusible ions on each side of the membrane. These are totaled in the column under T and the difference between inside and outside is given under D. One mole of solute dissolved in 1 liter of solvent at 25°C. would give rise to an osmotic pressure equal to 25,280 cm. of water. This value multiplied by the value D in each experiment would give the osmotic pressure which should be derived from the unequal distribution of diffusible ions across the membrane (assuming their osmotic activity to be equivalent to their concentrations). The value, α', is defined as the number of equivalents of ions derived from unit weight of the colloid and can be calculated from the equation

$$\alpha' = \frac{(\mathrm{Cl}^-)_i - [(\mathrm{H}^+)_i + (\mathrm{Na}^+)_i]}{A/V_i \times 1000}$$

A quantity not needed for calculating the relationship being tested but which is of interest is W, the equivalents of chloride combined with unit

TABLE 1

Osmotic pressure and ionic distribution data for solutions of crystallized egg albumin

NO.	SIDE OF MEMBRANE	TOTAL IN 320 CC. OF SOLVENT (i + o) Cl	TOTAL IN 320 CC. OF SOLVENT (i + o) Na	A	F	V	P_o	HYDROGEN-ION CONCENTRATION E.M.F.	HYDROGEN-ION CONCENTRATION pH	HYDROGEN-ION CONCENTRATION $[H^+] \times 10^4$	E	R	$[Na^+] \times 10^4$	$[Cl^-] \times 10^4$	$W \times 10^4$	$\alpha' \times 10^4$	α'/W	$[T] \times 10^4$	$[D] \times 10^4$	P_e	$P_e - P_o$	$E\alpha' \times 10^4$	$A/V_i \times 25{,}280$	P_p (M = 35,000)	$P_e - P_o + P_p$	$\frac{E\alpha'}{P_e - P_o + P_p} \times 10^4$	$-\log \frac{E\alpha'}{P_e - P_o + P_p}$	$[+]_i \times 10^4$	$-\log [+]_i$
		eq. × 10³	eq. × 10³	gms.	gms.	cc.	cm. H₂O	mv.		eq./l.	mv.		eq./l.	eq./l.	eq./g.	eq./g.		eq./l.	eq./l.	cm. H₂O	cm. H₂O			cm. H₂O	cm. H₂O			eq./l.	
1	i	0.75	0	0.60	17.16	16.50	129.0	449.4	3.460	347	40.2	4.790	0	7980	399	211	0.529	8327	4993	126.2	−2.8	84.8	916	26.1	23.3	3.64	3.439	347	3.460
	o					302.6		409.2	2.778	1667			0	1667				3334											
2	i	0.95	0.20	0.60	16.00	15.40	128.9	444.9	3.362	415	35.5	3.980	163	9170	402	220	0.547	9748	5141	129.9	+1.0	78.2	984	28.1	29.1	2.69	3.571	578	3.238
	o					304.0		409.4	2.782	1652			650	2305				4607											
3	i	1.25	0.50	0.60	15.19	14.59	128.3	440.0	3.300	501	30.5	3.280	492	10700	401	236	0.588	11690	5170	130.6	2.3	72.0	1038	29.7	32.0	2.25	3.648	993	3.003
	o					304.8		409.5	2.783	1646			1615	3260				6520											
4	i	1.55	0.80	0.60	14.20	13.60	128.4	437.4	3.254	557	27.6	2.930	879	12325	396	247	0.623	13760	5350	135.1	6.7	68.2	1114	31.8	38.5	1.770	3.752	1436	2.842
	o					305.5		409.8	2.788	1630			2575	4205				8410											
5	i	1.75	1.00	0.60	13.96	13.36	128.2	436.2	3.236	581	26.3	2.786	1155	13480	410	261	0.638	15215	5539	140.0	11.8	68.8	1135	32.5	44.3	1.554	3.809	1736	2.760
	o					306.0		409.9	2.790	1621			3217	4838				9676											
6	i	2.75	2.00	0.60	11.91	11.31	128.0	432.8	3.179	662	21.3	2.292	2780	18070	454	276	0.603	21510	5740	145.0	17.0	58.8	1345	38.4	55.4	1.050	3.978	3440	2 463
	o					308.1		411.5	2.820	1514			6370	7684				15770											
7	i	5.75	5.00	0.60	8.95	8.35	127.2	428.0	3.096	801	14.5	1.761	9000	30400	507	286	0.565	40200	5700	144.0	16.8	41.5	1816	51.9	68.7	0.604	4.219	9800	2.009
	o					311.1		413.5	2.850	1412			15840	17250				34500											
8	i	10.75	10.00	0.60	7.18	6.58	126.7	426.1	3.064	862	10.7	1.516	20800	49800	556	309	0.556	71420	5780	146.0	19.3	33.1	2305	65.8	85.1	0.390	4.410	21660	1.664
	o					312.9		415.4	2.882	1312			31520	32830				65640											
9	i	30.75	30.00	0.60	Coagulated		125.0																						
	o																												

Legend for the tables: i and o signify inside and outside the membrane. *Cl*, Na = equivalents (total) of each of these atoms present in system (i + o). A = weight (in grams) of dry isoelectric protein present inside the membrane. F = weight (in grams) of the protein-containing solution (inside) at equilibrium. V = volume (in cc.) of solvent present at equilibrium (i and o). P_o = constant pressure (cm. H_2O) (on inside solution) at which equilibrium was attained. $[H^+]$, $[Na^+]$, $[Cl^-]$ = concentrations (equivalents per liter) observed or calculated for these ions at equilibrium. $E = 59.1 \times (pH_i - pH_o)$ (in millivolts). R = antilog $E/59.1$ = ratio of distribution, $[H^+]_o/[H^+]_i$, of hydrogen ions at equilibrium. W = amount (equivalents) of hydrochloric acid which has combined with unit weight of protein (at equilibrium). α' = amount (equivalents) of chloride ion derived from unit weight of protein (chloride). α'/W = per cent dissociation of protein chloride. $[T]$ = total amount (equivalents per liter) of diffusible ions in the i and o solutions at equilibrium. $[D]$ = difference in amount (equivalents per liter) of diffusible ions inside and outside the membrane at equilibrium. $P_e = [D] \times 25280$ = calculated osmotic pressure due to diffusible ions alone. P_p = calculated osmotic pressure due to protein when the molecular weight has the value of M. $[+]_i$ = concentration (equivalents per liter) of diffusible ions inside the membrane and bearing the same sign of charge as the protein, i.e., a measure of foreign salt concentration inside.

TABLE 2

Osmotic pressure and ionic distribution data for solutions of cow serum albumin

No.	Side of membrane	Total in 320 cc. of solvent (i + o)		A	F	V	P_o	Hydrogen-ion concentration			E	R	$[Na^+] \times 10^6$	Chloride-ion concentration		$W \times 10^6$	$\alpha' \times 10^6$	α'/W	$[T] \times 10^6$	$[D] \times 10^6$	P_c	$P_c - P_o$	$B\alpha' \times 10^4$	$A/V_i \times 25{,}280$	P_p (M = 60,000)	$P_c - P_o + P_p$	$\frac{B\alpha'}{P_c - P_o + P_p} \times 10^4$	$-\log \frac{B\alpha'}{P_c - P_o + P_p}$	$[+]_i \times 10^6$	$-\log [+]_i$
		Cl	Na					E.M.F.	pH	$[H^+] \times 10^6$				E.M.F.	$[Cl^-] \times 10^6$															
		eq. × 10^3	eq. × 10^3	gms.	gms.	cc.	cm. H_2O	mv.		eq./l.	mv.		eq./l.	mv.	eq./l.	eq./g.	eq./g.		eq./l.	eq./l.	cm. H_2O	cm. H_2O			cm. H_2O	cm. H_2O			eq./l.	
1	i	0.50	0	0.40	11.43	11.03	128.2	464.2	3.710	195	45.7	5.930	0		6970	348	186	0.535	7165	4830	122.0	−6.2	85.2	917	15.3	9.1	9.37	3.028	195	3.710
	o					308.6		418.5	2.935	1162			0	153.0	1175				2335											
2	i	0.70	0.20	0.40	11.47	11.07	128.3	458.8	3.618	241	39.6	4.680	137		8170	373	215	0.577	8550	5035	127.2	−1.1	85.4	913	15.2	14.1	6.06	3.218	378	3.422
	o					308.5		419.2	2.948	1127			641	143.2	1745				3515											
3	i	1.00	0.50	0.40	11.40	10.90	127.6	454.7	3.547	284	33.6	3.705	433		9850	435	249	0.573	10565	5255	132.8	+5.2	83.6	927	15.4	20.6	4.06	3.392	717	3.144
	o					308.7		421.1	2.980	1047			1604	132.6	2660				5310											
4	i	1.30	0.80	0.40	10.74	10.34	127.9	452.5	3.512	307	30.4	3.270	783		11550	463	271	0.585	12640	5540	140.0	12.1	82.4	977	16.3	28.4	2.90	3.537	1090	2.963
	o					309.3		422.1	2.997	1007			2560	125.5	3530				7100											
5	i	1.50	1.00	0.40	10.25	9.75	127.2	451.9	3.500	316	28.7	3.060	1047		12680	497	276	0.555	14040	5730	144.8	17.6	79.2	1037	17.3	34.9	2.27	3.644	1360	2.86
	o					309.1		423.2	3.015	966			3200	121.8	4145				8310											
6	i	2.50	2.00	0.40	9.15	8.75	127.2	448.6	3.446	358	22.6	2.410	2640		17300	569	313	0.550	20300	5900	149.1	21.9	70.7	1155	19.2	41.1	1.72	3.764	2998	2.52
	o					310.8		426.0	3.062	867			6360	108.0	7175				14400											
7	i	5.50	5.00	0.40	7.00	6.60	126.9	445.2	3.386	411	15.4	1.820	8690		30340	661	351	0.531	39440	6230	157.5	30.6	54.1	1520	25.5	56.1	0.964	4.016	9101	2.041
	o					313.0		429.8	3.128	744			15800	87.6	16670				33210											
8	i	8.50	8.00	0.40	5.91	5.51	126.4	444.9	3.381	416	12.7	1.640	15370		42650	711	370	0.521	58440	6560	165.9	39.5	47.0	1833	30.6	70.1	0.670	4.174	15786	1.802
	o					314.1		432.2	3.168	679			25200	76.6	26000				51880											
9	i	10.50	10.00	0.40	5.28	4.88	126.6	444.8	3.381	416	11.6	1.571	20030		50800	729	370	0.507	71250	6760	170.8	44.2	42.9	2073	34.5	78.7	0.546	4.263	20446	1.689
	o					314.7		433.2	3.183	656			31480	72.0	32350				64490											
10	i	20.50	20.00	0.40	3.63	3.43	126.4	444.4	3.373	424	9.0	1.420	44210		89600	771	385	0.500	134230	7750	195.8	69.4	34.7	2948	49.1	118.5	0.293	4.533	44630	1.350
	o					316.2		435.4	3.222	600			62780	56.0	63100				126480											
11	i	50.50	50.00	0.40	1.68	1.28	124.7				Inside solution formed stiff gel																			
	o					318.3		439.1	3.284	520																				

TABLE 3

Osmotic pressure and ionic distribution data for solutions of crystallized horse serum albumin

NO.	SIDE OF MEMBRANE	TOTAL IN 320 cc. OF SOLVENT (i + o)		A	F	V	P_o	HYDROGEN-ION CONCENTRATION			E	R	$[Na^+] \times 10^6$	$[Cl^-] \times 10^6$	$W \times 10^6$	$\alpha' \times 10^6$	α'/W	$[T] \times 10^6$	$[D] \times 10^6$	P_e	$P_e - P_o$	$B\alpha' \times 10^4$	$A/V_i \times 25{,}280$	P_p (M = 80,000)	$P_e - P_o + P_p$	$\frac{B\alpha'}{P_e - P_o + P_p} \times 10^4$	$-\log \frac{B\alpha'}{P_e - P_o + P_p}$	$[+]_i \times 10^4$	$-\log [+]_i$
		Cl	Na					E.M.F.	pH	$[H^+] \times 10^6$																			
		eq. × 10³	eq. × 10³	gms.	gms.	cc.	cm. H_2O	mv.		eq./l.	mv.		eq./l.	eq./l.	eq./g.	eq./g.		eq./l.	eq./l.	cm. H_2O	cm. H_2O			cm. H_2O	cm. H_2O			eq./l.	
1	i	0.50	0	0.40	12.88	12.48	128.0	467.9	3.770	170	48.5	6.620	0	7425	383	227	0.590	7595	5350	135.2	7.2	109.8	810	10.1	17.3	6.35	3.197	170	3.770
	o					307.1		419.4	2.950	1122			0	1122				2244											
2	i	0.70	0.20	0.40	12.75	12.35	128.4	462.7	3.684	207	41.5	5.030	128	8510	440	253	0.575	8845	5461	138.0	9.6	104.7	819	10.2	19.8	5.29	3.277	335	3.475
	o					307.2		421.2	2.980	1047			644	1693				3384											
3	i	1.00	0.50	0.40	12.59	12.19	128.0	458.2	3.609	246	35.1	3.930	410	10140	499	289	0.580	10796	5636	142.5	14.5	101.4	829	10.3	24.8	4.09	3.388	656	3.183
	o					307.4		423.1	3.014	968			1610	2580				5160											
4	i	1.30	0.80	0.40	12.27	11.87	127.1	455.6	3.564	273	30.6	3.290	780	11410	548	307	0.560	12460	5520	139.5	12.4	94.1	852	10.6	23.0	4.09	3.388	1053	2.979
	o					307.7		425.0	3.045	902			2565	3470				6940											
5	i	1.50	1.00	0.40	11.62	11.22	127.7	454.3	3.542	287	28.5	3.030	1057	12330	570	308	0.540	13670	5530	139.8	12.1	87.8	901	11.2	23.3	37.7	3.424	1344	2.872
	o					308.4		425.8	3.060	871			3200	4070				8140											
6	i	1.80	1.30	0.40	11.17	10.77	127.8	453.1	3.521	301	26.0	2.750	1510	13700	603	320	0.530	15510	5550	140.3	12.5	83.2	939	11.7	24.2	3.44	3.463	1811	2.742
	o					308.9		427.1	3.082	828			4150	4980				9960											
7	i	2.50	2.00	0.40	9.94	9.54	127.4	449.5	3.462	345	21.7	2.328	2735	16780	610	327	0.530	19860	5500	139.0	11.6	71.0	1060	13.2	24.8	2.86	3.544	3080	2.511
	o					310.1		427.8	3.093	807			6370	7180				14360											
8	i	5.50	5.00	0.40	6.89	6.49	126.4	446.0	3.410	389	13.9	1.719	9190	28300	723	304	0.420	37880	4960	125.4	−1.0	42.2	1558	19.4	18.4	2.29	3.639	9580	2.019
	o					313.0		432.7	3.176	666			15790	16460				32920											
9	i	8.50	8.00	0.40	5.69	5.29	126.2	446.2	3.405	394	10.9	1.528	16480	39420	773	298	0.385	56290	4690	118.6	−7.6	32.5	1910	23.9	17.2	1.89	3.723	16874	1.773
	o					314.3		435.3	3.221	601			25200	25800				51600											
10	i	10.50	10.00	0.40	5.33	4.93	126.0	447.0	3.416	384	9.8	1.465	21460	46920	804	309	0.384	68760	4700	118.6	−7.2	30.3	2050	25.6	18.4	1.65	3.783	21844	1.660
	o					314.7		437.2	3.251	581			31470	32030				64060											

weight of the colloid. W is obtained from the knowledge of the equivalents of hydrochloric acid originally added to the system and the equivalents of hydrogen ion remaining in the system at equilibrium, according to the equation

$$W = \frac{\text{Total HCl added (equivalents)} - \left[\left([\mathrm{H}^+]_i \cdot \frac{V_i}{1000}\right) + \left([\mathrm{H}^+]_o \cdot \frac{V_o}{1000}\right)\right]}{A}$$

The percentage ionization of the protein chloride is given by the ratio α'/W.

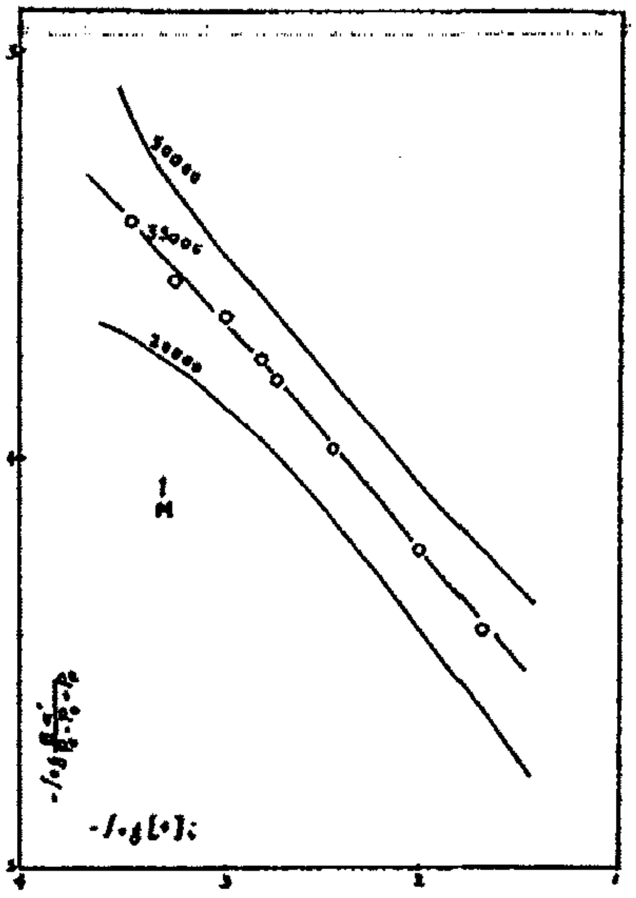

FIG. 1. OVALBUMIN

Any osmotic pressure due to the protein molecule, P_p, must be subtracted from the observed osmotic pressure, P_o, in order to obtain the fractional osmotic pressure due to the diffusible ions, before this can be analyzed to find if the same relationship exists when the colloid is a protein as has been found to exist for gum arabic. The value of P_p is obtained from the equation,

$$P_p = \frac{A/V_i \cdot 10^3 \cdot 25280}{M}$$

where M is the molecular weight of the protein. Plotting $\log \frac{E\alpha'}{P_c - (P_o - P_p)}$ against $\log\,[(\mathrm{H}^+) + (\mathrm{Na}^+)]_i$ should give a straight line if the proper value for M is chosen and if the relationship found in the case of the gum arabate also holds for the diffusible ions in the system containing the protein. If

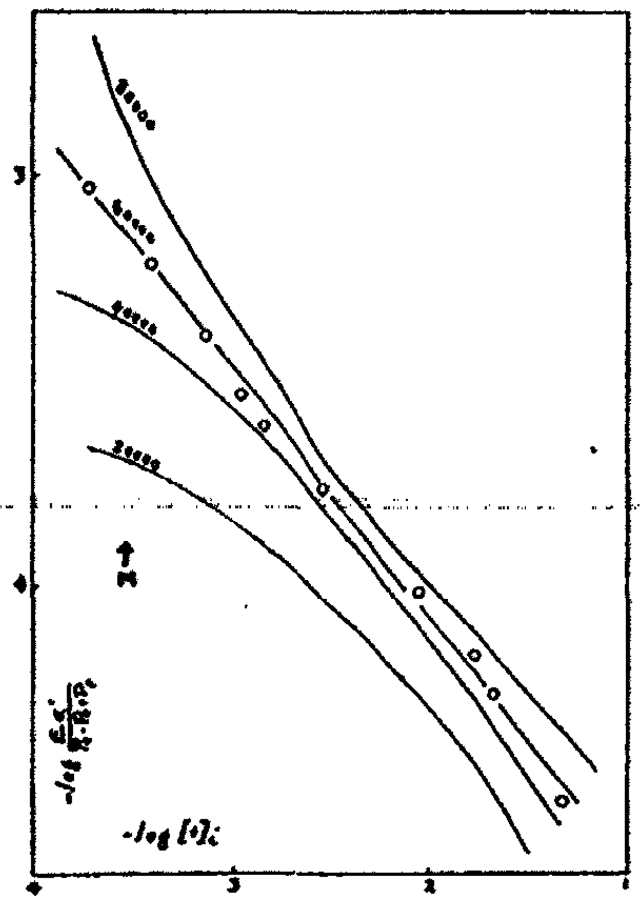

Fig. 2. Cow Serum Albumin

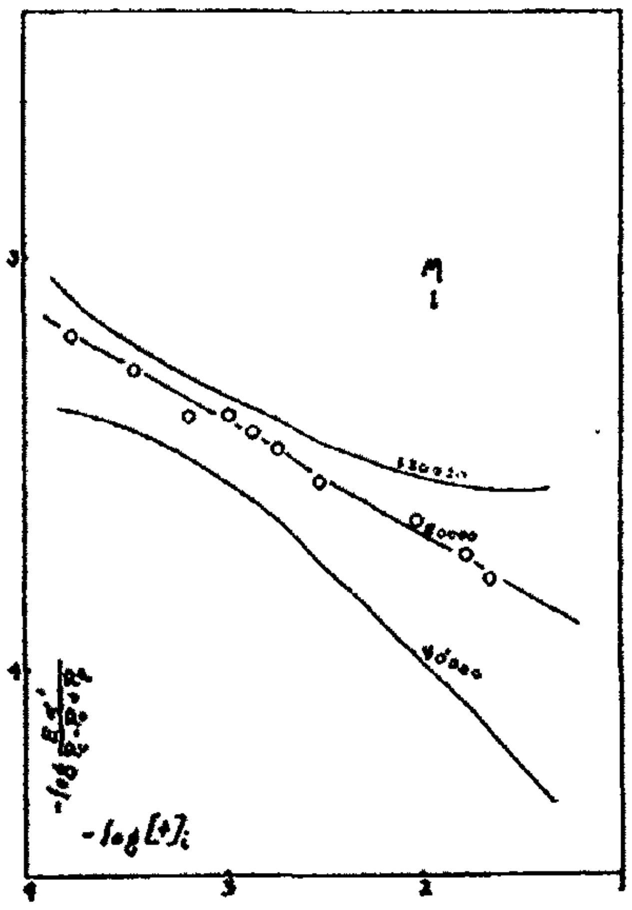

Fig. 3. Horse Serum Albumin

too high a value for M is chosen in calculating P_p, when the above factors are plotted a curve will be obtained convex in one direction; if M is too small a curve will be obtained which is convex in the other direction, and the proper value of M will give a straight line lying between these curves, as is shown by the figures.

DISCUSSION

Figures 1, 2, and 3 show the plotted values of log $\frac{E\alpha'}{P_c - P_o + P_p}$ against log $(+)_i$ for the experiments with egg albumin, cow serum albumin, and horse serum albumin, respectively. In each, varying values of M, the molecular weight of the protein, are used in calculating P_p. The graphs show straight lines when M is of the order of 35,000 for egg albumin, of 60,000 for cow serum albumin, and of 80,000 for horse serum albumin. Other values for M in each case give curved lines, the assumed values for M being indicated thereon.

The values for the molecular weights of egg albumin and horse serum albumin as determined by other methods are of the same order of magnitude as those for which straight lines are obtained in these graphs. This can be taken as proof that the empirical relationship found to exist for osmotic pressures derived from diffusible ions in the case of gum arabic solutions, holds also for protein solutions where the colloidal molecules are of sufficiently small dimensions to exhibit an appreciable osmotic pressure of their own. Also, it appears that the molecular weights and osmotic activities of the colloids under the conditions of the present experiments are not markedly different from those shown at the isoelectric point and in the absence of a Donnan equilibrium.

It cannot be claimed that this method is an accurate one for the determination of molecular weights of colloid electrolytes. So many calculations are involved that a small experimental error becomes a relatively large variation in the final values of $\frac{E\alpha'}{P_c - P_o + P_p}$. A change in M of over 15 per cent (greater at higher values of M) would be required before the straightness of the plotted line would be definitely destroyed. The method can, therefore, give only an approximation of the molecular weight of the colloid. The experiments show clearly that when the colloid osmotic pressure is corrected for, the relationships found to exist for osmotic pressures resulting from the unequal distribution of ions across the membrane in the case of gum arabic also hold in the case of proteins, where the molecules of colloid offer an appreciable fraction of the total osmotic pressure of the colloid-containing solutions. The membrane acts truly semipermeable for the colloid, which is retained mechanically from passing through, and its osmotic activity is proportional to its concentration difference across the membrane. For the diffusible ions, the equilibrium unequality across the membrane is due to electrostatic forces and not mechanical obstruction. The osmotic pressure due to these ions is not proportional to their total concentration difference across the membrane. The deviation ($P_c - P_o$) from this expected proportionality is proportional to the same factors as found in the gum arabic experiments. A theoretical basis for this obscured relationship has not yet been arrived at. Until this is done, the significance of slope and intercepts of the straight lines of figures 1, 2, and 3 cannot be given.

The number of equivalents of acid, W, which combine with unit weight of the protein in the various experiments is of interest. In the experiments shown in the tables the total equivalents of acid added were constant and increasing amounts of sodium chloride were added. This increase in salt content of the system caused a decrease in R, the ratio of distribution of ions across the membrane, thus causing a higher hydrogen-ion concentration to exist inside of the membrane, with a consequent greater binding of hydrochloric acid by the protein. The degree of ionization, α'/W, of this protein chloride appears to be only of the order of 50 to 60 per cent under the conditions of these experiments. In other experiments, the data for which are not included in this paper, it becomes apparent that as the pH of the protein solution is varied progressively away from the isoelectric point of the protein, W increases rapidly through the first increments of pH and then more slowly as saturation is reached in solutions of high acid content. At the same time the value of α'/W increases slowly at first then more rapidly, until in solutions of high acid content (i.e., most distant from the isoelectric point) the degree of dissociation approaches 100 per cent. This means that protein salts act as progressively stronger electrolytes as the pH of their environment deviates from the isoelectric point of the protein. From this it would be expected that the degree of ionization of the "Zwitterion" in the isoelectric protein solution would have a very low percentage of the total possible ionizable groups actually ionized.

SUMMARY

An empirical relationship which had already been found to exist for gum arabic solutions in defining the deviation between the observed osmotic pressure (P_o) and the calculated osmotic pressure (P_c) due to the unequal distribution of diffusible ions, is found to hold for protein solutions when correction is made for the osmotic pressure due to the colloid itself. (With gum arabic the size of the micellae was so large as to be negligible in comparison with that due to the diffusible ions.) Conversely, if this empirical correction for the osmotic pressure due to the diffusible ions is assumed to hold for protein solutions, it becomes possible to determine the molecular weights of the proteins in dilute solutions and in solutions having hydrogen-ion concentrations other than those at the isoelectric points of the proteins.

Three proteins were subjected to this analysis. Molecular weights were found to be 35,000, 60,000, and 80,000 (±ca. 15 per cent) for crystallized egg albumin, uncrystallized cow serum albumin, and crystallized horse serum albumin, respectively.

This relationship for the protein solutions is

$$\frac{E\alpha'([\pm]_i)^x}{P_c - P_o + P_p} = \text{a constant}$$

(at all values of hydrogen-ion, salt, and colloid concentrations) where:

P_o = observed osmotic pressure.

P_c = osmotic pressure (calculated) on basis of unequal distribution of diffusible ions.

P_p = osmotic pressure (calculated) due to protein of molecular weight = M.

E = 59.1 ($pH_o - pH_i$) = the membrane potential.

α' = equivalents of diffusible ion derived from unit mass of the protein.

$[\pm]_i$ = concentration of all ions, bearing same sign of charge as the protein, in the colloid-containing solution, i.e., foreign salt concentration inside the membrane.

x = a constant for a given colloid.

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INFLUENCE OF GASES ON SILVER SOLS

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In a previous paper (3) gases were found to have a stabilizing effect on Zsigmondy gold sols toward electrolytes, but no increase in charge was observed by measurement of cataphoretic velocity. The increase in stability was observed only with sols which apparently contained secondary particles. The study has been extended to other colloidal systems, and the results on silver sols are reported in this paper.

PREPARATION OF SOLS

Bredig silver sols

Bredig silver sols were prepared by the usual method of maintaining an arc between two silver electrodes. By use of a dismantled microscope for feeding the wire and a large inductance coil (1), a steady arc could be maintained. Owing to the formation of gases and the high per cent of silver oxide (8), Bredig silver sols were not entirely satisfactory for this investigation. Our experience in the preparation of other than a very dilute sol is not in accord with that of Best and Cox (2), who report no difficulty in preparing sols in water with a specific conductivity of 0.4 to 0.6 $\times 10^{-6}$ mhos. Difficulty was also encountered in preparing a sol of sufficient concentration for our studies by use of freshly purified sodium hydroxide at the optimum concentration reported by Pauli and Perlak (6). However, sodium hydroxide which had been standing in glass bottles gave good results. This led to an investigation which showed that sodium silicate in concentrations as low as 6×10^{-7} *N* produced a comparatively stable silver sol. Water which had been standing in soft glass bottles a short time or in Pyrex bottles for twenty to thirty days gave similar results. Consequently a study was made by one of the authors (7) to determine the extent and effect of the solution of glass from bottles under laboratory conditions.

Kohlschütter silver sols

These sols proved to be unsuitable for the study of the influence of gases on their properties, because hydrogen is used in the reduction of the silver oxide solution. Since silicates dissolved from glass were found to affect the stability of Bredig sols so markedly, it was thought that greater amounts of silicates would be dissolved at the higher temperatures used for reduction in Kohlschütter's method (50–60°C.) and would contribute much more to the sols' properties than has generally been attributed. Accordingly a rather extended study was made on the influence of surface and solubility of glass on these sols, but before the completion of this work a paper by Weiser and Roy (10) was published which corroborates the results obtained in this laboratory.

TABLE 1

Effect of bubbling gases on the precipitation value of silver sols

SOL. NO.	ORIGINAL	OXYGEN	NITROGEN	HYDROGEN	METHANE	ETHYLENE
Bredig 2	7.0	13.0	11.0	5.0		
3	8.0	14.0	14.0	6.0		
4	10.0	17.0	18.0	2.0		
5	22.0		23.0	12.0		23.0
Formol 1	7.0	20.0	20.0	22.0	32.0	34.0
2	20.0	32.0	28.0	34.0	42.0	45.0
3	34.0		38.0	44.0		44.0
4	40.0	40.0	40.0	40.0		40.0
5	42.0	42.0	43.0	43.0	42.0	42.0

TABLE 2

Effect of gas pressure on precipitation value of silver sols

SOL. NO.	ORIGINAL	OXYGEN	NITROGEN	HYDROGEN	METHANE	ETHYLENE
Bredig 1	7.0	12.3	10.0	5.0		
4	10.0	14.5		2.5		
Formol 1	7.0	12.0		16.0	20.0	18.0
2	20.0			28.0	28.0	30.0
4	40.0	40.0		40.0		40.0

Formol silver sols

Silver sols prepared by reduction of silver nitrate in the presence of a small amount of bromide or iodide with formaldehyde as described by the authors (8) proved to be particularly suited to the study of the effect of gases on their properties.

RESULTS

In order to study the influence of gases on the sols, measurements were made of their precipitation values, cataphoretic velocities, and conductances before and after treatment. Precipitation values were measured by diluting varying volumes of 0.1 *N* sodium nitrate to 15 cc. and mixing quickly with 10 cc. of the sol by use of a tube made as described by Weiser and Middleton (9). Cataphoresis measurements were made by the Burton moving boundary method in a set-up similar to that suggested by Kruyt and van der Willigen (4), and calculations were made as previously described (3).

TABLE 3

Effect of treatment on stability of silver sols

FORMOL SOL NO.		ORIGINAL SOL CORKED TIGHT	METHANE BUBBLED	STIRRING WITH MOTOR IN CORKED, FILLED FLASK	BOILING UNDER VACUUM	SHAKING IN FLASK OPEN TO AIR	STANDING OPEN TO AIR
6	Precipitation value........	8.0	22.0	10.0	2.0	20.0	12.0
	Color..........	Milky green	Yellow	Yellowish green	Green	Yellow	Greenish yellow
7	Precipitation value........	6.0	28.0	8.0	Precipitate	20.0	10.0
	Color..........	Milky green	Yellow	Yellowish green		Yellow	Greenish yellow

TABLE 4

Effect of gases on cataphoretic velocity of silver sols

Values in cm./sec./volt/cm. × 10^6 at 25°C.

SOL NO.	ORIGINAL	OXYGEN		NITROGEN		HYDROGEN		METHANE		ETHYLENE	
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Bredig 3	48	48		47	42						
4	41	41	47	41	46	40	41				
Formol 1	41	41	42			41	41	40	41	41	42
3	42	43	42			41	42	43	41	41	42
4	40	40	41	41	40	41	40	40	41	40	

(a) Gas bubbled through sol for 3 hours.
(b) Two atmospheres gas pressure.

Gases were run through the silver sols in well-leached Pyrex Erlenmeyer flasks for a period of about three hours, which was sufficient to give the maximum effect. The effects of gases on the Bredig and the formol silver sols are given in table 1. A portion of the sol was kept in a completely filled and tightly corked flask on which tests were made for the original value. The precipitation values are all given in millimoles of sodium nitrate just necessary to cause precipitation.

To determine whether the stabilizing action was due to the agitation or to the presence of gases, samples of the same sols were treated with gases under a pressure of 2 to 3 atmospheres for the same length of time. In general, gases under pressure stabilized the sol, but the effect was not as great as that caused by bubbling. The results are tabulated in table 2.

Experiments, as tabulated in table 3, were carried out to determine whether agitation alone, in the absence of gases, increased the stability.

The results of the cataphoresis measurements are given in tables 4 and 5. Table 4 gives a summary of some of the results for different gases, and table 5 gives detailed values taken during the measurements on two of the sols treated with hydrogen and methane respectively. Table 6 gives some of the results of conductance measurements before and after treatment with gases.

TABLE 5

Effect of methane and hydrogen on cataphoretic velocity

FORMOL SOL NO. 3	TIME IN MINUTES	VOLTS	DISTANCE BETWEEN ELECTRODES IN CM.	DISPLACEMENT TOWARD POSITIVE POLE IN CM. (UP)	DISPLACEMENT AWAY FROM NEGATIVE POLE IN CM. (DOWN)	VELOCITY IN CM./SEC./VOLT/CM. × 10^5
Original	20	70	28.6	1.35	1.05	40.9
Hydrogen	20	70	28.6	1.20	1.20	40.9
Methane	20	70	28.6	1.25	1.20	41.7
Methane, pressure	20	70	28.6	1.30	1.15	41.7

TABLE 6

Effect of gases on conductance of silver sols

Values in mhos × 10^6 at 25°C.

SOL NO.	ORIGINAL	OXYGEN	NITROGEN	HYDROGEN	HYDROGEN PRESSURE	ETHYLENE
Bredig 3	35.5	32.4	32.5	19.6	26.9	
4	49.2	48.4	49.0	26.3	33.0	
Formol 1	423	422		423	422	
2	453	452	452	453		452
4	511	511	512	511	511	512

DISCUSSION

The results given above show that the presence of gases produced a stabilizing effect on the silver sols except in the case of Bredig sol No. 5 and formol sols Nos. 4 and 5. Bredig sol No. 5 was made by adding slightly more sodium silicate than the amount necessary to produce a sol of fair concentration. Formol sols Nos. 4 and 5 were made by adding 5 cc. and 10 cc. of 0.01 *N* potassium bromide compared to 1.75 cc., 2.0 cc., and 2.5 cc. of 0.01 *N* potassium bromide for sols 1, 2, and 3 respectively. Formol sols Nos. 4 and 5 were yellow and clear by transmitted light, indicating a high and uniform degree of dispersion. The other three sols were cloudy and milky green when prepared and remained unchanged on standing in a stoppered flask. Bubbling gases through the cloudy sols changed the color from milky green to a clear yellow, indicating a higher and more uniform degree of dispersion. No effect on the color of the yellow sols having the larger amounts of potassium bromide was discernible after treatment with gases. Thus, it appears that gases affect only those sols which are on the border line of stability and which apparently contain secondary particles, that is, an agglomeration of two or more primary particles. If less than 1.75 cc. of 0.01 *N* potassium bromide was used, the sol was unstable, and gases would not stabilize it. Gases apparently do not take the place of stabilizing ions. Hydrogen decreased the stability of Bredig silver sols, owing to reduction of silver oxide and hydroxide as shown by conductance measurements in table 6.

A much larger number of experiments were made than those given in the tables, and in many of these the amount of electrolyte necessary for complete precipitation of *all* of the colloid in some of the milky green sols which had been tightly corked was rather high, even though 1 cc. to 2 cc. caused more than two-thirds of the colloid to settle out. This partial precipitation would indicate an inhomogeneous sol. In the case of the yellow sols greater uniformity was shown, because complete precipitation occurred when the characteristic color change was produced. More vigorous stirring during preparation should, therefore, tend to form a more homogenous sol.

The cataphoretic velocity measured and calculated as above is apparently not changed, within the limits of error, by treatment with gases. However, examination of the displacements in the positive and negative arms of the tube before and after treatment with gases as given in table 5 showed that there had been a change either in the electrical nature or in the size of the particles. Settling of the larger particles in the negative arm should tend to even up the displacements, so the effect was not due to a change in the size of the particles; moreover, since the conductance of the sols remained unchanged, the effect was due to differences in distribution of charges on the particles.

In all cases the sum of the displacements was the same within the limits of error in reading the boundary, but the displacement upward toward the positive pole for the original sol was 1.35 cm. while the displacement downward away from the negative pole was 1.05 cm. After treatment by bubbling gases, and for the yellow sols in general, the displacements were more nearly even, about 1.2 cm. in each arm. This indicates that before treatment some of the particles had a higher negative charge than others and were attracted to the positive pole faster than the less negative ones were repelled by the negative pole, thus giving different values for the displacements. After treatment with gases, it appears that the particles all had nearly the same charge. A redistribution of stabilizing ions must have resulted from the agitation during treatment with gases. This conclusion is borne out by the observations given in the previous paragraph on their behavior during precipitation. These observations show that the moving boundary method of determining cataphoretic velocity makes it particularly useful in obtaining the *average* charge on the colloidal particles. If the above explanations are true, then the contentions of Mukherjee (5) that the upper liquid used should always be adjusted so that the displacements of the upward and downward moving boundaries are the same are not entirely justified in all cases.

Since the values in table 3 show that agitation alone will not produce the increase in stability or effectively cause as even a distribution of stabilizing ions as treatment with gases, it may be assumed as in the previous paper (3) that the gases are adsorbed in a layer on the surface of the particle, thus modifying adsorption of ions from the precipitating electrolyte. Only those sols on the border line of stability are affected by gases. This apparently means that they furnish some surface on which the gases may be adsorbed. By use of larger amounts of potassium bromide the surface may be covered with the more strongly adsorbed layer of bromide ions. This is in accord with the theories of poisoning of catalytic surfaces. Just why the agitation in the presence of gases should cause a more uniform and more permanent distribution of stabilizing ions, we are not fully prepared to explain. However, in the presence of gases it may be assumed that as soon as secondary particles are broken up the adsorbed gas prevents re-formation of secondary particles. Also if the presence of a gas is not accompanied by agitation, the secondary particles may not be as readily broken up, and contact between the gas and the surface of the particle is limited.

SUMMARY

1. A discussion of the methods and difficulties involved in preparing silver sols has been given.
2. The influence of gases on silver sols treated in various ways has been determined by measurement of precipitation values, cataphoretic velocities, conductances, and color changes.
3. Gases seem to have a stabilizing effect on those sols which are on the border line of stability and which apparently contain secondary particles. Agitation with gases produces a uniform distribution of stabilizing ions giving an apparently homogeneous sol. When the secondary particles are

broken up, the adsorbed gas apparently prevents their re-formation. No increase in the *average* charge of the particles was observed by measurement of cataphoretic velocities.

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THE ELECTRIC MOMENTS OF SOME ORGANIC COMPOUNDS

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Many para-disubstituted benzene derivatives, like *p*-dichloro- and *p*-dinitrobenzene, have zero moments. This zero moment is to be expected if the benzene ring is flat, since the two substituted dipoles are exactly equal and act in diametrically opposite directions. That certain para compounds with identical groups do possess a definite dipole moment was first discovered by Hassel and Naeshagen (4). They report the moment of the *p*-phthalaldehyde molecule to be 2.85×10^{-18} E.S.U., but they offer no explanation for the apparent abnormal behavior.

This apparent anomaly has been explained by Bergman and Engle (1) on the basis of the theory that the moment of the aldehyde group does not act along the line joining the group to the benzene nucleus. Hence, considering the possibility of free rotation about the bond, the two vector moments may, or may not, act at an angle of 180°, as was previously supposed in all para compounds.

This type of anomalous moments has since been found to be a common characteristic of all molecules containing an —OR group attached to the benzene nucleus, where R may be a hydrogen atom, an alkyl group, an acyl radical, or groups containing oxygen, like —CHO and —COOR. It also occurs when the substituted groups are $—NH_2$, —NHR, or $—NR_2$.

The present paper contains the results obtained from a study of the electric moments of some substituted benzaldehydes, of the three ethanolamines, and of 2-ethylhexanol-1 and the corresponding aldehyde.

APPARATUS AND MATERIALS

The dielectric constants of the solutions were measured by the usual heterodyne beat method, using dynatron oscillators (3) for both variable and constant frequency circuits. The circuit diagram, shown in figure 1, was chosen because of its demonstrated frequency stability. The measuring cell, figure 2, consists of two gold-plated brass discs, one rigidly fixed and the other mounted on the end of a micrometer screw. With this arrangement the position of the plates may be changed and precisely duplicated. The plates were suspended from a tight-fitting Bakelite disc, which also serves as the cover of the Pyrex jar containing the solution under investigation.

The densities were determined by means of a 30-cc. Ostwald-Sprengel pycnometer and are accurate to one part in 300,000. The refractive indices of the liquids were measured by means of a large Pulfrich refractometer provided with a heating device. All measurements were made at 25°C. ± 0.01°. The weighings were made with certified weights and were corrected for air buoyancy.

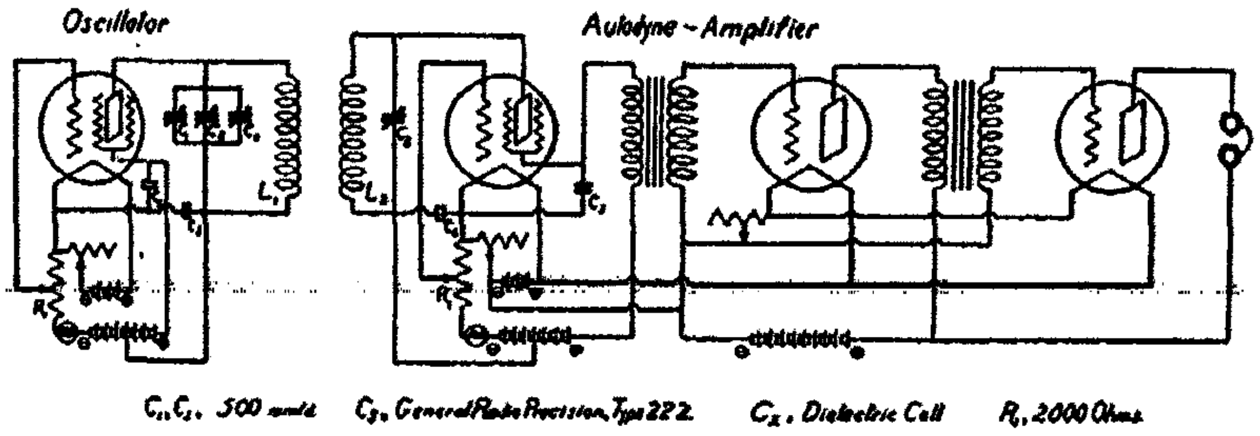

FIG. 1. THE CIRCUIT DIAGRAM

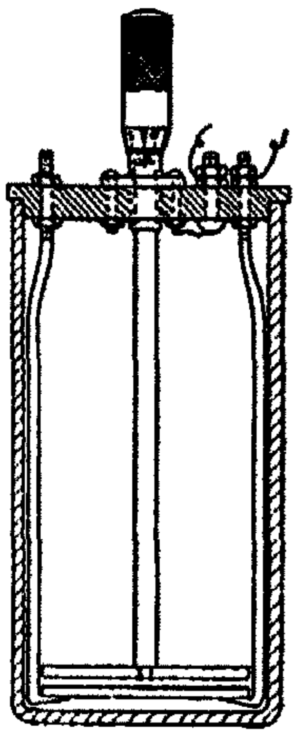

FIG. 2. THE MEASURING CELL

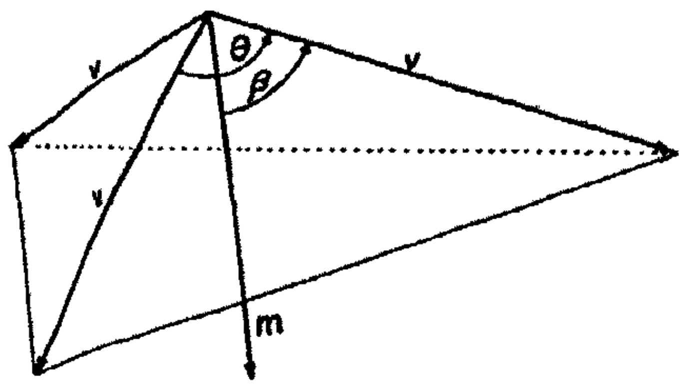

FIG. 3. THREE-VECTOR DIAGRAM

The benzene was made thiophene-free and then carefully purified in the approved standard way. It was finally dried over sodium wire, fractionally distilled, and fractionally crystallized. The boiling point of the middle fraction obtained by distillation through a Loveless column (7) was 80.1°C. at 760 mm.; its freezing point was 5.4°C. Commercial 1,4-dioxane was carefully purified by the method of Kraus and Vingee (6). The final distillation gave a middle fraction boiling at 101.3°C. at 760 mm.

The various aldehydes used were either Eastman's highest grade products, or they were specially prepared in our Division of Organic Manufactures under the direct supervision of Dr. George H. Coleman. They were further purified by accepted methods. Commercial triethanolamine from the Carbide and Carbon Chemicals Corporation was fractionally distilled under reduced pressure, using a small still of the Loveless type (7), modified for operating at reduced pressures. Repeated fractionation yielded the three pure amines. Their boiling points were: monoethanolamine, 65.0°C. at 5 mm.; diethanolamine, 134.0°C. at 3 mm.; triethanolamine, 175.0°C. at 2 mm.

The 2-ethylhexanol-1, also obtained from the Carbide and Carbon Chemicals Corporation, was first treated with metallic sodium wire to remove water and the lower alcohols. It was then fractionally distilled, and the middle fraction boiling at 185.5°C. at 760 mm. was retained. The α-ethylcaproaldehyde, from the same company, was dried over phosphorus pentoxide and fractionally distilled; its b.p. was 163.4–163.5°C. at 760 mm. Dioxane was used as the solvent for the three ethanolamines and *p*-bromo- and *p*-hydroxy-benzaldehyde, while benzene was the solvent for the remaining compounds.

EXPERIMENTAL

The experimental data are collected in table 1. Here, N_2 is the mole fraction of the dissolved substance, K is the dielectric constant, and d is the density of the solutions. Each value given is the mean of several closely agreeing, independent determinations. In table 2 are collected the values obtained for the total polarization, P_∞, the molar refractivity, MR_D, and the electric moment, μ, of the compounds studied.

The total polarization was calculated by means of the equation (5):

$$P_\infty = \frac{K_1 - 1}{K_1 + 2}\,\frac{1}{d_1}\left(M_2 - \frac{d - d_1}{N_2}\cdot\frac{M_1}{d_1}\right) + \frac{3M_1}{d_1(K_1 + 2)^2}\cdot\frac{K - K_1}{N_2}$$

where the subscript 1 refers to the pure solvent, subscript 2 to the pure solute, and the symbols without subscript refer to the solution of mole fraction N_2. The molar refractivities were calculated by means of the Lorenz–Lorentz equation

$$MR = \frac{n^2 - 1}{n^2 + 2}\cdot\frac{M}{d}$$

except for the two solid compounds for which the value given is the sum of the atomic refractivities. The dielectric constants are probably accurate to about 0.02 per cent and the densities to 0.005 per cent. Because of its limited solubility in dioxane, the electric moment of monoethanolamine was calculated from data on a single solution. Except for this one substance, the electric moments of the compounds are probably correct to within 1 per cent.

TABLE 1

The dielectric constants, densities, and mole fractions of solutions of certain aldehydes and ethanolamines in benzene and dioxane at 25°C.

N_2	K	$d_{4°}^{25°}$	N_2	K	$d_{4°}^{25°}$	N_2	K	$d_{4°}^{25°}$
p-Bromobenzaldehyde			*p*-Hydroxybenzaldehyde			*p*-Methoxybenzaldehyde		
0.04564	2.533	1.06185	0.04039	3.255	1.03659	0.05439	3.440	0.89152
0.02849	2.412	1.04885	0.02822	2.933	1.03400	0.02992	2.920	0.88324
0.02016	2.351	1.04317	0.01933	2.712	1.03230	0.02070	2.711	0.88010
0.01013	1.288	1.03600	0.00999	2.471	1.02900	0.01104	2.501	0.87674
p-Tolualdehyde			2-Ethylhexanol-1			*α*-Ethylcaproaldehyde		
0.07499	3.462	0.88659	0.04942	2.460	0.86805	0.04820	2.714	0.86863
0.04965	3.062	0.88226	0.02966	2.399	0.86997	0.02957	2.541	0.87086
0.03025	2.751	0.87875	0.01932	2.349	0.87094	0.01950	2.453	0.87146
0.01989	2.584	0.87633	0.00909	2.316	0.87204	0.01095	2.376	0.87230
0.01036	2.434	0.87476						
Triethanolamine			Diethanolamine			Monoethanolamine		
0.03964	2.928	1.03360	0.04514	2.174	1.03070	0.01016	2.288	1.02718
0.02857	2.743	1.03184	0.03261	2.568	1.02976			
0.01990	2.579	1.03074	0.02049	2.450	1.02910			
0.01960	2.577	1.03056	0.00933	2.323	1.02842			
0.00724	2.344	1.02884						

TABLE 2

Molecular polarization, molecular refractivity, and electric moments at 25°C.

COMPOUND	P_∞	MR_D	$\mu \times 10^{18}$ E.S.U.
p-Bromobenzaldehyde	134.1	35.03	2.19
p-Hydroxybenzaldehyde	396.0	33.38	4.19
p-Methoxybenzaldehyde	345.0	37.95	3.85
p-Tolualdehyde	262.0	36.43	3.30
2-Ethylhexanol-1	103.6	40.45	1.74
α-Ethylcaproaldehyde	183.3	39.19	2.64
Triethanolamine	301.0	37.82	3.57
Diethanolamine	189.9	26.95	2.81
Monoethanolamine	122.0	16.22	2.27

DISCUSSION

Applying the method of Bergman and Engle to the resolution of the moment of *p*-bromobenzaldehyde, we have calculated the angle between the aldehyde group moment and the line joining the 1 and 4 carbon atoms of the ring to be 127°. They also designate by α the angle between the planes in which the two moments lie and which also pass through the 1 and 4 carbon atoms of the benzene ring. This angle was calculated to be 153° for *p*-hydroxybenzaldehyde and 150° for *p*-methoxybenzaldehyde. In these calculations the moments and angles employed for the hydroxyl and methoxyl groups are the values recorded by Bergman and Engle, namely, 1.70×10^{-18} and 1.23×10^{-18} E.S.U., and 83° and 73°, respectively.

The moments of the monoethanolamine and the diethanolamine were calculated from bond and group moments on the basis of the following assumptions: (1) the moment of each of these amines is the vector sum of the N—H and the N—C_2H_4OH bonds; (2) the contribution of each such moment to the total moment is the same, regardless of the other bonds present. Thus, for example, the contribution of one N—H moment to the moment of the molecule is the same in diethanolamine as in ammonia.

From figure 3 it will be observed that for three equal vectors, v with an angle θ between them, each vector contributes one-third to the resultant vector, m. The angle β between any one vector and the resultant is given by

$$\cos \beta = m/3v$$

The angles θ and β are connected by the relation,

$$\sin \theta/2 = (\sqrt{3}/2) \sin \beta$$

If now we assume that the moment of the triethanolamine molecule is the resultant of three hydroxyl moments, each of $\mu = 1.70 \times 10^{-18}$ E.S.U., and acting at an angle θ to each other, this angle may be calculated by the above relations. The calculated value of θ is about 77°. However, the assumption made is not exactly true, since it omits from consideration the contribution of the N—C moment; the resultant error due to its omission is probably not large. We thus obtain a tetrahedral configuration of the vectors with the nitrogen atom at the apex. The angle, β, between each vector and the altitude is found to be 45°.

The angles θ and β were also calculated for the ammonia molecule, using Dennison and Uhlenbeck's values (2) for the interatomic distances, namely, N—H = 1.02 A.U. and H—H = 1.64 A.U. The angles for ammonia are: $\theta = 107°$ and $\beta = 68°$. With these angles and the moment of the ammonia molecule, 1.49×10^{-18}, the moment of the N—H bond was calculated to be 1.33×10^{-18} E.S.U. It is evident then that the N—H vectors for ammonia form a somewhat flatter tetrahedron than do the vectors of triethanolamine.

With these values for the moment vectors and the angles between them and the resultant vector we have calculated the moments of the monoethanolamine and diethanolamine to be 2.19×10^{-18} and 2.87×10^{-18}

E.S.U., respectively. The corresponding values obtained experimentally were 2.27×10^{-18} and 2.81×10^{-18}. In making these calculations it has been assumed that each N—H moment and each N—C_2H_4OH moment contributes the same moment to the total moment of monoethanolamine and diethanolamine that it contributes to the total moment of ammonia and triethanolamine. Considering the assumptions made, the agreement between the calculated and experimental values of the total moments is exceptionally good.

SUMMARY

1. The dielectric constants and the densities of dilute solutions of *p*-bromobenzaldehyde, *p*-hydroxybenzaldehyde, *p*-methoxybenzaldehyde, *p*-tolualdehyde, 2-ethylhexanol-1, α-ethylcaproaldehyde, triethanolamine, diethanolamine, and monoethanolamine have been measured at 25°C.

2. From these the total polarization and the dipole moments of each of the compounds have been calculated.

3. The spacial orientation of the group moments in the substituted benzaldehydes and in triethanolamine have been calculated.

4. The moments of diethanolamine and monoethanolamine calculated from theoretical considerations agree well with the values determined experimentally.

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A KINETIC INTERPRETATION OF THE COLORING OF GLASS BY X-RAYS[1]

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It is well known that glass becomes colored, usually brown or violet, when it is exposed to x-rays or other ionizing radiation. The color of glass which is exposed to a source of constant intensity increases at first rapidly and then gradually until it finally reaches a constant value, the saturation color. While a great deal of work has been devoted to the study of these effects (7, 12; see also 2, 3, 4, 9, 11), there is relatively little quantitative information[2] available on the rate of coloring of glass by x-rays. In this paper are presented measurements on the relative absorption of visible light as a function of wave length and on the relative absorption of monochromatic light as a function of duration of x-ray irradiation.

EXPERIMENTAL METHOD

Glass samples, 5 cm. square and about 4 mm. thick, were exposed to a Coolidge water-cooled x-ray tube during the routine treatments of patients in the Cancer Institute of the Minnesota General Hospitals. The exposures were not continuous, but consisted of 15- to 30-minute doses separated by 5- to 10-minute intervals. Approximately five hours were given per day. The glass was not exposed at night, nor on Saturday afternoons, Sundays, or holidays.

The deep therapy tube operated on 200 kv. (peak voltage) and 30 ma. current. The glass samples wrapped in black paper were placed inside of the cylindrical lead drum surrounding the tube. They were about 14 inches from the target and under the cathode end of the tube. The x-rays striking the glass were filtered only by the tube itself, except in a few cases where 1 mm. copper was used. The temperature inside of the drum was approximately 25°C.

The color changes were determined in terms of absorption of monochromatic rays in the visible spectrum. A Bausch and Lomb constant

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[1] This work was supported by a grant from the Graduate School of the University of Minnesota.

[2] See, however, reference 6.

deviation spectrometer and a photometer of the Konig-Martin type were used. The absorption of the colored glass was measured relative to that of a clear sample (not irradiated) cut originally from the same piece of glass. The irradiated and non-irradiated samples were interchanged in the photometer specimen holders in order to eliminate partially the errors due to reflection, unequal intensity of the two beams, and lack of perfect adjustment of the "zero" point of the photometer. The glass surfaces were cleaned thoroughly before each set of photometer match points were read. Immediately after each set of readings, the glass was returned to the x-ray protection cylinder and placed in the same position as before.

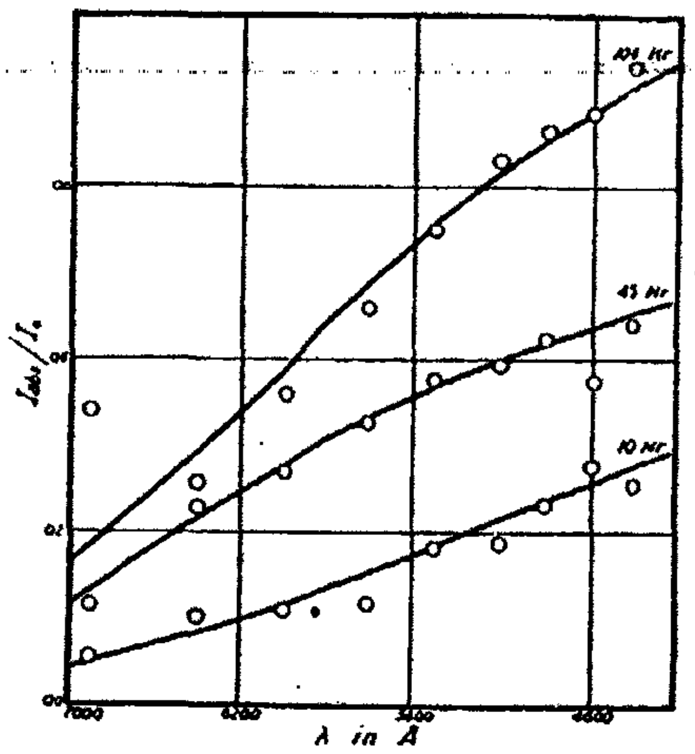

FIG. 1

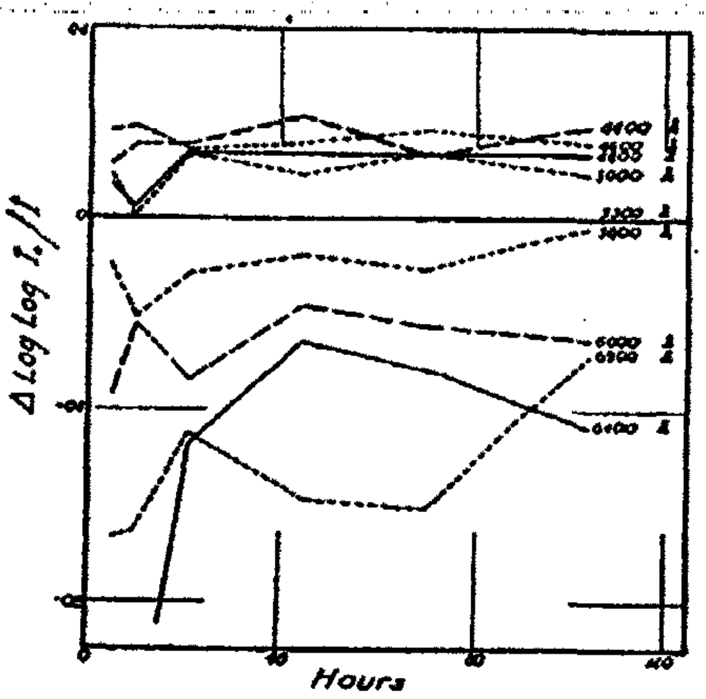

FIG. 2

FIG. 1. RELATIVE ABSORPTION AS A FUNCTION OF WAVE LENGTH

FIG. 2. TEST OF THE HYPOTHESIS THAT THE QUANTITY *cl* IS INDEPENDENT OF WAVE LENGTH

The x-ray intensities at the surface of the glass were the same for most samples. A few pieces of Pyrex, however, were exposed to rays filtered by 1 mm. copper. The intensities of the filtered and unfiltered rays were 45.5 and 185 roentgens per minute, respectively. Twelve per cent of the former and 25 per cent of the latter were absorbed by the glass. These measurements were made by means of a Victoreen Roentgen meter.

DISTRIBUTION OF COLOR

A brownish color, similar to that of commercial amber glass, appeared in all of the samples of glass used, upon irradiation. In figure 1, the relative absorption (I_{abs}/I_0) for a sample of Pyrex is plotted against the wave length of the analyzing light. The three curves correspond to irradiation periods of 10, 45, and 104 hours, respectively.

Probably the simplest interpretation of the change of color with time can be based upon the postulate that the color is due to one substance and that Beer's law applies to the absorption of monochromatic light of all wave lengths studied. On the basis of this assumption we may write[3]

$$\log\left(\frac{I_0}{I}\right)_\lambda = acl \qquad (1)$$

where a is the absorption coefficient, l the thickness of the glass, c the concentration of the colored substance, and I and I_0 the intensities, respectively, of the transmitted and incident light of wave length λ. If at a given time (t) we compare the absorption for two different wave lengths (λ and λ'), we may write

$$\log\log\left(\frac{I_0}{I}\right)_\lambda - \log\log\left(\frac{I_0}{I}\right)_{\lambda'} = \log a - \log a' = \text{constant} \qquad (2)$$

If the relation is obeyed, a plot of

$$\log\log\left(\frac{I_0}{I}\right)_\lambda - \log\log\left(\frac{I_0}{I}\right)_{\lambda,\ \text{reference}}$$

against time should consist of one horizontal straight line for each wave length, λ. Such a plot is presented in figure 2, for the same sample of Pyrex which was used in figure 1. It is apparent that the lines show no trend away from the horizontal, and that the erratic departures are due to experimental errors. Additional evidence for this hypothesis may be obtained by considering measurements which were made for λ 4800 and 6800 A.U. on four different samples of Pyrex, over somewhat longer periods of time. The data are briefly summarized in table 1.

Samples AV and AVII were cut from one plate of Pyrex, which presumably differed in batch from the plate from which samples BI and BII were cut. The constancy of

$$\log\log(I_0/I)_{4800\ \text{A.U.}} - \log\log(I_0/I)_{6800\ \text{A.U.}}$$

for each series of measurements is demonstrated by the magnitude of the average departure from the average value, column three. That this

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[3] It should be mentioned that this same relation may be based upon the assumption that any number of different colored substances are present, but that the ratios of their concentrations do not change with time or irradiation. The postulate implies also that the colored substance is distributed uniformly. This condition probably exists within the limits of sensitivity of our spectrophotometer. Moreover, it is not probable that the same surface of the glass was placed nearest the x-ray tube each of the many times it was returned for more irradiation. We intend to test in later experiments the distribution of colored material within the glass.

quantity is also constant for the different samples of glass is evident from the data in column two. The last two columns are included to indicate the range of values covered.

A series of measurements, similar to those summarized in figure 2, were made with a piece of flint glass, of unknown origin. The color distribution of this sample resembled that obtained for Pyrex within the limits of experimental error, and there is the same definite evidence that the ratio $a_\lambda/a_{\lambda,\text{reference}}$ is a constant. Qualitative experiments with "plate glass" and with Corex D indicated the same color distribution as was obtained for Pyrex.

TABLE 1

Evidence for the constancy of the quantity log $a_{4800\text{A.U.}}$ − log $a_{6800\text{A.U.}}$

SAMPLE	LOG LOG $(I_0/I)_{4800\text{A.U.}}$ −LOG LOG $(I_0/I)_{6800\text{A.U.}}$	AVERAGE ERROR OF THE AVERAGE VALUE	NUMBER OF MEASUREMENTS	DURATION OF EXPERIMENT IN HOURS
AV	0.63	0.02	21	110
AVII	0.63	0.01	11	310
BI	0.61	0.03	14	181
BII	0.67	0.02	16	186

RATE OF COLORING

The general form of the curve relating the absorption (for visible light) of glass to the duration of the exposure to x-rays has been established by the work of Kersten and Dwight (6). Quantitative interpretation of their results is difficult, since they measured the absorption of white light, and furthermore they used as their measuring instrument a photronic cell, the sensitivity of which is a function of wave length. In their experiments on the rate of fading of irradiated glass, they demonstrated that soft glass fades appreciably even at room temperature in the dark. This result was confirmed for samples of soft glass which were irradiated under our experimental conditions. However, the rate of fading of irradiated Pyrex proved to be much slower, amounting to not more than 2 or 3 per cent reduction in relative absorption[4] during a week at room temperature. For this reason, all of our experiments on rate of coloring were performed with samples of Pyrex.

In attempting to interpret our results, we have made the following assumptions. The rate at which the colored substance is formed is proportional to the product of the intensity of the absorbed x-rays and the concentration of some substance which reacts to form the colored material. Saturation is reached when this rate is counterbalanced by thermal fading

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[4] That is from, say, 0.45 to 0.44.

and by a second process, which is proportional to the product of the intensity of the absorbed x-rays and the concentration of the colored substance. These assumptions may be expressed by the equation

$$\frac{dc}{dt} = k(M - C) - k'C - f(C, M, T) \tag{3}$$

where M is the initial concentration of the substance which can be transformed into the colored material, C is the concentration of the colored substance, t is time, T is temperature, and k and k' are factors which are directly proportional to the intensity of the absorbed x-rays. The term $f(C, M, T)$ represents the thermal rate of fading. In the following treatment, this last term (which is of unknown form) will be neglected, and the resulting equation will be applied to the experimental data for the first sixty hours of irradiation, during which time the rate of coloring (and therefore dc/dt) is relatively large compared to the thermal rate of fading.[5] With this term omitted, the equation may be written as

$$\frac{dc}{kM - (k + k')C} = dt \tag{4}$$

Integrating between the limits 0 and t and 0 and C,

$$C = \frac{kM}{k + k'}[1 - e^{-(k+k')t}] \tag{5}$$

Eliminating C between equations 1 and 5,

$$\log\frac{I_0}{I} = alM\frac{k}{k + k'}[1 - e^{-(k+k')t}] \tag{6}$$

$$= \alpha(1 - e^{-\beta t}) \tag{7}$$

where α is a positive coefficient, which is directly proportional to the thickness of the glass (l) and the absorption coefficient (a) for the analyzing light, but is independent of the intensity of the absorbed x-rays, and β is a positive exponent which is directly proportional to the intensity of the absorbed x-rays.

It is interesting to note that equation 7 is consistent with two widely different hypotheses. Either that the initial concentration M is extremely small and that saturation is reached when this substance is used up, no

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[5] Glass samples which were irradiated for two or three hundred hours did not gradually approach a constant saturation value (as was expected), but showed an erratic fluctuation, of from 5 to 10 per cent of the relative absorption, around this constant value. This fluctuation was probably the result of our experimental technique, being due chiefly to changes in the room temperature and to changes in the intervals which elapsed between irradiation periods. We are planning to repeat this work under conditions which will minimize these factors.

radiochemical back reaction being assumed; or that the initial concentration M is large enough so that the concentration $M - C$ is not sensibly altered by irradiation, and that saturation is a steady state at which the radiochemical forward and back reactions are equal.

Equation 7 was tested by fitting it (graphically) to the experimental data. The curves in figures 3, 4, and 5 are plots of the equation. The corresponding experimental points are represented by circles. The values used for the constants α and β are summarized in table 2. The first two columns of this table refer to the numbers of the figures and of the glass samples. The wave length of the analyzing light is given in column three, and the thickness of the glass in column four. The values of the constants are given in the last two columns; of these, the four values printed in heavy type were determined empirically. The constants of the equation were first determined to fit the data for sample BIII, figure 3. The same value for β was used for all experiments, except those on sample BI. For all data obtained with λ4800 A.U. as the analyzing light, the value of α used was 0.81 × l/3.94 mm. To allow for the difference in the absorption coefficient (a), the values of α for experiments with λ6800 A.U. were obtained by multiplying the corresponding value (i.e., for the same sample and irradiation) for λ4800 A.U. by the empirical factor 0.25. The value of β was determined empirically from the data for BI, λ4800 A.U., since this sample was not exposed directly to the x-rays, but was surrounded by a copper filter which decreased the intensity and increased the average requency of the absorbed x-rays.

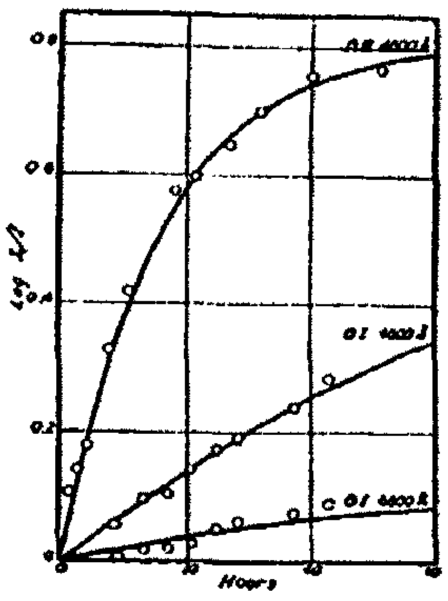

FIG. 3
RATE OF COLORING

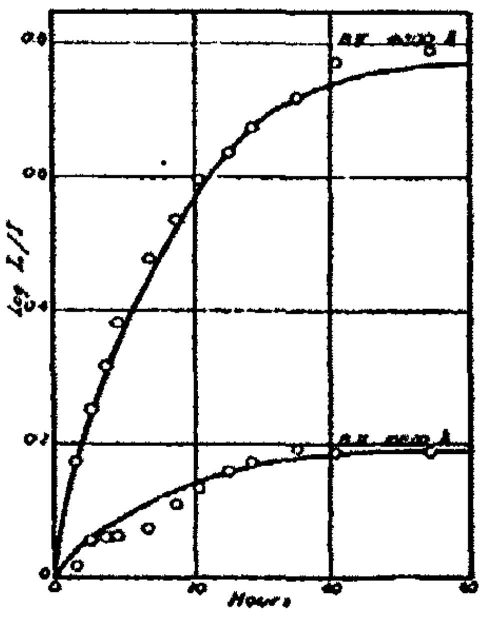

FIG. 4
RATE OF COLORING

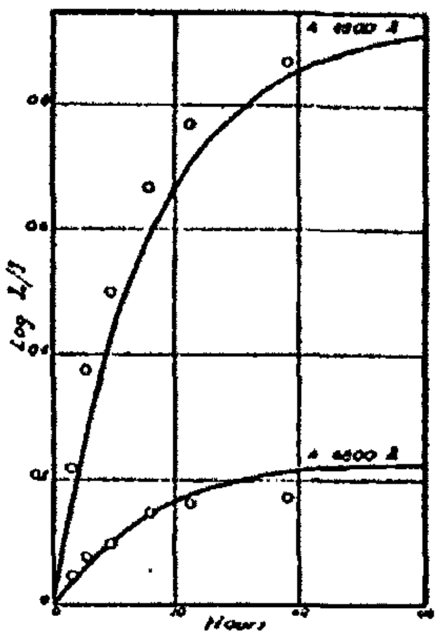

FIG. 5
RATE OF COLORING

The graphs demonstrate that, with the exception of the data for sample

A, figure 5, the experimental points are fitted by equation 7 within the limits of experimental accuracy. The curve for sample A is uniformly about 10 per cent lower than the experimental points. However, it must be remembered that samples A and B were not taken from the same lot of Pyrex, and there is no *a priori* reason for assuming (as we have) that the values of α and β will be the same for different batches of Pyrex. If the initial concentration M were 10 per cent greater in sample A than in sample B, the discrepancy would be explained.[6]

Since we have assumed that k and k' are directly proportional to the intensities of the absorbed x-rays, we should expect that the ratio of the values of β, for the experiments with filtered and unfiltered x-rays, would be equal to the ratio of the energies absorbed from the x-rays. The ratio of the values of β is 0.064/0.0096 = 6.7; the experimentally determined ratio of the intensities of the absorbed x-rays is 8.3. While these ratios are substantially in agreement, their difference is probably larger than the experimental error. The difference may be ascribed either to a departure from direct proportionality between k_2 (and possibly k_1) and the intensity, or to a relatively greater efficiency of the more penetrating x-rays transmitted by the copper filter.

TABLE 2

Summary of data of figures 3, 4, and 5. A test of equation 7

FIGURE	SAMPLE	λ	l	α	β
		A.U.	*mm.*		
3	BIII	4800	3.94	0.81	0.064
4	BII	4800	3.85	$0.79 = \frac{3.85}{3.94}\,0.81$	0.064
5	A	4800	4.54	$0.93 = \frac{4.54}{3.94}\,0.81$	0.064
4	BII	6800	3.85	$0.20 = 0.25 \times 0.79$	0.064
5	A	6800	4.54	$0.23 = 0.25 \times 0.93$	0.064
3	BI	4800	3.85	$0.79 = \frac{3.85}{3.94}\,0.81$	0.0096
3	BI	6800	3.85	$0.20 = 0.25 \times 0.79$	0.0096

The coloring due to α-, β-, and γ-rays

The effect of x-rays on glass is, in many respects, similar to the effects of the radiations from radioactive substances. The distribution of absorption, as a function of the wave length of the analyzing light, seems to be quite independent of the type of radiation. The color of glass irradiated

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[6] This assumption is consistent with the first hypothesis, that M is very small, being the concentration of some impurity.

by hard x-rays appears to be quite homogeneous, but glass which is exposed to the complete radiation from radon or radium salts develops three layers of differing intensity. α-Rays produce a thin skin of intense color, about 0.04 mm. thick (10). β-Rays produce a layer of intermediate intensity, which shades off gradually but appears to be about 2.5 mm. thick (2). The energy absorbed from the accompanying γ-rays is very much smaller, and the coloring of glass by them is correspondingly slow, but is of course uniform. Some measurements made on the coloring of the plane ends (3.4 mm. thick) of a cylindrical Pyrex cell, of 30 cc. volume, which was filled with about 100 millicuries of radon, may be of interest in this connection. The color increased very rapidly at first, and appeared to a casual inspection to have reached saturation after forty-eight hours. However, sensitive photometric measurements revealed that the color was still increasing slowly after three hundred hours had elapsed. A second and even a third charge of radon (of approximately 100 millicuries each) failed to bring the color to a saturation value. In our opinion, these facts indicate that a source which produces either α- or β-rays is not well adapted to quantitative measurements on the coloration of glass. On the other hand, a pure γ-ray source is (except for the inconvenient slowness of its action) an ideal one for the purpose.

Experiments on the rate of coloring of glass subjected to the complete radiation from radium sulfate have been reported by Kabakjian (5). His absorption measurements appear to have been made with white light. The equation which he develops to fit the data is based upon the assumption that saturation is reached when the rate of thermal fading is equal to the rate of coloring due to the absorbed radiation. As the author points out, the known extremely slow rate of thermal fading (at room temperature) and certain inconsistencies in the empirically determined values of the constants make it practically certain that the agreement between the experiments and the equation is fortuitous.

An equation similar to that derived in this paper was presented in 1923 by Belar (1) to represent the rate of coloration of rock salt subjected to β- and γ-radiation. In 1926, Przibram (8) subjected the question to a thorough analysis and decided that the formula of Belar was not sufficient to represent all of the facts; he derived a more complex expression which was consistent with the available data on the coloring of rock salt by β- and γ-radiation. In these experiments it was established that the saturation value of the absorption is a function of the intensity of the absorbed β, γ-radiation. Kabakjian's claim that the saturation limit is a function of intensity for glass irradiated by α, β, γ-radiation does not appear to be definitely proven. There is at present no evidence to indicate that a similar effect exists in the coloring of glass by x-rays. Further experiments should be performed, using hard x-rays or γ-rays under carefully controlled conditions to test this point and to throw some light on the various questions raised by the present work.

SUMMARY

Some experiments have been performed on the rate of coloring of Pyrex glass by irradiation with hard x-rays, and on the distribution of relative absorption, of the colored glass, as a function of wave length for visible light. A simple hypothesis of the rate of coloring has been suggested, an equation has been derived from this hypothesis, and it has been shown that the experimental measurements are in agreement with the equation. Some discussion of the analogous effects of radiations from radium is included.

In conclusion we wish to express our appreciation of the coöperation and interest of Dr. Wilhelm Stenstrom, of the Cancer Institute, and of Prof. S. C. Lind, Director of the School of Chemistry.

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THE PHYSICAL CHEMISTRY OF FLOTATION. VI

THE ADSORPTION OF AMINES BY SULFIDE MINERALS

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Wark and Wark (4) have used the measurement of contact angle at the line of triple contact air–solid–water as a means of studying adsorption by the solid of the class of compounds known in flotation as "collectors." It was shown that, for a group of soluble collectors containing the —SH group or its alkali metal salts, the angle of contact is dependent only upon the specific non-polar group of the adsorbed collector. Though the collectors most commonly used today for the flotation of the sulfide minerals are almost all of this type, several other types are of considerable theoretical interest, namely: (1) soluble salts of the fatty acids, in which, as in the xanthate type, the non-polar group is in the negative ion; (2) soluble salts of the amines, in which the non-polar group is in the positive ion; (3) sparingly soluble oils. The first of these types is being investigated elsewhere by the contact angle method. Work on the second type is described in this paper. Work on the third type is to be undertaken shortly.

Amines have been chosen to facilitate a comparison between (a) different members of the series of primary amines from the methyl to the hexyl derivatives, (b) different members of the series of quaternary amines from the methyl to the amyl derivatives, (c) the ethyl derivatives of the primary, secondary, tertiary, and quaternary series, and (d) the aliphatic and the aromatic amines.

EXPERIMENTAL METHOD

Preparation of amines

The primary, secondary, and tertiary amines were recrystallized as the hydrochlorides, usually from alcohol, by addition of ether. The quaternary ammonium salts were recrystallized from water.

Determination of contact angle

The experimental procedure of the preceding papers was followed, but in the present work higher concentrations of the collector were generally necessary to induce contact. Since limited amounts of the amines were available, the response of the minerals could not be tested in solutions of greater concentration than 1 g. per liter. In every test, the reaction of the mineral to the amine was observed over a period of at least half an hour, and the bubble was pressed against the mineral for approximately fifteen seconds to see whether true contact was established.

The pH value of the solution was found to influence the adsorption of amines. Consequently, if a mineral failed to respond to the natural solution of the amine hydrochloride, its behavior was observed also in acid (pH = 1) and alkaline (pH = 12) solutions. Even with this procedure, adsorption of isoamylamine by sphalerite was not detected. Gaudin, Haynes, and Haas (1) have shown that flotation in this case occurs only within the pH range 9 to 11. It is possible, therefore, that in a few cases contact angles are reported as "nil" where tests at other pH values would have shown contact to be possible.

RESULTS

No matter what the concentration of an amine may be, a characteristic contact angle is never exceeded. Near the minimum effective or "threshold" concentration of amine, or near the critical pH value—at which contact ceases to be possible—there is a range of solution compositions over which the maximum contact angle is not attained. However, over a wide range of concentrations and of pH values, the contact angle is constant within an experimental error of ±2°. The determined *maximum* contact angles are recorded in table 1. Over a wider range of pH values than other minerals, bornite and chalcocite do not give the usual maximum angles for the aliphatic amines. On the other hand, both these minerals adsorb sulfur-bearing collectors more readily than does chalcopyrite, and the incomplete response to amines may be due to fouling of the surface by cuprous chloride or iodide. Certainly both minerals float readily with hexylamine under solution conditions that lead to angles of contact of only 40° to 50°, the amine itself serving as frother. With triethylamine, however, for which the measured contact angles were still lower, only a very rapidly collapsing mineralized froth could be obtained, even in the presence of an added frother.

When placed in amine-free distilled water, a chalcopyrite surface that has previously responded to hexylamine or to a quaternary ammonium salt retains for some time the ability to attract an air bubble. It is evident, therefore, that the amine changes the surface of the mineral. The change, attributed to adsorption of the amine, is most permanent for those amines that are most readily adsorbed.

Methylamines. Trimethylamine hydrochloride and tetramethylammonium iodide were tested. Within the pH range considered, none of the minerals with which the investigation was concerned would have responded to a 1 g. per liter solution of the primary or secondary methylamines.

None of the minerals responds to a concentration of 1 g. per liter of trimethylamine hydrochloride at pH values of 7 or 12. To a solution of 1 g. per liter at a pH value of 1.0, only chalcopyrite and bornite responded, and then but weakly; in normal hydrochloric acid, however, the response of chalcopyrite to the amine was complete. Sphalerite that had been previously activated[1] responded in acid solution in a manner similar to chalcopyrite.

TABLE 1

Maximum values of contact angle for various minerals and amines

AMINE	MAXIMUM VALUES OF CONTACT ANGLES FOR VARIOUS MINERALS						
	Chalcopyrite $CuFeS_2$	Sphalerite, ZnS	Sphalerite activated by $CuSO_4$	Bornite, Cu_3FeS_3	Chalcocite, CuS	Pyrite, FeS_2	Galena, PbS
Trimethylamine hydrochloride	61*	Nil	59*	(49)*	Nil	Nil	Nil
Monoethylamine hydrochloride	58*	Nil	Nil	(42)*	Nil	Nil	Nil
Diethylamine hydrochloride	61*	Nil	Nil	(44)*	Nil	Nil	Nil
Triethylamine hydrochloride	61	Nil	63	(52)*	Slight	Nil	Nil
Isoamylamine hydrochloride	63	Nil	60	(52)	Slight*	Nil	Nil
Isohexylamine hydrochloride	63	61	56	(47) 64†	(49) 62†	63	Nil
Aniline hydrochloride	56	Nil	57	59	57	Nil	Nil
α-Naphthylamine hydrochloride	62	(55)*	62	Slight Slight†	59	Nil	Nil
Piperidine hydrochloride	61	Nil	58*	56	Slight*	Nil	Nil
Tribenzylamine hydrochloride‡	61	Nil	62	62	(56)	Nil	60
Tetramethylammonium iodide	60	Nil	61	61	(50)	Nil	Nil
Tetraethylammonium iodide	61	Nil	61	60	61	Nil	(54)*
Tetrapropylammonium iodide	61	Nil	60	56	(52)	Nil	(52)
Tetrabutylammonium iodide	62	60	59	61	61	Nil	62
Tetraamylammonium iodide	59	60	57	60	60	Nil	62

* At pH = 1.0.
† At pH = 12.0.
‡ Maximum pH value 3.5.

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[1] Sphalerite that has been immersed in a dilute copper sulfate solution becomes coated by a copper-bearing film, probably of cupric sulfide. When in this condition, it responds more readily to most collectors, and is regarded as being "activated."

The copper minerals respond to 1 g. per liter of tetramethylammonium iodide, but neither galena, sphalerite, nor pyrite responds within the pH range 1 to 12. Chalcopyrite, however, responds to so low a concentration as 25 mg. per liter, and the response of bornite, chalcocite, and sphalerite activated by copper sulfate, to neutral 1 g. per liter solutions is rapid. The contact angle for chalcocite (see table 1) was influenced by the formation of a heavy precipitate, presumably of cuprous iodide. In neutral solution, the angle of contact for bornite was 61°, but contact was slower and less complete (= 50°) at pH = 12.

Ethylamines. The mono-, di-, tri-, and tetra-substituted ammonium salts indicate a slight increase in the readiness with which adsorption occurs as the number of non-polar groups in the adsorbed molecule increases. Solutions of a constant concentration (1 g. per liter) were used for all four amines. The differences between them would have been slightly greater had equivalent concentrations been taken.

Monoethylamine is a slightly less potent collector than trimethylamine. None of the minerals responds to 1 g. per liter of ethylamine hydrochloride in neutral or alkaline solutions (pH = 12) and only chalcopyrite responds completely in an acid solution of pH value = 1. Bornite gives an angle of approximately 40° at pH = 1, the response being irregular over the surface.

Diethylamine hydrochloride was adsorbed only by those minerals that adsorbed the primary amine. Again, none of the minerals responds to 1 g. per liter in neutral solution or at pH = 12, and only chalcopyrite and bornite respond in acid solution. The response of bornite is again incomplete.

With triethylamine the response of the minerals is slightly more general. Pyrite, sphalerite, and galena, however, fail to respond to 1 g. per liter of the hydrochloride over the whole pH range 1 to 12. Activated sphalerite does respond, particularly in acid solution. Chalcocite responds incompletely, the angle of contact being only 38° at pH = 1, and it does not respond in alkaline solution. Though bornite responds over the whole pH range, the contact angle is low, a maximum angle of 51° being obtained at pH = 1. Chalcopyrite responds rapidly to the neutral solution.

The quaternary ammonium salt is more effective than triethylamine as a collector. The copper minerals and activated sphalerite respond rapidly to a 1 g. per liter solution of tetraethylammonium iodide in neutral solution; indeed, much lower concentrations than 1 g. per liter may be used. Galena responds in a strongly acid solution (pH = 1), but the full contact angle is not attained. Neither pyrite nor sphalerite responds to a 1 g. per liter solution within the pH range 1 to 12.

Isoamylamine. Though more effective as a collector than monoethylamine, isoamylamine is no more effective than triethylamine. Galena and pyrite do not respond to a 1 g. per liter solution of isoamylamine hydrochloride at pH values 1, 6, and 12. However, sphalerite, which does not respond at pH values of 6 and 12, does respond at 10. The copper minerals and activated sphalerite respond to a 1 g. per liter solution at the natural pH value (3.8). Chalcopyrite responds to very low concentrations in acid solution (see figure 2).

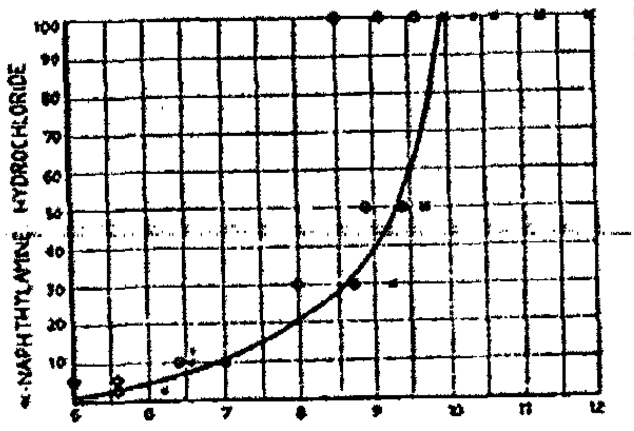

FIG. 1

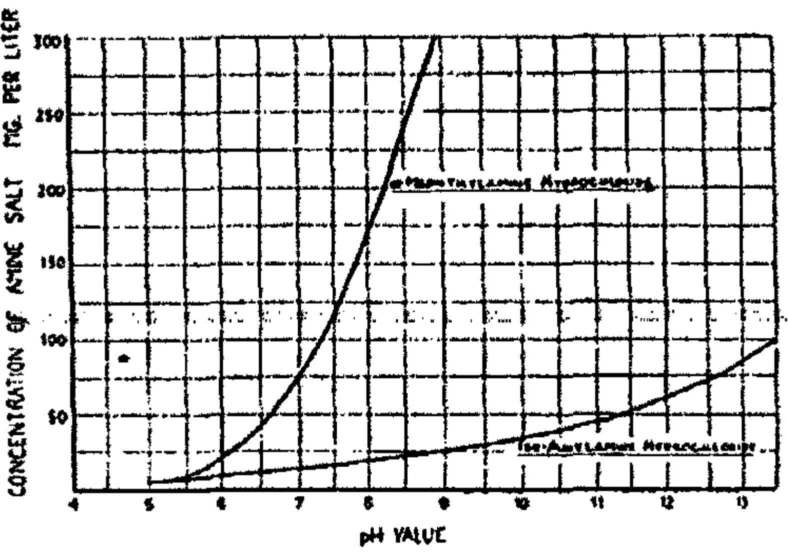

FIG. 2

FIG. 1. RELATIONSHIP BETWEEN THE pH VALUE AND THE CONCENTRATION OF α-NAPHTHYLAMINE HYDROCHLORIDE NECESSARY TO INDUCE CONTACT BETWEEN AN AIR BUBBLE AND A CHALCOPYRITE SURFACE

⊙, contact possible; × contact impossible. Contact possible only to left of curve.

FIG. 2. RELATIONSHIP BETWEEN THE pH VALUE AND THE CONCENTRATION OF AMINE HYDROCHLORIDE NECESSARY TO INDUCE CONTACT BETWEEN AN AIR BUBBLE AND A SURFACE OF CHALCOPYRITE

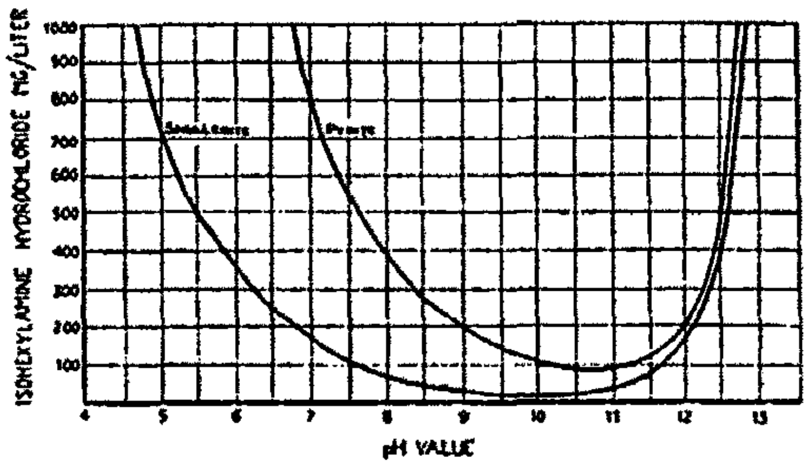

FIG. 3. RELATIONSHIP BETWEEN THE pH VALUE AND THE CONCENTRATION OF ISOHEXYLAMINE NECESSARY TO INDUCE CONTACT BETWEEN AN AIR BUBBLE AND SURFACES OF SPHALERITE AND PYRITE

Contact possible only above curves

Isohexylamine. Isohexylamine is a still more effective collector than the corresponding amylamine. It is a good collector for sphalerite, the optimum pH value being about 10 (see figure 3). Even pyrite responds to sufficiently concentrated solutions of the hydrochloride over a limited pH range. Galena alone fails to respond at the pH values tested.

Aniline. As a collector, aniline resembles isoamylamine. Sphalerite, galena, and pyrite do not respond to a 1 g. per liter solution of aniline hydrochloride within the pH range tested, but the copper minerals and activated sphalerite do respond to a solution at the natural pH value of 3.5.

α-Naphthylamine. α-Naphthylamine is a little more effective than aniline; sphalerite responds slowly and incompletely to 1 g. per liter of the hydrochloride in acid solutions. However, neither galena nor pyrite responds to it. Accordingly, sphalerite can be floated away from galena by a 1 g. per liter solution of the amine hydrochloride at a pH value of 3.5. The amine itself serves as a frother.

Piperidine. Piperidine and α-naphthylamine are of approximately equal value as collectors, the former being slightly the more active.

Tribenzylamine. The solubility of tribenzylamine hydrochloride in water is less than 200 mg. per liter; a saturated solution was therefore employed. Since alkalis precipitate the amine from this solution, no tests could be made in alkaline solution. Only the natural solution (pH = 3.5) and a solution of pH value = 1 were tested. This amine is the strongest collector of the aromatic derivatives tested. Even with this low concentration, only sphalerite and pyrite failed to respond to it in acid solutions.

Tetrapropylammonium iodide. Of the minerals tested, only pyrite and sphalerite do not respond to 1 g. per liter of this reagent within the pH range 1 to 2. The response of chalcocite is masked by the formation of a precipitate of cuprous iodide, and though galena responds to a neutral 1 g. per liter solution, its response is not fully developed. The copper minerals respond in the natural solution (pH = 6.6) to considerably less than this concentration of the amine; indeed, chalcopyrite responds fully to 25 mg. per liter.

Tetrabutylammonium iodide. With the increase in the size of the non-polar portions of the amine, adsorption becomes still more general, and sphalerite responds to this collector without the need for activation. Pyrite, however, remains uninfluenced by 1 g. per liter of the reagent over the pH range 1 to 12. Concentrations as low as 25 mg. per liter are effective for the copper minerals and activated sphalerite.

Tetraamylammonium iodide. Of the minerals tested, pyrite alone does not respond to a 1 g. per liter solution of tetraamylammonium iodide within the pH range 1 to 12. The other minerals respond to considerably lower concentrations.

INFLUENCE OF pH VALUE

In general, the amines are more readily adsorbed from acid than from alkaline solutions. However, in two cases at least—namely, for sphalerite and pyrite with hexylamine—adsorption ceases to be possible in acid solutions, and in fact takes place more readily from alkaline solutions. In these cases, there is an optimum pH value between 9 and 11 *for contact* between air and mineral; Gaudin, Haynes, and Haas (1) give an optimum pH value of about 10 *for flotation* of sphalerite by isoamylamine. The copper minerals exhibit no such optimum pH value within the range tested (3.4 to 13). With them there is, for each pH value, a concentration of collector above which contact is possible between mineral and air and below which contact is impossible. This concentration is dependent both on the mineral and on the amine.

Curves have therefore been determined to show the influence of pH value on the threshold concentration of the amine for a number of minerals and amines. The method of determining the curves is best illustrated by figure 1, which shows for chalcocite the relationship between pH value and concentration of α-naphthylamine hydrochloride. The response of chalcocite to a number of solutions of differing concentration and pH value was determined. The compositions of solutions in which contact with an air bubble was possible appear on the diagram as circles; those of solutions in which contact was not possible appear as crosses. Where the response over the surface was irregular, or where the contact angle fell short of 60°, the solution composition appears on the diagram as a crossed circle. A smoothed line is then drawn between the two sets of points; obviously it separates solutions in which contact is possible from those in which contact is not possible. Fuller details of the method are given elsewhere (2). In general, the curves for amines cannot be determined with the same precision as those for xanthate, the range of incomplete contact being bigger. In figure 2 are shown the curves for chalcopyrite with two different amines, and in figure 3, the curves for sphalerite and pyrite with isohexylamine.

DISCUSSION OF RESULTS

The maximum angles of contact cited in table 1 are approximately constant for all the amines tested; the mean value is 60° and the variation therefrom is usually within the experimental error. This angle is independent both of the nature of the mineral and of the concentration of the collector, provided that the latter exceeds a "threshold concentration" characteristic of the mineral, the amine, and the pH value of the solution. The threshold concentration is lowest for the copper minerals, and then follow, in order of their susceptibility to the quaternary ammonium salts, galena, sphalerite, and pyrite. Sphalerite preactivated by copper sulfate closely resembles chalcopyrite in its response to amines; this is in accord with its response to the sulfur-bearing collectors.

Though galena responds more readily than sphalerite to the quaternary amines, sphalerite responds more readily to hexylamine. Using 50 mg.

per liter of hexylamine at a pH value of 10.5, sphalerite can be floated away from galena. The amine serves both as collector and frother. With collectors of the xanthate type, galena can be floated away from sphalerite; in this case a frother is necessary. It follows that the function of the collector in selective flotation is not merely to enhance differences in the inherent floatability of the minerals to be separated, as has been suggested by some writers, but actually to alter the surface of the desired mineral so that it can be floated.

Of the amines tested, the quaternary ammonium salts are the most readily adsorbed. Further, the higher the homolog the lower is the concentration necessary for the mineral to respond. For example, considering the ethylamines, the primary compound induces a marked response only in one mineral, chalcopyrite, and then only in strongly acid solutions; the secondary compound is little if any more active; the tertiary compound is, however, very much more active, though it does not influence pyrite or galena, and only slowly influences sphalerite in acid solutions; while the quaternary compound induces a response from all the minerals except pyrite and sphalerite. Similarly, tetraamylammonium iodide is very much more active than primary amylamine.

Among the primary amines the higher members of the series are far more active than the methyl and ethyl compounds. Three of the four aromatic amines considered are of about the same order of activity as isoamylamine, but tribenzylamine is more active.

An analysis of the influence of acids and alkalis suggests that in general the amine may be adsorbed in the form of an ion, e.g. $(N(Et)_4)^+$, $(N(Et)_3H)^+$, $(NEt_2H_2)^+$, $(NEtH_3)^+$, etc. The greater the hydrogen-ion concentration the greater will be the percentage of the amine present in the ionic form (and the less in the form of the amine itself or of the hydroxide) and consequently a smaller addition of amine would produce the threshold concentration of the amine ion necessary for adsorption.

The loss of floatability with decrease of pH value for sphalerite and pyrite in the presence of hexylamine cannot be explained in this manner. There, up to a certain point, an increase in alkalinity permits of a smaller addition of amine; thereafter (figure 3), the curves are of the normal form. No explanation is offered for the increase in concentration shown on the left of these two curves. Gaudin, Haynes, and Haas have shown (1) that the relationship between flotation and pH value may be very complex.

The approximate constancy of the angle of contact for all the amines tested indicates that the forces responsible for the adsorption of the amines differ from those responsible for the adsorption of the soluble collectors of the xanthate type. This is perhaps due to the fact that the non-polar groups are in the positive ion in amines and in the negative ion in xanthates.

If, as has been suggested (3), ionic forces bind the xanthate ion to the surface, the forces of adsorption *must* be of a different nature in the two cases.

Using sphalerite and hexylamine, it has been possible, for the first time, to determine experimentally how closely contact angle tests parallel actual flotation tests carried out in identical solutions. Concentrations of this amine that are sufficient to cause contact between air and mineral are also sufficient to produce frothing. Moreover, the amount of the amine abstracted by the mineral is low and the concentration of the amine in solution can therefore be calculated approximately from the amount added.

By means of flotation tests carried out in test tubes (3) a curve can be constructed showing the relationship between the pH value and the amount of amine necessary to induce flotation. Such a curve approximately coincides with the corresponding contact curve of figure 3, but there is not absolute agreement between them. In comparing flotation tests with the contact curve, it was found that, keeping the amine concentration constant at 1 g. per liter, flotation of sphalerite is impossible at pH values below 5; that at a pH value of between 5.5 and 6 an ephemeral mineralized froth forms; that when the pH value is increased to 8, flotation becomes stable; but that at a pH value of 13 only the very fine material floats.

Keeping the pH value constant and gradually increasing the concentration of the amine it was found that: (a) with the pH value at 9.5, no flotation occurs with 15 mg. per liter, only an ephemeral mineralized froth forms at 25 mg. per liter, and a permanent mineralized froth forms at 50 mg. per liter; (b) with the pH value at 6.6, no flotation occurs at 100 mg. per liter or 200 mg. per liter, slight flotation occurred at 250 mg. per liter, and good flotation occured at 300 mg. per liter; (c) with the pH value at 13, good flotation occurred at 2 g. per liter. Except in the last-mentioned case these results are in agreement with the contact curve.

A similar comparison has been made for chalcopyrite and α-naphthylamine (compare figure 2). With a concentration of 500 mg. per liter in strongly acid solutions no froth is produced, but the mineral gives good film flotation. As alkali is added the solution acquires the capacity to form a froth, and between pH values of 6 and 9 a stable mineralized froth is produced. Beyond pH = 10, although the frothing power increases, flotation falls away, until at pH = 12 no permanent mineralized froth can be formed. At lower concentrations an additional frother is necessary, and the comparison loses significance.

SUMMARY

1. Table 1 shows that the maximum contact angle is independent of the particular amine chosen, being within a few degrees of 60° for all amines.

2. The amine induces a more or less permanent effect on the mineral surface, and it is concluded that adsorption of the amine is responsible for this.

3. Of the minerals tested, the copper minerals respond most readily, and pyrite least readily, to amines; activated sphalerite closely resembles chalcopyrite in its response.

4. Using hexylamine, sphalerite can be floated away from galena.

5. Of the amines tested, the quaternary ammonium salts are most readily adsorbed.

6. The higher the homolog, the lower is the concentration necessary for the mineral to respond, i.e., the ethylamines are more effective than the methylamines, the propylamines than the ethylamines, etc.

7. The primary amines are the least active, the secondary amines are more active, and the tertiary amines are still more active.

8. Three cyclic amines—aniline, α-naphthylamine, and piperidine—are of about the same order of activity as isoamylamine, but tribenzylamine is much more active.

9. Contact tests closely parallel actual flotation tests carried out in identical solutions.

10. Figures 1, 2, and 3 show how the contact induced at certain mineral surfaces by certain amines is prevented by addition of alkali or acid.

We wish to record our thanks to Professor E. J. Hartung for having made available a laboratory for this work, and to Messrs. H. Hey and A. B. Cox for help during its progress. The cost of the work was borne by the University of Melbourne and the following Companies: Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Company of Australasia Ltd., Mount Lyell Mining and Railway Company Ltd., and the Burma Corporation Ltd.

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THE APPARENT VOLUMES AND APPARENT COMPRESSIBILITIES OF SOLUTES IN SOLUTION. II

Concentrated Solutions of Lithium Chloride and Bromide

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In the first paper (11) of this series it was shown that, from the standpoint of the apparent molal volume and compressibility, concentrated solutions of lithium chloride and bromide differ significantly from solutions of other strong electrolytes. It was impossible, however, with the limited data at hand to determine at what concentration these solutions become abnormal or to study the nature of the irregularity. The object of this paper is to report new measurements of the density and compressibility coefficient of concentrated solutions of these salts and to present a more complete picture of the anomalous properties of these solutes.

The results of seven new experiments are summarized in table 1. No detailed description of these experiments will be given here, because the procedure followed throughout was the same as that described fully in a previous communication (10). It should be noted, however, that new stock solutions of both lithium chloride and lithium bromide were prepared for these experiments, and that all other solutions investigated were prepared by dilution of weighed portions of these stock solutions.

From these data have been calculated the apparent molal volume ϕ, the apparent molal compressibility $(\bar{B} + f)$, and the volume concentration of the solute in the several solutions. Values of these calculated quantities are given in table 2, which may be regarded as a supplement to table 2 given in paper I. With the exception of some of the f values, the method of calculating these quantities is the same as that already described (11). The modification in the method for calculating f may be outlined briefly. It will be recalled that by definition

$$\phi = V - n_1 V_1$$

and

$$B = \frac{-\mathrm{d}\phi}{\mathrm{d}P} = V\beta - n_1 V_1 \beta_1$$

where V = volume of solution containing 1 gram-mole of solute,
V_1 = volume of 1 gram-mole of pure water at the temperature of the solution,
n_1 = number of moles of water present in the solution, and
β, β_1 = compressibility coefficients of solution and water, respectively.

ϕ, however, is a function of two independent variables, pressure and concentration,

$$\phi = F(P, c)$$

and we can write for the total differential

$$\mathrm{d}\phi = \left(\frac{\partial\phi}{\partial P}\right)_c \mathrm{d}P + \left(\frac{\partial\phi}{\partial c}\right)_P \mathrm{d}c$$

Dividing through by $\mathrm{d}P$, we get

$$-\bar{B} = \frac{\mathrm{d}\phi}{\mathrm{d}P} = \left(\frac{\partial\phi}{\partial P}\right)_c + \left(\frac{\partial\phi}{\partial c}\right)_P \frac{\mathrm{d}c}{\mathrm{d}P}$$

The quantity f is the last term of this expression

$$f \equiv \left(\frac{\partial\phi}{\partial c}\right)_P \frac{\mathrm{d}c}{\mathrm{d}P}$$

whence

$$\bar{B} + f = -\left(\frac{\partial\phi}{\partial P}\right)_c$$

The method of calculating f, given in paper I, was for the special case where ϕ is a linear function of $c^{\frac{1}{2}}$ at constant pressure (Masson's rule). For the concentrated solutions of the lithium halides where this relationship is not valid, it has been necessary to proceed as follows. The numerical value of the slope $\frac{\partial\phi}{\partial c}$ was found graphically from a plot of ϕ against c. Further, since

$$c = 1000/V$$

it follows that

$$\frac{\mathrm{d}c}{\mathrm{d}P} = \frac{-1000}{V^2}\frac{\mathrm{d}V}{\mathrm{d}P} = \frac{1000}{V}\beta = c\beta$$

The product $c\beta$ affords a simple means of getting the numerical value of the second term necessary for the evaluation of f. It should perhaps be noted here again that the calculated values of $\bar{B}$ derived from our data refer to solutions under a pressure of 200 metric atmospheres, and that therefore the f values must be calculated for the same condition. This requirement was met in the calculation of the f values given in table 2.

The graphical method of computing f just described has also been applied to the calculation of the f values omitted from table 1 of the first paper (11). For the sake of completeness these new values as well as some recalculated ones are included in table 3. For purpose of identification only the $\bar{B}$ values given in the table referred to are repeated here.

TABLE 1

Table of results

SOLUTION NO.	WEIGHT PER CENT OF SALT	DENSITY AT 35°C.	$\beta \times 10^6$	AVERAGE DEVIATION
		Lithium chloride solutions		
1	41.020	1.25597	20.44	0.01
2	37.003	1.22536	21.86	<0.01
3	27.450	1.15772	25.62	<0.01
		Lithium bromide solutions		
1	45.183	1.44911	27.12	
2	39.999	1.37671	28.63	<0.01
3	34.706	1.31036	30.11	<0.01
4	18.076	1.13859	35.28	

TABLE 2

Values of the various solution factors at 35°C.

SOLUTION NO.	c	c_{200}	ϕ	ϕ_{200}	$-\bar{B} \times 10^4$	$f \times 10^4$
			Lithium chloride solutions			
1	12.152	12.201	20.97	21.14	8.82	0.11
2	10.695	10.734	20.89	21.08	9.91	0.11
3	7.496	7.534	20.68	20.95	12.94	0.09
			Lithium bromide solutions			
1	7.5385	7.5793	26.64	26.82	8.31	−0.05
2	6.3400	6.3762	26.66	26.85	9.60	−0.12
3	5.2359	5.2675	26.61	26.83	10.94	0.16
4	2.3696	2.3863	26.02	26.35	16.57	0.25

The relationships existing between the apparent properties and concentration in solutions of these lithium salts are portrayed in figures 1 and 2, which were constructed by plotting the values of ϕ_{200} (left-hand scale) and $(\bar{B} + f)$ values (right-hand scale), against the corresponding c_{200} values. The plotted values are those given in tables 2 and 3 of this paper and table

1 of paper I. Quantities for solutions under a pressure of 200 metric atmospheres have been used as in paper I in order to have them under the same conditions with the least loss in the precision of the original measurements. To show the molecular composition of the more concentrated solutions another scale is given at the top of each graph, which indicates the number of moles of water, n_w, per mole of solute in the solution, the concentration of which is given below on the abscissa scale.

TABLE 3

Values of f by graphical method

Lithium chloride solutions

$-B \times 10^4$.....	8.83	10.55	13.90	14.91	17.34	18.62	22.69	27.09
$f \times 10^4$.....	0.11	0.11	0.23	0.24	0.29	0.33	0.34	0.26

Lithium bromide solutions

$-B \times 10^4$.....	5.25	6.38	7.27	8.22	8.62	10.74	12.05	14.13	17.20	17.58	20.00
$f \times 10^4$.....	−0.15	−0.27	−0.32	−0.05	−0.07	0.16	0.16	0.16	0.24	0.21	0.18

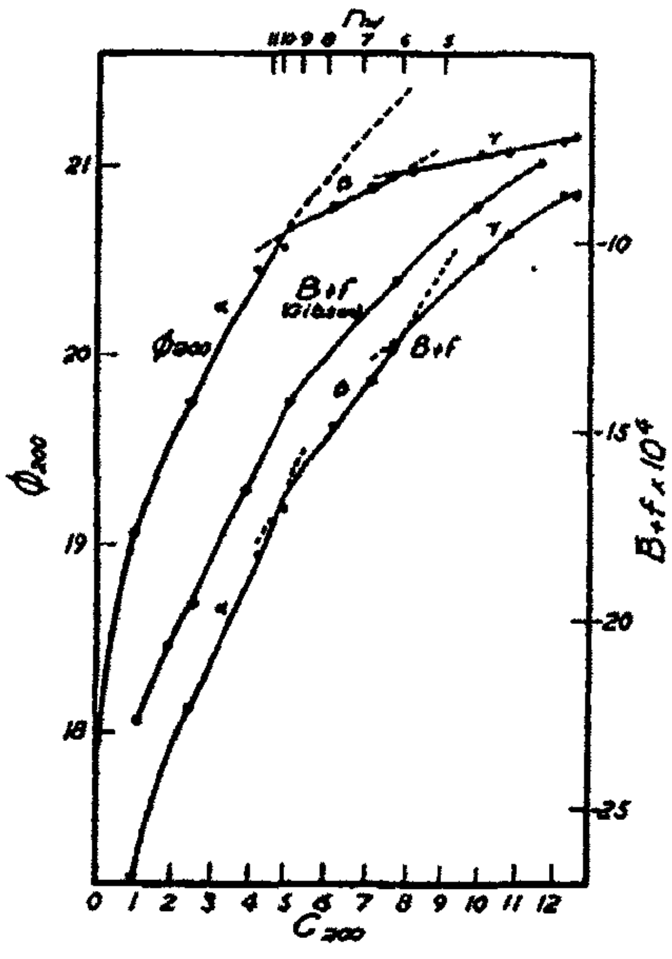

FIG. 1

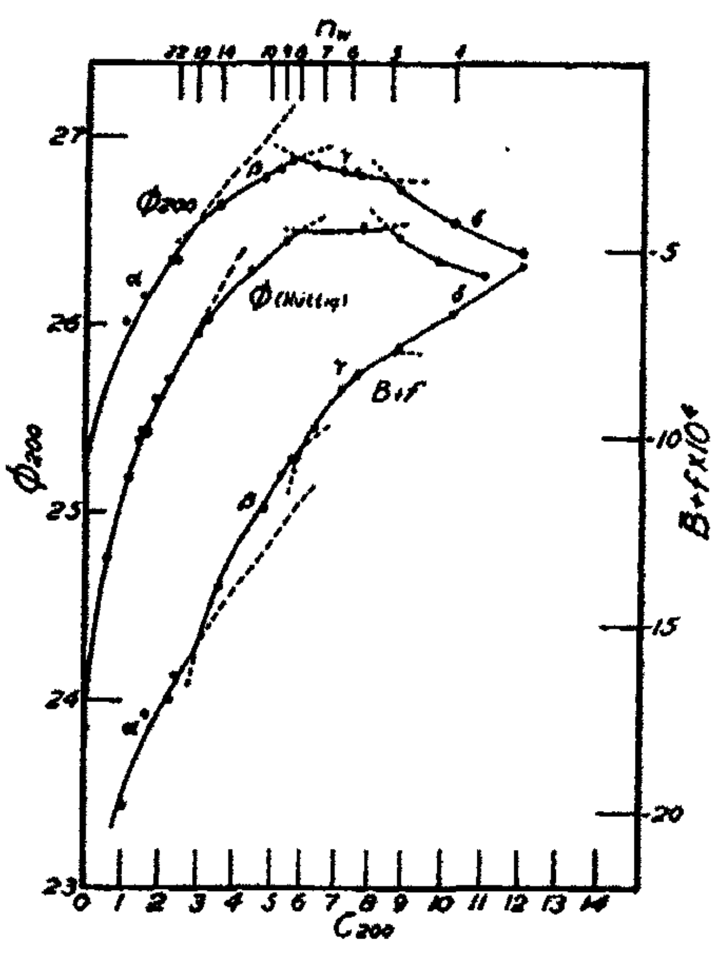

FIG. 2

FIG. 1. APPARENT MOLAL VOLUMES AND APPARENT MOLAL COMPRESSIBILITIES OF LITHIUM CHLORIDE PLOTTED AGAINST CONCENTRATION

FIG. 2. APPARENT MOLAL VOLUMES AND APPARENT MOLAL COMPRESSIBILITIES OF LITHIUM BROMIDE PLOTTED AGAINST CONCENTRATION

On the basis of several recent studies (3, 6, 7) of the question it may be stated that the variation of ϕ with c in solutions of strong electrolytes is represented satisfactorily by the Masson equation:

$$\phi = kc^{\frac{1}{2}} + \phi^0$$

where k and ϕ^0 are constants dependent on temperature and pressure. From the Masson relationship a similar expression can be deduced for the relationship between $(\bar{B} + f)$ and c:

$$(\bar{B} + f) = -\frac{\partial k}{\partial P} c^{\frac{1}{2}} + \bar{B}^0$$

These normal relationships have been shown (11) to be valid for dilute solutions of lithium halides and are depicted in the graphs by the curves marked α. The numerical values of the constants of the above equations which were used in computing the α curves were estimated from the figures given by Geffcken (3) for solutions at atmospheric pressure and from the additive relationships found in paper I. The values of these constants are:

SALT	k_{300}	ϕ^0_{300}	$-\left(\frac{\partial k}{\partial P}\right)_{300} \times 10^4$	$\bar{B}^0_{300} \times 10^4$
LiCl	1.28	17.75	8.05	−34.90
LiBr	1.05	24.71	5.99	−26.00

An inspection of the graphs shows clearly that the simple square-root relationship (α curves) is not valid in concentrated solutions. Since our present interest is a detailed description of these irregularities, we shall examine the chloride and bromide graphs separately.

The ϕ–c plot for solutions of lithium chloride gives evidence of three distinct relationships between ϕ and c, depending on the concentration range: α (normal), β, and γ. The critical concentrations which mark the limits of these relationships, that is, the concentrations at which discontinuities in the ϕ–c plot occur, correspond, so far as can be ascertained, to solutions containing an integral number of moles of water per mole of solute. Thus reading from the graph we get:

Intersection of curves	*Values of n_w*
α–β	10
β–γ	6

The critical $n_w = 10$ value is the same as that which Masson (6) showed to be the limit of validity of his relationship at 18°C. and atmospheric pressure. The second critical value has not been reported before. As might be anticipated, discontinuities in the $(\bar{B} + f)$–c plot occur at the same critical concentrations, but they are less marked than in the ϕ–c plot. For the sake of comparison we have included in the graph another plot of $(\bar{B} + f)$ values derived from the recent measurements by Gibson (2). These values of $(\bar{B} + f)$ are for solutions under a mean pressure of 500 atmospheres and are therefore not directly comparable with our values. The fact that the difference between the two curves is sensibly uniform is to be expected. The absence in Gibson's plot of clear evidence of breaks at the two critical concentrations is at first sight disturbing. This failure to conform to our results, however, is probably due to two facts: first, Gibson's compressibility measurements are slightly less precise than ours, and second, the distribution of the plotted points would tend to obscure rather than enhance the appearance of the breaks in question. In concluding the description of this graph attention may be called to the fact that Scott and Blair (9) also found definite breaks in the variation of the magnetic susceptibility of lithium chloride solutions with concentration at concentrations $n_w = 10$ and 6.

The anomalies of lithium bromide solutions are more striking than those of the chloride solutions. In the ϕ–c plot of these bromide solutions there appear to be three critical concentrations as follows:

Intersection of curves	*Values of n_w*
α–β	18
β–γ	8
γ–δ	5

The first of these concentrations cannot be determined with the same certainty as the others, but the value 18 is unquestionably a minimum figure.

Evidence bearing on the irregularities in these concentrated bromide solutions has been reported by other investigators. Hüttig and Keller (4) in 1925 published the results of an extensive series of density measurements on the basis of which they concluded that the relation of ϕ to n_w undergoes abrupt changes when $n_w = 6$, 30, and 75. Discontinuities were believed to exist at practically the same concentrations in similar plots of the molar refractivity and absorption coefficients against log n_w. Prompted by the critical discussion of these conclusions, Hüttig and Kükenthal (5), three years later, reported the results of new density and composition measurements at 20°C. which were not entirely in agreement with the earlier series. From the new data it was concluded that the only unambiguous discontinuity in the ϕ–log n_w plot occurs when $n_w = 6$. The ϕ and c values (at atmospheric pressure) calculated from the published data of these investigators are included also in figure 1, where they appear as the middle curve. In order to simplify the mechanical features of the graph it was necessary, in plotting the comparison data, to increase all the ϕ values by exactly

0.500 cc. There is an unmistakable resemblance between the two ϕ–c plots, a fact which we have attempted to bring out more clearly by drawing through the plotted points depicting the data of Hüttig and Kükenthal curves similar to those representing our own measurements. It appears that the ϕ–c plot representing the data of these investigators agrees in general with the plot of our data, but does not necessarily confirm our conclusion regarding the exact location of the three discontinuities.

Although no complete interpretation of these unusual irregularities in the concentrated solutions of lithium chloride and bromide is possible at this time, a number of general conclusions may be suggested. The traditional approach to a problem of this kind would be to assume that the irregularities in question arise from alterations in the degree of hydration of the lithium ion which is common to both salts. Thus, Hüttig and Keller, in order to account for the supposed irregularities in their solutions at concentrations $n_w = 6, 30,$ and 75, argued that these critical concentrations corresponded to the theoretical composition of one ($n_w = 6$), two ($n_w = 30$), and three ($n_w = 76$) layers of water molecules packed around the lithium ion. From the standpoint of our results, this simple hydration hypothesis falls down, because the critical concentrations of the solutions of the chloride and bromide are not the same.

We would hardly expect an hydration hypothesis to be applicable to solutions of high concentration where a large fraction of the ions must be in contact with each other. It seems much more to the point to consider the question whether irregularities in these solutions can be ascribed simply to changes in the arrangement or packing of the ions (i.e., the domain of the solute). In attempting to formulate a tentative answer to this question we shall make use of an argument which was developed in paper I. It may be recalled that the quantities ϕ and $(\bar{B} + f)$ have only an *apparent* physical significance, and that a change in magnitude of either of these quantities is possibly the net result of variations in two factors, one related to the domain of the solute and the other related to the number of solvent molecules which, under the influence of ionic forces, have suffered a contraction in volume. In the case of ϕ the possible magnitude of changes in either factor may be of the same order, and therefore it would be impossible from the nature of the changes in ϕ to determine which factor is responsible for the change. On the other hand, in the case of $(\bar{B} + f)$ the possible variation in the compressibility of the solute is so small relative to the possible change in the second factor that the individual effects of the two factors can be partially distinguished. In brief, unless the variation in $(\bar{B} + f)$ with concentration is extremely small, it can be assumed to involve a change in the number of molecules of water in the contracted state.

If we examine the $(\bar{B} + f)$–c plots with this method of analysis in mind, we find no evidence of unusual variation in the amount of water in the contracted state. This negative conclusion is important, because it rules out of consideration one explanation of the irregularities in the ϕ–c plots and therefore means that changes in the domain of the solute must occur in the concentrated solutions. As a matter of fact a more detailed application of this argument leads to the conclusion that the actual changes in the domain of the solute are much greater than the variation in ϕ.

No inferences can be drawn regarding the changes in packing of the ions and water molecules, which we assume to be the cause of the change in the domain of the solute. It is worth noting, however, that Bassett and his collaborators (1), in seeking to elucidate the structures of various lithium salt hydrates and complexes, have been obliged to postulate the existence of various types of polynuclear cations and even complex anions containing lithium. If such complexes exist in the solid state, they doubtless exist also in solution, and it may be suggested that a certain complex may be stable in solution only in a limited concentration range and that the characteristic properties of the several concentration regions depend on the complex or complexes present. The magnetic susceptibility measurements of lithium chloride mentioned above can be looked upon as supporting this viewpoint. The susceptibility of the salt was found to be constant in dilute solutions up to the concentration $n_w = 10$, and to be constant also in very concentrated solutions, $n_w < 6$. In other words, one structural arrangement or complex may be supposed to be stable in dilute solution, another in very concentrated solutions, and in the concentration range (β) a transition between these two types of arrangement may be supposed to take place. It is likely that a determination of the susceptibilities of the bromide solutions would throw some light on these more complex solutions and possibly on the problem as a whole.

SUMMARY

New measurements of the densities and compressibility coefficients of concentrated solutions of lithium chloride and bromide are reported. On the basis of these and previous measurements, the irregular properties of the concentrated solutions of these electrolytes are discussed.

A graphical method for calculating the factor

$$f\left[= \left(\frac{\partial \phi}{\partial c}\right)_P \frac{\mathrm{d}c}{\mathrm{d}P}\right]$$

is described.

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COMMUNICATION TO THE EDITOR

ON THE $(C—C)_{diam.}$ BOND ENERGY

In a recent communication (Lasareff, W.: J. Phys. Chem. **39**, 913 (1935)) with the above title, there was suggested a value of 123 Cal. for the energy of the C—C bond. Since this value is so much larger than that currently accepted, and since this quantity is of great importance in thermochemistry, it seems worth while to examine some of the assumptions made in its derivation. It was assumed that the most probable value for the heat of sublimation of carbon is 154 ± 10 Cal. The recent work of W. Lozier(Phys. Rev. **46**, 268 (1934))on the heat of dissociation of CO leads to two alternate values for this heat of sublimation, 136 ± 2 and 182 ± 2 Cal. Thus the magnitude of this quantity is still rather uncertain. Even if 154 Cal. is accepted, it does not necessarily follow that the energy of the C—C bond is 123 Cal. In the thermodynamic cycle that was used, it was assumed that the diamond dissociates to give ^5S atoms, which then drop to the ^3P state. There is, however, another possibility, that the quadrivalent carbon in diamond, presumably in the ^5S state, may dissociate adiabatically into ^3P atoms. This has been more completely discussed in previous work (Kistiakowsky, G. B., and Gershinowitz, H.: J. Chem. Physics, **1**, 432 (1933); Gershinowitz, H.: Thesis, Harvard University, 1934). If this should be the actual process, the energy of the C—C bond would be 77 ± 5 Cal., which is in much better agreement with the available data than is the larger figure. Even though the energy of a bond is not a constant which is entirely independent of the compound in which the bond occurs, an energy of 123 Cal. for the C—C bond in diamond seems to be quite incompatible with the energy of dissociation of cyanogen into cyanide radicals (77 ± 4 Cal.) (see preceding reference), and with the energy of activation for the decomposition of ethane into methyl radicals (79.5 Cal.) (Rice, F. O., and Johnston: J. Am. Chem. Soc. **56**, 214 (1934)). Neither the theory nor the data from which the value of 123 Cal. has been derived is sufficiently certain to allow one to prefer it to other values.

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September 7, 1935.

FLOTATION OF GALENA AND CHALCOCITE OF NEAR-COLLOIDAL SIZE WITH POTASSIUM AMYL XANTHATE AND AMYL DIXANTHOGEN

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In the beneficiation of ores by ore-dressing processes the treatment of the finest portion of an ore has always been a problem difficult, if not sometimes impossible, of solution. Flotation has proved no exception to this rule. In the "near-colloidal" size-range of mineral particles embracing the entire scale from 5 microns to the size of the truly colloidal particles recovery by flotation has been found to be very unsatisfactory (1, 5).

A study directed to improve the flotation behavior of these particles has been carried on at the Montana School of Mines since 1931. It resulted in the discovery of a successful experimental solution of the problem of flotation of near-colloidal pulps (6). By adding the collector into the pebble mill, so that it is present while the minerals are being ground, satisfactory flotation results can be obtained. This holds true for a number of collectors that comprise a group of the most common ones and of some of their less common derivatives (6).

The present paper deals with the investigation of the effect of some arbitrary variables on the flotation behavior of two mineral mixtures (galena–aplite and chalcocite–aplite) when the collector is present during the grinding.

The variables investigated are: (a) the effect of increasing amount of collector; (b) the effect of some alkaline pH-modifying agents; and (c) the effect of substituting a "neutral" grinding atmosphere for air atmosphere. The study of the effect of the three variables was confined to two collectors: potassium *n*-amyl xanthate and its oxidation derivative, *n*-amyl dixanthogen (*n*-amyl thioformate disulfide).

EXPERIMENTAL METHOD

The grinding and flotation procedure employed was such that all conditions were kept as nearly constant as was experimentally possible. Accordingly the minerals used, galena, chalcocite, and aplite (consisting chiefly of quartz and orthoclase, with a little plagioclase), were specially purified and sized to 20/100 mesh. In all the tests 70 g. of the sulfide mineral and 280 g. of the gangue (aplite) were charged together with the collector into an assay-size Abbé porcelain pebble mill with 225 cc. of water and ground for twenty-one hours. This grinding reduced all the minerals to the size of 3 microns or finer. Flotation of the ground mixtures was conducted in a 500-g. Fahrenwald flotation machine. When necessary, terpineol[1] was used as a frother in amount sufficient (0.05 to 0.20 lb. per ton) to produce froth requisite for normal rate of flotation. Flotation products were analyzed for the metal of the sulfide mineral.

In the tests in which the minerals were ground in a "neutral" atmosphere, i.e., in virtual absence of oxygen, the mill atmosphere was successively evacuated and refilled with nitrogen, grinding being done in an evacuated mill after two flushings with nitrogen. Disregarding the oxygen adsorbed on solid surfaces and that dissolved by water, the oxygen remaining in the mill atmosphere was calculated to be approximately 0.000045 mole. Flotation in these tests was conducted in air, as usual.

Effectiveness of flotation was quantitatively evaluated by means of the selectivity index (3). Recovery of the sulfide mineral was calculated for each test. For graphic presentation of the experimental results the selectivity index was plotted as ordinate against the arbitrary variable as abscissa.

The experimental method outlined above has been found useful in fields of research outside that for which it was originally designed. Thus, by means of this method it was possible to undertake an investigation from which a hypothesis for the non-flotation of minerals of near-colloidal size was formulated (7). Also, it was found possible to substantiate some conclusions regarding the formation of reaction products of the reagent with the mineral base on a more direct study of their formation (4).

EXPERIMENTAL RESULTS

Effect of increasing amount of collector

A series of tests was conducted in which progressively greater amounts of the collectors were used while all other conditions were kept constant. The results for galena and chalcocite with potassium amyl xanthate and with amyl dixanthogen at a "natural" pH (i.e., that obtaining in the pulp after the completion of the flotation operation when no pH modifiers are used) are presented in tables 1 and 2, and graphically in figure 1. In figure 1 along the abscissa the quantity of potassium xanthate (pounds per ton) is plotted. In order to make the results obtained with dixanthogen strictly comparable to those obtained with potassium xanthate, the

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[1] Terpineol does not appear to affect the effectiveness of flotation but merely its rate.

amounts of dixanthogen used are plotted in terms of potassium xanthate containing xanthate radical $(—S\overset{\overset{S}{\|}}{C}OC_5H_{11})$ equivalent to that contained in dixanthogen.

A very curious phenomenon was encountered in the case of the test in which dixanthogen equivalent to 32.0 lb. of potassium xanthate per ton was used for flotation of galena. After grinding, the pulp appeared pinkish white (color of ground aplite), indicating absence of galena within it (usually the presence of galena is indicated by the gray color of the pulp). The galena was finally discovered among the washed pebbles in the form of a hard, compressed, nearly perfect sphere. In addition, there were occasional fragments of compressed galena of irregular shapes adhering to the rubber gasket of the cover of the pebble mill. Upon charging of the white pulp into the flotation machine, instead of the usual froth a greasy and

TABLE 1

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of galena-aplite mixtures

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Pb, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
1.4		24.6	14.4	1.4	17.9
1.4		31.0	14.2	1.8	17.5
2.0		39.0	5.9	3.3	71.7
2.8		50.2	0.39	17.5	98.10
2.8		51.3	0.35	19.0	98.41
2.8		44.7	0.21	21	99.08
4.0		45.9	0.20	22	99.12
4.0		45.4	0.18	23	99.21
5.7		46.2	0.30	18.3	98.68
5.7		44.4	0.26	18.7	98.89
8.0		45.0	0.30	17.7	98.61
8.0		46.2	0.30	18.2	98.56
11.4		47.2	0.17	25	99.21
16.0		56.0	0.22	27	99.00
32.0		56.6	0.16	33	99.23
	1.4	18.0	15.0	1.1	4.1
	2.8	48.0	0.40	17.3	98.14
	4.0	56.0	0.40	20	98.11
	5.7	45.4	0.48	14.1	97.76
	8.0	44.8	0.36	16.1	98.23
	16.0	51.8	0.36	19.1	98.32
	32.0	79.3	0.11	98	99.38

TABLE 2

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of chalcocite-aplite mixtures

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
0.4		24.0	12.5	1.5	9.6
1.0		30.4	13.2	1.8	16.8
2.0		41.2	2.17	6.4	89.8
4.0		36.2	1.13	7.8	94.6
4.0		44.3	1.13	9.6	93.8
8.0		38.1	3.46	4.6	81.8
8.0		31.3	3.20	4.0	84.0
16.0		34.9	1.73	6.0	90.2
16.0		41.3	2.98	5.4	82.7
	0.55	20.7	13.1	1.3	5.9
	1.4	40.5	5.1	4.0	72.0
	2.8	47.9	1.25	10.1	93.3
	5.5	39.8	1.28	8.0	92.7
	11.0	38.1	3.14	4.8	82.6
	22.0	41.6	3.7	4.9	79.8

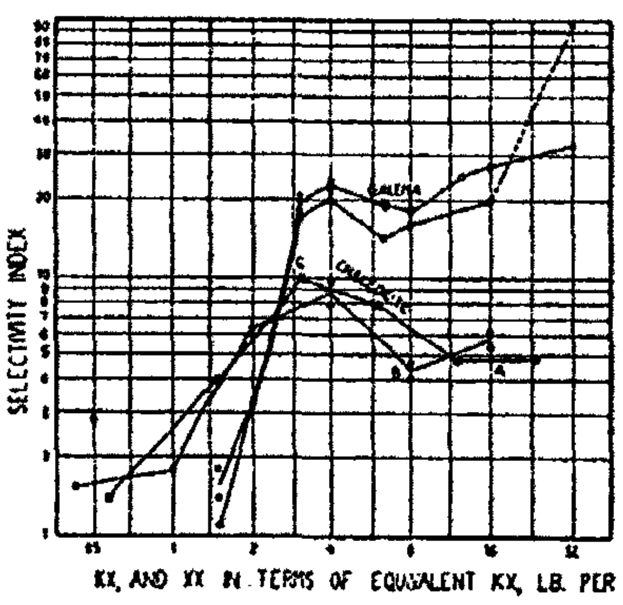

FIG. 1. EFFECT OF INCREASING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF AMYL DIXANTHOGEN ON FLOTATION OF GALENA-APLITE AND OF CHALCOCITE-APLITE MIXTURES

⊠ chalcocite with amyl dixanthogen (XX); ⊕ chalcocite with potassium amyl xanthate (KX); ● galena with amyl dixanthogen (XX); ○ galena with potassium amyl xanthate (KX).

shiny film formed, which was scraped off. The pulp remaining in the machine after this operation was termed tailing, and analyzed for lead. In table 1 the data for the concentrate for this test were calculated by difference from the amount of galena originally put in. The selectivity index obtained for this test is not entirely comparable to the other tests of the series because concentration was not effected in the flotation machine but in the pebble mill during grinding. The selectivity index is so high, chiefly because the concentrate contained very little gangue.

In the case of both galena and chalcocite the results obtained with potassium xanthate and with dixanthogen agree within the limits of experimental error, so that only one curve for both the reagents could be drawn. If this is warranted and the action of both the reagents on the mineral can be assumed identical, one could postulate that the flotation-inducing non-polar coatings produced on the mineral by the reaction of the reagents with the mineral are the same for dixanthogen and potassium xanthate. This speculation is confirmed by the more direct study of the reaction of dixanthogen and of potassium xanthate with chalcocite and with galena (4).

The peculiar shape of the curves for chalcocite in figure 1, that is, the dip of the curves with amounts greater than 4.0 lb. per ton, and the rise with amounts greater than 8.0 lb. per ton, may be explained on the basis of the reaction products formed. Froths from tests in which the amounts of reagents were used that corresponded to the maxima and the dips of the curves yielded upon extraction with benzene different reaction products. These products were identified with those obtained by F. Dewey (6, 5): at point *A* of the curve as cuprous xanthate (Cu_2X_2), and at point *C* as a compound of the type $xCu_2S \cdot yCu_2X_2$. From the knowledge of the reaction of xanthate and dixanthogen with chalcocite given elsewhere (4), the following explanation is proposed:[2] At point *A* the reaction product on the mineral surface is copper xanthate. As the amount of the reagent is decreased while the extent of chalcocite surface remains constant, deficiency of xanthate radical for the formation of Cu_2X_2 causes the formation of complex compounds containing less xanthate per molecule (of the type $xCu_2S \cdot yCu_2X_2$). These compounds are more non-polar; hence they induce better flotation and the curve rises to *C*. With less than the amount of reagent at *C* there is insufficient reagent to coat effectively the mineral surface exposed and flotation is incomplete, as is evidenced by the drop in the curve.

The non-conformance of the dixanthogen and the xanthate curves in the region of high amounts of reagent might not be entirely due to experimental error. When high amounts of potassium xanthate are used the hydroxyl-ion concentration (OH^- ion is derived from hydrolysis of xanthate and from the reaction of xanthate with the oxidation coating of chalcocite, which is a basic carbonate) is possibly increased enough to cause the formation of copper monothiocarbonate (4), which is presumably more

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[2] After Franklin Dewey (2).

polar than the copper xanthate; hence the depression of the xanthate curve at point *B* below the dixanthogen curve.

It may be conjectured that the dip and rise in the galena curves are also due to the formation of different reaction products. Positive evidence for this is not available to date.

It is noteworthy that the rise and dip in the galena and in the chalcocite curves occur at approximately the same amounts of reagents.

Effect of alkaline pH modifiers on flotation of galena

Using galena–aplite mixtures, a series of tests was conducted in which some pH modifiers were added with the collector into the pebble mill. Flotation was carried on as usual. Table 3 summarizes the results of these tests. Unfortunately in most cases it was impossible to determine pH for the different amounts of modifiers used; the pulp was highly dispersed so that clear solution could not be obtained for colorimetric determinations of pH by any method of filtration or clarification available in the laboratory.

It is clear from an examination of the results in table 3 that hydroxyl-ion concentration in the grinding system is very injurious to subsequent flotation. The action of all of the pH modifiers seems to affect flotation adversely if enough modifier be used. Because with a larger amount of collector more modifier is needed to inhibit flotation of galena, it may be conjectured that the action of the modifier is to consume or change the collector or reaction products of the collector with galena so as to render them useless for flotation.

That flotation of galena with amyl dixanthogen is also adversely affected by high pH is shown by the tests given in table 4.

Effect of pH modifiers on flotation of chalcocite

A series of tests was conducted in which chalcocite–aplite mixtures were floated using increasing amounts of potassium xanthate and of dixanthogen with 20.0 lb. of lime per ton. The results are presented in table 5 and in figure 2.

Whereas the use of pH modifiers was injurious to flotation of galena, in the case of chalcocite, lime, one such modifier, seems to be highly beneficial. Again, as in the case when no modifiers were used, within limits of experimental error the results obtained with both the potassium xanthate and with dixanthogen appear to indicate that the action of the two reagents is identical. Conformance of the two curves in the region of large amount of reagents is better than in figure 1 for chalcocite. This is possibly because the concentration of hydroxyl ion remains substantially the same for both reagents, as an excess of hydroxyl ion is present, derived from the lime added.

TABLE 3

Effect of some pH modifiers on flotation of galena-aplite mixtures with potassium amyl xanthate

POTASSIUM AMYL XANTHATE	POTASSIUM HYDROXIDE	CALCIUM* HYDROXIDE	SODIUM CARBONATE	CONCENTRATION OF TOTAL AVAILABLE OH	GRADE, Pb, PER CENT		SELECTIVITY INDEX	RECOVERY
					Concentrate	Tailing		
lb. per ton	*lb. per ton*	*lb. per ton*	*lb. per ton*	*equiv. per liter*				*per cent*
4.0					45.4	0.18	23	99.21
4.0	5.2‡			0.0058	16.6	14.9	1.1	18.6
4.0	10.5§			0.0115	16.2	14.5	1.1	18.1
4.0	26.2¶			0.0288	14.8	14.9	1.0	20.3
4.0		4.0		0.0058	27.6	4.8	2.8	81.0
4.0		4.0		0.0058	36.2	7.7	2.7	62.9
4.0		8.0		0.0115	14.4	14.2	1.0	16.6
4.0		20.0		0.0288	25.2	12.5	1.6	39.0
4.0		40.0		0.0576	27.0	7.0	2.3	71.3
4.0			4.0	0.0053†	43.2	0.68	11.2	96.37
4.0			8.0	0.0106	18.0	14.5	1.1	17.5
4.0			20.0	0.0265	17.4	14.4	1.1	13.2
4.0			40.0	0.0530	17.4	14.9	1.1	13.9
8.0					46.2	0.30	18.2	98.56
8.0		4.0		0.0058	48.2	0.34	17.8	98.37
8.0		8.0		0.0115	45.2	0.22	21	98.96
8.0		20.0		0.0288	48.4	0.28	19.8	98.67
8.0		40.0		0.0576	45.0	0.48	14.0	97.82
16.0					56.9	0.22	27	99.00
16.0		8.0		0.0115	47.2	0.18	24	99.20
16.0		20.0		0.0288	48.0	0.28	19.5	98.67

* Commercial slaked lime, 76 per cent pure.

† Assuming complete hydrolysis of sodium carbonate.

‡ Equivalent to 4.0 lb. $Ca(OH)_2$ per ton.

§ Equivalent to 8.0 lb. $Ca(OH)_2$ per ton.

¶ Equivalent to 20.0 lb. $Ca(OH)_2$ per ton.

TABLE 4

Effect of high pH on flotation of galena with amyl dixanthogen

	DIXANTHOGEN EQUIVALENT TO 4.0 LB. POTASSIUM XANTHATE PER TON	
	20.0 lb. calcium hydroxide per ton	No pH modifier
Per cent lead in concentrate	37.0	56.0
Per cent lead in tailing	5.8	0.40
Selectivity index	3.2	20
Recovery, per cent	75.2	98.11

TABLE 5

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of chalcocite-aplite mixtures with 20.0 lb. of lime per ton

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
1.0		11.7	13.6	0.9	7.9
1.6		24.2	13.3	1.5	5.6
2.0		52.4	0.66	16.4	95.6
2.6		55.4	0.43	22	97.5
2.6		55.7	0.50	20	97.5
4.0		47.0	0.31	19.9	97.2
4.0		41.8	0.33	16.8	98.3
8.0		43.6	0.31	18.3	98.5
9.7		43.2	0.29	18.6	98.5
32.0		49.0	0.16	27	98.8
	1.6	15.3	13.40	1.1	5.3
	2.6	56.6	0.47	22	97.6
	5.5	46.0	0.47	15.6	97.8
	5.5	46.6	0.52	15.2	97.8
	7.2	47.0	0.36	18.4	98.2
	11.0	44.7	0.31	18.3	98.5

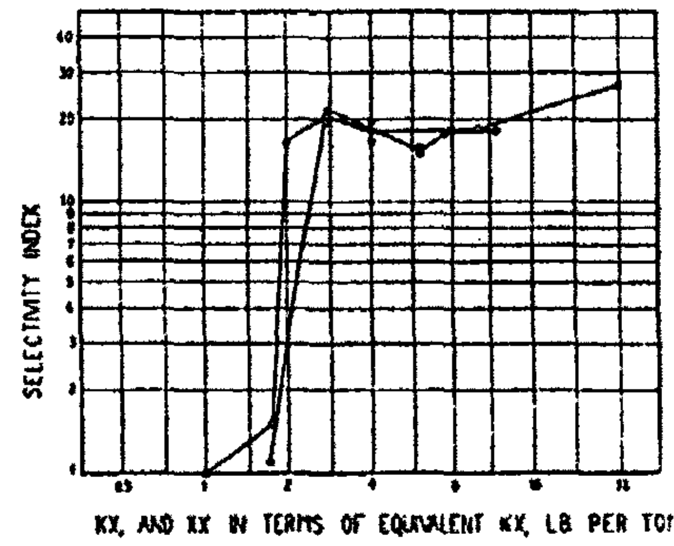

FIG. 2. EFFECT OF INCREASING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF AMYL DIXANTHOGEN ON FLOTATION OF CHALCOCITE-APLITE MIXTURES WITH 20.0 LB. OF LIME PER TON (COMPARE WITH FIGURE 1)

● Chalcocite with amyl dixanthogen (XX) and 20.0 lb. CaO per ton; ○ chalcocite with potassium amyl xanthate (KX) and 20.0 lb. CaO per ton.

In order to investigate fully the effect of lime on flotation of chalcocite a series of tests was conducted in which both the amount of potassium xanthate and the amount of lime were the arbitrary variables. These tests are presented in table 6. The results are presented graphically in figure 3, in which the selectivity index is plotted as the coördinate perpendicular to the plane of the paper, and contour lines are drawn connecting projections in the plane of the paper of points of equal selectivity index.

The effect of potassium hydroxide and of lime on flotation of chalcocite with constant amount of amyl dixanthogen is shown by table 7 and by figure 4. Excessively high amounts of potassium hydroxide were necessary to induce the requisite pH. This is possibly because the hydroxide was consumed by reaction with the gangue.

TABLE 6

Effect of varying amounts of potassium amyl xanthate and of lime on flotation of chalcocite-aplite mixtures

POTASSIUM AMYL XANTHATE	CALCIUM OXIDE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
1.8	4.3	47.6	0.85	12.2	95.5
2.0	8.0	48.6	0.70	13.8	96.3
4.0	8.0	51.6	1.76	9.5	91.0
8.0	8.0	51.7	1.09	12.1	94.7
16.0	8.0	49.5	0.52	16.5	97.4
1.4	10.3	25.9	13.4	4.9	11.5
2.0	12.0	56.2	0.43	22	96.8
4.0	12.0	51.6	0.45	18.8	97.7
16.0	12.0	46.3	0.34	18.6	97.1
1.3	13.1	16.3	14.0	1.1	1.7
32.0	14.3	47.8	0.24	23	99.5
7.2	15.4	51.9	0.38	21	98.2
1.7	16.0	32.4	12.4	6.2	16.8
2.3	16.0	48.5	0.49	18.9	98.0
16.0	17.1	48.6	0.32	20	98.4
5.7	18.3	47.0	0.34	19.0	98.6
2.9	18.9	48.5	0.39	18.5	98.0
5.7	22.9	39.8	0.44	13.7	97.8
5.7	28.6	45.2	0.19	24	99.1
11.4	28.6	51.6	0.29	24	98.6

Effect of "neutral" grinding atmosphere

A series of tests was conducted in which the minerals were ground in a pebble mill whose atmosphere was practically devoid of oxygen. Oxygen was removed by the procedure given earlier in the paper. In the series of tests using chalcocite, 20.0 lb. of lime per ton was added together with the collector, whereas in galena tests no modifying agents were used. The results are presented in tables 8 and 9 and in figure 5.

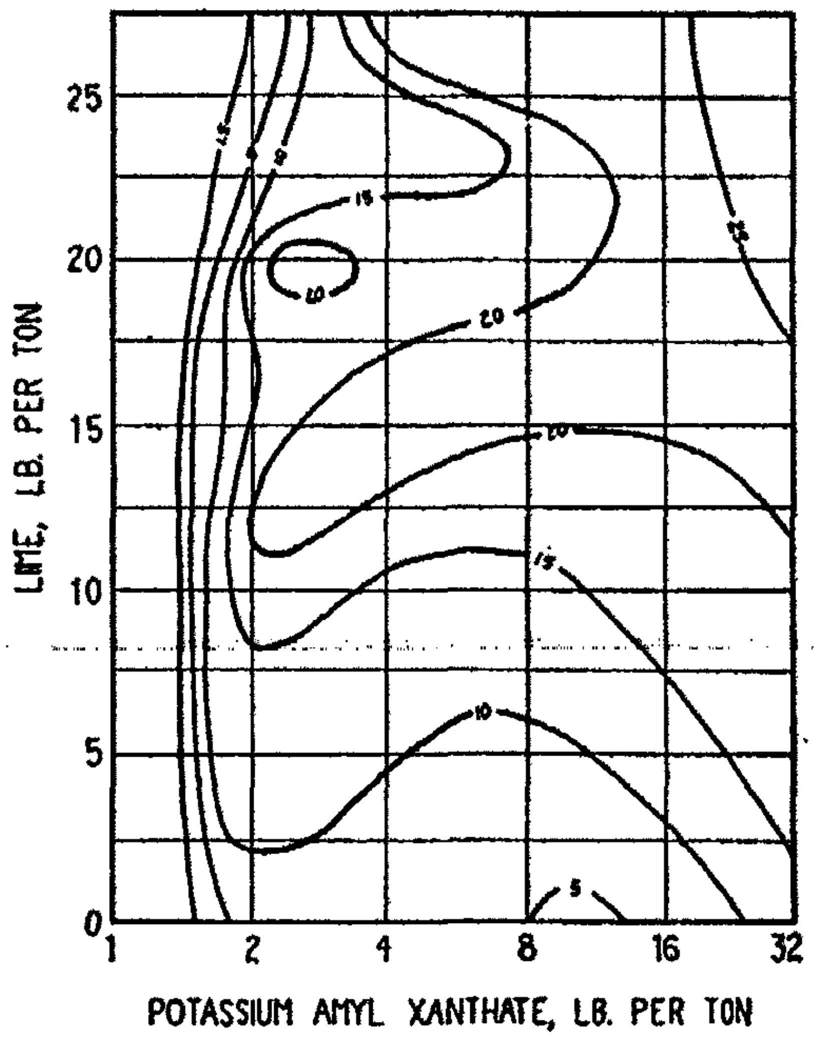

FIG. 3. EFFECT OF VARYING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF LIME ON FLOTATION OF CHALCOCITE–APLITE MIXTURES

TABLE 7

Effect of pH resulting from increasing amounts of potassium hydroxide and of lime on flotation of chalcocite-aplite mixtures with amyl dixanthogen equivalent to 5.4 lb. of potassium amyl xanthate per ton

POTASSIUM HYDROXIDE	CALCIUM OXIDE	pH	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
			Concentrate	Tailing		
lb. per ton	*lb. per ton*					*per cent*
23.0*		10.2	39.6	0.62	11.2	96.9
57.0		11.7	39.8	0.46	13.1	97.6
114.0		12.4	38.9	0.59	11.3	96.8
	4.0	8.6	40.2	0.67	11.2	96.4
	11.4	10.2	39.1	0.27	17.1	98.7
	20.0	11.2	46.0	0.47	15.6	97.8
	40.0	12.0	41.9	0.36	16.0	98.3

* Amount yielding OH^- ions equivalent to OH^- ions yielded by half as many pounds of CaO per ton.

Again, as in figures 1 and 2 and in tables 1, 2, and 5 the two reagents, dixanthogen and potassium xanthate, seem to yield results for which only one curve need be drawn for a given mineral. Also, the shapes of the

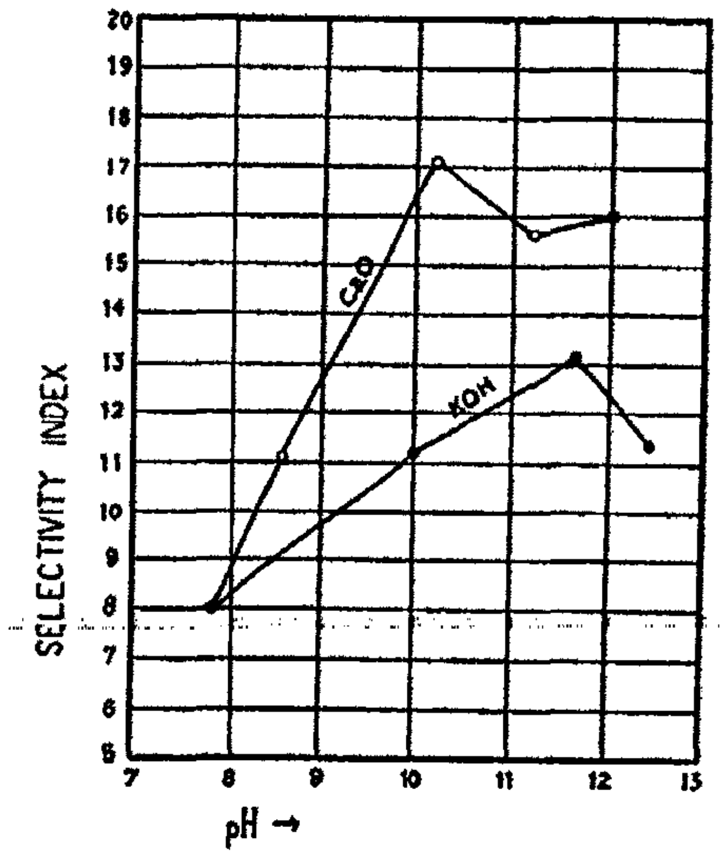

Fig. 4. Effect of pH Resulting from Increasing Amounts of Potassium Hydroxide and of Lime on Flotation of Chalcocite-Aplite Mixtures with Amyl Dixanthogen Equivalent to 5.4 lb. Potassium Amyl Xanthate per Ton

TABLE 8

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of chalcocite-aplite mixtures ground in absence of air

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Cu, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
0.46		No flotation		1.0	0
0.73		36.6	1.06	8.1	95.1
1.14		45.9	0.61	13.8	98.4
1.6		53.6	0.19	27	99.0
2.9		46.6	0.15	29	99.3
2.9		48.1	0.14	30	99.4
2.9		48.3	0.12	32	99.5
5.5		48.3	0.13	32	99.3
11.4		50.1	0.069	46	99.7
	0.46	No flotation		1.0	0
	0.9	43.5	0.29	18.7	98.6
	1.6	44.9	0.18	25	99.1
	2.9	48.5	0.122	33	99.5
	5.5	49.8	0.11	26	99.4
	11.4	48.9	0.077	42	99.6

TABLE 9

Effect of increasing amounts of potassium amyl xanthate and of amyl dixanthogen on flotation of galena-aplite mixtures ground in absence of air

POTASSIUM AMYL XANTHATE	AMYL DIXANTHOGEN IN TERMS OF EQUIVALENT POTASSIUM XANTHATE	GRADE, Pb, PER CENT		SELECTIVITY INDEX	RECOVERY
		Concentrate	Tailing		
lb. per ton	*lb. per ton*				*per cent*
0.57		No flotation		1.0	0
1.0		No flotation		1.0	0
2.0		58.9	0.30	25	98.54
4.0		53.6	0.21	26	99.06
8.0		55.8	0.18	30	99.20
16.0		54.9	0.18	29	99.17
32.0		58.1	0.19	33	99.24
	1.0	42.4	3.6	4.7	85.3
	1.4	54.6	0.80	13.3	96.31
	2.8	52.0	0.30	21	98.65
	5.7	54.6	0.165	30	99.27
	8.0	54.2	0.124	35	99.45
	32.0	63.9	0.103	49	99.47

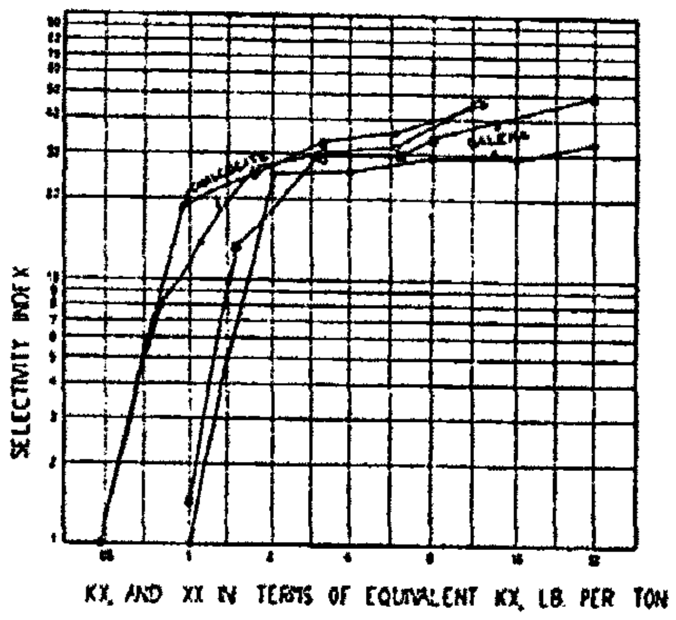

FIG. 5. EFFECT OF INCREASING AMOUNTS OF POTASSIUM AMYL XANTHATE AND OF AMYL DIXANTHOGEN ON FLOTATION OF CHALCOCITE-APLITE AND OF GALENA-APLITE MIXTURES GROUND IN ABSENCE OF AIR (COMPARE WITH FIGURES 1 AND 2)

● chalcocite with amyl dixanthogen (XX) and 20 lb. CaO per ton; ○ chalcocite with potassium amyl xanthate (KX) and 20 lb. CaO per ton; ✖ galena with amyl dixanthogen (XX); ⊕ galena with potassium amyl xanthate (KX).

curves for galena and for chalcocite are similar, as they were in figure 1. However there is no dip in the curves as there was in those of figure 1.

If one compares the chalcocite curves of figure 2 with those of figure 5, it can be noted that to induce flotation when chalcocite is ground in the absence of air the amount of reagent necessary is approximately half that required to induce flotation when it is ground in presence of air.

Apparently no such simple relation exists in the case of galena, although markedly less reagent is required to induce flotation when galena is ground in "neutral" atmosphere than that required when it is ground in air.

It is to be noted that, likewise, to induce flotation of chalcocite the amount of reagent required is approximately one half that necessary in the case of galena.

All these facts may have a significance in the interpretation of floatability in the light of reaction products. But such an interpretation cannot be given at present, because our knowledge of the reactions has not as yet been put on a strictly quantitative basis.

The results obtained when the minerals are ground in neutral atmosphere are superior to any hitherto obtained in this research. This seems to indicate that oxygen has some undetermined injurious action when it is present, as it always is in practice, in the grinding atmosphere.

CONCLUSIONS

1. The action of potassium amyl xanthate and of amyl dixanthogen on galena and on chalcocite of near-colloidal size appears to be identical when the mineral is ground in air.
2. Concentration of hydroxyl ion influences profoundly the flotation of sulfides, and its influence is specific to each of the sulfides.
3. High pH is conducive to better flotation of chalcocite of near-colloidal size with amyl dixanthogen and with potassium amyl xanthate, whereas it is destructive to flotation of galena with the same reagents.
4. It is proposed that the hydroxyl radical influences the formation of reaction products whose formation in turn affects flotation of the sulfide mineral.
5. Under the experimental conditions employed, oxygen in grinding has a noticeable injurious effect on the flotation of chalcocite and of galena with potassium amyl xanthate and with amyl dixanthogen, as evidenced by the results obtained when the minerals are ground in virtual absence of oxygen; they are superior to any hitherto obtained in this research.
6. The action of potassium amyl xanthate and of amyl dixanthogen on galena and on chalcocite appears to be identical when the mineral is ground in a "neutral" atmosphere, i.e., in virtual absence of air.

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THE KINETICS OF THE REACTION BETWEEN PERMANGANATE AND MANGANOUS IONS[1]

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INTRODUCTION

The reaction between permanganate and manganous ions (the Guyard reaction (1); manganese dioxide is formed) is slow in acid solutions, even at high temperatures. This is a familiar fact, since the recognition of the end point in the permanganate–oxalate titration depends on it. The present paper contains a brief description of the writer's recent observations showing that the reaction has an incubation period and that it is autocatalytic. For the sake of continuity, the main observations and general conclusions will be given first, followed by the experimental details. In order to facilitate cross reference, corresponding sections and the figures illustrating them will be given the same numbers (sections A–I to A–VIII, sections B–I to B–VII, and figures 1 to 7). In the present discussion a solution containing manganous and permanganate ions will be referred to as a Guyard solution. The heterogeneous mixture resulting from such a solution will be called a Guyard mixture.

A–I. This investigation is a side product of an unpublished study of the permanganate–thiosulfate reaction, undertaken by the writer. It is known that each mole of thiosulfate ion reduces one equivalent of a mild oxidizing agent, such as iodine. It reduces a larger number of equivalents when reacting with manganese dioxide. Finally, thiosulfate ion reduces a still larger number of equivalents when it reacts with permanganate ion.

It was to be expected, therefore, that, if a small amount of thiosulfate ion is added to an acid Guyard mixture, the quantitative results should depend on the age of the latter at the time of mixing, in other words, on the amount of manganese dioxide formed at the expense of the permanganate. This prediction was tested and verified in a series of experiments. The curve obtained in this series of experiments gave the first indication that the reaction between permanganate and manganous ions is autocatalytic in acid solution. This was supported by visual observations on the Guyard

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[1] This investigation is a part of a project carried out on a grant from the National Research Council, to which the writer takes pleasure in expressing his obligation.

[2] Present address: San Francisco City Junior College, San Francisco, California.

solution; the latter remained clear and purple for a measurable time (incubation period), after which the reaction proceeded at a rapidly increasing rate.

A–II. In order to study the effect of acid on the Guyard reaction, visual observations were made on mixtures containing the same amounts of potassium permanganate and manganous sulfate, but varying amounts of perchloric or sulfuric acid. It was found that both the incubation period and the total reaction time were proportional to the concentration of the perchloric acid. When sulfuric acid was used, the results were complicated by the tendency of sulfate ion to shunt the reduction of permanganate by manganous ion into another reaction path. This tendency was linked with the formation of manganic sulfate complex ion.

A–III. Visual observations were next carried out on mixtures containing constant amounts of potassium permanganate, manganous sulfate, and sulfuric acid, and varying amounts of potassium fluoride. It was found that fluoride ion also modifies the process of reduction of permanganate ion. The effect of fluoride ion was stronger than that of sulfate ion, and this was linked with the greater tendency to form the manganic fluoride complex.

A–IV. The observations described in sections A–II and A–III were visual and therefore subjective, to a certain extent. After several attempts to develop an objective method of following the Guyard reaction, the writer decided to use oxalic acid for this purpose. (The use of thiosulfate ion was avoided because the stoichiometry of the several reactions is not sufficiently well understood.) The oxalic acid method depends on the fact that under certain conditions the acid is oxidized by manganese dioxide but not by permanganate ion. In the presence of a small excess of manganous ion both react rapidly with the acid, forming manganic oxalate complex. In this fast reaction one half of the manganese dioxide is reduced by the acid, whereas very little of the permanganate ion is reduced by the oxalic acid; it is practically entirely reduced by the manganous ion:

$$MnO_4^- + 4Mn^{++} + 10H_2C_2O_4 = 5Mn(C_2O_4)_2^- + 4H_2O + 12H^+ \quad (1)$$

$$2MnO_2 + 5H_2C_2O_4 = 2Mn(C_2O_4)_2^- + 2CO_2 + 4H_2O + 2H^+ \quad (2)$$

It follows that, if excess oxalic acid is added to a Guyard mixture, the loss of oxidizing titer will give a measure of the amount of manganese dioxide formed at the expense of the permanganate ion. It will be shown in the experimental part of this paper that the oxalic acid method is applicable only when the concentration of the manganous ion is low. If the concentration of manganous ion is high, the manganese dioxide will dissolve in oxalic acid without reduction.

A–V. With the use of oxalic acid it was shown once more that the Guyard reaction in acid solution is autocatalytic. It was also shown that the rate of reaction in a Guyard mixture was increased by a decrease in acidity or by an increase in the concentration of either the manganous or the permanganate ion.

A–VI. In an attempt to find the cause of the autocatalysis, the assumption was tested that the manganese dioxide formed in the reaction was the responsible agent. In several series of experiments manganese dioxide was added to the initial solution. It was found that this procedure eliminated the incubation period and accelerated the reaction. It was further found that the effectiveness of the manganese dioxide as a catalyst depended on the mode of its preparation; the solid prepared in neutral solution was much more effective than that prepared in acid solution. From visual observations it was clear that the "neutral" solid was much more highly dispersed than the "acid" solid.

A–VII. It was realized that the difference between the catalytic activities of manganese dioxide prepared in neutral and in acid solution might have been due in part to a difference in chemical composition. The two solids were analyzed iodometrically and were both found to contain tetravalent manganese only. If there was any difference at all in the composition of the "neutral" and "acid" manganese dioxide, it could have been only in the degree of hydration of the oxide.

EXPERIMENTAL

B–I. The reaction of thiosulfate ion with excess acid mixture of permanganate and manganous ions. In this series of experiments the following procedure was used: 150 cc. of a solution was prepared containing 0.00333 *M* potassium permanganate, 0.00867 *M* manganous sulfate, and 0.0666 *M* sulfuric acid. At the time t after mixing, 10 cc. of 0.01 *M* sodium thiosulfate was added. The thiosulfate was oxidized rapidly in all cases. Thirty seconds later aqueous potassium iodide was added (the time of addition of potassium iodide is immaterial). The iodine formed was titrated with standardized sodium thiosulfate solutions. The ratio

$$\frac{\text{number of equivalents of oxidizing agent reduced}}{\text{number of moles of thiosulfate added}}$$

was calculated from the observed loss of oxidizing titer.

The experimental results are shown in figure 1. Briefly, they can be summarized as follows: Freshly prepared solutions, containing only permanganate and manganous ions, lose four equivalents of oxidizing agent per mole of thiosulfate added. Old solutions, containing only manganese dioxide and manganous ion, lose only two equivalents of oxidizing agent. Intermediate results are obtained with intermediate solutions. The shape of the curve gives a clear indication of the autocatalytic nature of the Guyard reaction. This is verified by the visual observations given in figure 1. In this particular Guyard solution the color remained unchanged about twenty seconds.

If the manganous sulfate is omitted (experiment 2062, figure 1), thiosulfate ion reduces six equivalents of oxidizing agent. The deviation of experiment 2062 from the main series is significant: although the manganous ion reacts slowly with permanganate ion, it exerts a strongly modifying influence on the rapid permanganate–thiosulfate reaction.

B–II. Visual observations on the effects of acid and of sulfate ion on the rate of the Guyard reaction. The effect of perchloric acid is shown in figure 2 (lines 2090). In each experiment of this series the initial solutions contained the same amount of permanganate and manganous ions but a variable amount of perchloric acid. The points on lines 2090 show the duration of the incubation period and the total reaction time for the respective experiments. It will be seen that the rates were inversely proportional to the concentration of the acid.

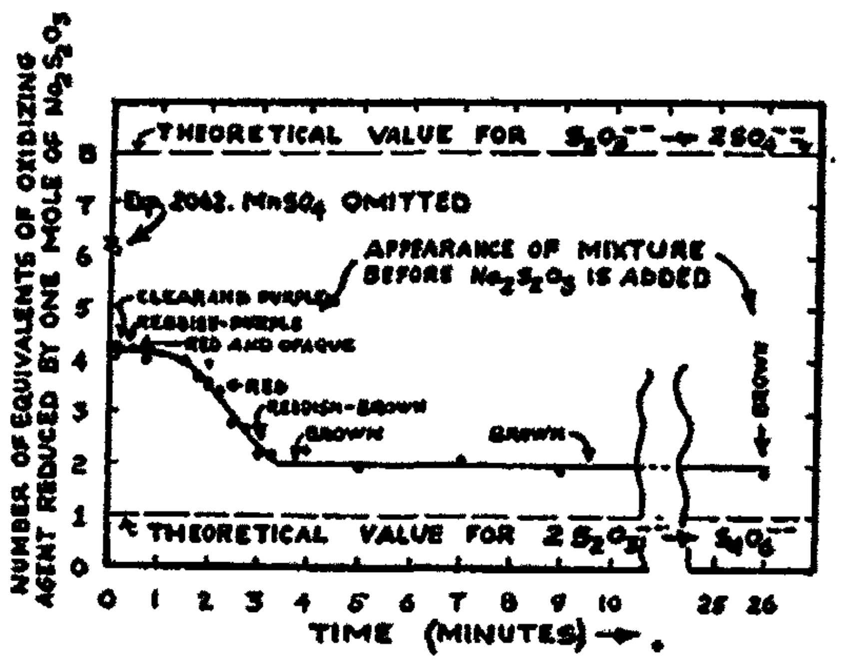

FIG. 1. FIRST EVIDENCE OF THE AUTOCATALYTIC NATURE OF THE GUYARD REACTION

The oxidation of sodium thiosulfate by a large excess of a mixture containing 0.00333 *M* potassium permanganate, 0.00867 *M* manganous sulfate, and 0.0667 *M* sulfuric acid, as a function of the age of the mixture. The figure also shows the appearance of the Guyard mixture, as a function of time.

The effect of sulfuric acid is less simple. The color change and the complete disappearance of permanganate ion take place earlier than in an equal concentration of perchloric acid. Sulfate ion tends to form a red complex with manganic ion. It will be shown in the theoretical part of this paper why this tendency exerts a strong influence on the course of the Guyard reaction. At this time it will suffice to state that the complex contains more than one sulfate radical, and for this reason the sulfate effect predominates over the acid effect at the higher concentrations of sulfuric acid. As a result, curve 2083 is bent toward the horizontal axis.

B-III. The effect of fluoride ion on the Guyard reaction. In series 2085 (figure 3) the concentration of potassium fluoride was the only variable. Fluoride ion forms a much more stable manganic complex than sulfate ion does. On the other hand, the color of manganic fluoride complex is not so pronounced that a small amount of it could be detected in the presence of a large amount of permanganate. Since fluoride ion also retards the precipitation of manganese dioxide, the net result is that small amounts of fluoride *appear* to increase the incubation period (the time at the end of which the solution begins to differ in appearance from a standard permanganate solution). When large amounts of fluoride are used, the consumption of

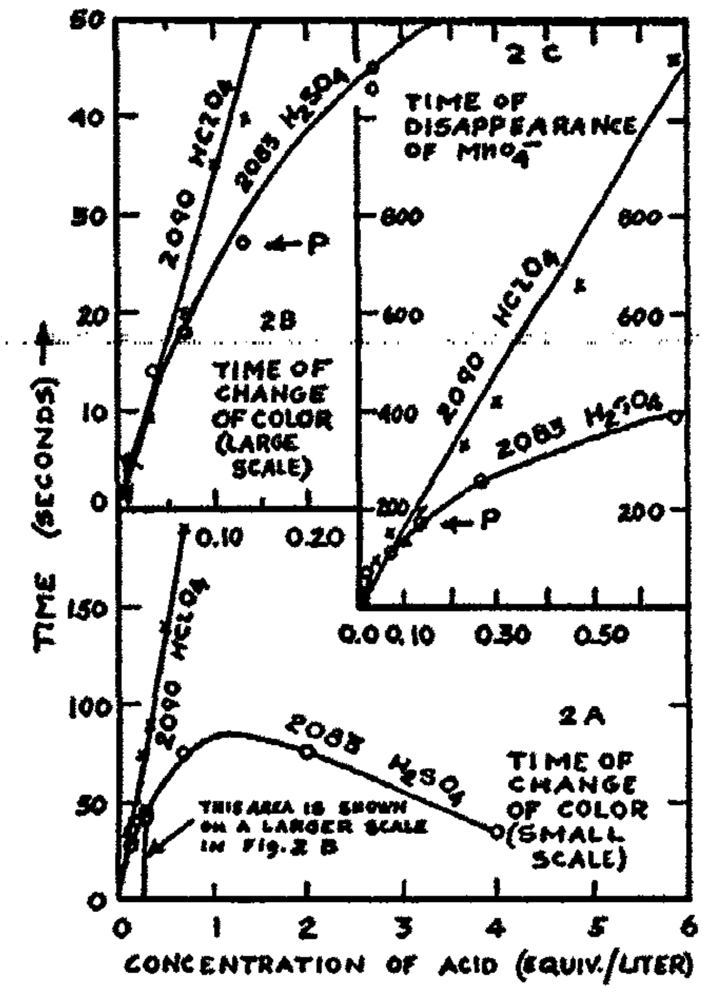

FIG. 2

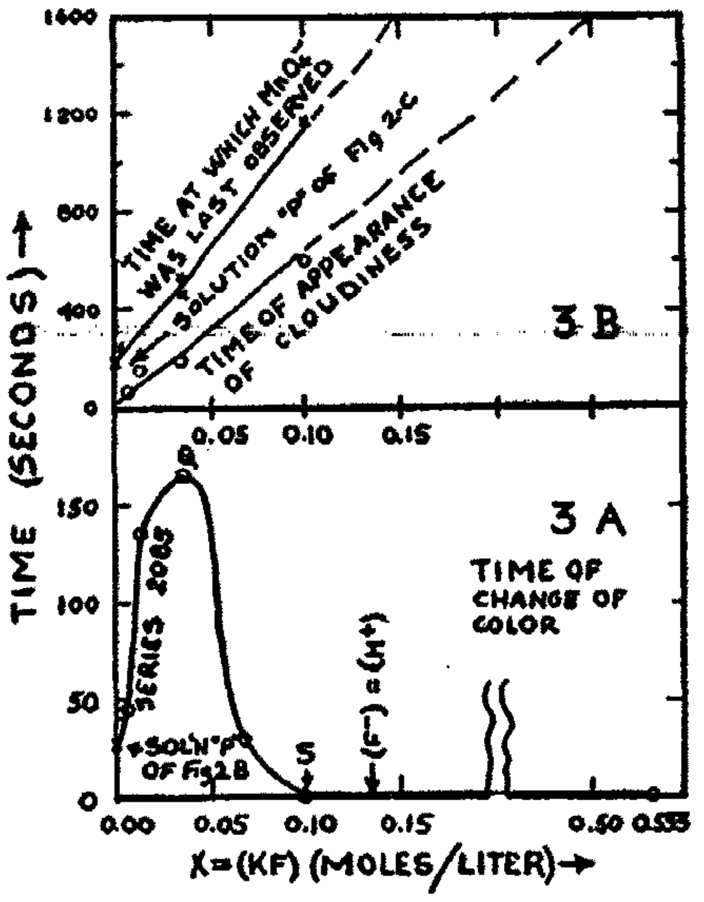

FIG. 3

FIG. 2. TIME-COLOR OBSERVATIONS ON SOLUTIONS CONTAINING 0.00333 M POTASSIUM PERMANGANATE, 0.00835 M MANGANOUS SULFATE, AND VARYING CONCENTRATIONS OF PERCHLORIC OR SULFURIC ACID

The incubation period, preceding the change of color toward red, is shown in figures 2A and 2B. The total reaction time is shown in figure 2C. The precipitate appears soon after the color begins to change.

FIG. 3. THE INCUBATION PERIOD, THE TIME OF APPEARANCE OF THE PRECIPITATE, AND THE TOTAL REACTION TIME IN SOLUTIONS CONTAINING 0.00333 M POTASSIUM PERMANGANATE, 0.00835 M MANGANOUS SULFATE, 0.133 N SULFURIC ACID, AND VARYING AMOUNTS OF POTASSIUM FLUORIDE

In the ascending branch of curve 2085 the accelerating effect of the fluoride ion is masked by the retardation of the precipitation of manganese dioxide.

permanganate manifests itself in a weakening of the purple color. Under such conditions it becomes obvious that fluoride ion speedily converts permanganate and manganous ion into manganic fluoride complex (descending part of curve 2085). The precipitation of manganese dioxide is progressively retarded by increasing amounts of fluoride ion (figure 3B).

It will be recalled that fluoride ion combines with hydrogen ion, forming a weak acid. This is a factor which should be taken into consideration when interpreting curve 2085. A vertical arrow indicates the concentration of fluoride which is equivalent to the acid present. It is obvious that a rapid color change takes place even in solutions in which not all the hydrogen ion was used up by the fluoride.

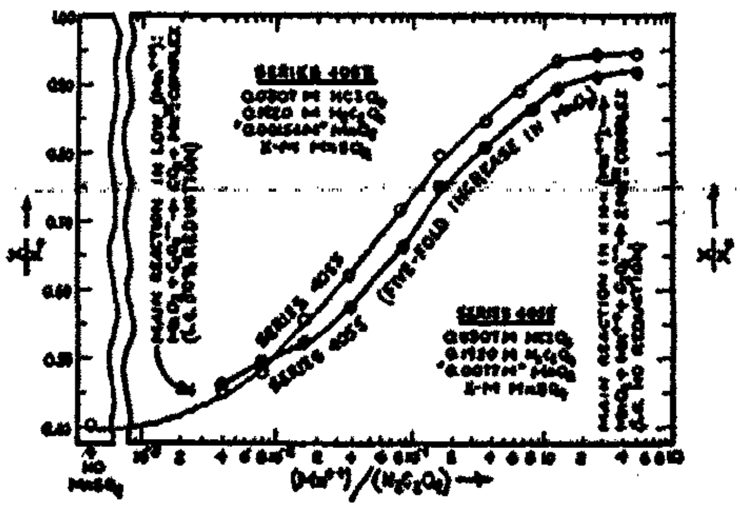

Fig. 4

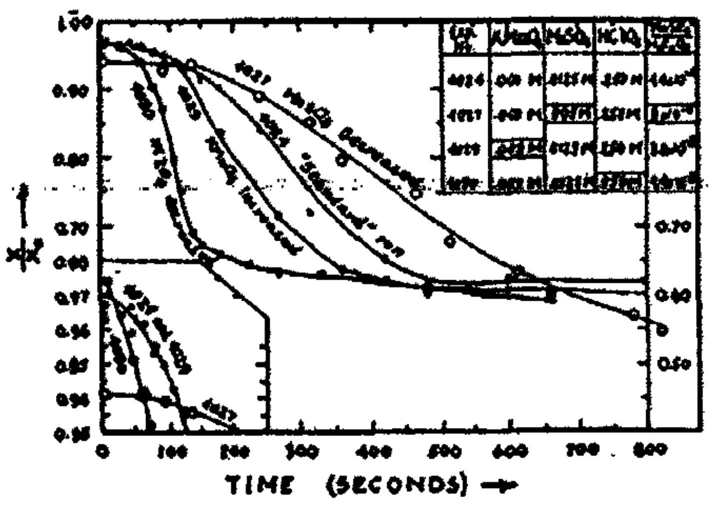

Fig. 5

Fig. 4. The Influence of Manganous Ion on the Manganese Dioxide–Oxalic Acid Reaction

X/X_0 is the ratio of the number of equivalents of manganic ion formed to the number of equivalents of manganese dioxide used. In the absence of manganous ion the reaction can follow only one path. In the presence of manganous ion the reaction can follow two paths. When the ratio $(Mn^{++})/(H_2C_2O_4)$ is large, the second path predominates. The extreme limits of the curve fall below the theoretical values 0.50 and 1.00 because of induced oxidation of oxalic acid.

Fig. 5. The Effect of Perchloric Acid, Potassium Permanganate, and Manganous Sulfate on the Course of the Guyard Reaction

X/X_0 gives a measure of the amount of manganese dioxide formed. The lower left insert shows the initial portions of the four curves, with a larger vertical scale. The upper right insert gives the initial concentrations in the four solutions. The last column gives the value, toward the end of each run, of the ratio which determines the final titer value of the solution (cf. figure 4).

B-IV. The reaction of manganese dioxide with oxalic acid. A semiquantitative method of analyzing a changing Guyard mixture. Curves 4053 and 4055, figure 4, show the results of two series of experiments in each of which known quantities of freshly precipitated manganese dioxide were treated with solutions containing the same amount of oxalic acid and varying amounts of manganous sulfate. The oxalic acid was immediately followed with potassium iodide. It is obvious from figure 4 that at low concentrations of manganous ion the manganese dioxide dissolves by oxidizing the oxalic acid. At high concentrations of manganous sulfate the manganese dioxide dissolves without an appreciable loss of oxidizing titer, by oxidizing the manganous ion. It follows that oxalic acid can be used to differentiate between manganese dioxide and permanganate ion only in those solutions in which the concentration of manganous ion is not too large (see section A–IV).

B–V. The effects of acid, of permanganate ion, and of manganous ion on the course of the Guyard reaction. The course of the Guyard reaction, as revealed by the oxalic acid method, is shown in curve 4024, figure 5. The initial composition of the solution is given in the figure. At the desired time the reaction was stopped by adding excess oxalic acid. This was followed at once with potassium iodide. The loss of oxidizing titer gave a measure of the amount of manganese dioxide formed. Each point on the curve represents one such experiment. The other three curves in figure 5 show the effects of acid, of permanganate ion, and of manganous ion. A decrease in the acid concentration or an increase in the concentration of either one of the two reacting ions increases the rate of the Guyard reaction.

In a separate series of experiments it was found that direct sunlight has only a small effect, if any, on the rate of the reaction.

B–VI. Manganese dioxide catalyzes the Guyard reaction in acid solution. Curve 4042, figure 6, shows the usual course of the Guyard reaction in a solution whose composition is the same as in series 4030, figure 5. In series 4043, 10 per cent of the permanganate had been converted into manganese dioxide before the acid and the remainder of the manganous ion were added. In calculating the loss of oxidizing titer, allowance was made for the fact that manganese dioxide was present to start with. The catalytic effect is pronounced.

The manganese dioxide used as initial catalyst in series 4043 was prepared in neutral solution. As shown in figure 6, the effectiveness of the catalyst did not change on "aging" it either in neutral or in acid solution. Curves 4046 and 4050 show that the activity of manganese dioxide prepared in acid solution is smaller. Visual observations on the color and the rate of settling of the precipitate gave convincing evidence that the "neutral" solid was more highly dispersed than the "acid" one. Once the solid had formed, its degree of dispersion was affected only very little by aging it either in neutral or in acid solution.

B–VII. The chemical composition of the solid used as catalyst. Since the catalytic activities of the "acid" and the "neutral" catalysts differed so markedly, the solids were analyzed to determine the valence of the manganese in each. In preparing the catalyst, a small amount of manganous ion was added to excess permanganate. The composition of the solid was determined iodometrically; the heterogeneous mixture was filtered, and the distribution of oxidizing titer between precipitate and filtrate was studied. The following results were obtained (see figure 7).

Experiment 4061. Catalyst was prepared in acid solution. The reagents were introduced into a flask in the indicated order: 10.0 cc. of 0.002 *M* potassium permanganate; 1.0 cc. of 1 *M* perchloric acid; 0.30 cc. of 0.01 *M* manganous sulfate. Theoretical distribution of oxidizing titer, if manganese dioxide is formed: 10 per cent in the solid phase, 90 per cent in the precipitate. Theoretical distribution if manganic oxide (Mn_2O_3) is formed: 3.75 per cent and 96.25 per cent. Observed distribution: 10.3 per cent and 87.0 per cent.

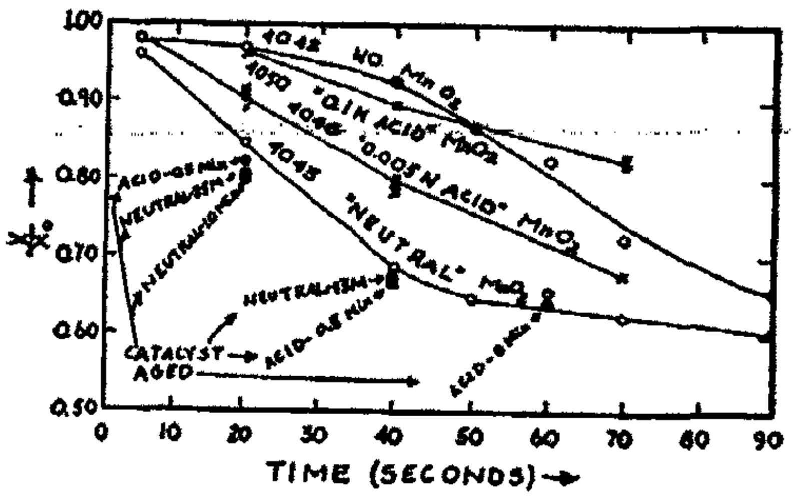

FIG. 6

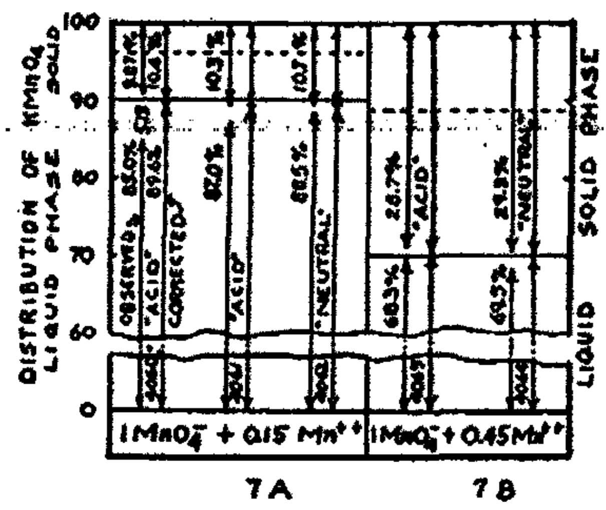

FIG. 7

FIG. 6. THE CATALYTIC EFFECT OF MANGANESE DIOXIDE IN THE GUYARD REACTION IN ACID SOLUTION

Manganese dioxide prepared in neutral solution is more active than that prepared in acid solution. "Aging" the catalyst, either in neutral or in acid solution, does not affect its activity. This is due to the fact that the highly dispersed "neutral" manganese dioxide does not coagulate into larger particles on acidulation.

FIG. 7. THE CHEMICAL COMPOSITION OF THE CATALYST

The solid horizontal lines indicate the theoretical titer distribution between the liquid and the solid phase if the catalyst is MnO_2. The dotted lines give the theoretical distribution if the catalyst is Mn_2O_3. The experimental values were corrected by the same factor, to add up to 100%. It is obvious that the manganese in the catalyst is tetravalent.

Experiment 4062. "Neutral" catalyst was prepared (perchloric acid omitted). Observed distribution: 10.6 per cent and 88.5 per cent.

In experiments 4061 and 4062 the same procedure was used as had been previously used in experiments 4050 and 4043, of figure 6. In the following two experiments the amount of manganous sulfate added was increased threefold. In these two experiments the theoretical distributions for manganese dioxide and manganic oxide are, respectively, 30 to 70 per cent and 11.25 to 88.75 per cent.

Experiment 4064. "Acid" catalyst was prepared. Observed distribution: 29.3 per cent and 68.3 per cent.

Experiment 4065. "Neutral" catalyst was prepared. Observed distribution: 28.7 per cent and 69.5 per cent.

The experimental results show that both in the "acid" and in the "neutral" catalyst the manganese was tetravalent. Thus, it is highly probable that the difference in catalytic activity was due entirely to the difference in surface exposed.

DISCUSSION OF RESULTS

In the light of recent evidence on the equilibrium existing in an acid mixture containing permanganate and manganous ions (2), it is possible to give a tentative explanation of the experimental results described in this paper. In an acid mixture of manganous and permanganate ions a *rapid* equilibrium is established, in which the concentrations of Mn^{+++} and of Mn^{++++} are extremely small. The tetravalent ion hydrolyzes, forming a hydrate of manganese dioxide. The formation of the precipitate is slow; it takes a measurable time before the presence of the solid changes the color of the solution, hence the incubation period. The solid catalyzes the further precipitation of manganese dioxide. The effect of the acid is due partly to its influence on the degree of dispersion of the solid and partly to some other, as yet unknown, influence.

The complex-forming sulfate ion modifies the reaction by shifting the equilibrium and directing the reaction through a new path, involving the manganic sulfate complex. Fluoride ion has a more pronounced effect because it forms a more stable complex.

The immeasurably fast rate of the reaction taking place when oxalic acid is added to an acid mixture of manganous and permanganate ions is due to the rapid formation of manganic oxalate ion and the resulting rapid shift of equilibrium. A more detailed discussion of this reaction will appear elsewhere (3).

In a mixture containing manganese dioxide, manganous ion, and oxalic acid two competitive reactions seem to take place. In one of these the oxalic acid merely forms manganic oxalate complex; in the other reaction the oxalic acid is oxidized. The data shown in figure 4 seem to indicate that the rates of these two reactions are of the same order of magnitude. At the present time it would be premature to speculate whether the competition is between the rates of formation of Mn^{++++} and of Mn^{+++} or between the rates of reaction of these two ions with oxalic acid.

Thiosulfate ion probably forms a manganic thiosulfate complex analogous to the red ferric thiosulfate complex. It is highly probable that thiosulfate ion, when added to an acid mixture of manganous and permanganate ions, shifts the equilibrium, forming manganic thiosulfate ion. The latter decomposes at once, forming manganous ion (early part of the curve shown in figure 1). If manganous ion is absent, as in experiment 2002, figure 1, the thiosulfate reacts with the permanganate by some other reaction path, and this results in a higher consumption of oxidizing agent. Thus, the apparently anomalous effect of manganous ion, discussed in section B-I, is probably due to this rapid shift of equilibrium.

SUMMARY

In acid solution the reaction between manganous and permanganate ions has an incubation period and is catalyzed by the manganese dioxide formed in the course of the reaction.

The rate of the reaction is increased by a decrease in the acidity or by an increase in the concentration of either the manganous or the permanganate ion.

Sunlight has only a small effect, if any, on the rate of the reaction.

The reaction can be accelerated by the addition of manganese dioxide to the initial solution. The catalyst prepared in a neutral solution is more effective than that prepared in acid solution. The difference is probably due to the larger degree of dispersion of the "neutral" manganese dioxide.

Sulfate and fluoride ions modify the reaction by carrying it through another path involving the intermediate formation of moderate amounts of the respective manganic complex ion.

Oxalate ion not only diverts the reaction rapidly into a new path, but also leads to the formation of entirely different reaction products.

When a solution containing both oxalic acid and manganous ion is added to freshly precipitated manganese dioxide, the amount of oxalic acid oxidized depends chiefly on the ratio: $(Mn^{++})/(H_2C_2O_4)$.

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ACTION OF RADON ON POLYMETHYLENES: CYCLOPENTANE AND CYCLOPENTENE

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In a previous paper (5) the action of radon on cyclopropane was reported. The study of the action of radon on this type of hydrocarbon was continued to permit comparisons of their behavior with that of the aliphatic hydrocarbons to be made and to study the relation of the values of the $-M/N$, the heats of formation, and the

$$\frac{\Delta(H_2 + CH_4)}{-\Delta HC}$$

The procedures and methods of calculation of the $-M/N$ values were those used in a previous paper (4). The results of the present work are summarized in the upper part of table 1. The lower figures are given for purposes of comparison.

A comparison of the values of $-M/N$ and

$$\frac{\Delta(H_2 + CH_4)100}{-\Delta HC}$$

for cyclopentane with the corresponding values for the saturated aliphatics and those of cyclopentene with those of ethylene show a very striking similarity—in fact the values are practically identical.

In a previous paper (6) the writer pointed out the fact that the $-M/N$ values for compounds with positive heats of formation from diamond and hydrogen are low—ordinarily about 2. The values of $-M/N$ for those compounds whose heat of formation was negative were larger than 2, and the values increased with the increase of the negative heat of formation. The heat of formation of cyclopentane from diamond and hydrogen was calculated from the heat of combustion by means of the general expression

$$m\text{C}_{\text{diamond}} + \frac{n}{2}\text{H}_2 \rightarrow \text{C}_m\text{H}_n + 92.1m + 34.2n - \text{heat of combustion}$$

The heat of combustion of cyclopentane is 783.6 (9), and the heat of formation is 18.9 kg-cal. The value of the $-M/N$ is 1.7. The heat of combustion of cyclopentene has not been determined experimentally, but was calculated by the method of Kharasch (10) and was found to be 735.9. The heat of formation from hydrogen and diamond based on this value is −1.8 kg-cal., and the $-M/N$ is 4.5. The correlation of these values of the heats of formation and the $-M/N$ is very satisfactory.

Inasmuch as very pure samples of these substances were available, their vapor pressures were determined.

TABLE 1

Summary of results

HYDROCARBON	$-\Delta P_{HC}$ IN MM.	PER CENT $-\Delta P$ USED IN CALCULATION	$\frac{\Delta(H_2 + CH_4)}{-\Delta HC}$	$-M/N$	HEAT OF FORMATION (DIAMOND $+ H_2$)	PRODUCT
Cyclopentane...	32.9	100	73.7	1.7	18.9	Light colored mobile liquids
Cyclopentene...	91.0	97.0	19.2	4.5	−1.8	
Methane........			75.7	2.2	20.4†	
Ethane.........			91.1	1.7	25.5	Light colored liquids
Propane........			82.3	1.7	30.3	
Ethylene........			16.0*	4.8	−6.4	

* During the first part of the reaction. The ratio increases, owing to action on the product.

† Calculated from heats of combustion given in International Critical Tables Vol. V, p. 163 (1929).

EXPERIMENTAL

Preparation of cyclopentane

This substance was prepared by the reduction of (a) cyclopentadiene and (b) cyclopentene in an Adams hydrogenation apparatus using a platinum oxide catalyst. Since these methods of preparation have not been previously described, they are given in some detail.

Dicyclopentadiene (60 cc.) was depolymerized by heating the polymer in a Clarke flask contained in a metal bath at 185°C. The temperature was gradually increased to 215°C. at the end of the process. Thirty cc. of cyclopentadiene dissolved in 175 cc. of 95 per cent ethanol to which 0.5 g. of platinum oxide catalyst (prepared according to the directions in Organic Syntheses, Vol. VIII, p. 92) were reduced in the Adams hydrogenation apparatus. Only 80 per cent of the calculated amount of hydrogen was taken up. The portion distilling to 78°C., but chiefly between 40–45°C., was thoroughly agitated successively with water, concentrated sulfuric acid, and dilute sodium hydroxide, and then dried over fused calcium chloride. The sample distilled between 49–50°C. On treating the alcohol used as a solvent with water, an oily solid separated which was identified as tetrahydrodicyclopentadiene by its melting point. This compound had been described by Eijkman (1). Its formation undoubtedly accounts for the low absorption of hydrogen.

Forty cc. of cyclopentene dissolved in 150 cc. of ethanol was hydrogenated using 0.25 g. of the oxide catalyst. The calculated amount of hydrogen was absorbed in about an hour. The product was removed by distilling at 78°C. and was purified as described previously. Any traces of unsaturated impurity were removed by thoroughly agitating with an alkaline permanganate solution until a portion did not decolorize a very dilute solution. After drying over calcium chloride, the sample distilled at 48.8°C. at 738.4 mm. The boiling point at 760 mm. was calculated to be 49.6°C. (3). The boiling point given in the International Critical Tables is 49.5°C. (8).

Purification of cyclopentane

The cyclopentane prepared from the cyclopentene was held over bright sodium under its own vapor. Fresh sodium was used each day. The surface was not coated after standing thirty-six hours. The sample was distilled three times under its own vapor pressure from a trap maintained at 0°C. and condensed in a trap at −80°C. The vapor pressure was 107.3 mm. at 0°C. and was unchanged by the distillations. After two distillations from −20°C. to a trap at −80°C. the vapor pressure at 0°C. was 107.3 mm. The vapor pressure of the first fraction and of the last fraction at 0°C. was 107.3 mm.

Action with radon

Very shortly after mixing the cyclopentene with radon a fog appeared. The product collected as a mobile nearly colorless oil on the bottom of the reaction sphere, and was not appreciably affected by further action of radon as shown by the constancy of the ratio

$$\frac{\Delta(H_2 + CH_4)}{-\Delta HC}$$

Typical data is given in table 2.

Preparation of cyclopentene

Cyclopentene was prepared by the dehydration of cyclopentanol by heating with hydrated oxalic acid. The cyclopentanol was made by the reduction of cyclopentanone, using a Raney nickel catalyst and hydrogen under high pressure. Cyclopentanone (148.5 g. or 1.77 moles) from the Eastman Kodak Co. was reduced with hydrogen at an initial pressure of 1600 lbs., using 8 g. of Raney nickel catalyst but no solvent. After four hours at 150°C., 90 per cent of the calculated amount of hydrogen was absorbed. The contents of the bomb were filtered through a sintered glass crucible, and the residue was washed with a little absolute alcohol. The filtrate was distilled through a Widmer column with an electrically heated jacket. An oil bath was used to heat the sample. The following fractions were collected.

TABLE 2

Polymerization of cyclopentene by alpha rays from radon

$C_5H_8 \rightarrow$ liquid. Temp. 25°C.; is = 3.95; i = 1.23; s = 3.21. Reaction sphere: volume = 35.309 cc.; diameter = 4.070 cm.; E_0 = 0.03395 Curie

TIME		RADON	PRESSURE			$\Delta P_{H_2 + CH_4}$	$\frac{\Delta(H_2+CH_4)}{-\Delta C_5H_8} \times 100$	$k\mu/\lambda$	$-M/N$
Days	Hours		Total	C_5H_8	$H_2 + CH_4$				
		per cent	*mm.*	*mm.*	*mm.*				
		100.000	168.7	168.7					
	1.03	99.231	166.9	163.9				40.5	5.0
	3.15	97.665	163.6	163.6				37.7	4.7
	7.18	94.757	158.3	152.3	1.0	1.0	15.9	39.9	4.9
	9.32	93.260	155.6	154.3	1.3	0.3	10.00	37.6	4.7
	14.6	89.629	149.3	147.3	2.0	0.7	10.00	37.7	4.7
	23.65	83.747	140.0	136.3	3.7	1.7	15.45	38.9	4.8
1	3.57	81.311	137.0	132.8	4.2	0.5	14.26	31.5	3.9
1	9.40	77.832	132.4	126.4	6.0	1.8	28.08	41.7	5.2
1	12.73	75.928	129.8	123.1	6.7	0.7	21.20	41.0	5.1
2	0.23	69.648	122.9	114.2	8.7	1.0	11.24	35.2	4.4
2	5.23	67.086	120.2	110.8	9.4	0.7	22.90	34.9	4.4
3	1.38	59.679	111.8	100.0	11.8	2.4	26.10	32.1	4.2
3	5.98	55.719	110.3	97.9	12.4	0.6	28.60	31.8	4.0
4	9.11	45.461	103.0	88.3	14.7	2.3	23.99	29.6	3.7
5	0.37	40.546	99.9	83.8	16.1	1.4	31.10	31.5	4.0
6	0.10	33.935	96.1	77.7	18.4	2.3	37.64	33.6	4.2
6	8.15	31.947	94.8	75.1	19.7	1.3		50.5	6.3
Weighted average.							19.15		4.5

Fraction I.	77-78°C.	Solvent discarded
Fraction II.	135-136°C.	Discarded
Fraction III.	136-137.5°C.	Collected
Fraction IV.	Above 137.5°C.	Discarded

Fraction III weighed 134.7 g. and 95 per cent of it boiled between 137-137.5°C. The yield was 91 per cent.

The reduction of cyclopentanone to the cyclopentanol has also been carried out by Godchot and Tabourg (2). They obtained some unreacted cyclopentanone, cyclopentane, 50 per cent of the weight of the starting substance as cyclopentanol, and 40 per cent as a ketone having the formula $C_{10}H_{16}O$.

Cyclopentanol (110 g. or 1.17 moles) and 600 g. of hydrated oxalic acid (4.8 moles) were placed in a 1-liter Claisen flask. The flask was heated in a Wood's metal bath until the contents began to liquefy. A condensate began to appear in the condenser when the temperature of the mixture was 80°C. The heating was then gradually increased until no more solid was present (110°C.), and held at that temperature for 30 minutes. The temperature of the distillate gradually increased to 80°C. The temperature of the metal bath was increased until the temperature of the vapors distilling was 100°C. Very soon after this temperature was reached, the condensate was clear, indicating that no more product was being obtained: the heating was then stopped. The time of heating was about two hours.

The cyclopentane was separated from the aqueous layer and dried over calcium chloride. The crude material weighed 55.5 g., making a yield of 70 per cent. The dried product was then distilled from sodium. The distillation started at 43°C. and the temperature quickly rose to 43.8°C. When the temperature reached 45.5°C. the distillation was stopped. The 49.0 g. of the product (62 per cent yield) was mixed with the products obtained in preliminary runs, and allowed to stand overnight over sodium. On distilling, the material boiled between 43.5°C. and 43.8°C. A small fraction boiling between 43.8°C. and 44.1°C. was also obtained. The barometric pressure was about 740 mm.

In order to dry it thoroughly and to remove any trace of unchanged cyclopentanol, a portion of the material was placed in a vessel previously filled with dry nitrogen containing bright pieces of sodium; after freezing in liquid oxygen the nitrogen was pumped off. After standing twelve hours under its own vapor at 0°C. a brown sludge was formed; the sample was then distilled at low temperatures into a second evacuated vessel containing a few pieces of bright sodium. After remaining three days in contact with the sodium no sludge was formed and the surface of the sodium was bright.

Purification of cyclopentene

The sample was then distilled from a trap maintained at 0°C. and was condensed at −182°C. The first and last 1.5 cc. were discarded. A second distillation was made from 0°C., and condensation took place at −182°C. Then the sample was cooled to −182°C. and any non-condensable gases were pumped off. The temperature was raised to 0°C. and, after cooling, the pumping operation was repeated to remove any residual non-condensed gas. The vapor pressure of the sample at 0°C. was 131 mm. The sample was then distilled two times from −30°C. to −182°C. When two-thirds of the sample had distilled, the vapor pressure of the residue was found to be 131 mm. at 0°C. A second distillation under the same conditions was carried out. The vapor pressure of the low-boiling fraction was

131 mm. at 0°C. The vapor pressure of the middle sample was also 131 mm. at 0°C. A sample to use in determining the vapor pressure at various temperatures and to subject to the action of α-particles was taken, after about a third of the material had been distilled off. The vapor pressure of this sample was 131 mm. at 0°C.

TABLE 3

Polymerization of cyclopentane by alpha rays from radon

C_5H_{10} gas → liquid. Temp. 25°C.; $is = 4.3$; $i = 1.24$; $s = 3.48$. Reaction sphere: volume = 35.805 cc.; diameter = 2.045 cm.; $E_0 = 0.03718$ Curie

TIME		RADON	PRESSURE			$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta P_{C_5H_{10}}}$	$k\mu/\lambda$	$-M/N$
Days	Hours		Total	C_5H_{10}	$H_2 + CH_4$			
		per cent	*mm.*	*mm.*	*mm.*			
		100.000	105.5					
	2.22	98.364	105.5	105.2	0.3	100.0	4.9	0.6
	4.08	96.987	105.5	104.6	0.9	100.0	11.2	1.3
	7.22	94.729	104.9	103.2	1.7	57.2	15.9	1.8
	9.83	92.892	104.6	101.9	2.7	77.0	18.5	2.1
	22.90	84.219	103.2	97.2	6.0	70.3	14.7	1.7
1	1.77	82.426	103.0	96.0	7.0	83.3	18.7	2.2
1	19.33	72.253	101.5	90.8	10.7	64.8	14.2	1.7
2	9.58	64.931	101.0	87.7	13.3	83.8	12.8	1.5
2	20.75	59.715	100.4	85.7	14.7	70.0	11.9	1.3
3	8.56	54.653	100.1	83.1	17.0	88.5	16.3	1.9
4	4.20	47.168	99.3	79.3	20.0	78.8	16.8	1.9
4	18.8	42.276	99.1	77.8	21.3	86.7	16.2	1.9
7	19.8	24.450	98.0	72.3	25.7	79.9	11.3	1.3
Weighted average..................................						73.7		1.7

TABLE 4

Vapor pressures of cyclopentane and cyclopentene

t	VAPOR PRESSURE OF CYCLOPENTANE	t	VAPOR PRESSURE OF CYCLOPENTENE
°C.	*mm.*	*°C.*	*mm.*
−52.0	4.4	−77.5	1.0
−47.5	6.1	−50.8	6.1
−38.8	12.1	−26.8	31.0
−25.9	27.3	−9.2	81.9
−14.4	53.0	0.0	129.3
0.0	107.4	+6.8	178.1
6.0	140.7	+12.3	226.6
13.6	197.6	15.0	253.1
18.4	241.8	19.9	309.4
		43.5	731.2

Action with radon

The action with radon was practically identical with that of cyclopentane. The data is given in table 3.

Vapor pressures

The vapor pressures of cyclopentane and cyclopentene at various temperatures were determined using the method and apparatus previously described (7). The results are given in table 4.

SUMMARY

1. Pure cyclopentane and cyclopentene have been prepared, and the vapor pressures at several temperatures have been determined.

2. The action of radon on these compounds has been studied. The $-M/N$ values are in agreement with the heats of formation and with

$$\frac{\Delta(H_2 + CH_4)100}{-\Delta HC}$$

The writer wishes to acknowledge the grant from the Graduate School to aid in carrying out this work and the assistance of Lucille M. Heisig in determining the vapor pressures.

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ELECTROMETRIC AND ANALYTICAL EVIDENCE FOR THE COMPOSITION OF PRECIPITATED BASIC COPPER PERCHLORATE

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The composition of the precipitate formed when carbonate-free alkali is added to solutions of copper salts can be estimated, without analysis, by electrometric titration, using the quinhydrone electrode as pH indicator. The application of the method to several copper salts has been previously described (1, 6). In all cases where evidence was obtained for a definite basic salt, the composition was that of the 1:3 salt, for example, $CuCl_2 \cdot 3CuO \cdot (?)H_2O$. Such 1:3 precipitates have been formed under favorable conditions from solutions of the following copper salts: sulfate, chloride, nitrate, and trichloroacetate.

To extend the list further, the precipitation of basic copper perchlorate has been studied by the electrometric method. Unlike the cases previously investigated a 1:6 salt is formed, i.e., $Cu(ClO_4)_2 \cdot 6CuO \cdot (?)H_2O$. Because of this anomalous behavior, the composition of the precipitated basic salt has been tested further by direct analysis for the copper to perchlorate ratio. The results confirm the formula derived by the electrometric method.

EXPERIMENTAL

Preparation of solutions

A solution of carbonate-free sodium hydroxide was prepared by the method of Cornog (5).

Copper perchlorate solutions were made by two methods. For solution A; barium chloride was added in slight excess to a solution of copper sulfate, and the precipitated barium sulfate was removed by centrifuging. A small weighed excess of perchloric acid was added to prevent hydrolysis. In making solution B, an excess of vacuum-distilled perchloric acid was allowed to react with basic copper carbonate. Aside from the excess acid, this solution contained only copper and perchlorate ions. The acid present was estimated by the position of the initial breaks in the curves, as shown in figure 1 (7). Both solutions were standardized for copper content by the iodometric method. A blank test showing no liberation of iodine from potassium iodide by perchlorate ion in weak acid solution demonstrated that the method was applicable.

Electrometric titrations

Both direct and delayed titrations were used as previously described in the case of copper trichloroacetate (1). Using a saturated calomel reference electrode, an E.M.F. value of + 0.007 volt was chosen as the end-point, this being the point of maximum slope of the titration curves. In all of the titrations of solutions of initial concentration greater than 0.1 N, very nearly 1.714 moles of alkali were required per mole of copper salt. This indicates a 1:6 basic salt.[1] The results for the direct titrations are shown

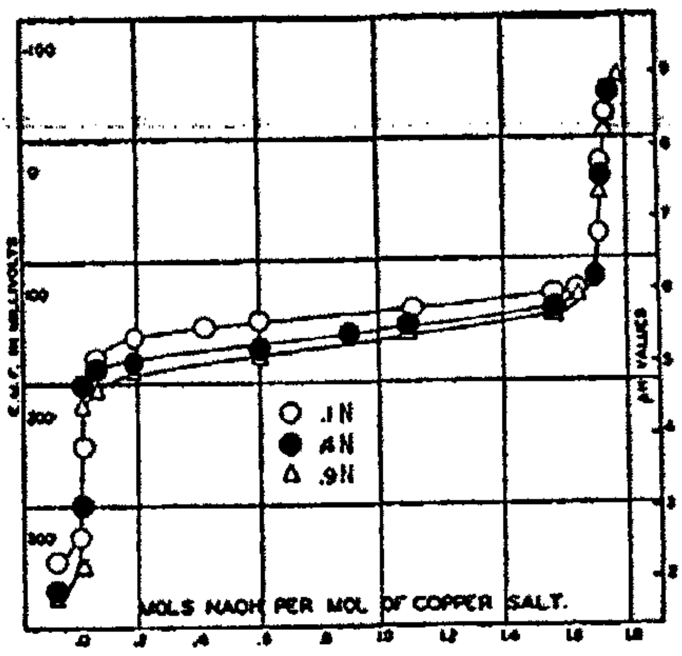

FIG. 1

TABLE 1

Use of direct titrations in determination of alkali required per mole of copper perchlorate

(1.7143 required for 1:6 basic salt)

SOLUTION A		SOLUTION B	
Normality of copper perchlorate solution	Moles of NaOH	Normality of copper perchlorate solution	Moles of NaOH
1.000	1.710	1.000	1.713
0.400	1.714	0.400	1.714
0.266	1.714	0.100	1.715
0.100	1.711		

---

[1] According to the equation, $7Cu(ClO_4)_2 + 12NaOH = Cu(ClO_4)_2 \cdot 6CuO \cdot (?)H_2O + 6Na_2SO_4$, the ratio of moles of sodium hydroxide to moles of copper salt is 1.7143:1.

in figure 1 and table 1;[2] those for the delayed titrations, in table 2. In the delayed titrations it is certain that sufficient time was allowed to let the system come to equilibrium. Because the results were identical for the direct and the delayed titrations, it may be concluded that the precipitates were in equilibrium with the solutions even in the direct titrations.

For solutions less concentrated than 0.1 *N*, more than 1.714 moles of alkali were required. This indicates that under these conditions the precipitate was probably a mixture of the 1:6 salt and hydrated copper oxide.

TABLE 2

Use of delayed titrations in determination of alkali required per mole of copper perchlorate

SOLUTION OF $Cu(ClO_4)_2$ USED	NORMALITY OF $(CuClO_4)_2$	TIME OF STANDING	TREATMENT	MOLES NaOH ADDED INITIALLY	TOTAL MOLES NaOH
A	0.10	20 hours	a[*]	1.633	1.712
A	0.10	20 hours	b[†]	1.633	1.712
A	0.10	8 days	b	1.626	1.711
A	0.27	20 hours	a	1.636	1.711
A	0.27	20 hours	b	1.633	1.711
A	0.27	8 days	b	1.633	1.712
B	0.40	20 hours	a	1.557	1.714
B	0.40	20 hours	b	1.557	1.714
B	0.40	8 days	b	1.557	1.714
B	0.10	20 hours	a	1.557	1.715
B	0.10	20 hours	b	1.557	1.716
B	0.10	8 days	b	1.557	1.715
B	0.93	20 hours	a	1.557	1.714
B	0.93	20 hours	b	1.557	1.713
B	0.93	8 days	b	1.557	1.714

[*] a denotes constant stirring.

[†] b denotes occasional shaking.

Analysis of the precipitate

To 0.4 *N* copper perchlorate, alkali was added in amounts somewhat less than 1.714 moles per mole of copper salt.[3] After three washings by centrifuging and decantation, the moist precipitate was dissolved in dilute sulfuric acid to make a stock solution. Separate aliquot portions of this solution were analyzed for copper iodometrically, and for perchlorate by

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[2] Points on the curves above pH 7, approximately, do not represent equilibrium conditions. On standing a rather rapid decrease in pH is observed, owing to the interaction of the excess hydroxyl ions with the precipitated basic salt.

[3] More than 1.7143 moles of alkali would, of course, convert a part of the basic salt into hydrated copper oxide, so that the precipitate would not have definite composition.

the nitron method (4). In the basic salt $Cu(ClO_4)_2 \cdot 3CuO \cdot (?)H_2O$, the ratio of moles of copper to moles of the perchlorate radical should be 7:2. Analysis of one precipitate from copper perchlorate solution A yielded a ratio of 6.96:2. Two precipitates from solution B each yielded a ratio of 6.99:2.

DISCUSSION

Previously both electrometric (1, 6) and phase rule studies (2) have established the individualities of several 1:3 basic salts of copper of which $CuSO_4 \cdot 3CuO \cdot 4H_2O$ is an example. Britton (3) has given a review of the various theories, based on constitution, which have been proposed to account for this regularity of behavior. Now, with definite evidence for a 1:6 basic copper perchlorate, any future theories must explain the structure of this salt as well. The authors believe that no satisfactory theory has yet been advanced.

SUMMARY

1. When alkali is added to an excess of copper perchlorate in solutions above 0.1 *N*, the precipitate has the constitution: $Cu(ClO_4)_2 \cdot 6CuO \cdot (?)H_2O$. This compound has not been reported in the literature.

2. This 1:6 salt is unlike any other basic salts of copper previously known.

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SOLUBILITY OF SEVERAL COMPOUNDS OF THE MANNOSE SERIES IN ALCOHOLS

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INTRODUCTION

This investigation records solubilities of *l*-rhamnose, α-*d*-mannose, β-*d*-mannose, *d*-mannonic-γ-lactone, *d*-mannonic-δ-lactone, α-methyl-*d*-mannoside, and *d*-mannitol in methyl, ethyl, allyl, propyl, isopropyl, and the four isomeric butyl alcohols. An attempt has been made to compare the solvent properties of this series of alcohols for a given sugar, and in addition to compare the effect of structure of the sugar derivatives on solubility in a given solvent. Practically no data of this kind are now available. The results of Creighton and Klauder (4) for the solubility of mannitol in ethyl alcohol at 60°C. do not agree with those presented here, since they report mannitol as much more soluble than we have found it to be.

EXPERIMENTAL

Materials

l-Rhamnose hydrate was purified by recrystallization from methyl alcohol, m.p. 92°C., $[\alpha]_D^{20°} = -7.7°$ (initial) and $+8.85°$ (final). α-*d*-Mannose was obtained according to the method of Levene (6), m.p. 132–135°C., and β-*d*-mannose was obtained according to the method of Riiber and Minsaas (7). Its constants were m.p. 133.5°C., $[\alpha]_D^{20°} = -18°$ (initial) and $+14.6°$ (final). The constants for the *d*-mannonic-γ-lactone were m.p. 152°C. and $[\alpha]_D^{20°} = +52.3°$ with no change in twenty-four hours. For the *d*-mannonic δ-lactone, m.p. 162.5°C., $[\alpha]_D^{20°} = +112°$ two minutes after solution. α-Methyl-*d*-mannoside had a melting point of 195°C. and a rotation $[\alpha]_D^{20°} = +80.6°$. *d*-Mannitol melted at 167°C. and its rotation $[\alpha]_D^{20°} = +24.5°$ in the presence of borax.

The physical constants as above given established the purity of the different solutes used.

Each of the alcohol solvents was purified by means of a prolonged drying process with calcium oxide and was then subjected to careful fractionation, using an efficient fractionating column. The fractions selected corresponded very closely in boiling point and density with the best values recorded in the literature. These constants are summarized in table 1.

Procedure

The solubility determinations were made by the synthetic method of Alexejew (1). Among the other workers who have used the method are Carrick (2), Collett and Johnston (3), Kendall and his students (5), Schroder (8), Sidgwick and his students (9), Sunier (10), and Ward (11).

TABLE 1

Summary of constants for alcohols

ALCOHOL	BOILING TEMPERATURE (CORRECTED)		DENSITY IN GRAMS PER CC. AT 20°C.	
	Found	Accepted	Found	Accepted
	°C.	°C.		
Methyl	65.2	64.5	0.7916	0.7917
Ethyl	78.6	78.5	0.7883	0.7893
Allyl	96.4–96.6	97.0	0.8530	0.855
Propyl (normal)	97.5–97.7	97.8	0.8034	0.804
Propyl (iso)	82.4	82.3	0.7853	0.7854
Butyl (normal)	117.5	117.7	0.8093	0.810
Butyl (secondary)	99.4–100.0	99.5	0.8067	0.808
Butyl (iso)	107.7–107.9	107.3	0.8016	0.802
Butyl (tertiary)*	82.5–82.6	82.8	0.7810†	0.781†

* Melting temperature = 24°C.

† At 25°C.

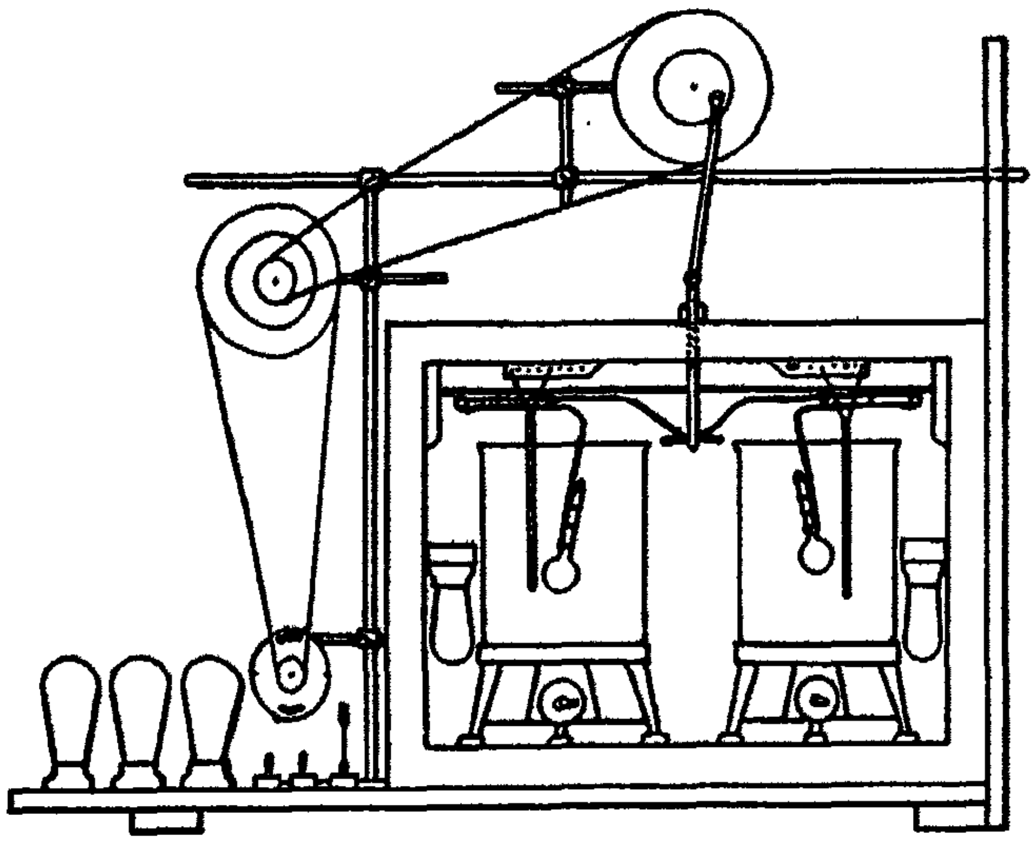

FIG. 1. THE APPARATUS

The essential feature of this method is to ascertain the temperature at which the last crystal just disappears when a known mixture of solvent and solute is slowly heated. Collett and Johnston (3) checked this method in comparison with the usual analytical method and found very good agreement between the two.

Small glass bulbs of 3 to 15 ml. capacity similar to those described by Collett and Johnston (3) were used, and their technique was followed in filling the bulbs and obtaining the weight of solvent and solute.

TABLE 2

Solubility in methyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)	
35.9	16.7
42.6	24.4
49.1	35.5
53.3	44.0
56.0	49.9
60.5	61.4
α-*d*-Mannose	
44.8	2.18
46.1	2.29
50.1	2.83
50.2	2.84
53.9	3.38
58.9	4.22
62.6	5.07
β-*d*-Mannose	
41.5	1.84
45.0	2.19
51.3	2.82
55.0	3.26
59.1	3.95
64.2	4.97
d-Mannonic-γ-lactone	
40.0	0.813
47.9	1.083
53.4	1.325
60.9	1.797
67.4	2.367
α-Methyl-*d*-mannoside	
40.2	0.458
43.7	0.523
49.8	0.652
54.9	0.776
58.4	0.867
62.4	1.010
64.6	1.094
66.8	1.205
d-Mannonic-δ-lactone	
35.8	0.235
45.3	0.341
50.4	0.415
54.9	0.508
56.8	0.581
63.4	0.779
66.9	0.957
d-Mannitol	
47.0	0.0766
49.7	0.0874
60.8	0.136
66.0	0.173
69.7	0.210
72.9	0.256
76.6	0.298
77.3	0.316
80.5	0.367

Figure 1 is a rough sketch of the apparatus used. The bath was a large beaker heated by means of an electric hot plate and filled with water for temperatures up to 95°C. and with paraffin oil for higher temperatures. Two determinations were made at one time. The bulbs were fastened to the shaker arms by means of rubber bands as indicated, and the whole was contained in a cabinet to reduce temperature variation to the minimum. The shaker arms made two hundred complete vibrations per minute; this was found to produce adequate stirring of the bath. Total immersion calibrated thermometers graduated in 0.2°C. intervals were used.

The temperature was raised fairly rapidly at first and then more slowly toward the end of a determination. The rate of heating could be controlled by the placing of one or more light bulbs in series with the heating elements. Usually approximately twenty minutes was required in raising the temperature the last degree. By means of the switch the shaking machine could be stopped momentarily for observation of the bulbs. The temperature recorded, as nearly as could be determined, was that point at which the last crystal of solute just disappeared. Usually two or three determinations of the solution temperature were made with each bulb. Recrystallization was carried out as rapidly as possible by cooling the bulbs

TABLE 3

Solubility in ethyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)	
42.0	7.93
49.3	12.6
53.6	17.2
54.5	18.7
56.1	21.5
59.2	26.1
59.8	27.5
59.9	27.9
61.1	30.7
α-*d*-Mannose	
43.3	0.353
52.0	0.490
57.9	0.627
58.3	0.639
61.1	0.695
67.6	0.895
β-*d*-Mannose	
48.2	0.337
51.8	0.394
55.3	0.455
61.2	0.568
65.4	0.697
71.4	0.867

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
d-Mannonic-γ-lactone	
44.1	0.207
48.3	0.250
55.9	0.357
60.4	0.427
64.5	0.519
α-Methyl-*d*-mannoside	
37.9	0.0940
47.4	0.177
48.5	0.186
52.4	0.229
53.9	0.241
54.6	0.247
62.0	0.342
66.1	0.413
76.2	0.615
81.0	0.761
84.6	0.905

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
d-Mannonic-δ-lactone	
42.0	0.0853
49.8	0.124
53.6	0.144
60.4	0.192
66.8	0.262
68.2	0.279
d-Mannitol	
53.6	0.0293
62.0	0.0463
63.3	0.0494
69.6	0.0634
73.0	0.0768
77.2	0.0989
80.3	0.122
85.2	0.166
92.5	0.255

in a refrigerator and shaking them by hand occasionally in order to obtain the solutes in the form of small crystals. Two careful determinations, the results of which showed a divergence not greater than 0.2°C., were considered satisfactory.

The determinations with *l*-rhamnose were difficult because the rather concentrated solutions were cloudy, and because rhamnose has a tendency to form large crystals. The usual time required to make the determination with either of the *d*-mannoses was three hours. Only one determination was made with each bulb, since the α- and β-*d*-mannose both undergo more or less mutarotation in alcohol solution and the recrystallized product is not a single substance. The two *d*-mannonic-lactones and the α-methyl-*d*-mannoside gave no difficulties. With *d*-mannitol initial determinations were not reliable, since it was found to recrystallize in one of two different

TABLE 4

Solubility in allyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
35.8	4.05	47.2	0.235	42.0	0.0806
38.2	4.49	51.8	0.281	46.6	0.0964
46.1	6.28	55.5	0.338	53.0	0.127
49.2	7.58	58.4	0.392	57.7	0.156
54.5	10.72	65.0	0.511	62.0	0.192
59.8	14.90	68.2	0.586	67.6	0.247
60.5	15.62				
62.4	18.60	*d*-Mannonic-γ-lactone		*d*-Mannitol	
α-*d*-Mannose		46.4	0.215	55.9	0.0296
		49.7	0.250	59.4	0.0352
48.2	0.323	55.1	0.320	63.6	0.0460
52.0	0.378	60.4	0.404	69.3	0.0627
55.3	0.438	63.4	0.464	75.0	0.0854
56.5	0.455			79.7	0.112
66.6	0.672	α-Methyl-*d*-mannoside		84.7	0.141
		46.2	0.197		
		49.4	0.229		
		53.3	0.275		
		55.9	0.313		
		58.5	0.345		
		60.5	0.391		
		63.2	0.436		
		70.3	0.581		

TABLE 5

Solubility in n-propyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
31.0	2.43	48.7	0.123	45.9	0.0476
40.0	3.32	53.0	0.149	50.2	0.0566
41.3	3.61	59.8	0.192	53.9	0.0679
46.1	4.43	65.6	0.250	59.7	0.0945
51.2	6.04	70.3	0.306	65.4	0.123
56.5	8.04	75.7	0.419	71.4	0.157
61.1	10.33				
63.2	12.44	*d*-Mannonic-γ-lactone		*d*-Mannitol	
α-*d*-Mannose		42.2	0.0849	58.8	0.0193
		47.3	0.105	61.5	0.0236
41.3	0.129	55.3	0.158	67.3	0.0328
47.1	0.164	64.6	0.244	73.7	0.0474
56.4	0.248	68.6	0.296	78.6	0.0631
60.0	0.290			89.2	0.108
63.1	0.320	α-Methyl-*d*-mannoside		90.9	0.122
68.4	0.396	45.8	0.077	97.7	0.174
		48.9	0.099		
		54.6	0.148		
		60.1	0.194		
		68.1	0.270		
		75.3	0.386		
		86.5	0.622		

TABLE 6

Solubility in isopropyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
36.8	3.01	47.1	0.130	45.6	0.0607
44.5	4.06	51.7	0.159	51.0	0.0748
49.3	5.37	58.3	0.206	55.4	0.0935
53.8	6.86	62.4	0.250	61.1	0.121
55.3	7.49	67.6	0.312	65.3	0.146
61.2	10.70	71.1	0.371	69.7	0.181
α-*d*-Mannose		*d*-Mannonic-γ-lactone		*d*-Mannitol	
40.2	0.131	43.8	0.109	55.2	0.0180
49.3	0.191	51.6	0.163	59.5	0.0224
52.3	0.227	57.4	0.215	65.7	0.0318
57.7	0.297	64.4	0.294	69.5	0.0459
59.3	0.321	67.9	0.349	79.3	0.0775
64.2	0.388	α-Methyl-*d*-mannoside		81.5	0.0882
		46.3	0.0876		
		51.6	0.129		
		57.3	0.164		
		60.8	0.206		
		65.7	0.254		
		68.0	0.276		
		73.8	0.362		
		79.7	0.486		

TABLE 7

Solubility in n-butyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
32.3	1.85	41.3	0.0679	48.1	0.0379
40.9	2.27	51.2	0.0815	50.8	0.0414
47.6	3.38	55.8	0.101	53.9	0.0472
53.6	4.39	60.1	0.127	59.6	0.0634
55.2	4.89	65.1	0.165	65.0	0.0822
61.0	6.66	72.6	0.245	69.4	0.103
α-*d*-Mannose		*d*-Mannonic-γ-lactone		*d*-Mannitol	
42.9	0.0888	47.1	0.0719	58.5	0.0131
47.1	0.101	51.3	0.0868	65.8	0.0199
51.0	0.116	54.7	0.106	67.1	0.0207
55.6	0.141	60.1	0.139	77.0	0.0407
55.8	0.142	63.0	0.163	84.2	0.0648
62.9	0.199	71.5	0.242	89.4	0.0887
69.6	0.281	α-Methyl-*d*-mannoside		95.2	0.1337
		45.8	0.0539		
		56.1	0.107		
		56.2	0.109		
		62.7	0.165		
		67.5	0.219		
		73.1	0.290		
		91.1	0.632		

TABLE 8

Solubility in secondary-butyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
43.1	3.25	45.1	0.0933	44.9	0.0415
49.1	4.04	48.7	0.116	49.2	0.0487
51.8	4.53	53.9	0.144	54.0	0.0637
52.5	4.68	58.0	0.175	58.5	0.0827
58.6	6.41	65.2	0.239	64.9	0.115
65.4	8.74	70.6	0.301	71.9	0.152
72.4	13.86	*d*-Mannonic-γ-lactone		*d*-Mannitol	
α-*d*-Mannose		43.1	0.0807	53.5	0.0164
46.1	0.132	46.6	0.0927	60.3	0.0227
50.8	0.162	52.0	0.125	66.1	0.0286
55.4	0.199	57.4	0.167	69.5	0.0356
56.4	0.209	64.7	0.238	73.0	0.0432
64.0	0.281	68.7	0.286	83.3	0.0772
76.1	0.438	α-Methyl-*d*-mannoside		100.8	0.1904
		49.7	0.107		
		53.9	0.140		
		58.6	0.175		
		66.7	0.251		
		75.6	0.367		
		80.5	0.440		
		93.9	0.768		

TABLE 9

Solubility in isobutyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		*d*-Mannonic-γ-lactone		*d*-Mannonic-δ-lactone	
40.4	2.18	49.5	0.0659	46.8	0.0307
44.8	2.85	51.7	0.0770	52.3	0.0402
51.4	3.78	56.9	0.102	55.4	0.0461
55.0	4.51	63.3	0.142	59.5	0.0582
61.2	6.17	66.4	0.164	63.0	0.0693
66.6	7.83	75.1	0.236	68.1	0.0842
α-*d*-Mannose		α-Methyl-*d*-mannoside		*d*-Mannitol	
47.1	0.0848	46.1	0.0528	57.5	0.0110
52.1	0.102	51.1	0.0746	61.3	0.0149
55.1	0.118	56.0	0.104	67.4	0.0195
57.6	0.135	63.5	0.154	72.1	0.0269
62.6	0.180	69.4	0.221	73.6	0.0300
72.5	0.269	74.3	0.285	83.3	0.0538
		80.1	0.363	89.5	0.0754
		83.0	0.420	101.8	0.1636
β-*d*-Mannose					
47.0	0.0608				
49.8	0.0679				
54.0	0.0820				
58.2	0.103				
63.8	0.137				
72.1	0.203				

TABLE 10

Solubility in tertiary-butyl alcohol

TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT	TEMPERATURE IN °C.	MOLES OF SOLUTE PER 100 MOLES OF SOLVENT
l-Rhamnose (hydrate)		β-*d*-Mannose		*d*-Mannonic-δ-lactone	
42.4	3.97	47.9	0.204	39.4	0.0638
53.2	5.99	52.3	0.246	43.4	0.0752
57.1	7.10	58.1	0.318	47.6	0.0907
62.3	8.72	65.0	0.411	53.7	0.125
67.4	11.40	69.5	0.487	57.7	0.153
α-*d*-Mannose		74.0	0.589	67.1	0.226
45.3	0.208	*d*-Mannonic-γ-lactone		*d*-Mannitol	
47.3	0.227	35.2	0.0938	43.1	0.0203
52.8	0.272	41.9	0.123	46.3	0.0250
54.2	0.308	48.7	0.173	55.0	0.0391
61.6	0.409	55.6	0.250	62.7	0.0574
64.2	0.447	59.0	0.288	71.5	0.0845
68.7	0.521	70.0	0.424	79.7	0.1115
		α-Methyl-*d*-mannoside		90.3	0.1487
		38.0	0.102		
		41.4	0.114		
		55.0	0.200		
		60.9	0.258		
		71.7	0.402		
		83.8	0.613		

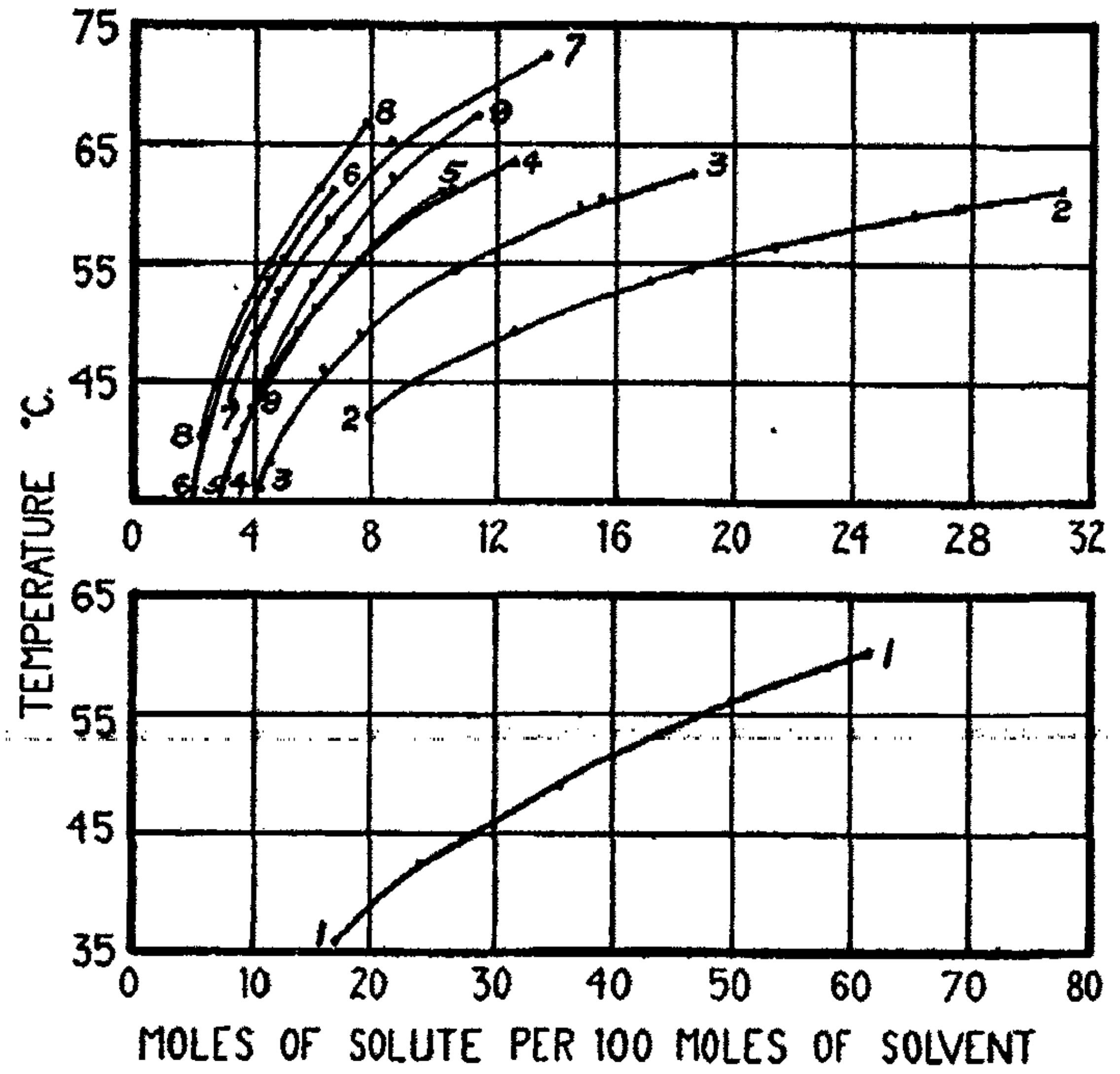

FIG. 2. SOLUBILITY OF *l*-RHAMNOSE IN ALCOHOLS

Curve 1, methyl alcohol; curve 2, ethyl alcohol; curve 3, allyl alcohol; curve 4, *n*-propyl alcohol; curve 5, isopropyl alcohol; curve 6, *n*-butyl alcohol; curve 7, *sec.*-butyl alcohol; curve 8, isobutyl alcohol; curve 9, *tert.*-butyl alcohol.

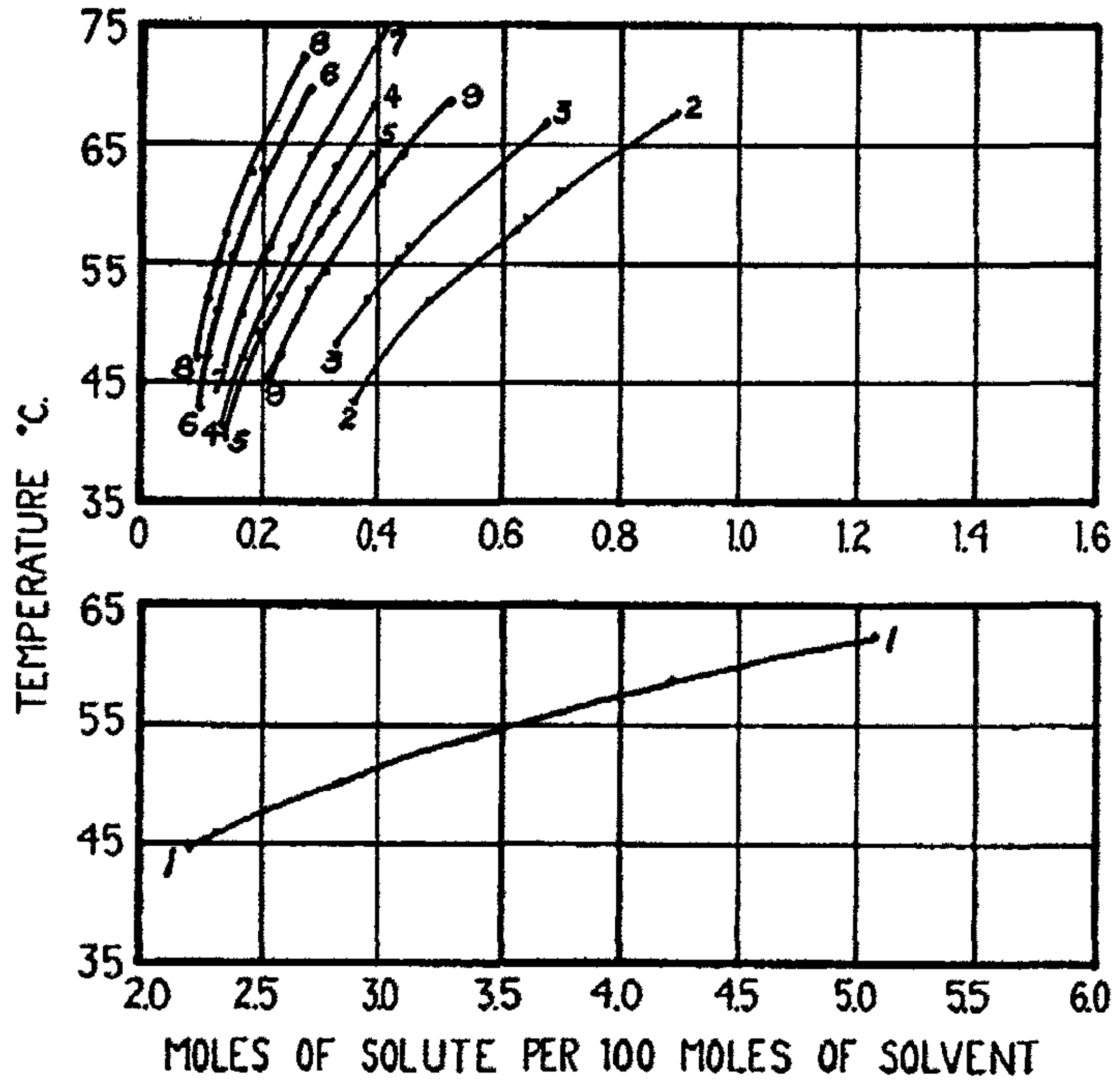

FIG. 3. SOLUBILITY OF α-*d*-MANNOSE IN ALCOHOLS (SEE FIGURE 2)

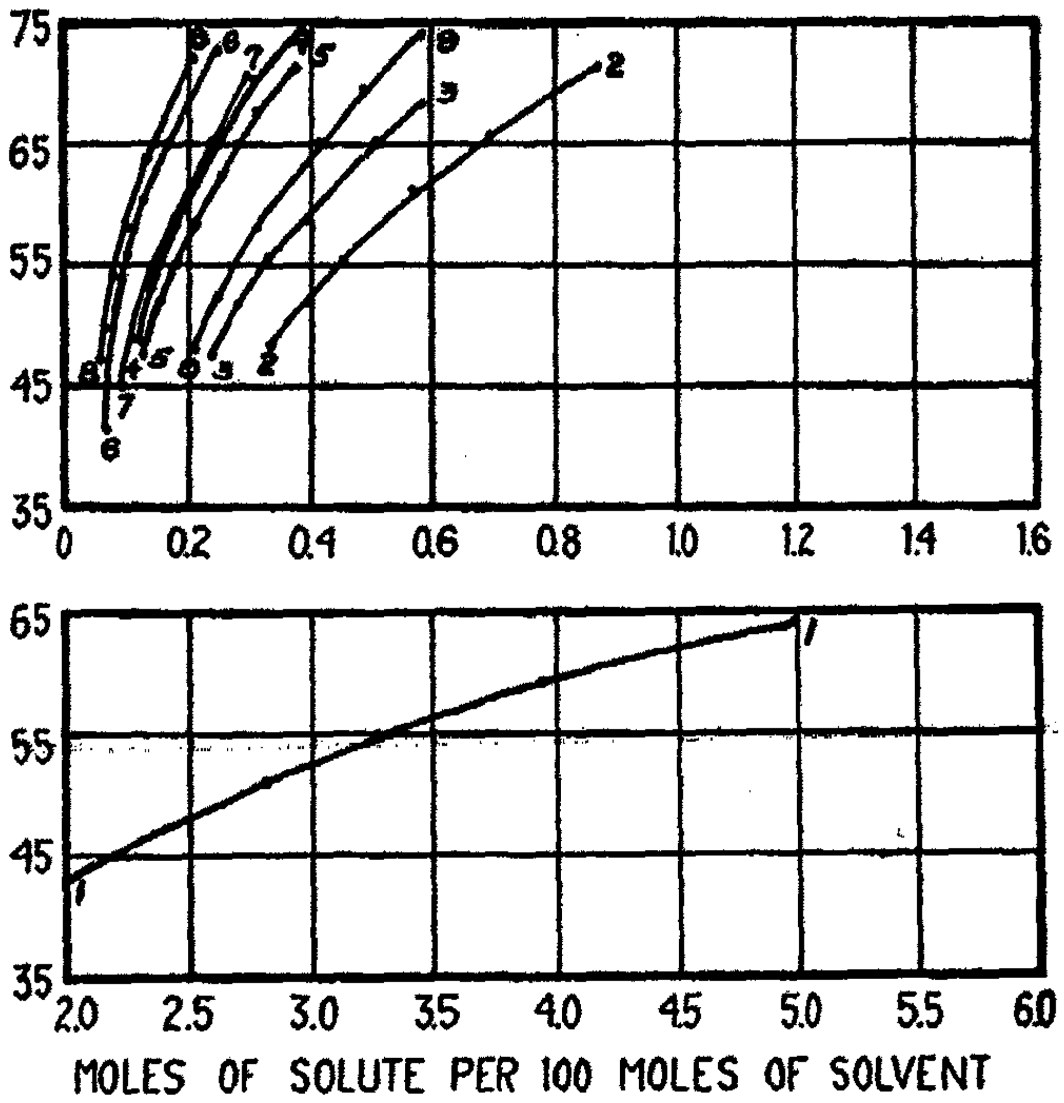

Fig. 4. Solubility of β-*d*-Mannose in Alcohols (See Figure 2)

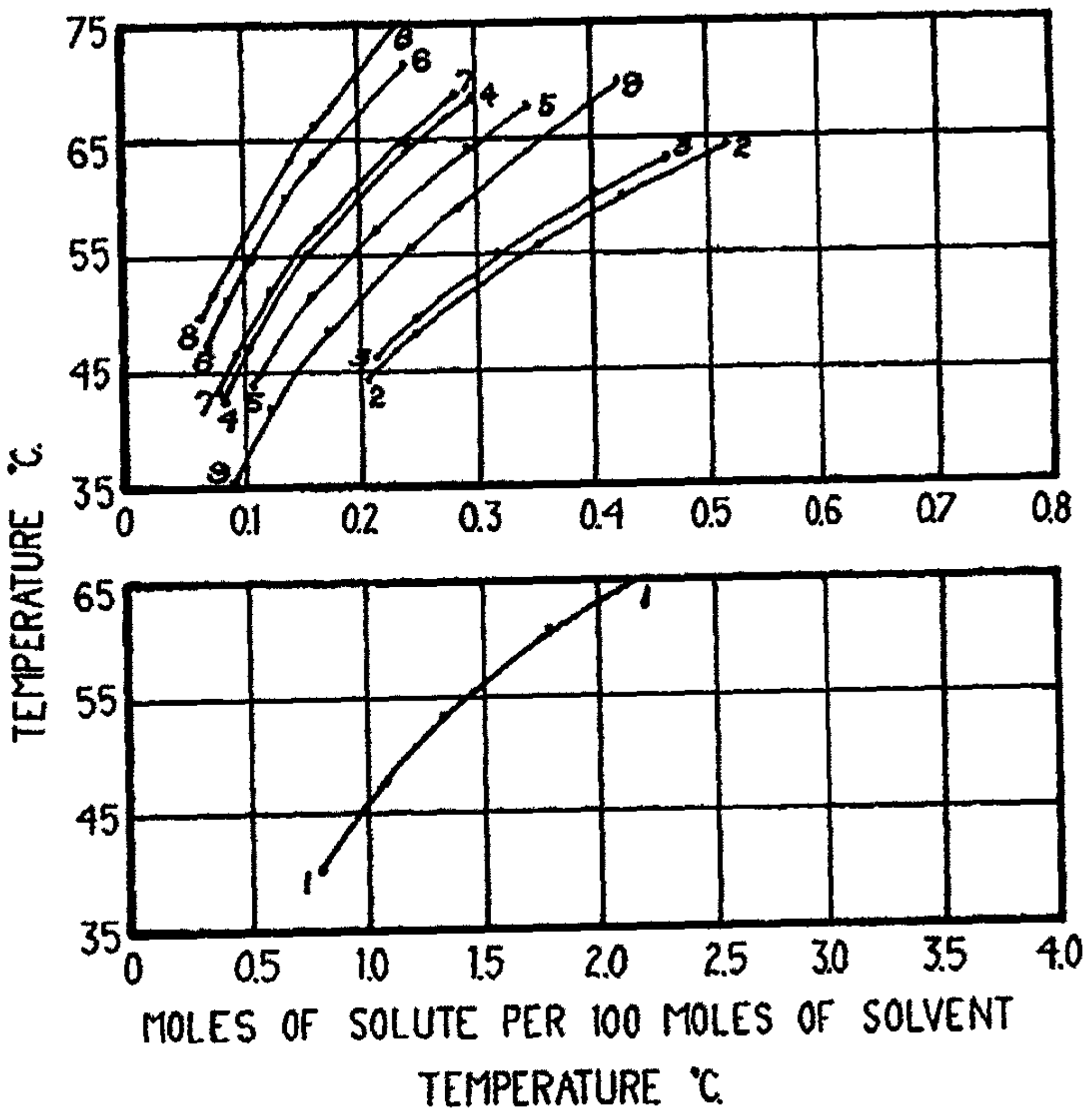

Fig. 5. Solubility of *d*-Mannonic-γ-lactone in Alcohols (See Figure 2)

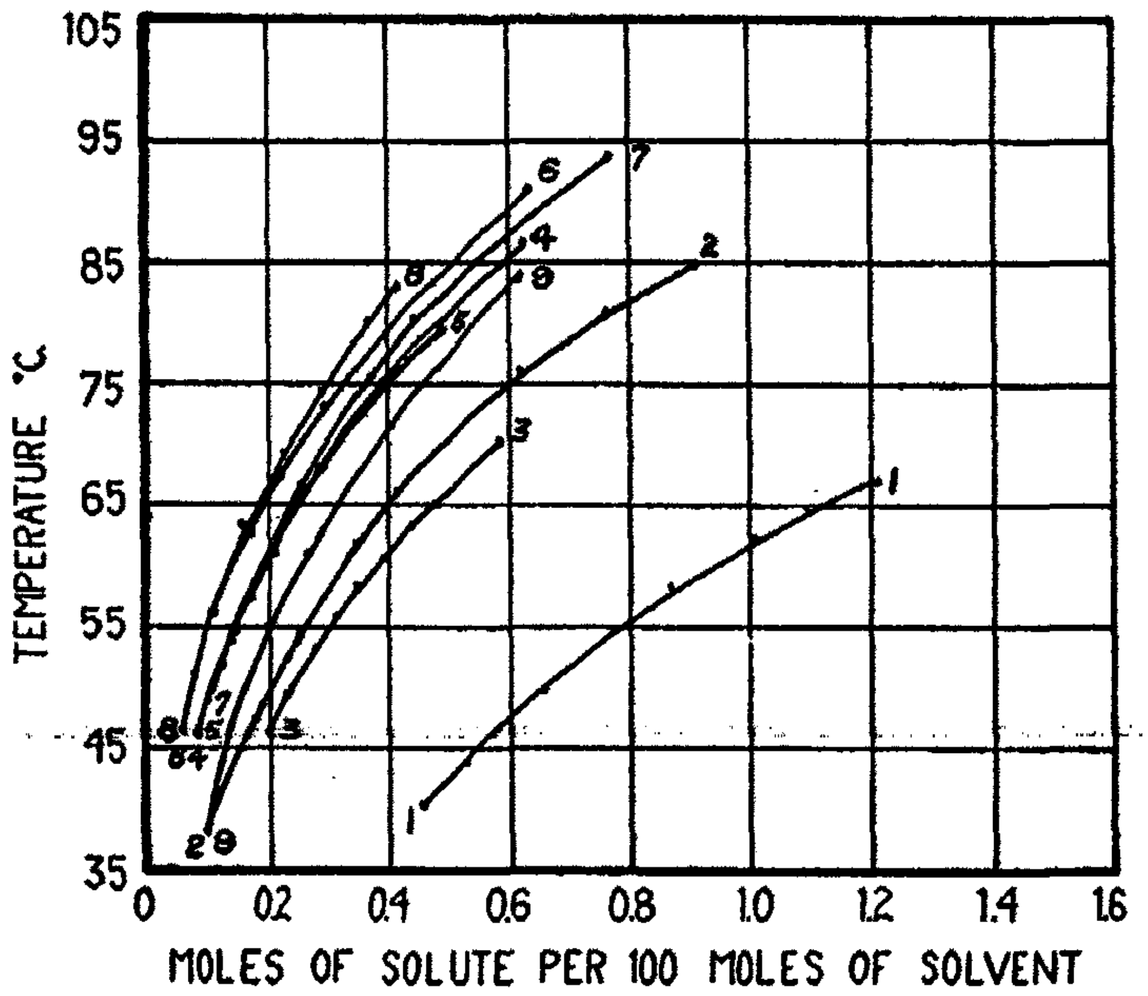

FIG. 6. SOLUBILITY OF α-METHYL-*d*-MANNOSIDE IN ALCOHOLS (SEE FIGURE 2)

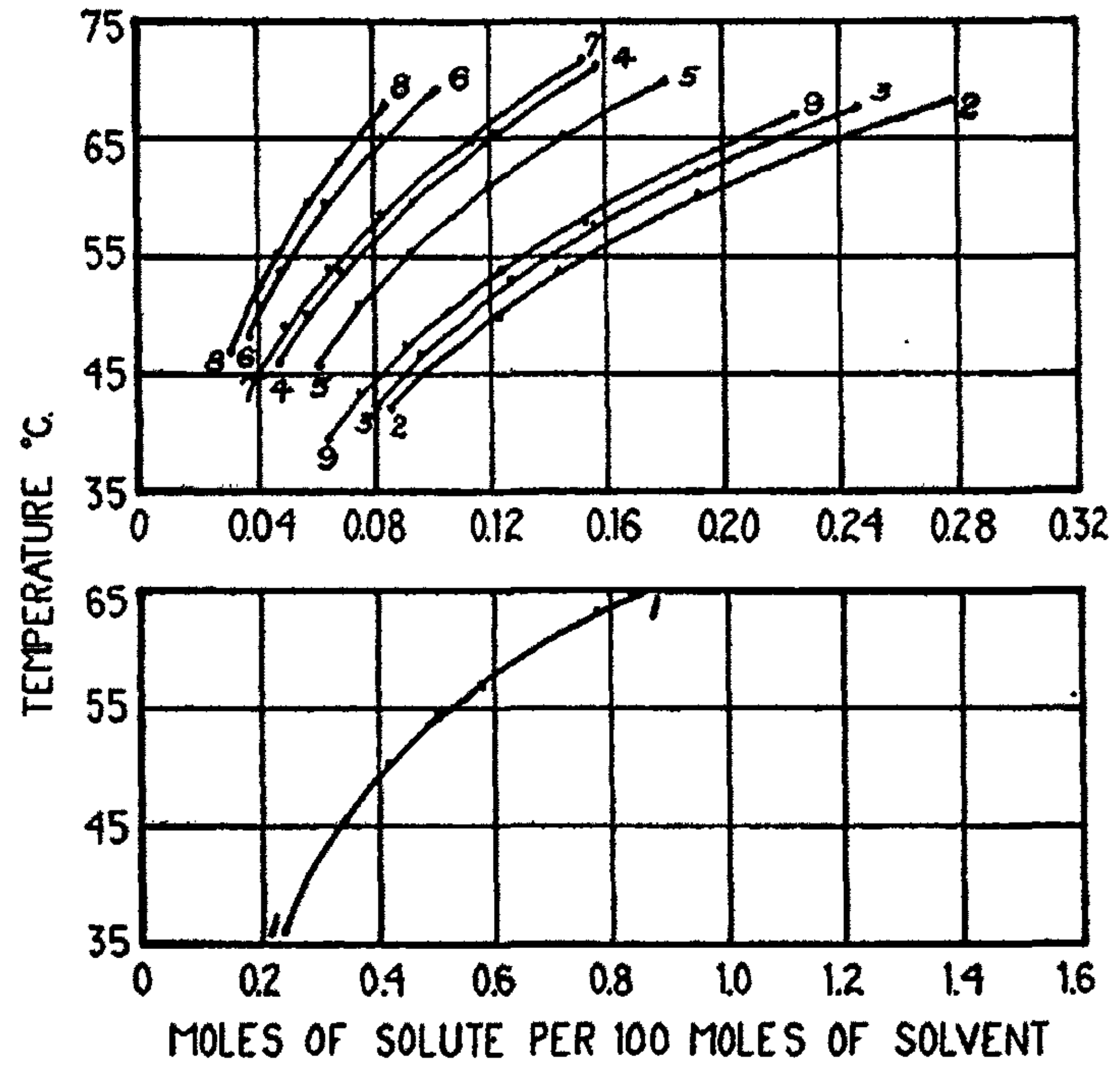

FIG. 7. SOLUBILITY OF *d*-MANNONIC-δ-LACTONE IN ALCOHOLS (SEE FIGURE 2)

crystal forms having different solubilities. The temperatures reported are for the type having the lower solution temperature.

Determinations made at temperatures higher than 90°C. are less reliable, owing to difficulty in controlling the temperature and in keeping the oil bath clear. No corrections were made for the alcohol in the vapor phase.

Solution temperatures for the seven sugar derivatives in the nine different alcohols are recorded in tables 2 to 10. The temperature is in degrees Centigrade and the concentration is expressed in moles per one hundred moles of solvent. The data are expressed graphically in figures 2 to 8.

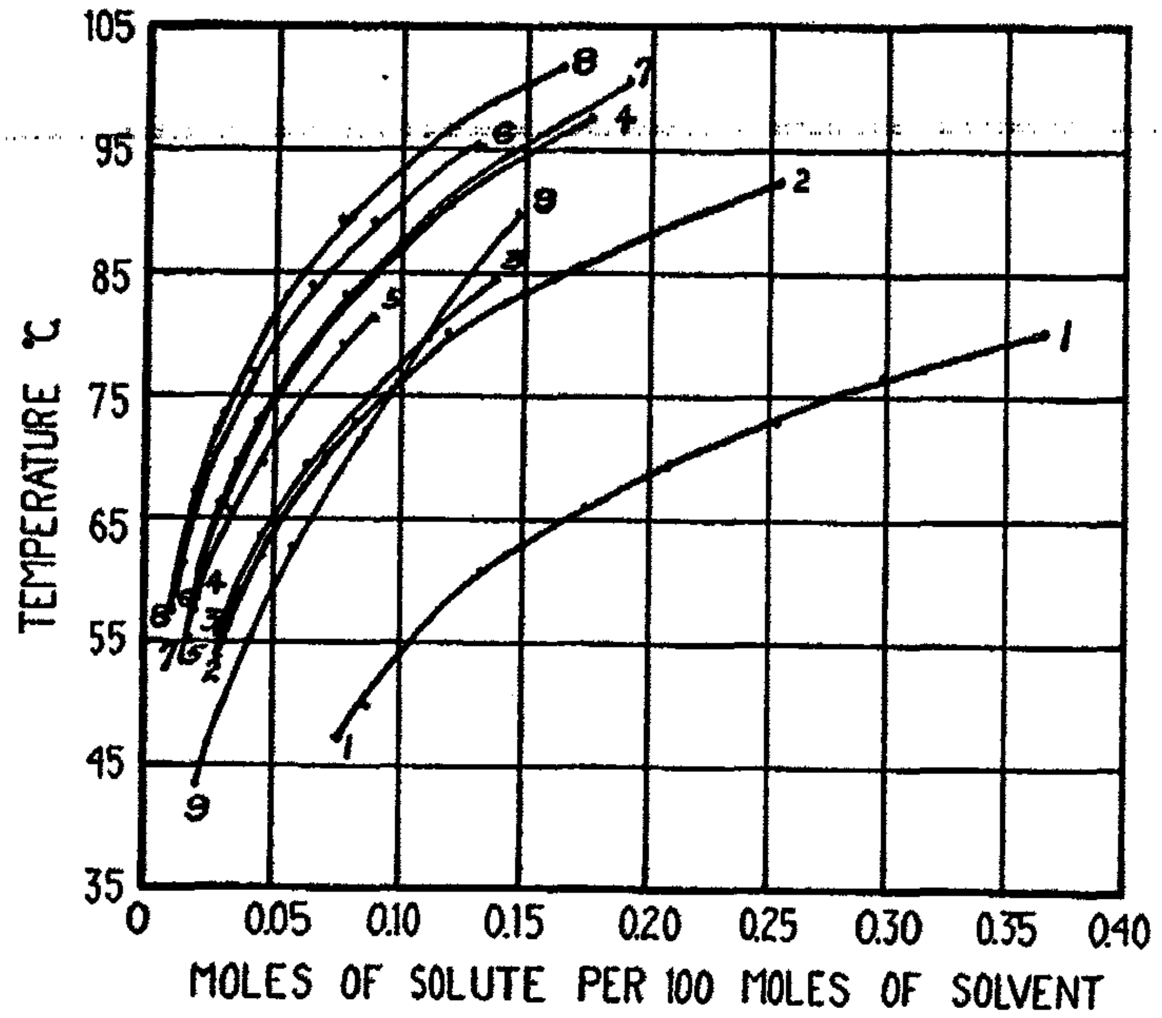

FIG. 8. SOLUBILITY OF *d*-MANNITOL IN ALCOHOLS (SEE FIGURE 2)

DISCUSSION OF RESULTS

In this study it has been possible to obtain information regarding the solubilities of a series of seven closely related isomeric compounds, of which six are of the *d*-rotatory variety and one of the *l*-rotatory variety.

In every solvent *l*-rhamnose, which was used in the form of its monohydrate, is many times as soluble as the next most soluble substance studied. α-*d*-Mannose is more soluble in all the alcohols than β-*d*-mannose, in the ratio of approximately 1.4 to 1. This is of special interest, since these isomeric forms of mannose differ only as regards the groups on the first asymmetric carbon atom. In most solvents α-methyl-*d*-mannoside is only slightly less soluble than β-*d*-mannose, but is considerably less soluble than α-*d*-mannose from which it is derived. The difference in solubility of *d*-mannonic-γ-lactone and *d*-mannonic-δ-lactone is pronounced.

The former is the more soluble in the ratio of approximately 2 to 1 in most alcohols, but over 3 to 1 in methyl alcohol. The relatively unstable δ-lactone thus has the lower solubility. The γ-lactone is more soluble than β-*d*-mannose in all the solvents. Of all the compounds studied, the polyhydric alcohol *d*-mannitol has the lowest solubility in all the alcohols.

The results of these studies confirm the general rules of solubility. All the solutes are polar compounds and hence their solubility in general decreases with increasing length of the carbon chain in the alcohols studied. All seven sugars are much more soluble in methyl alcohol (curve 1) than in any of the other alcohols. Second in solvent properties stands ethyl alcohol (curve 2), and allyl alcohol (curve 3) stands third. There is one exception; α-methylmannoside is somewhat more soluble in allyl alcohol than in ethyl alcohol. With the exception of rhamnose and of mannitol above 75°C., *tertiary*-butyl alcohol (curve 9) comes next in the series after allyl alcohol in the order of decreasing solvent action. We should expect it to be a better solvent than the other butyl alcohols, but not a better solvent than the propyl alcohols. With two exceptions, isopropyl alcohol (curve 5) is a slightly better solvent than normal propyl alcohol (curve 4). In the case of rhamnose and methylmannoside, the two alcohols have almost identical solvent properties. For all the sugars the remaining three butyl alcohols stand in the order secondary (curve 7), normal (curve 6), and isobutyl (curve 8). Thus there is agreement in the case of the propyl and butyl alcohols in that the secondary is a better solvent than the normal alcohol.

SUMMARY

1. Solubility data were determined by the synthetic method for seven carbohydrate derivatives in nine alcohols.
2. The concentration in terms of moles of solute per hundred moles of solvent and the solution temperature are given for each determination. The data are also presented graphically.
3. A comparison of the solubilities of the different solutes in the nine alcohols has been made.

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THE THERMAL DECOMPOSITION OF NITROMETHANE[1]

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In attempts during recent years to isolate data for unimolecular reactions the decomposition of various organic halides, ethers, azo compounds, amines, and nitrites has been studied kinetically, and though superficial results would suggest that in most cases a net reaction of the first order was occurring, extremely few are so free from secondary changes that the results may be accepted unequivocally. The multiplication of such attempts is thus justified. No nitro compounds have so far been studied. The simplest, nitromethane, was therefore chosen.

The apparatus and method used for the study were identical with those used previously by Taylor (3) in similar work, and involved the determination of the rate of pressure change of the reactant with time. To prevent condensation of the nitromethane vapor the apparatus outside the furnace was maintained at about 80°C. throughout the work. The nitromethane used was carefully fractionated from a Kahlbaum sample, the fraction boiling between 100.5 and 101°C. being collected. Temperatures from 390 to 420°C. were found to yield a convenient velocity of decomposition. The percentage increase in pressure during reaction was found to be 130, independent of temperature and pressure, as is shown in table 1.

Data of a typical experiment are given in table 2 showing the observed pressure increases occurring at the specified times at 420°C. with an initial pressure of 198 mm. of nitromethane.

The complete data are presented in table 3 in the form of fractional lives calculated as the times necessary for 25, 50, and 75 per cent of the total pressure increase to occur. This procedure is justified, since from the constancy of the end points under all conditions studied the same reaction is proceeding in each case.

From the general constancy of the above values, particularly for the quarter-lives at the higher temperatures, the reaction may be taken as of the first order, at least early in the reaction. The changing values of the three-quarter-lives would suggest the presence of secondary reactions of higher order than the first. In view of this possibility, the observed in-

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1934.

crease in the quarter-lives with decrease in initial pressure especially at the lower temperatures may be due either to a real deviation of the reaction from unimolecularity or to these secondary reactions of higher order which, if they should have lower temperature coefficients than the unimolecular

TABLE 1

Increase in pressure during decomposition of nitromethane

INITIAL PRESSURE	PER CENT INCREASE	INITIAL PRESSURE	PER CENT INCREASE
Temperature = 390°C.			
201	129	55.5	131
148	130	25.5	133
100.5	130		
Temperature = 400°C.			
201.5	130	52	133
156.1	130	26.5	130
101.5	131		
Temperature = 410°C.			
187.5	130	55	130
145	131	26.5	131
105.5	130		
Temperature = 420°C.			
198	130	51	130
157	130	27	129
104	131		

TABLE 2

Data of a typical experiment

Temperature, 420°C.; initial pressure, 198 mm.

TIME	PRESSURE INCREASE	TIME	PRESSURE INCREASE
minutes	*mm.*	*minutes*	*mm.*
1	40	25	234.5
2	67	30	240
3	89	35	243.5
4	108	40	246
5	124	45	247
6	138	75	249.5
8	161	334	251.5
10	179	469	253.5
15	208	1354	257
20	224.5		

reaction, would have a relatively larger effect on the overall rate at lower temperatures and higher pressures.

TABLE 3

Complete data for the decomposition expressed as fractional lives

INITIAL PRESSURE	FRACTIONAL LIVES		
	t_{25}	t_{50}	t_{75}
	Temperature = 420°C.		
mm.	*minutes*	*minutes*	*minutes*
198	1.40	4.00	7.50
157	1.40	4.00	7.00
104	1.50	4.00	7.50
51	1.40	3.50	7.50
27	1.38	4.00	7.50
	Temperature = 410°C.		
189	2.50	7.40	15.4
153	2.60	7.40	15.2
97.5	2.60	7.80	15.4
46.5	2.70	7.60	15.6
23.5	2.60	7.40	15.4
	Temperature = 400°C.		
201.5	5.10	14.0	28.0
156	5.12	14.0	28.0
101.5	5.50	14.0	28.0
52	5.20	13.0	25.0
26.5	5.30	14.0	24.0
	Temperature = 390°C.		
307	6.50		
202.5	8.00	21.0	42.0
148	10.40	27.0	51.6
100.5	10.35	27.5	52.1
55	10.40	29.0	61.0
25.5	10.40	32.0	63.0
	Temperature = 380°C.		
199.5	16.0		
146	16.5		
101	17.5		
49.5	21.0		
24.5	22.5		

To find the effect of increased surface the reaction vessel was filled with short lengths of Pyrex tubing, the ratio of surface to volume being increased 6.3 times. A comparison between experiments on the normal and increased surface is afforded by a typical run as shown in table 4. Taking the total pressure increase as 130 per cent for the reaction in the packed vessel as in the empty vessel, the quarter- and half-lives for the above reactions are 1.40 and 4.00 minutes in the empty vessel and 1.45 and 4.10 minutes in the packed vessel. The reaction in its early stages does not therefore appear to be influenced to any marked extent by surface.

TABLE 4

Comparison between experiments on the normal and increased surface

Temperature, 420°C.

TIME	INITIAL PRESSURE	
	Empty, 198 mm.	Packed, 216.5 mm.
	Pressure increase	
minutes	*mm.*	*mm.*
1	40	50
2	67	87.5
3	89	115
4	108	136
5	124	152
6	138	162
8	161	181
10	179	190
20	224.5	205
40	246	206
50	247	202
60	248.5	199
80	249.5	193
170	250	188
260	251	192
1350	257	199

That the later reactions, however, are changed by the extent of surface can readily be seen from the peculiar pressure changes in the packed vessel given above, wherein the pressure increase reaches a maximum, falls, and then later rises again. This pressure decrease always observed in the packed vessel, though never found with the empty vessel, can be traced, as is shown later, to a condensation in the capillaries of some of the products of reaction. This fact is responsible for the apparent changed end point in the packed vessel.

The influence of foreign gases in the course of reaction was very thoroughly investigated for the following gases,—helium, nitrogen, nitric oxide, carbon dioxide, and oxygen. With the exception of oxygen all these gases were found to be without effect, the observed results, indeed, duplicating those already given. The addition of oxygen resulted in an appreciable change of the reaction rate and a somewhat different end point. The data are presented in table 5.

The energy of activation of the reaction in its early stages was found by application of the Arrhenius equation to the average values of the quarter-lives at the higher pressures as previously given. The logarithms of these times plotted against the reciprocals of the absolute temperatures gave a good straight line with a slope corresponding to 61,000 calories.

The actual mechanism of the reaction seems to be so extremely complex that it will be simplest to outline it step by step and to attempt to justify each step as given. The primary step postulated involves a split of oxygen according to the equation

$$CH_3NO_2 \rightarrow CH_3NO + \frac{1}{2}O_2$$

TABLE 5

The influence of oxygen on the reaction rate

Temperature, 420°C.; initial pressure of nitromethane, 102.5 mm.; initial pressure of oxygen, 79.5 mm.

TIME	PRESSURE INCREASE	TIME	PRESSURE INCREASE
minutes	*mm.*	*minutes*	*mm.*
1	29.5	12	118.5
2	49.5	15	122.5
3	65	20	125.5
4	77.5	40	126
5	87.5	70	126
6	99.5	250	129
8	106	1350	130
10	113.5		

That nitrosomethane is formed fairly readily was demonstrated by refluxing nitromethane at its boiling point for forty-eight hours. The liquid was then fractionated and a small fraction boiling at 84°C. collected. This is the boiling point of formaldoxine, the isomer of nitrosomethane. Upon refluxing a small portion of this liquid with water for some hours and subsequent addition of silver nitrate a copious precipitate of silver cyanide was obtained, according to the reaction

$$CH_2{:}NOH \rightarrow HCN + H_2O$$

Another portion of the formaldoxime was hydrolyzed in presence of acid and gave a subsequent test for aldehyde

$$CH_2{:}NOH + H_2O \rightarrow CH_2O + NH_2OH$$

The proven presence of formaldoxime is indirect substantiation for the postulated nitrosomethane which is known to be unstable and to isomerize as stated (2).

Nitromethane is known to oxidize according to the reaction (1),

$$CH_3NO_2 + \tfrac{3}{4}O_2 \rightarrow CO_2 + \tfrac{3}{2}H_2O + \tfrac{1}{2}N_2$$

and gas analyses of the products of reaction showed their presence in large quantities. The reaction indeed must be a rapid one, as is demonstrated by the increased rate observed in the experiments with added oxygen as compared with those in its absence.

The third step involves the fate of the nitrosomethane; the simplest assumption would be the splitting into nitric oxide and free methyl radicals, which would give ethane alone or a mixture of methane, ethylene, and hydrogen, as frequently appears in hydrocarbon decompositions. Assuming the former,

$$2CH_3NO \rightarrow C_2H_6 + 2NO$$

there would be for the overall reaction occurring

$$10CH_3NO_2 \rightarrow 6NO + 6H_2O + 4CO_2 + 3C_2H_6 + 2N_2$$

The presence of large amounts of nitric oxide continually made itself felt during the conduct of the experiments. Copious brown fumes of the dioxide were always observed upon evacuating the system after each run.

In an effort to identify the above products and their relative amounts at the end of the decomposition a number of bombs were made up containing nitromethane; they were then heated to allow complete reaction to occur. The bombs upon cooling always showed large amounts of water. In some, definite tests for cyanides were obtained and others contained a white solid. A microanalysis of the solid[2] gave it the empirical formula CH_5NO_3, and it later proved to be ammonium bicarbonate. Analysis of the gases remaining in the bomb gave on the average 23 per cent carbon dioxide, 30 per cent carbon monoxide, 16 per cent methane, 4 per cent nitric oxide, about 1 per cent each of hydrogen and an unsaturated hydrocarbon reckoned as ethylene, with the residual 25 per cent of nitrogen. These analyses, bearing only superficial resemblance to the amount of products postulated above, suggested the possibility that concentration and surface conditions existing in the bombs might have a marked effect on the later progress of reaction. It will be recalled that although no effect of increased surface was found early in the reaction, the later stages were greatly changed. An observation of significance too, was that instead of copious brown fumes being observed on evacuating the system after runs

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[2] Thanks are due Dr. Joseph B. Niederl for this analysis.

with the increased surface, vapors with a strong ammoniacal odor alone were found. Close inspection of the capillaries after a number of these runs showed traces of the white solid, ammonium bicarbonate. Apparently one of the later reactions in the series is capable of being catalyzed to yield varying products; it is suggested as most likely that the nitrosomethane decomposition is responsible, since it is this reaction which yields the observed nitric oxide in large amounts with the empty vessel. The condensation of ammonium bicarbonate in the capillaries accounts satisfactorily for the pressure decrease observed with the increased surface and the reduced end point as compared with runs in the empty vessel. As stated previously, nitrosomethane will isomerize to formaldoxime, which in the presence of water from the nitromethane oxidation will hydrolyze to yield hydroxylamine and formaldehyde. The latter would be decomposed at the temperature in question into carbon monoxide and hydrogen. The hydroxylamine would yield ammonia, and hence give rise to ammonium bicarbonate in the system. It seems quite reasonable then, that the specific surface effect may be in the isomerization of the nitrosomethane to formaldoxime and, in view of the large amounts of nitric oxide produced in the runs in the unpacked vessel, to assume the mechanism given above. The overall reaction would then correspond to a pressure increase of 110 per cent as compared with the observed 130 per cent. If the reactions of the free radicals from the nitrosomethane should not give ethane alone, and the 16 per cent of methane in the bomb experiments would seem to suggest this, the total pressure change would be greater than that given above and more nearly in agreement with the observed.

In summary then, the main reaction being studied appears to be a homogeneous unimolecular split of nitromethane into nitrosomethane and oxygen, with an energy of activation of about 61,000 calories. The complexity of the subsequent reactions does not permit a further analysis of the observed kinetic data.

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THE THERMAL DECOMPOSITION OF TRIETHYLAMINE[1]

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The marked similarity that has appeared up to the present in the decompositions of primary and secondary amines (3, 4, 5, 6) is significant, suggesting an explanation in the presence of the replaceable hydrogen in the amine group. The removal of this in a tertiary amine might be expected to cause a considerable change, since now the bond broken must certainly be C — N and hence data on this bond alone would be definitely available. At the same time it appeared possible that a study of the mechanism of the decomposition, hitherto neglected, might shed further light on existing difficulties in the reactions of the other amines.

The method of study again adopted was the static one, as in all previous cases, supplemented by analyses at significant points during the reaction. The triethylamine, originally an Eastman product, was stored over sodium to remove alcohol and water and distilled three times, the portion boiling between 88.7 and 90.3°C. being collected each time. The high boiling point of the amine necessitated that the capillaries and stopcocks connecting the amine reservoir, reaction vessel, and manometer be heated to prevent condensation. Since most of the measurements were made at pressures below atmospheric, a temperature of 80°C. was maintained throughout the parts of the system outside the furnace, proving sufficient for the purpose. The rate of pressure increase with time was measured at pressures from about 20 to 400 mm. at temperatures of 450, 470, 485, and 500°C.

The percentage increase in pressure for the end point of the reaction was extremely difficult to obtain, owing presumably to very slow secondary reactions occurring. Thus a sample of amine left in the system for six days at 450°C. increased in pressure 2 mm. between the sixth and seventh day. A rather arbitrary time limit was thus set at forty-eight hours at 450°C., this being reduced at the other temperatures studied by an amount in accordance with the observed temperature coefficient. In this way the pressure increase was found to vary from 200 to 250 per cent for the initial

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1933.

pressure range 350 to 20 mm. These values, however, were uninfluenced by temperature, as table 1 will show.

Data for the individual experiments are most conveniently given as the times necessary for the pressure to increase by 25, 50, 75, 100, and 175 per cent of its initial value. At the lowest temperatures the times corresponding to the latter were not measured at all pressures and are therefore not listed in table 2.

The above values, especially those for 25 and 50 per cent pressure increase, being constant above about 150 mm. at 450°C., about 120 mm. at 470°C., about 50 mm. at 485°C., and at all pressures studied at 500°C. suggest that the reaction is of the first order, passing towards the bimolecular range at pressures below the limits stated.

TABLE 1

Relation between temperature and pressure increase

TEMPERATURE	INITIAL PRESSURE	PER CENT PRESSURE INCREASE
°C.	mm.	
450	25	258
450	128	221
450	242	205
470	21	256
470	317	201
485	33	254
485	286	205
500	17	268
500	161	216
500	347	194

The usual test for homogeneity of the reaction was made. The reaction vessel was packed with short lengths of Pyrex tubing sufficient to increase the surface to volume ratio a little more than seven times. Examples are given in table 3 of reactions in this packed vessel at 450°C. where no difference from the normal rates is shown.

The effect of additions of foreign gases was determined for nitrogen, ammonia, and hydrogen. The data given in table 4 were obtained.

It will be observed that experiments were made at the highest and lowest temperatures studied in each case and also at various pressures to include the effect of the added gas on the reaction in the pressure range where it appeared to have deviated from its unimolecular course. The effect of nitrogen is negligibly small at all temperatures and pressures studied. The same also applies to ammonia. Hydrogen on the other hand has a

TABLE 2

Times required for pressure to increase by certain per cent of its initial value

INITIAL PRESSURE	FRACTIONAL LIVES				
	t_{25}	t_{50}	t_{75}	t_{100}	t_{125}
			Temperature = 500°C.		
mm.	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
15	0.25	0.56	0.91	1.30	2.9
50	0.28	0.62	0.97	1.45	3.9
69	0.25	0 57	0.96	1.40	4.0
122	0.26	0.57	0.95	1.43	4.9
138	0.28	0.63	1.04	1.55	5.35
161	0.27	0.55	0.90	1.37	4.8
185	0.27	0.58	0.97	1.48	5.4
245	0.26	0.60	0.99	1.50	5.7
285	0.27	0.61	1.01	1.57	6.6
322	0.26	0.60	1.01	1.60	7.0
347	0.26	0.59	1.04	1.60	7.8
			Temperature = 485°C.		
33	0.80	1.60	2.50	3.70	4.9
36	0.74	1.53	2.39	3.40	5.0
48	0.65	1.31	2.08	3.05	4.4
50	0.55	1.22	1.95	2.95	4.1
59	0.52	1.14	1.85	2.65	7.7
92	0.50	1.12	1.90	2 85	8.7
154	0.50	1.17	1.95	2.98	10.0
197	0.50	1.11	1.94	2.96	10.0
224	0.48	1.09	1.87	2.93	9.9
258	0.50	1.16	1.97	3.10	11.9
286	0.50	1.17	2.06	3.19	12.8
358	0.53	1.20	2.12	3.32	14.5
377	0.48	1.17	2.04	3.21	14.4
			Temperature = 470°C.		
21	1.59	3.21	5.01	7.07	
29	1.44	2.78	4.40	6.88	
62	1.31	2.81	4.73	7.11	
66	1.22	2.65	4.53	6.93	
108	1.10	2.80	4.71	7.20	
130	1.03	2.55	4.45	6.78	
162	1.02	2.49	4.40	6.82	
217	1.05	2.59	4.47	6.91	
242	0.99	2.45	4.42	6.87	
207	1.03	2.57	4.46	6.89	
317	1.03	2.54	4.40	6.89	
407	1.02	2.47	4.42	6.92	

TABLE 2—*Concluded*

INITIAL PRESSURE	FRACTIONAL LIVES				
	t_{25}	t_{50}	t_{75}	t_{100}	t_{175}
Temperature = 450°C.					
mm.	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
25	4.0	9.0	16.0	23.2	
34	3.8	8.9	16.0	24.3	
50	3.7	8.7	14.8	22.5	
80	3.6	8.6	14.9	22.8	
102	3.3	8.2	14.5	22.5	
128	3.0	7.8	13.8	21.5	
150	2.7	6.9	12.2	18.9	
199	2.6	6.7	12.3	19.7	
242	2.8	7.4	13.5	21.3	
297	2.7	7.4	13.4	21.2	
330	2.7	7.3	13.3	21.2	
369	2.7	7.3	13.3	21.1	

marked effect. There is evidence that it accelerates the reaction slightly in its early stages both at low and at high pressures; the low pressure rate, however, is not raised to its high pressure value. Later in the reaction, as will be seen from a comparison of the times for 175 per cent increase in pressure in the presence and absence of hydrogen, the rate of pressure increase is markedly reduced and to such an extent that the pressure–time curve reaches a sharp maximum and actually decreases again slightly on continued heating. Whether the effect in the earlier stages is a true effect due to fruitful collisions cannot be said, but certainly the effect later in the reaction must be due to a hydrogenation.

To obtain the energy of activation of the reaction the logarithms of the average values of the times for 25, 50, and 75 per cent pressure increase in the high pressure range were plotted against the reciprocal of the absolute temperature. Excellent straight lines were obtained, the slopes however increasing steadily so that the energies calculated from them were 52,080 calories for 25 per cent, 55,550 calories for 50 per cent, and 57,300 calories for 75 per cent pressure increase. In itself this is sufficient indication that the reaction is complex and that the energy of activation of the earliest reaction occurring is less than 52,000 calories and would most probably be of the order of 50,000 calories. This value is higher than that found for the primary amines, namely 44,000 calories, but is in fair agreement with the value of 49,000 calories found for diethylamine.

The first attempt to obtain some idea of the products of reaction was made by interrupting a static run when only partially completed, removing the furnace from around the reaction vessel, and replacing it with liquid air. Only fixed gases should then remain, namely methane, hydrogen, or nitrogen. Thus, 222 mm. of amine after 10 minutes at 500°C. gave enough permanent gas at liquid air temperature to yield a pressure of 17 mm. Again, 384 mm. of amine after 23 hours at 450°C. gave a residual gas pressure of 28.5 mm. Assuming the simple gas laws to hold approximately, these figures show that the fixed gases constituted 65 and 60 per cent respectively of the initial pressures. This would indicate that only slight amounts of ammonia and unsaturated hydrocarbons were produced during the reaction. To decide this definitely about 0.2 g. of amine was sealed under its own vapor pressure at room temperature in a glass bomb and

TABLE 3

Reaction in vessel packed with Pyrex tubing

Temperature, 450°C.

INITIAL PRESSURE	FRACTIONAL LIVES			
	t_{25}	t_{50}	t_{75}	t_{100}
mm.	*minutes*	*minutes*	*minutes*	*minutes*
346	2.8	7.2	13.3	21.7
190	2.9	7.4	13.1	20.8

TABLE 4

Effect of added foreign gases

INITIAL PRESSURE		TEMPERATURE	FRACTIONAL LIVES				
Amine	Added gas		t_{25}	t_{50}	t_{75}	t_{100}	t_{125}
mm.	*mm.*	*°C.*	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
126	100 N_2	500	0.25	0.61	0.91	1.42	4.2
80	102 N_2	500	0.30	0.64	1.02	1.50	4.4
240	155 N_2	450	2.7	6.8	12.6	21.4	
170	150 N_2	450	2.7	7.0	12.5	19.4	
146	101 N_2	450	2.7	7.2		19.6	
81	100 N_2	450	3.5	8.1	14.4	21.6	
110	124 NH_3	500	0.28	0.61	1.03	1.55	5.3
73	143 NH_3	500	0.28	0.61	1.00	1.55	5.0
214	183 NH_3	450	2.8	7.2	13.0	20.0	
24	179 NH_3	450	4.0	8.7	14.4	22.0	
214	159 H_2	500	0.25	0.56	0.95	1.50	6.8
154	151 H_2	500	0.24	0.55	0.94	1.45	5.9
96	99 H_2	500	0.27	0.57	0.97	1.47	6.2
51	153 H_2	500	0.24	0.60	0.97	1.53	7.0
51	100 H_2	500	0.27	0.57	0.95	1.43	4.8
257	102 H_2	450	2.5	6.6	11.6	18.6	
175	143 H_2	450	2.4	6.2	11.2	17.7	
25	153 H_2	450	3.6	9.4	20.7		

thoroughly decomposed at 500°C. The gas remaining was then analyzed,[2] showing on the average of several determinations 58 per cent methane, 20 per cent ethane, 3 per cent ammonia, 2 per cent unsaturated hydrocarbon (bromine absorption), no hydrogen, and the residue 17 per cent nitrogen. In all such bomb experiments, owing to the high concentration of the reactant, large amounts of a tarry deposit always form—an occurrence never observed in the individual static runs.

Samples of the triethylamine were heated at 400°C. for from one to three hours to test for intermediate products early in the reaction. In the liquid which remained after heating, the presence of some primary amine was demonstrated by the Rimini test and of a hydrazine in quantity by reduction of alkaline silver nitrate. Cyanides, by the ferrocyanide and thiocyanate tests, acetonitrile by hydrolysis with hydrochloric acid, and secondary amines by the Simon test were shown to be absent. Analysis of the gas formed under these conditions showed the presence of 8 per cent ammonia, 3 per cent unsaturated hydrocarbon, less than 1 per cent of hydrogen, and the residue on combustion gave a CO_2 to H_2O ratio of 3 to 4. This would indicate the residual gas to be either propane or a mixture of methane and butane. A further sample of this gas therefore was kept in solid carbon dioxide until no further contraction in volume occurred. The uncondensed gas gave a CO_2 to H_2O ratio of 1:2.06. The condensed gas on vaporizing and combustion gave a ratio of 4:5.2. The residual hydrocarbon is then a mixture of methane and butane, the percentages of the total gas being 22 for methane and 35 for butane, leaving a residual 32 per cent of nitrogen.

Analysis shows then that butane is present in considerable quantities in the early stages of reaction. To account for this at the same time as a hydrazine the following reaction would seem to be indicated.

$$2(C_2H_5)_3N \rightarrow (C_2H_5)_2N{-}N(C_2H_5)_2 + C_4H_{10}$$

This would probably be a second-order reaction and would be followed by the decomposition of the hydrazine and also of the butane. If it is assumed that nitrogen and butane are formed by the hydrazine, the butane in turn yielding finally methane and ethane with residual carbon as always found, two molecules of amine would yield seven molecules of gaseous products corresponding to the pressure increase of 250 per cent observed. The butane decomposition, known to be relatively slow at 500°C., would account for the slow approach to the end point. If the hydrazine decomposition is relatively fast, as appears probable from the absence of any noticeable induction period, which would be expected since the initial

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[2] These analyses and the subsequent tests after partial decomposition were kindly made by W. Takacs of this laboratory.

bimolecular reaction involves no volume change, then the overall reaction in the intermediate stage would correspond to two molecules of amine yielding three of butane and one of nitrogen, approximately a two for one split. Now by the analytical method of Guggenheim (1) we can judge approximately the end point towards which a reaction is heading at any stage in its course, from three readings equally separated in time. The larger the time intervals the more accurate is the result. Applying this in three cases it is found that, at 500°C. for the first two minutes of reaction, corresponding to a pressure increase of 100 per cent, the end point should be 164 per cent and for two runs at 485°C. the end point should be 150 per cent. The errors involved in this determination do not justify the acceptance of these figures as absolute, but one fact would appear certain, namely, that the reaction in its early stages is more nearly a two for one split than the three or four for one necessary to account for the observed pressure increases of between 200 and 250 per cent.

The mechanism suggested would appear so far to be satisfactory. The decomposition of the hydrazine would most probably be unimolecular, as is known to be the case for butane. The pressure increases herein measured would thus be those of a unimolecular volume increase reaction succeeding a bimolecular reaction without volume change. The relative rates of these would control the apparent order of reaction, but at a certain lower pressure the bimolecular reaction must eventually take control and the apparent order pass to more nearly two. Extremely little is known of the postulated tetraethylhydrazine, so that further speculation must be avoided.

In view of the presence of free ammonia and unsaturated hydrocarbon and in relatively larger quantities in the earlier than later stages of reaction, it would seem that some immediate decomposition of the amine into ammonia and an unsaturated hydrocarbon was occurring. The actual amounts found, however, preclude this possibility as of real significance in the major mechanism. The simultaneous presence of ammonia and unsaturated would account for the traces of primary amine found in the analyses. The effect of added ammonia, slight if any, could only be to aid such a reaction. The effect of added hydrogen, which is the more marked in the later stages of the reaction and especially on the end point, is to be accounted for by its known hydrogenation of unsaturateds formed in the butane decomposition (2).

SUMMARY

The thermal decomposition of triethylamine has been investigated over a pressure range from 15 to 400 mm. at temperatures from 450 to 500°C. The reaction is homogeneous with an energy of activation in its early stages of the order of 50,000 calories. The mechanism suggested by analysis of

intermediate products involves the formation of tetraethylhydrazine and butane with subsequent decompositions yielding chiefly methane and nitrogen.

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THE CHLORINATION OF PROPANE. II

The Heterogeneous Reaction

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In a previous communication (6) the results of studies on the homogeneous reaction occurring between chlorine and propane were presented. The present paper deals with the results obtained in the presence of catalysts.

PROCEDURE

The same flow method was used in this research as in the previous work on the homogeneous reaction. The per cent of chlorine converted was calculated from the iodine and hydrochloric acid titrations in the potassium iodide absorbers. The reactants were purified, measured, and mixed before being passed into the heated contact mass.

At the beginning of a series of runs, a new catalyst was placed in the reaction chamber and activated with nitrogen at 400°C. for about two hours. This was followed with chlorine at about 200°C. for thirty minutes, and the excess chlorine was swept out with nitrogen at room temperature.

MATERIALS

The silica gel used as a catalyst base was obtained through the courtesy of the Silica Gel Corporation. It was a gel prepared by the method of Patrick and contained some iron. The gel was purified by boiling with concentrated nitric acid and then with distilled water until acid-free, dried on a steam bath, and activated with clean dry air at 270°C.

The catalysts were prepared by the method of Smith and Reyerson (5). A solution of $Cu(NH_3)_4(NO_3)_2$ or $Cu(NH_3)_4Cl_2$, depending upon the catalyst wanted, was made while the gel was activated at 350–400°C. The gel was allowed to cool and the copper solution poured over it. The impregnated gel, which was blue, was placed between filter papers to dry. The method from here on depended upon the type of catalyst wanted, namely, metallic copper, or cupric chloride on the gel.

If the copper gel was wanted the $Cu(NH_3)_4(NO_3)_2$ gel was placed in the furnace and dry air or oxygen passed over it. This was then reduced to metallic copper by passing a stream of hydrogen at 450°C. over it until reduction was complete. In the production of the cupric chloride catalyst, the gel impregnated with $Cu(NH_3)_2Cl_2$ was placed in the catalyst tube and activated as described previously.

TABLE 1

Chlorination of propane using Al_2O_3 *as catalyst*

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
98	535	473	21	494	4.3
135	516	428	57	485	11.8
151	503	380	100	480	20.8
166	475	315	172	487	35.3
179	427	207	279	486	57.3
187	413	175	338	513	65.9
191	454	54	425	479	88.7
199	415	4	619	623	99.2

TABLE 2

Chlorination of propane using Al_2O_3 *as catalyst*

30 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 2:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
62	632	368	2	320	0.6
97	662	304	5	309	1.6
139	637	272	31	303	10.2
148	635	288	41	329	12.5
160	643	263	73	336	21.8
171	625	233	109	342	31.8
182	619	187	130	317	41.0
187	601	161	176	337	52.1
193	600	122	213	335	63.5
201	600	75	280	355	78.9
205	564	50	301	351	85.6
208	588	50	304	354	86.0
208	574	54	304	358	84.8
211	575	10	365	375	97.4

The aluminum oxide catalyst was furnished through the kindness of the Aluminum Company of America. It was an excellent uniform product of 8–14 mesh that had been specially activated. Its catalytic behavior was tested in dehydration reactions in which olefins were pyrogenically made from the corresponding alcohol. The results showed the catalytic activity to be excellent.

This activated alumina was slightly reddish in color, which was probably due to the presence of traces of iron. After activating it for eight hours with nitrogen, the temperature rose from 20°C. to 40°C. when the reactants were passed through it, indicating good absorptive powers.

DISCUSSION OF RESULTS

The runs in this group were divided into two series, namely, determinations at 10 liters per hour for the total rate of flow and at 20 liters per hour. One series of runs was made at 2 liters per hour using a copperized gel catalyst. No further runs were made at this rate, as poisoning is high at such low space velocities. A few runs were made at 50 liters per hour, but the problem of heat transfer was so great that the results obtained were not valid.

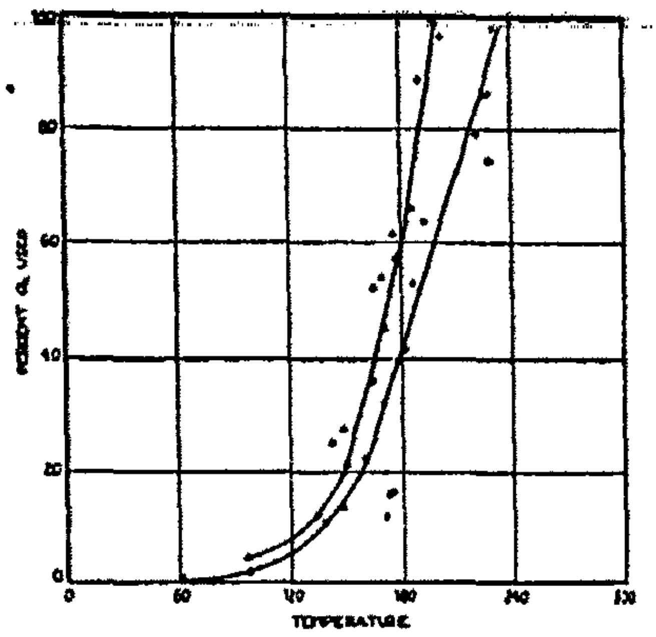

Fig. 1

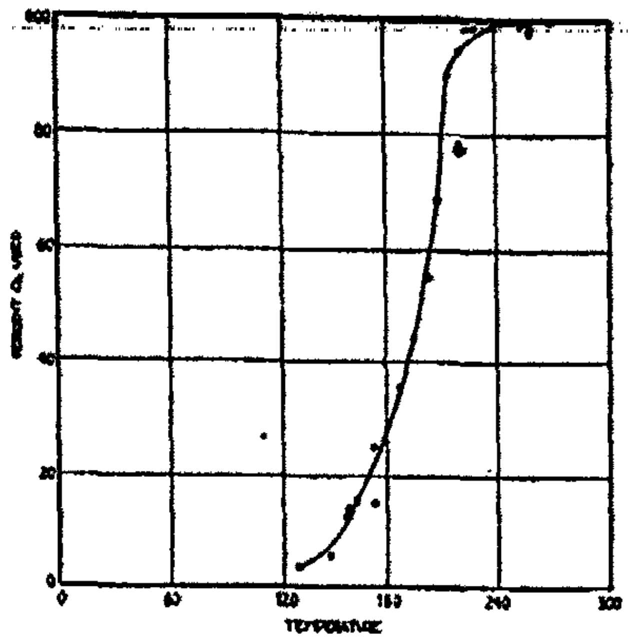

Fig. 2

Fig. 1. Chlorination of Propane Using Al_2O_3 as Catalyst and a Rate of Flow of Two Liters per Hour

⊙ $C_3H_8:Cl_2 = 2:1$; △ $C_3H_8:Cl_2 = 1:1$

Fig. 2. Chlorination of Propane Using $CuCl_2 \cdot SiO_2$ Catalyst and a Rate of Flow of Ten Liters per Hour

$C_3H_8:Cl_2 = 2:1$

A series of runs was made using an activated aluminum oxide catalyst, the results of which are summarized in figure 1 and tables 1 and 2. It was believed that a layer of aluminum chloride would form on the aluminum oxide base and thus give a very active catalyst. The $AlCl_3 \cdot Al_2O_3$ combination was desired, as aluminum chloride if used alone would sublime and leave the reaction chamber. It was hoped that the aluminum oxide would prevent this.

In comparing the data represented in figure 1 with similar data in the other catalytic runs it can be seen that the aluminum oxide catalyst was quite active. Nevertheless, it proved to be undesirable. Water was found to be continually coming over with the products of the reaction, and on examination the catalyst proved to be saturated with water. The probable reaction is as follows:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

This water undoubtedly reacted with chlorine to give hypochlorous acid. How this would affect the propane or the course of chlorination is unknown, but it would not simplify matters. The use of this catalyst was consequently discontinued, and only the $CuCl_2 \cdot SiO_2$ gel catalyst used. The latter catalyst was active and easy to prepare.

The question of the dehydrogenation of propane prior to chlorination arises in the catalytic reaction. Frey and Huppke (2) have recently studied the dehydrogenation of propane. They give the following equation for the affinity of the reaction:

TABLE 3

Chlorination of propane using Cu–SiO$_2$ *catalyst*

60 minutes duration. Total rate of flow 2 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
52	1030	1018	2	1020	0.2
103	1012	1184	12	1196	1.0
145	819	976	106	1082	9.8
153	1056	921	135	1056	12.8
164	955	786	224	1010	22.2
184	843	580	463	1043	44.3
204	726	411	742	1153	64.3
209	595	193	923	1116	82.7
225	632	34	994	1028	96.7
246	413	14	1132	1146	98.8
276	448		1397	1397	100.0

$$A = 25{,}920 - 9.21T \log_{10}T - 0.21T$$

Since all of the chlorinations were made below 300°C., we shall use this temperature for the calculation.

Then

$$A = 25{,}775 \text{ cals.}$$

$$A = -RT \ln \frac{(C_3H_6)(H_2)}{(C_3H_8)}$$

Substituting the proper values, we find the equilibrium partial pressure of propylene at 300°C. to be 1.3×10^{-5} atmospheres. This small concentration should scarcely affect the results at even the higher temperatures. The factor involving the addition of chlorine to propylene, formed by the pyrolysis of propane, may then be disregarded.

An examination of the graphs giving the results of the catalytic reaction shows the difficulty of obtaining uniform results. Only the runs having a high partial pressure of propane will give a uniform curve. This is due to two effects: first, the high chlorine partial pressure causes the production of relatively large amounts of the higher chlorinated propanes which act as poisons, and second, the occurrence of a new phenomenon which we have called catalytic hysteresis (to be mentioned later). If a poisoning of the wall in the empty chamber reaction had an appreciable effect on the reaction, certainly such a powerful adsorbent as silica gel, with its enormous surface, should greatly affect the rate of the reaction.

TABLE 4

Chlorination of propane using $CuCl_2 \cdot SiO_2$ *catalyst*

5 minutes duration. Total rate of flow 10 liters per hour. $C_3H_8:Cl_2 = 2:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
107	547	258		258	
146	533	242	14	256	5.5
222	485	15	256	271	94.3
158	542	227	37	264	14.0
173	591	210	68	278	24.5
187	529	175	96	271	35.4
205	492	118	141	259	54.4
221	500	63	207	270	76.7
226	470	5	287	292	98.2
156	541	242	34	276	12.3
173	532	217	37	254	14.6
196	514	139	108	247	43.7
222	498	57	203	260	78.0
163	538	231	41	272	15.1
210	498	80	172	252	68.2
229	468	4	291	295	98.5
240	465	4	284	288	98.5
216	480	27	246	273	90.0
240	465	5	303	308	98.2
256	452	4	287	291	98.5
270	450		301	301	100.0
224	477	61	195	256	76.2
260	452	8	258	266	96.8
260	448	1	293	294	99.8
223		115	147	262	56.0
129	565	270	10	280	3.6

In order to calculate the heat of activation, a series of runs is chosen having a high partial pressure of propane, as the results are fairly uniform under these conditions. Using the data in figure 2 (table 4), the ratio of the velocity constants k_2/k_1 is equal to 2 in the temperature range 168°C. to 192°C.

$$\ln \frac{k_2}{k_1} = \frac{H}{R} \frac{T_2 - T_1}{T_2T_1}$$

$$H = \frac{RT_2T_1 \ln k_2/k_1}{T_2 - T_1}$$

$$= \frac{2 \times 465 \times 441 \times \ln 2}{465 - 441}$$

$$= 11{,}900 \text{ calories per mole } (\mathrm{CuCl_2 \cdot SiO_2} \text{ catalyst})$$

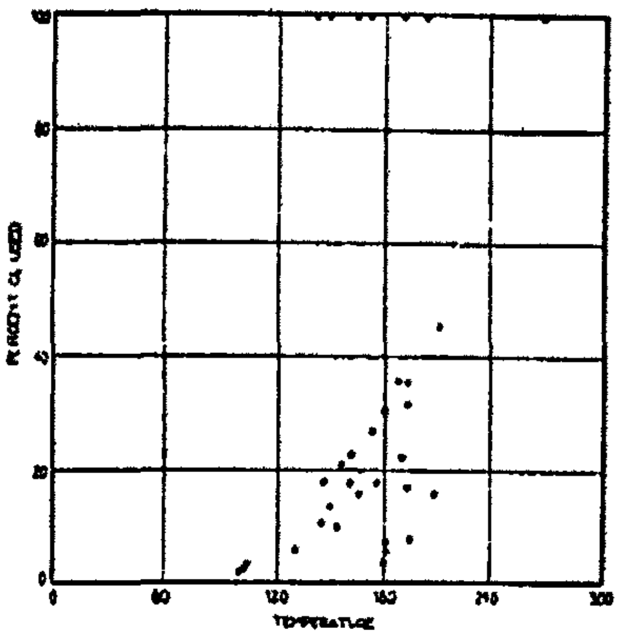

FIG. 3

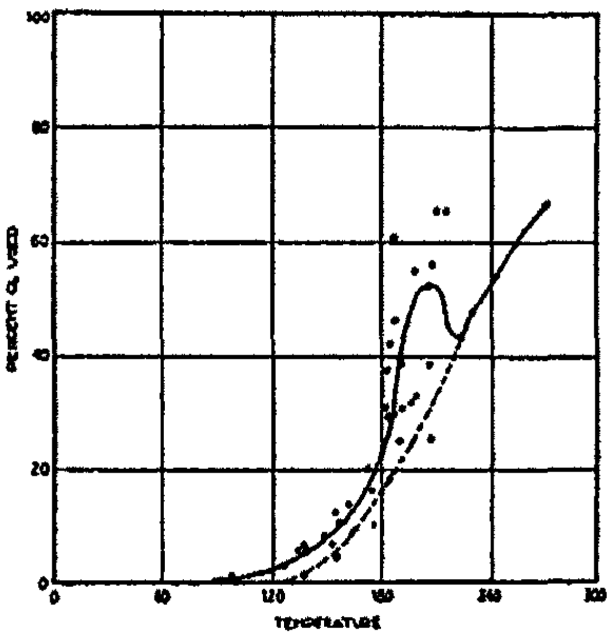

FIG. 4

FIG. 3. CHLORINATION OF PROPANE USING $CuCl_2 \cdot SiO_2$ CATALYST AND A RATE OF FLOW OF TEN LITERS PER HOUR

$C_3H_8:Cl_2 = 1:2$

FIG. 4. CHLORINATION OF PROPANE USING $CuCl_2 \cdot SiO_2$ CATALYST AND A RATE OF FLOW OF TWENTY LITERS PER HOUR

$C_3H_8:Cl_2 = 1:1$

The heat of activation is almost half of that calculated for the empty chamber results. Not only is the heat of activation less in the catalytic reaction, but an examination of corresponding data will show a greater extent of chlorination at a given temperature and a given rate of flow when the contact agent is present.

The heats of activation for the copperized gel catalyst and the aluminum oxide catalyst were calculated and found to be 14,400 and 12,900 calories per mole, respectively. The data from the copperized gel (see table 3) were taken when the partial pressures of the reactants were equal. In these catalytic reactions, very little change in rate was detected when the partial pressures of the reactants were varied.

Figure 4 gives a good example of the effect of poisoning on the catalyst. The continuous curve represents one series of successive runs. The negative temperature coefficient of reaction is shown here just as in the empty chamber runs. In order to prove that this effect was due to poisoning, the catalyst was used for some time and another series of runs was made. The results followed the broken line curve, which makes a normal uniform chlorination curve with the upper part of the original curve. After the contact agent had been completely poisoned or when it had reached a steady state of activity, no abnormalities were noticed.

MECHANISM OF THE CATALYTIC REACTION

Cupric chloride at higher temperatures dissociates (4) and gives off free chlorine. This chlorine is probably in the atomic form when first liberated.

$$CuCl_2 + \text{heat} \rightarrow CuCl + Cl$$

Such a contact mass should be a good agent for the production of chlorine atoms with this possible mechanism.

$$\begin{gathered} CuCl + Cl_2 \rightarrow CuCl_2 + Cl \\ CuCl_2 + \text{heat} \rightarrow CuCl + Cl, \text{ etc.} \end{gathered}$$

These chlorinations may initiate chains just as in the mechanism postulated for the gas phase chlorination.

$$\begin{gathered} C_3H_8 + Cl \rightarrow C_3H_7 + HCl \\ C_3H_7 + Cl_2 \rightarrow C_3H_7Cl + Cl, \text{ etc.} \end{gathered}$$

It may be that the free propyl radicals also combine with chlorine atoms on the surface:

$$C_3H_7 + Cl \rightarrow C_3H_7Cl$$

Cuprous chloride has the property of combining with hydrogen chloride to give a complex.

$$CuCl + HCl \rightarrow HCuCl_2$$

This property of cuprous chloride should make it a good catalyst for chlorination, as it aids in the removal of the hydrogen chloride. We may represent the reaction at the surface as follows:

$$\begin{gathered} CuCl_2 + \text{heat} \rightarrow CuCl + Cl \\ CuCl + Cl + C_3H_8 \rightarrow HCuCl_2 + C_3H_7 \\ HCuCl_2 + \text{heat} \rightarrow CuCl + HCl \\ CuCl + Cl_2 \rightarrow CuCl_2 + Cl \\ Cl + C_3H_7 \rightarrow C_3H_7Cl \end{gathered}$$

Since some of the chlorination takes place in the gas phase, both the gas phase and surface mechanism would take place simultaneously. The quantitative extent of the two processes has not been determined.

CATALYTIC HYSTERESIS

A new and peculiar effect occurred in the catalytic runs using partial pressures of chlorine of 0.5 atmosphere or over. Starting a series of runs at a low temperature and going up the temperature scale gave a curve that was quite normal up to the point where all the chlorine had reacted. In dropping the temperature, the points did not fall along the curve obtained with a successively rising temperature. One hundred per cent of the chlorine continued to be used as the temperature in the reaction chamber was dropped to as low a point as 140°C. The series of points at 100 per cent on figure 3 illustrate this phenomenon. Figure 5 gives a typical hysteresis curve with the points numbered in the order in which the determinations were made.

The possibility of hysteresis at lower conversions than 100 per cent was tested, but in each case, on lowering the temperature, the points followed the original curve. It seemed necessary to carry the reaction to 100 per cent conversion before this reaction inertia set in.

A freshly activated catalyst produced this effect with greater ease than one that had been used for some time. In two cases, with extremely active catalysts, the catalytic hysteresis set in between 170°C. and 190°C. This was at a much lower temperature than usual.

An examination of the figure showing this effect indicates 100 per cent conversion where the normal conversion at the same temperature would be around 5 per cent. Equilibrium had been established at the lower temperatures, as runs made over a period of two or three hours gave constant results. The hysteresis effect remained as long as five hours after its inception, this period of time being certainly sufficient for the attainment of equilibrium. The temperature indicated by the thermometer was correct, as the thermometer well went to the center of the contact mass.

One of the possible explanations advanced for this phenomenon was briefly this: chlorination at a low temperature permits the adsorption of chloropropanes (not so strongly adsorbed at higher temperatures) which poison the catalyst. Higher temperatures favor the activation of the catalyst by removing the adsorbed products. This autoactivation enhances the activity of the contact mass, thereby producing a high percentage of chlorination.

To test this possible theory, nitrogen was passed over the catalyst at 300°C. to activate it thoroughly. The temperature was then dropped to 140°C. and the reactants passed through the reaction zone. If the theory was correct, 100 per cent chlorination should be the result, but such was not the case. A second explanation was advanced, which involved the origin of the heat of activation. This energy is derived from two sources: the heat of reaction and the heat of the electric furnace.

$$H_{\text{furnace}} + H_{\text{reaction}} = E_{\text{activation}} + H_{\text{losses}}$$

At the beginning of a series of runs the extent of reaction is such that $H_F + H_R$ is insufficient to activate all of the molecules. As soon as there is energy enough to activate all of the molecules, there will be 100 per cent conversion. Once this condition is attained, $H_F + H_R$ is more than enough to activate all of the molecules, and even though H_F is decreased (the temperature dropped), all of the molecules will still be activated. A point will be reached when the two sides of the equation will be exactly equal. Any decrease in temperature beyond this point will decrease the heat resulting from reaction (H_R) as well as H_F, which in turn means that the energy available for activation is cut. These two factors H_R and E_A will affect one another progressively, and there should be a sudden drop in the extent of chlorination.

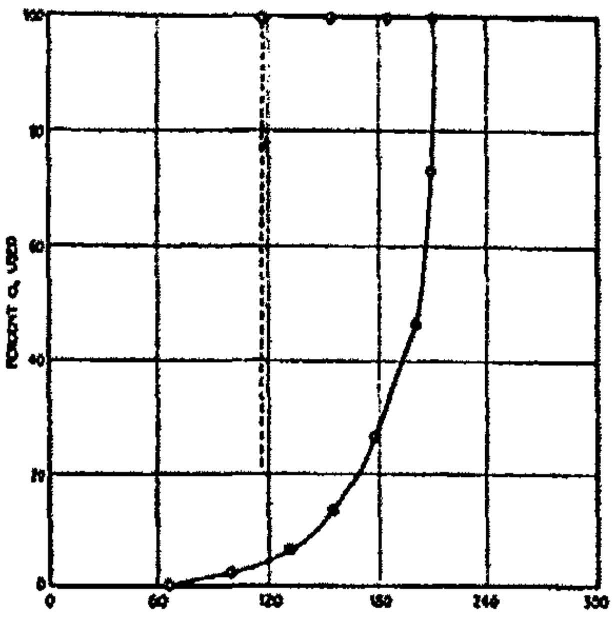

Fig. 5

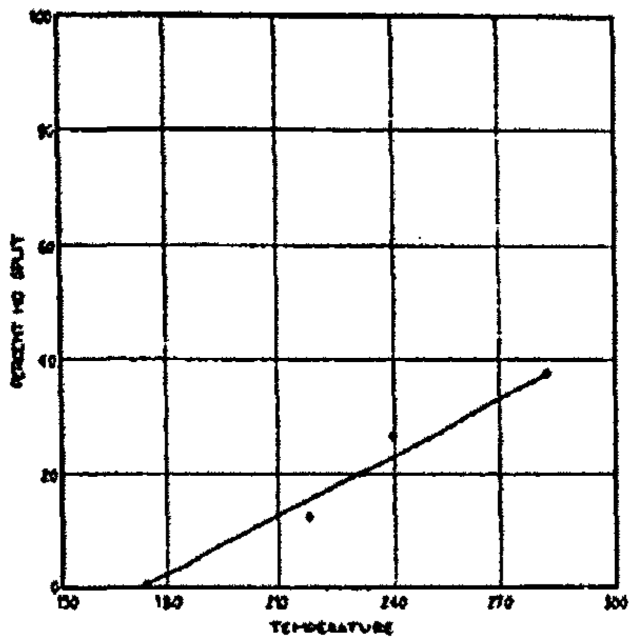

Fig. 6

Fig. 5. A Typical Hysteresis Curve

Fig. 6. Relationship between Amount of Hydrogen Chloride Split and the Temperature

The question arises as to why this effect does not take place in the homogeneous reaction. In all probability it does, but to such a small extent, because of the small surface involved, that it has not been detected. In addition, the heat of activation of the catalytic reaction is almost half of that of the gas phase reaction.

PYROLYSIS OF PROPYL CHLORIDES

Hurd (3) gives many examples of the pyrolysis of the alkyl halides. No mention of the propyl chlorides is made, but Aronstein (1) studied the effect of heat on *n*-propyl bromide. At 280°C. this compound rearranged into the iso-form. Such a behavior might involve the splitting out of hydrogen bromide. A similar behavior would be expected in the case of propyl chlorides.

The catalytic hysteresis offered an excellent means of studying this pyrolysis. It had been postulated that secondary chlorination of paraffins having two or more carbon atoms could take place in two ways. The first method was by direct substitution.

$$RCH_2CH_2Cl + Cl_2 \rightarrow RCHCl \cdot CH_2Cl + HCl$$

and the second by pyrolysis followed by addition:

$$\begin{array}{l} RCHCl \cdot CH_3 \\ \quad \text{or} \\ RCH_2 \cdot CH_2Cl \end{array} + \text{heat} \rightarrow RCH{=}CH_2 + HCl$$

$$R \cdot CH{=}CH_2 + Cl_2 \rightarrow RCHCl \cdot CH_2Cl$$

Both of these mechanisms give the same final products, and there would be no way of determining the ratio of the two processes. The equation for the first mechanism gives the more symmetrical chloropropane, but it would have been possible to attach the second chlorine atom to the terminal carbon. In such a case the product obtained by the two mechanisms would not have been the same. The analysis of products of chlorination showing relatively high quantities of the 1,2-dichloro compounds might indicate the pyrolytic mechanism of secondary chlorination but would not definitely prove it.

In a normal chlorination, one molecule of hydrogen chloride is formed for each chlorine molecule used, regardless of the mechanism of chlorination. This supposition is the basis of the calculations for obtaining the per cent of chlorine used in this research. The unused chlorine and the hydrogen chloride formed during chlorination were passed through a solution of potassium iodide. After removing this solution from the absorption chambers it was progressively titrated with standard thiosulfate and potassium hydroxide.

$$(\text{cc. } Na_2S_2O_3) \times \text{normality factor} \times 11.2 = \text{cc. } Cl_2 \text{ unused}$$
$$(\text{cc. KOH}) \times \text{normality factor} \times 22.4 = \text{cc. } Cl_2 \text{ used}$$

The sum of these two quantities will give the total chlorine admitted into the system. This should agree with the setting of the chlorine flowmeter, if the reaction is behaving in a normal manner.

Once the reaction reaches the stage where all the chlorine is used, the effect of the hydrogen chloride split will be noticed, as there is no excess chlorine to satisfy the unsaturation of the substituted and unsubstituted propylenes. At this point, the calculated chlorine input (from chemical data) will be higher than that indicated by the flowmeter.

$$RCH_2 \cdot CH_2Cl + \text{heat} \rightarrow RCH{=}CH_2 + HCl$$

When such a process takes place and the unsaturated compound formed is not saturated by the addition of chlorine, two molecules of hydrogen chloride will be formed for each chlorine molecule used. The product collected should have unsaturated compounds present. The difference between the calculated chlorine input and that indicated by the flowmeter should give a measure of the hydrogen chloride split.

The hysteresis effect enables us to go to lower temperatures while still retaining 100 per cent chlorine used, which in turn allows a study of the relationship between the amount of hydrogen chloride split and the temperature. A regular decrease in pyrolysis would be expected with a decrease in temperature. This was actually the case, as is illustrated by figure 6 (see table 5).

TABLE 5

Chlorination of propane using $CuCl_2 \cdot SiO_2$ *catalyst*

5 minutes duration. Total rate of flow 10 liters per hour. $C_3H_8:Cl_2 = 1:1$

TEMPERATURE	C_3H_8 UNUSED	Cl_2 UNUSED	Cl_2 USED	Cl_2 RUN IN	PER CENT Cl_2 USED
°C.					
240	256	1	527	528	99.9
218	212		469	469	100.0
174	195		418	418	100.0
282	250		572	572	100.0

Since this elimination of hydrogen chloride takes place when the chlorine used is not 100 per cent, we have a rough way of estimating the extent of chlorination due to the addition of chlorine to the unsaturated compounds. For instance, at 200°C. the per cent of hydrogen chloride split out of the chlorinated propanes would be roughly the same if there was an excess of chlorine gas or if the hysteresis was present. It would be expected then that the amount of 1,2-dichloropropane formed when an excess of chlorine was present would be measured by the extent of the hydrogen chloride split under hysteresis. This is, of course, supposing that every molecule which has had hydrogen chloride removed, remains as such and does not add either hydrogen chloride or chlorine at the double bond. The figure shows that secondary chlorination by the pyrolytic mechanism is quite appreciable at the higher temperatures. It might well be that most of the secondary chlorination takes place by this process.

Cuprous chloride can combine with hydrogen chloride to form a complex:

$$CuCl + HCl \rightarrow HCuCl_2$$

This should favor its catalytic property for the removal of hydrogen chloride from a compound.

COUPLING REACTION

Evidence of coupling reactions has been obtained by the analysis of products from chlorinations. Any discrepancy between the calculated and flowmeter input when an excess of chlorine was present should indicate a coupling reaction.

$$RCH_2Cl + CH_3R \rightarrow RCH_2{\cdot}CH_2R + HCl$$

In this way some of the chlorine molecules would give two molecules of hydrogen chloride instead of one as in a normal chlorination. A few runs were made which brought out this coupling reaction. In all the cases there was an excess of chlorine in the exit gases, but the calculated chlorine input exceeds the value indicated by the flowmeter. The catalyst was always poisoned by use, reducing its ability to remove hydrogen chloride from the propyl chlorides. The temperature of reaction was high (324°C.). The formation of free radicals would be favored by such a condition and the possibility of coupling taking place was increased.

PRODUCT

The product obtained from the catalytic runs was more highly chlorinated than the chloropropanes resulting from the gas phase reaction. A high partial pressure of propane favored the production of the lower chloro derivatives. 1,2-Dichloropropane was found in relatively large amounts in all of the samples collected. This would indicate that a large amount of the secondary chlorination takes place by the addition of chlorine to propylene formed by the pyrolysis of monopropyl chloride. The product collected at low temperatures during hysteresis showed a lower chlorine content than the higher temperature runs under the same conditions. Under the conditions studied, no orientation tendency was shown by the catalysts towards the chlorination.

In all cases in which there was 100 per cent chlorine used, the product had a peculiar pungent odor that was not characteristic of saturated chlorohydrocarbons. Along with this peculiarity in odor, etc., it was found that the composite samples were unsaturated, as was shown by their bromine adsorption.

SUMMARY

1. The catalytic reaction of propane with chlorine has been studied under various conditions.

2. A mechanism for the reaction has been postulated.
3. Heats of activation were calculated for the three catalysts used.
4. High partial pressures of chlorine tend to poison the catalyst.
5. A "hysteresis effect" was found and an explanation postulated.
6. Secondary chlorination in part was shown to be due to the addition of chlorine to propylene formed by the pyrolysis of propyl chlorides.
7. A coupling reaction was shown to be present.
8. High chlorine partial pressures, high temperatures, and high rates of flow all favored the formation of more highly chlorinated products.
9. A relatively large per cent of 1,2-dichloropropane in the products supported the statement made in 6.
10. Unsaturation was found in all products collected when the chlorine used was 100 per cent.

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THE ALUMINUM ALKYL OXIDES AND THEIR PARACHORS

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Sugden (9), in deriving the atomic parachor of aluminum from measurements on the acetylacetonate, propionylacetonate, and bromide, found it necessary to formulate these compounds with singlet linkages (i.e., one-electron valency bonds) in order to obtain reasonable values for the parachor of aluminum, each singlet linkage decreasing the observed parachor by 11.6 units. No measurements have been made on simple compounds of aluminum. In the case of thallium the singlet linkage formulation of analogous compounds has been supported by measurements on the ethoxide, nitrate, formate, and acetate, because both types gave the same value for the parachor of thallium, provided that the chelated compounds were assigned a singlet linkage formulation. The force of this argument was, however, diminished by the demonstration (7) that thallium ethoxide is a fourfold polymer, while the chelated ethyl acetoacetate is bimolecular. Since the parachor of aluminum has not been obtained from simple unchelated compounds, work was commenced on the alkyl oxides of aluminum, a group of liquids and low-melting solids, but it was found that these compounds are by no means simple in structure. Nevertheless, a number of points of interest have been noted which are worthy of record.

EXPERIMENTAL

Alumino acetylacetonate, prepared by Sugden's method (9) for the propionylacetonate, melted at 192°C. after recrystallization from alcohol and benzene. Density determinations were made in a U-shaped pyknometer (8), and surface tensions were estimated by the double capillary method. The method was checked frequently by determinations on standard liquids.

T	γ	D	P
°C.			
195	20.17	1.007	686.5
210	18.74	0.989	686.8
220	17.92	0.976	683.6

Mean P = 682.9, whence P_{Al} = 43.9

Alumino ethyl acetoacetate was prepared by adding the ester to aluminum under petroleum ether, the aluminum being activated by the method of Wislicenus and Kaufman (12). Reaction proceeded for an hour without warming, yielding a pale green viscous oil, b.p. 190–200°C. at 11 mm., which solidified in the presence of petroleum ether; after recrystallization from this solvent the substance melted at 78–79°C.

T	γ	D	P
°C.			
80	27.20	1.101	859.0
95	25.80	1.088	857.6
110	24.32	1.074	857.0
125	23.00	1.059	856.5
140	21.60	1.042	857.0

Mean P = 857.4, whence P_{Al} = 41.4

Alumino diethyl malonate was prepared by the prolonged heating of aluminum and mercuric chloride with malonic ester. The petroleum ether extract deposited white crystals melting at 95–96°C. after several recrystallizations from petroleum ether.

T	γ	D	P
°C.			
100	24.02	1.084	1030
120	22.13	1.064	1029
140	20.62	1.047	1027

Mean P = 1029, whence P_{Al} = 36.0

Chromium acetylacetonate. Equivalent quantities of chromium sulfate and acetylacetone were mixed in aqueous solution, and the chromium was precipitated by ammonium hydroxide. After forty-eight hours the acetylacetonate crystallized in red needles which were extracted with benzene; the benzene layer was dried and evaporated. The acetylacetonate was then purified by sublimation *in vacuo*; it melted at 212°C.

T	γ	D	P
°C.			
213	21.24	1.072	699.5
225	20.20	1.059	699.2
240	18.92	1.042	698.8

Mean P = 699.2, whence P_{Cr} = 60.2

Aluminum alkyl oxides were prepared by the method of Tistschenko (11) and purified by distillation under reduced pressure. As the whole preparation always distilled over approximately a five-degree range with very small head and tail fractions, no special precautions were taken for fractionation, the material being evidently homogeneous. Parachor determinations were made on a redistilled middle fraction. Obtained in this way the oxides were viscous liquids or white non-crystalline solids with ill-defined melting points, often exhibiting marked supercooling, the extreme case being the isopropoxide, m.p. 118°C., which has been supercooled to −20°C. without solidification. Analyses were made by dissolving the oxides in acid, and precipitating and weighing the alumina in the usual manner. Analysis was also attempted by evaporation of the oxide with water and ignition of the resulting alumina, but this method invariably gave high results, e.g., the butoxide gave 11.60 and 11.29 per cent Al (calculated, 10.95 per cent). The same peculiarity is to be found in the analyses of Gladstone and Tribe (3), although no reference was made to it. The error may be associated with the difficulty of completely dehydrating the very granular alumina produced in this way, although ignition over a blow-pipe yielded no better results, or with the formation of a stable carbon-nitrogen compound of the cyanamide type. Whatever the cause, it is worth while emphasizing the error. No difficulty was encountered in the acid treatment.

Aluminum ethoxide distilled at 210–214°C. at 13 mm. and melted at 146–151°C. Analysis gave 16.78 and 16.70 per cent of aluminum; the calculated value is 16.63 per cent. Molecular weight in naphthalene: 631. Calculated molecular weight for $[Al(OEt)_3]_4$: 648.

T	γ	D	P
°C.			
150	13.98	0.919	341.0
165	13.11	0.904	340.9
180	12.24	0.890	340.6
Mean value of P			340.8

A redetermination on another sample gave mean value of P = 341.5.

Aluminum n-propoxide distilled at 271–275°C. at 14 mm. and melted at 106–108°C. Analysis gave 13.30 per cent of aluminum; the calculated value is 13.21 per cent. Molecular weight in naphthalene: 865. Calculated molecular weight for $[Al(OPr)_3]_4$: 816.

T	γ	D	P
°C.			
110	19.18	0.957	445.9
130	17.92	0.938	447.4
150	16.66	0.921	447.5
Mean value of P			446.9

Aluminum isopropoxide distilled at 151–153°C. at 15 mm. and melted at 118°C. Analysis gave 13.20 per cent of aluminum. Molecular weight in naphthalene: 775. Calculated molecular weight for $[Al(OPr)_3]_4$: 816.

T	γ	D	P
°C.			
60	20.28	0.944	458.6
80	18.84	0.926	459.1
100	17.04	0.904	458.3
120	15.68	0.881	460.5
Mean value of P			459.1

Aluminum n-butoxide distilled at 274–278°C. at 9 mm. and melted at 102–106°C. Analysis gave 10.98 per cent of aluminum; the calculated value is 10.95 per cent. Molecular weight in naphthalene: 968. Calculated molecular weight for $[Al(OBu)_3]_4$: 984. Molecular weight by boiling point in benzene: 1050. Molecular weight by boiling point in *n*-butyl alcohol: 1025. Electrical conductivity in *n*-butyl alcohol (1 g. in 50 cc.) $< 4 \times 10^{-5}$ mhos.

T	γ	D	P
°C.			
80	20.48	0.925	565.4
100	19.11	0.909	565.7
120	17.69	0.893	565.2
140	16.33	0.875	565.0
Mean value of P			565.3

Aluminum isobutoxide distilled at 248–250°C. at 11 mm. and melted at 208–210°C. It exhibited no supercooling. Analysis gave 11.05 per cent of aluminum. Molecular weight in naphthalene: 968.

T	γ	*D*	*P*
°*C.*			
209	11.84	0.827	551.7
217	11.52	0.819	553.3
Mean value of *P*......................................			552.5

Owing to the high melting point and viscosity and the consequent difficulty of making parachor determinations, great reliance cannot be placed on this result.

Aluminum sec-butoxide distilled at 174–176°C. at 5 mm. It did not solidify even after standing for two months. Analysis gave 10.94 per cent of aluminum. Molecular weight by boiling point in benzene: 994.

T	γ	*D*	*P*
°*C.*			
50	23.19	0.937	576.4
70	21.49	0.917	577.5
90	19.96	0.894	581.7
110	18.10	0.868	584.8
Mean value of *P*......................................			580.1

Antimony ethoxide was prepared by the interaction of antimony trichloride and sodium ethoxide in absolute alcohol. It distilled smoothly at 99.5°C. at 13 mm. or 95°C. at 11 mm., without any sign of ebullition, to a colorless liquid. Molecular weight in naphthalene: 302. Calculated molecular weight for $Sb(OEt)_3$: 257.

T	γ	*D*	*P*
°*C.*			
17	28.36	1.524	389.0
37	26.58	1.490	391.2
57	24.77	1.455	393.6
77	23.16	1.420	396.7
130	17.66	1.328	396.4
150	16.18	1.295	397.4
170	14.53	1.262	397.3
190	12.87	1.229	395.9
Mean value of *P* (77–190°C.)...............................			396.7

DISCUSSION

The unsuitability of the alkyl oxides as a means of determining the parachor of aluminum (*vide infra*) necessitates the tentative acceptance of the value derived from chelated compounds. This has now been confirmed by measurements on the acetylacetonate and new measurements on the ethyl acetoacetate and the diethylmalonate, from which, assigning singlet linkage formulations to these compounds, values of 43.9, 41.4, and 36.0, respectively, are obtained for the parachor of aluminum. The latter value is probably somewhat erroneous because it is derived from a large molecular parachor, but taking the mean of these three values together with the three values of the parachor given by Sugden (9), a figure of 39.5 results for the parachor of aluminum.

This value may be checked by taking the parachor of chromium as 53.7 from the data for chromyl chloride (2) and comparing the acetylacetonates of chromium and aluminum which are found to differ in their parachors by 16.3 units. It then follows that the parachor of aluminum is 37.4. This fixes the order of the atomic parachor independent of the validity of the singlet linkage formulation of the acetylacetonate.

TABLE 1

Comparison between observed parachors of alkyl oxides and those calculated for the formula, $Al(OR)_3$

OXIDE	P (OBSERVED)	P (CALCULATED)	ANOMALY
Ethoxide	340.8	384.8	−44.0
n-Propoxide	446.6	501.8	−55.2
Isopropoxide	459.1	501.8	−42.7
n-Butoxide	565.3	618.8	−53.5
Isobutoxide	552.5	618.8	−66.3
sec-Butoxide	580.1	618.8	−38.7

Assuming the value of 39.5 for the parachor of aluminum obtained with the aid of singlet linkage formulations, a comparison can be made between the observed parachors of the alkyl oxides and those calculated for the simple formula, $Al(OR)_3$, as shown in table 1.

The hypothesis that the liquids have an angle of contact which would reduce the apparent surface tension can be shown to be an inadequate explanation, since an angle of contact of at least 60° would be necessary to account for the anomalies and such an angle would have been easily detected in the microscope. In every case the meniscus was normal.

Molecular weight determinations from the freezing point of naphthalene solutions and the boiling point of benzene and *n*-butyl alcohol solutions showed that the molecules are polymerized fourfold in solution, and since the parachor was constant over a considerable temperature range (except in the case of the *sec*-butoxide), it is probable that any polymerization which occurs in the pure liquid is not affected by temperature. Application of the Ramsay-Shields equation to the surface tension data favors the simple formula $Al(OR)_3$, but the validity of this equation may be questioned. It was hoped to obtain conclusive evidence on this point by a vapor density determination under reduced pressure with the apparatus previously described (5), but, although excellent results could be obtained with other compounds, some decomposition always occurred with these alkyl oxides. This is remarkable in view of the ease with which the compounds could be distilled without decomposition, but all attempts to vaporize them in the Victor Meyer tube resulted in decomposition, although vaporization was carried out under a variety of conditions. The results, however, are not entirely without significance because in whatever way decomposition occurs, e.g.,

$$2Al(OEt)_3 \rightarrow Al_2O_3 + 3Et_2O$$

or

$$2Al(OEt)_3 \rightarrow Al_2O_3 + 3H_2O + 6C_2H_4$$

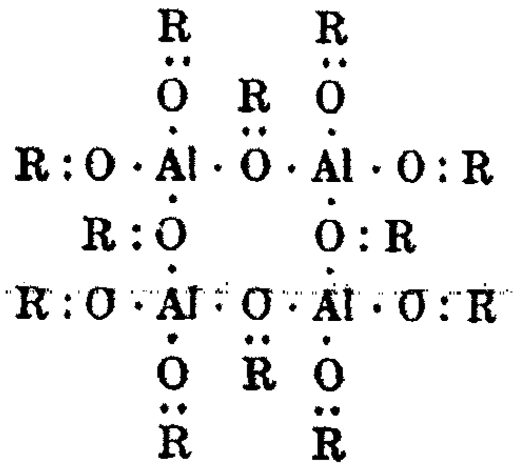
the number of molecules produced by decomposition must be larger than the number of alkyl oxide molecules even if these are unpolymerized. Thus decomposition would lower the apparent molecular weight. The observed molecular weights were with one exception larger than those calculated from the simple formula, and in the single case in which agreement was obtained it was apparent that considerable decomposition had occurred. Vapor density determinations therefore show that polymerization occurs, but afford no estimate of the degree of polymerization.

The balance of evidence is in favor of the formula $[Al(OR)_3]_4$, in which case the compounds are analogous to the thallous alkyl oxides which Sidgwick and Sutton (7) have shown to be tetramolecular in alcohol and benzene solution but which, surprisingly, give a normal value for the parachor of thallium (9). The parachor anomaly of the aluminum alkyl oxides is paralleled to a lesser extent in antimony ethoxide, which presents the phenomenon of an increasing parachor at low temperatures (presumably due to slight polymerization), followed by a constant parachor at higher temperatures. This constant parachor, which indicates complete depolymerization, falls short of that calculated from the known parachor of antimony by 14 units. Germanium ethoxide also exhibits a deficiency of seven units (6). Methyl and ethyl orthosilicates have parachors increasing with temperature (10), differences of approximately 5.3 and 6.3 units being observed over a 54°C. range. The boron esters are normal (1).

The formula $[Al(OR)_3]_4$ would bring these compounds into line with the "alkoxo salts" of Meerwein and Bersin (4), if $[Al(OR)_3]_4$ is written

$Al[Al(OR)_4]_3$, but a polar formulation is improbable because the aluminum alkyl oxides, like the "alkexo salts," have the non-polar properties associated with covalent links, e.g., they melt and distil at low temperatures and the *n*-butoxide has a very small conductivity in *n*-butyl alcohol solution.

By analogy with the ring structure assigned by Sidgwick and Sutton (7) to thallous ethoxide, aluminum ethoxide may be written as in formula I,



I

but because of the ring structure in I the parachor anomaly must be raised to 45.8, and a negative anomaly of this magnitude can only be accounted for by four singlet linkages associated with each aluminum atom. A model constructed with the four aluminum bonds arranged tetrahedrally and the Al—O—Al bonds making an angle of 110° shows that a ring structure of this type is practically strainless, although the eight atoms in the ring do not all lie in the same plane. However, although this formulation may be supported on steric grounds, it seems highly improbable that stability can be attained with only four electrons in the valency shell of each aluminum atom and five unshared electrons to each oxygen atom.

A further difficulty is encountered in the fact that larger negative anomalies are found in the higher alkyl oxides of aluminum. This is not peculiar to this series of homologues. Thus the parachor of beryllium propionylacetonate is higher than that of the acetylacetonate by 68.6 (calculated, 78), while the difference between the parachors of acetyl- and propionylacetone is 34.3 (calculated, 39), and that between sulfonal and trional is only 28.3 units.

SUMMARY

1. Aluminum alkyl oxides have been prepared from ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *secondary*-butyl alcohols; also prepared were the acetylacetonates of chromium and aluminum, alumino ethyl acetoacetate, alumino diethylmalonate, and antimony ethoxide.

2. Molecular weight determinations indicate a fourfold polymerization of the alkyl oxides of aluminum, which is supported qualitatively by vapor density measurements.

3. Antimony ethoxide with a normal molecular weight exhibits a parachor deficiency of 14 units, deficiencies also being found in the ethoxides of silicon and germanium. The parachor deficiency found in the aluminum alkyl oxides is of a larger magnitude and varies with the nature of the alkyl group. The only reasonable formulation of these compounds which will account for these deficiencies by means of singlet linkages consists of an eight-membered ring with all the oxygen atoms attached to the aluminum atoms by singlet linkages. In this formulation the electron octets of all the atoms are filled with the exception of those of the aluminum atoms, which only possess four electrons each.

We wish to acknowledge the valuable assistance rendered by Mr. W. S. Rapson, M.Sc., in the preparation of many of the compounds used in this investigation.

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NOTES ON ACETYLMETHYLCARBINOL

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The N. V. Nederlandsche Gist-en Spiritusfabriek, Delft, Holland, has recently marketed acetylmethylcarbinol or acetoin, $CH_3 \cdot CO \cdot CH(OH)CH_3$, a slightly yellow liquid which changes spontaneously into a white crystalline polymer. The authors have to thank the above company for a sample of acetoin, which they have examined briefly, since the literature (1, 2, 3, 4, 5) indicates that the polymerization is incompletely understood.

The authors' samples of acetoin were obtained by melting or distilling the original solid polymer. Samples were kept at various temperatures, portions were withdrawn from time to time, and the refractive indexes were determined at 20°C.; typical results are given in tables 1 and 2. The initial value of n varied with the conditions of melting or distilling; the minimum may be 1.4175. At 100°C. and 130°C. the acetoin became browner and more viscous and developed a "burnt sugar" odor. Evidently molecular complexity (polymerization) occurs on keeping the liquid acetoin; the polymer however does not accumulate in the liquid, but forms the solid polymer.

Acetoin, kept in an open beaker in the air, absorbed water; n fell from 1.4186 to 1.4141 in five days. When acetoin was kept over sulfuric acid, the value of n rose to 1.4435 in seven days, but the acetoin volatilized into the acid, darkened it, and formed a substance of sharp odor.

The densities and viscosities of acetoin kept at 30.0°C. were determined, and the results are given in table 2. These properties varied similarly to the refractive index, but to a greater degree. By extrapolation, the freshly distilled acetoin would have $d_{4°}^{30°} = 0.9860$ and $\eta^{30°} = 0.0175$. The density of acetoin is lowered (by about 9 parts in 1000) after boiling, i.e., depolymerization occurs on heating.

The normal freezing point of acetoin was at -72°C., i.e., it repeatedly froze and melted at this temperature. The following vapor pressures of acetoin were found by the static method: 162 mm. at 0°C.; 164 at 10°C.; 168 at 20°C.; 174 at 30°C.; 183 at 40°C.; 210 at 60°C.; 256 at 80°C.; 330 at 100°C.; 449 at 120°C.; 664 at 140°C.; 760 at 144°C.

At ordinary temperatures the acetoin deposited crystals of the polymer in from two to nine days. The polymer was slightly soluble in water, methyl and ethyl alcohols, cyclohexanol, acetone, ethyl acetate, acetic acid, and paraldehyde, and sparingly soluble in ether, benzene, carbon tetrachloride, ethylene bromide, bromoform, and acetophenone. The

TABLE 1

The change of refractive index, $n_D^{30°}$, of acetoin with time

AGE OF SAMPLE	REFRACTIVE INDEX, $n_D^{30°}$, OF SAMPLES OF ACETOIN				
	Distilled sample 2 at −10°C.	Melted sample 1 at room temperature	Melted sample 2 at 30°C.	Melted sample 3 at 100°C.	Melted sample 4 at 130°C.
days					
0	1.4192	1.4178	1.4184	1.4180	1.4186
1		1.4191	1.4203	1.4198	1.4247
2		1.4202	1.4199	1.4211	Cooled
3		1.4205*	1.4202		1.4278
4	1.4187*	1.4207*		1.4254	1.4421
5		1.4208*	1.4201	1.4278	1.4546
6			1.4200	1.4312	1.4762
7	1.4190*	1.4205*	1.4204	1.4328	
15			1.4200	1.4471	
20	1.4199*		1.4201		

* Denotes that crystals are present in the sample.

TABLE 2

The change of properties of acetoin when kept at 30°C.

AGE OF SAMPLE	MELTED SAMPLE 2	DISTILLED SAMPLE 1		DISTILLED SAMPLE 2		
	$d_{4°}^{30°}$	$d_{4°}^{30°}$	$\eta^{30°}$	$d_{4°}^{30°}$	$\eta^{30°}$	$n_D^{30°}$
1 hr.	0.9889	0.9861	0.0178	0.9865	0.0180	
2¼ hrs.				0.9878	0.0187	1.4192
21 hrs.	0.9949		0.0208	0.9930	0.0207	
26 hrs.				0.9934	0.0209	1.4198
50 hrs.	0.9950		0.0211	0.9938	0.0211	1.4200
4 days			0.0212	0.9938	0.0211	1.4199
5 days	0.9950					
6 days		0.9944	0.0213	0.9939	0.0212	1.4201
7 days	0.99515					
12 days	0.99515					
16 days	0.9952					1.4198
29 days						1.4205

polymer was appreciably volatile at room temperatures; if it held traces of liquid acetoin, it liquefied and volatilized more rapidly. The pure well-crystallized polymer may be kept unchanged for several months, either in closed vessels or between watch-glasses. The crystals are flat, monoclinic, transparent prisms, smooth and greasy to the touch, and of density 1.26.

Many melting-point determinations were done on this polymer. The crystals tended to become opaque at 60–110°C., and they melted at 110–128°C., and in rare cases at 150–160°C.; the general melting point was about 124°C. The crystals also sublimed rapidly at 150–160°C., and less rapidly at 100°C. and lower temperatures. The melting point depended on the rate of heating, on the time the sample was held at a given temperature, and on the use of an open or closed tube; the results hint that a chemical change (polymer → liquid) is involved. This polymer then has no simple or definite melting point; it passes to liquid acetoin at any temperature above 30°C., and perhaps at lower temperatures, in longer or shorter times.

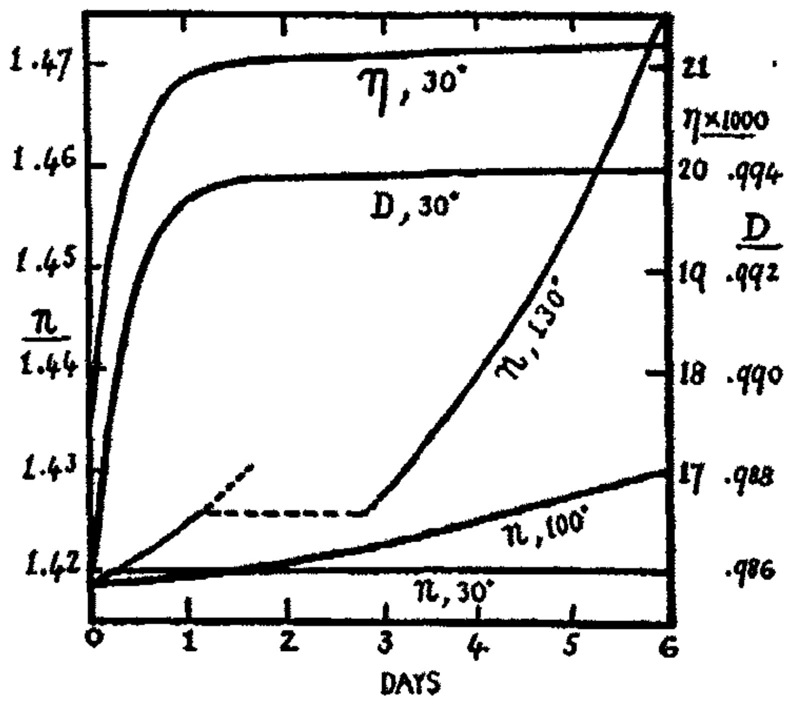

Fig. 1

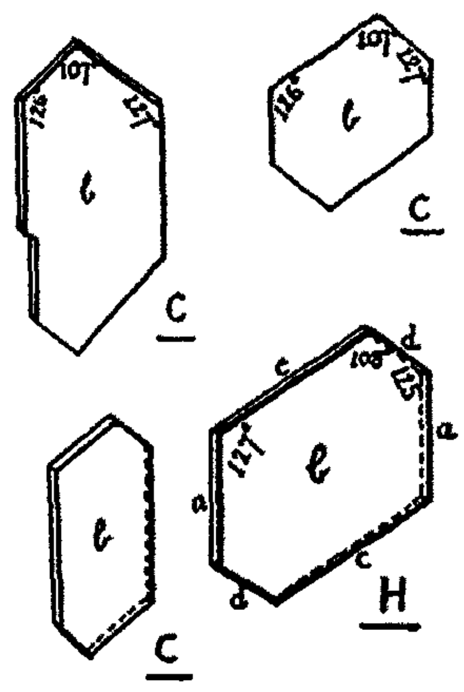

Fig. 2

Fig. 1. Variation of the Properties of Acetoin with Time

Fig. 2. Crystals of the Polymer of Acetoin

By dilatometer experiments the transition temperature between the polymer and liquid acetoin was placed at 16°C.; but in entire absence of the liquid the solid was stable at higher temperatures (*v.s.*).

By the cryoscopic method the polymer was found to be monomolecular in water, acetic acid, and paraldehyde.

In contact with zinc at −10° to 0°C. acetoin became solid within twenty-four hours; the crystals appeared to be the same as before, and they too were monomolecular in the above solvents.

Acetoin was kept by itself for eighteen days at temperatures between −20° and 0°C.; crystals appeared on the fourth day, and about one-third of the sample had crystallized at the last. These crystals, C, had the same form and density as the polymer, H, deposited at room temperatures.

The authors thank Mr. Yates for the following notes and figure 2 about these crystals:—"Three crystals of each substance, C and H, were sketched as seen under the microscope, and their angles on the clino-pinacoidal face were measured. All the crystals were practically identical; they had tabular habit, being very thin in the direction perpendicular to the clino-pinacoidal face, b; their interfacial angles were similar; the symmetry was monoclinic, though the departure from rhombic symmetry was only about 1°. The ortho- and basal-pinacoid faces are a and c, and d is the orthodome face."

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18-130

STUDIES ON ORGANIC DEPOLARIZERS[1]

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Determinations of single potentials of cathodes against organic depolarizers made by Hunter and Wernlund (8) as a preliminary to comparing electrolytic reductions of organic compounds with those carried out by chemical reagents showed that the order of the cathodes used, based on their single potentials, was essentially the same with different depolarizers. The present work extended these measurements using the electrodes platinum, nickel, gold, silver, and tin. The results obtained agree with those of Hunter and Wernlund and have led to a further simplification of the theory of depolarization values by including the idea of the "electron affinity" of the depolarizer.

Physicists have made a very thorough study of the emission of electrons into gases in their work on the photoelectric effect, contact potentials, resonance and ionization potentials, and electron emission from hot bodies. They have made it clear that the emission of electrons by metals into gases involves the performance of work, and that the work required is different for each metal and is greatly influenced by the nature of the gas surrounding the emitting surface. It is thus certain that their values found for the work function can not be transferred without change to aqueous solutions, but it is equally certain that the idea of the work function should be used in a study on organic depolarizers.

When an electrode with no current flowing is placed in a solution containing a depolarizer, which may be defined as anything whose presence causes a cathode to become more positive against a solution than it was before the material was added, electrons will be removed from the electrode by the depolarizer. This will result in a continuous and usually rapid increase in the positiveness of the electrode until equilibrium is reached. The single potential of the cathode with the current turned on passes through a minimum "positive" value, owing to the fact that when a depolarizer molecule takes an electron from the metal it then unites with a hydrogen

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[1] This article is based upon the thesis of L. F. Stone, submitted to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1927. The manuscript was prepared by the junior author after the death of Dr. Hunter in 1931.—L. I. Smith.

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ion, thus producing a change in the ratio of the depolarizer to its reduction product and resulting in a gradual increase in the potential.

The magnitude of the increased positiveness obtained with any one depolarizer will depend to a large extent on the work required to remove electrons from that cathode or on the work function under the conditions of the experiment. Other effects will have an influence on the actual value of the single potential, but in general their magnitude will be small and will be of the same order with any one depolarizer except insofar as the effects are due to the electrode material. Thus the value of the single potential of a cathode in contact with a given depolarizer will be largely dependent on the work function of that electrode and will therefore vary with different metals. As shown in figure 1 the values of the single potentials of the cathodes in contact with a given depolarizer, such as quinone, become more negative in the following order: platinum, gold, silver, nickel, and tin. The values of the work function of these electrodes, under the conditions of our experiments, increase in the same order.

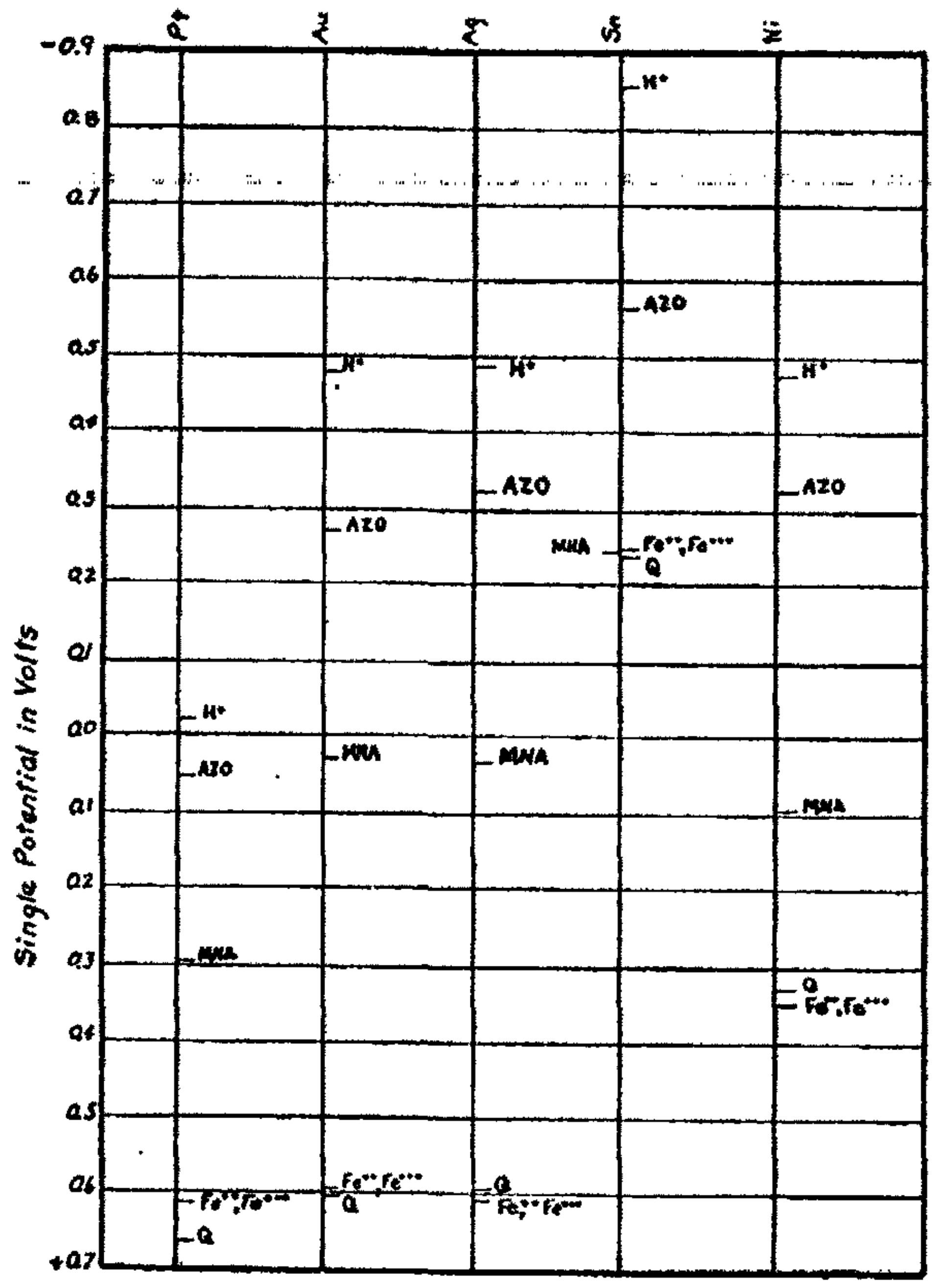

FIG. 1. SINGLE POTENTIALS OF CATHODES AGAINST DIFFERENT DEPOLARIZERS

The values of the single potentials of nickel and tin are often complicated, owing to the fact that in the presence of some depolarizers these cathodes become sufficiently positive to send their ions into solution. When a tin electrode, for example, is placed in a depolarizer solution, some of the electrons will be removed and the force holding the tin ions in the metal therefore becomes less. As the normal potential of the electrode is approached, this force is overcome and metal ions enter the solution. The potential will then remain close to the value of the normal potential for tin, the actual value depending on the number of ions sent into the solution as well as on the depolarizer and its reduction products. Solution of metal ions will occur with any electrode that is in contact with a depolarizer that has a sufficient force of attraction for electrons, or "electron affinity," to reduce the potential of the electrode to its normal potential against its own ions. The effect of the work function thus appears to be masked to some extent in these cases, owing to the introduction of a new depolarizer,—the metal ion.

In determining the single potential of a cathode against various depolarizers it will be found that some of the latter decrease the potential very slightly, while with others the effect is very marked. Every depolarizer will have a definite potential with a given cathode, and that position will be determined by the electron affinity of that depolarizer. It is well known that the potential of a pure substance has an infinite value and will not give the "definite potential" noted above except when a finite quantity of the reduced material is also present, and the value under these conditions will be dependent upon the ratio of the concentration of the depolarizer to its reduction product.

The value of the electron affinity of any one depolarizer depends on two parts of the molecule: the "characteristic group," which is that part of the compound that takes up electrons from the cathode, and the rest of the depolarizer molecule. Different groups vary considerably in their force of attraction for electrons, while the rest of the compound has very little effect on the single potential and probably exerts its influence only through the characteristic group. The difference between the single potentials of nitrobenzene and nitrosobenzene, for example, would be much larger than that between nitrobenzene and *m*-nitroaniline.

Although the actual values of electron affinity can not be determined, we believe that relative values for different depolarizers can be deduced from a study of the data obtained in our experiments. The values of the single potentials obtained in our work with different depolarizers against the cathodes platinum, gold, silver, nickel, and tin are given in figures 1 and 2. The values of the single potentials of several of the depolarizers against platinum, given in figure 2, were obtained from data given by other investigators. The single potential values of formaldehyde, acetaldehyde, pyridine, and acetone were obtained from the work carried out by Hunter and Wernlund (8) under conditions identical with those of the present work. The values for I^-, I_2 (solid) given by Thompson (11) and those for OH^-, O_2; Br^-, Br_2 (liquid); Cl^-, Cl_2 (gas); and F^-, F_2 (gas) given by MacDougall (9) were obtained in studies in which there was no external electromotive force impressed on the cell, and are therefore slightly more positive than they would be under the conditions of our experiments.

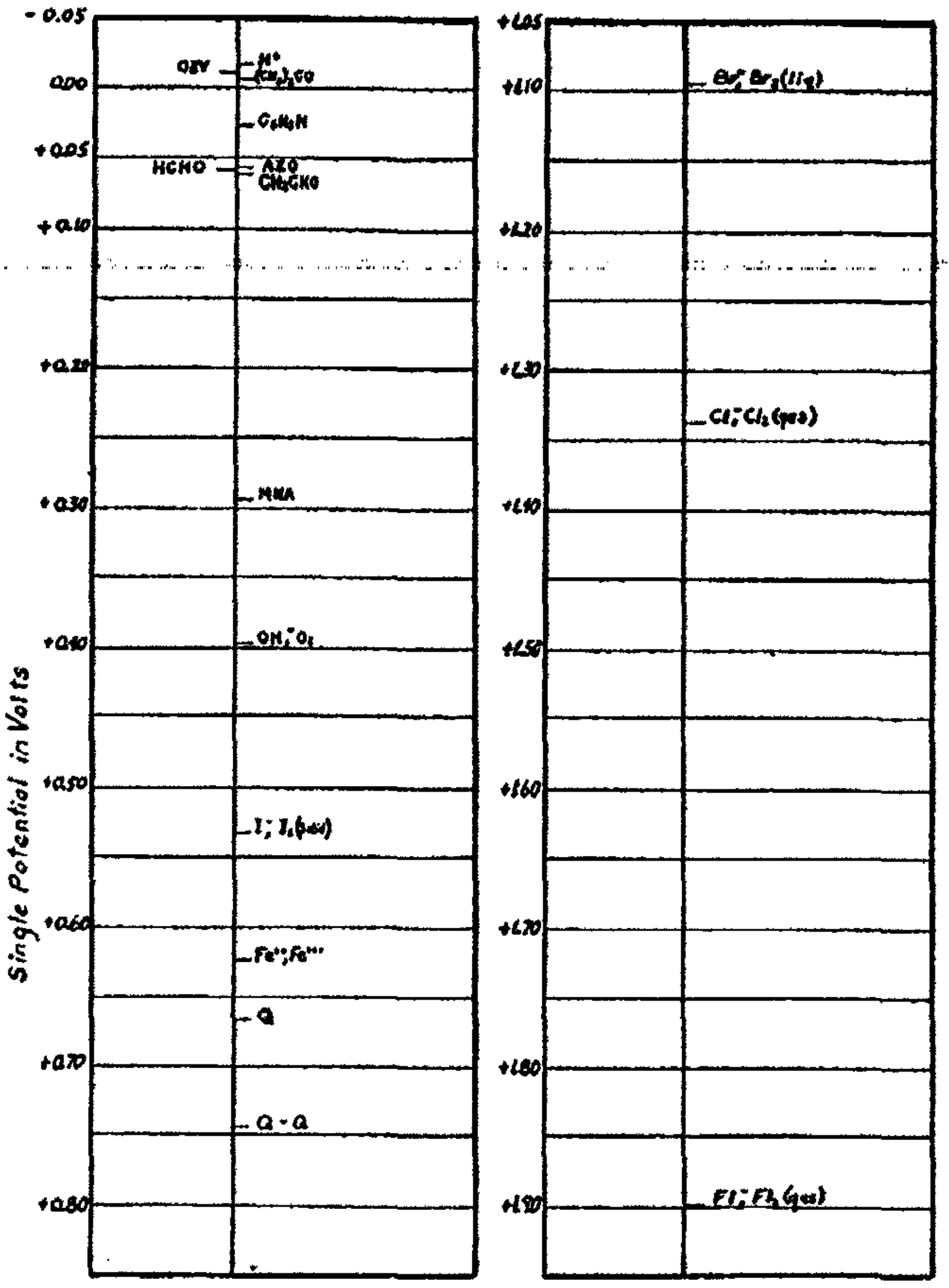

FIG. 2. SINGLE POTENTIALS OF PLATINUM AGAINST DIFFERENT DEPOLARIZERS

In figure 1 it may be seen that the depolarizers tested against gold, in the order of decreasing positiveness of single potential, are as follows: quinone; ferro-ferri; *m*-nitroaniline; azobenzenesulfonic acid; and hydrogen ion. On the basis of our theory the relative values of the electron affinity of these depolarizers decrease in the same order. This order of the depolarizers is the same as that obtained on the other electrodes with the exception of three points. In these cases the difference in the values is very small and may well be due to other effects not considered by us.

Assuming that all cations present in a catholyte may be considered as depolarizers brings the concept of hydrogen overvoltage into accord with our general picture of cathodic action. Thus, the single potential of quinone against the cathodes tested becomes more negative in the order: platinum, gold, silver, nickel, and tin. This is also the order of the metals against the hydrogen ion. In the latter case the actual value of the single potential on a given cathode is probably not dependent on the electron affinity of the depolarizer alone but also on other effects, such as adsorption of hydrogen into the metal and gas films. The failure of the hydrogen discharge point to "space" as well as other depolarizers as regards their distances on the scale of potentials given in figure 1 may well be due to these latter, acting not as primary causes of overvoltage but as secondary effects superimposed on that of electron affinity. It therefore seems possible to speak of the overvoltage of any depolarizer as well as of hydrogen and with the same meaning,—the increase of potential necessary to discharge it on a given cathode over and above that required on platinum.

It thus appears that the "electron affinity" of the depolarizer and the "work function" of the electrode are definite properties of the depolarizer and electrode, respectively, and that it should be possible to estimate the single potential of a depolarizer on a given cathode when its value on platinum is known. Although the present work did not include the formulation of an equation for calculating the electromotive force of a cell, we believe that an equation, perhaps of the Nernst type, should also include other terms that are a function of the "electron affinity" of the depolarizer and the "work function" of the electrode.

EXPERIMENTAL

Electrodes

All electrodes were 3.8 cm. in diameter and 1.5 mm. in thickness. Gold electrodes made from sheet metal, 99.99 per cent pure, were plated using the solution given by Blum and Hogaboom (1). The silver electrode made from sheet silver, 99.99 per cent pure, was plated using the solution given by Blum and Hogaboom (2). Platinum electrodes made from sheet platinum were plated using the bath recommended by Findlay (7). Tin electrodes containing 99.97 per cent tin and 0.03 per cent lead were plated using the solution given by Blum and Hogaboom (3). Nickel electrodes, prepared from electrolytic nickel, were plated using the solution recommended by Blum and Hogaboom (4).

Depolarizers

Quinone, prepared from hydroquinone by the method given by Vliet (12), was recrystallized from benzene and sublimed twice. A fresh 0.015

molar solution in 2 N sulfuric acid was made for each run. Twenty-five grams of *m*-nitroaniline, m.p. 112.5°C. after recrystallization twice from water, was treated with 10 cc. of concentrated sulfuric acid to form the sulfate, and dissolved in 2 N sulfuric acid to give the 0.181 molar solution used in the experiments. The ferrous-ferric solutions, having a ratio of 1:1, were made from Merck's Blue Label iron sulfates. Azobenzenesulfonic acid, prepared from azobenzene, was recrystallized from water and dissolved in 2 N sulfuric acid to give a 0.01 molar solution. 3,3′-Diaminoazoxybenzene, m.p. 145–147°C., made from *m*-nitroaniline according to the procedure given by Meldola and Andrews (10), was recrystallized from alcohol, and a 0.002 molar solution in 2 N sulfuric acid was made for use in the runs on platinum.

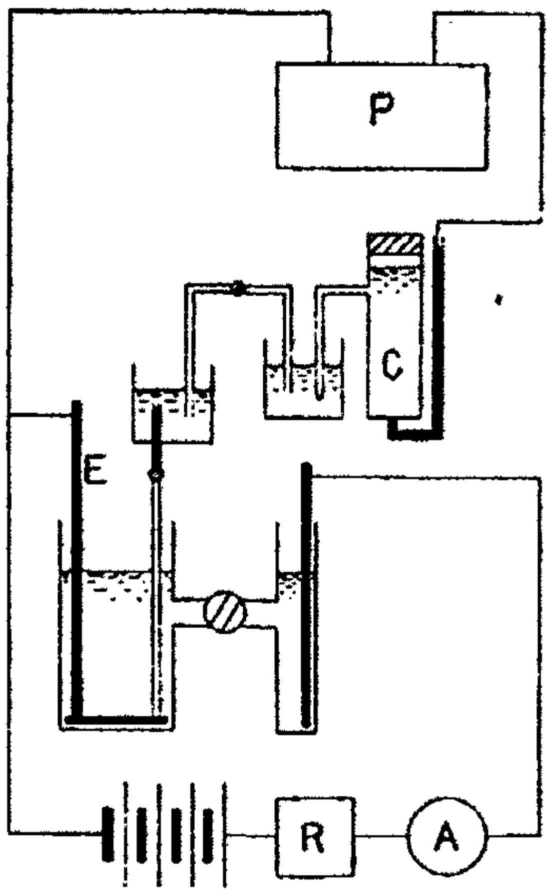

FIG. 3. THE APPARATUS

Apparatus (*see fig. 3*)

The cathode chamber of the cell was 10 cm. in height and 4.5 cm. in diameter, and was separated from the anode chamber by a stopcock. Current from the storage batteries, used to impress an external electromotive force on the cell, was regulated by a resistance box (R) and was measured by a milliammeter (A). The cathode (E) was connected to a Leeds and Northrup type K potentiometer (P) and the cell completed by the calomel electrode (C), salt bridge, and capillary tube. The calomel electrodes, prepared from distilled mercury, fresh calomel, and a saturated solution of recrystallized Merck's Blue Label potassium chloride, were frequently checked against each other and showed variations of the order of 0.1 to 0.05 millivolt.

Typical runs

In method A 75 cc. of 2 *N* sulfuric acid was added to the cell after all connections were made. A constant current of 50 milliamperes was passed through the cell and readings taken, constant stirring being maintained by means of an electrically driven glass stirrer. The stopcock separating the chambers was then closed and 50 cc. of the 2 *N* sulfuric acid in the cathode chamber was replaced with 50 cc. of a depolarizer solution. The stopcock was then opened and readings again taken. In method B the depolarizer solution was added to the cell, and readings taken before and after turning on the current of 50 milliamperes.

TABLE 1

Results obtained with the depolarizers m-nitroaniline, 3,3′-diaminoazoxybenzene, quinhydrone, and hydrogen ion

ELECTRODE MATERIAL	DEPOLARIZER IN 2 *N* H_2SO_4	METHOD	AVERAGE VALUE OF E_h AFTER 5 MINUTES AT 50 MILLIAMPERES	AVERAGE VALUE OF E_h AT 0 MILLIAMPERES
Platinum	M.N.A.	A	0.3012^{+}	
Platinum	M.N.A.	B	0.2889^{+}	
Gold	M.N.A.	A	0.0467^{+}	
Gold	M.N.A.	B	0.0162^{+}	
Silver	M.N.A.	A	0.0404^{+}	
Silver	M.N.A.	B	0.0272^{+}	
Tin	M.N.A.	A	0.2441^{-}	
Tin	M.N.A.	B	0.2451^{-}	0.2101^{-}
Nickel	M.N.A.	A	0.1020^{+}	
Nickel	M.N.A.	B	0.0964^{+}	0.2276^{+}
Platinum	Oxy	B	0.0116^{-}	
Platinum	Quinhydrone*			0.6970^{+}
Platinum	2 *N* H_2SO_4†	B	0.0212^{-}	
Gold	2 *N* H_2SO_4	B	0.4752^{-}	
Silver	2 *N* H_2SO_4	B	0.4889^{-}	
Tin	2 *N* H_2SO_4	B	0.8642^{-}	
Nickel	2 *N* H_2SO_4	B	0.4738^{-}	

* Saturated solution.

† Data given are the average of the final, nearly constant values determined over a period of three to four hours.

Preliminary runs indicated that the values of the single potentials of the electrodes in contact with the various depolarizers passed through the minimum "positive" value noted above, and were becoming more negative very slowly, approximately five minutes after the addition of the depolarizer, in the case of method A, and five minutes after the current of 50

TABLE 2

Results obtained with the depolarizers quinone, ferro-ferri, and Sn^{++}

ELECTRODE MATERIAL	DEPOLARIZER IN 2 N H_2SO_4	METHOD	AVERAGE VALUE OF E_h AFTER 5 MINUTES AT 50 MILLIAMPERES	AVERAGE VALUE OF E_h AT 0 MILLIAMPERES
Platinum	Quinone	B	0.6703^+	
Gold	Quinone	B	0.6045^+	0.7804^+
Silver	Quinone	B	0.5925^+	0.6481^+
Tin[*]	Quinone	B	0.2363^-	0.2063^-
Nickel[†]	Quinone	B	0.3268^+	0.3569^+
Platinum	Fe^{++}-Fe^{+++}	A	0.6197^+	
Platinum	Fe^{++}-Fe^{+++}	B	0.6244^+	0.6684^+
Gold	Fe^{++}-Fe^{+++}	A	0.5938^+	
Gold	Fe^{++}-Fe^{+++}	B	0.5965^+	0.6666^+
Silver	Fe^{++}-Fe^{+++}	A	0.6073^+	
Silver	Fe^{++}-Fe^{+++}	B	0.6159^+	0.6604^+
Tin[*]	Fe^{++}-Fe^{+++}	A	0.2488^-	
Tin[*]	Fe^{++}-Fe^{+++}	B	0.2482^-	0.2067^-
Nickel[†]	Fe^{++}-Fe^{+++}	A	0.3418^+	
Nickel[†]	Fe^{++}-Fe^{+++}	B	0.3491^+	0.3797^+
Tin	Sn^{++}[‡]	B	0.2348^-	0.2036^-

[*] A positive test for tin ions in the solution was obtained at the end of the run.

[†] A positive test for nickel ions in the solution was obtained at the end of the run.

[‡] Molar solution of tin ions.

TABLE 3

Results obtained with the depolarizers azobenzenesulfonic acid and quinone-quinhydrone

ELECTRODE MATERIAL	DEPOLARIZER IN 2 N H_2SO_4	METHOD	AVERAGE VALUE OF E_h AFTER 5 MINUTES AT 50 MILLIAMPERES	AVERAGE VALUE OF E_h AT 0 MILLIAMPERES
Platinum	Azo	B	0.0584^+	
Gold	Azo	B	0.2745^-	
Silver	Azo	B	0.3203^-	
Tin[*]	Azo	B	0.5729^-	
Nickel[†]	Azo	B	0.3273^-	
Platinum	Q-Q[‡]			0.7452^+
Gold	Q-Q			0.7433^+
Silver	Q-Q			0.6792^+
Nickel	Q-Q			0.3517^+
Tin	Q-Q			0.1994^-

[*] A negative test for tin ions in the solution was obtained at the end of the run.

[†] A negative test for nickel ions in the solution was obtained at the end of the run.

[‡] Saturated solution quinone–quinhydrone. Constant values for the platinum and gold electrodes were reached in about five minutes. An initial value of 0.6552 was obtained for silver, the final constant value of 0.6792 being reached in about two hours. The value for the nickel electrode was not constant, probably owing to the complexity of the solution. The value given for the tin electrode was fairly constant. Tests on the solutions in contact with the latter two electrodes showed the presence of nickel and tin ions, respectively.

milliamperes was turned on, in the case of method B. All of the values given in the tables are based on readings taken five minutes after the start of the run. These readings were corrected to 25°C. and 760 mm., using the data given by Fales and Mudge (6). These corrected values were reduced to the normal hydrogen scale (E_h) by adding algebraically +0.2464, the value given by Clark (5) for the saturated calomel electrode, referred to the normal hydrogen electrode at 0°C. Although readings were taken to four places, the true value is not certain closer than a few millivolts when measurements are made during reduction.

Tables

The data obtained on the cathodes against the various depolarizers tested are given in tables 1, 2, and 3, and in figures 1 and 2. Abbreviations used are as follows: azo = azobenzenesulfonic acid; oxy = 3,3'-diaminoazoxybenzene; M.N.A. = *m*-nitroaniline; Q = quinone; Q-Q = quinone-quinhydrone.

SUMMARY

1. The single potentials of several depolarizers have been measured against different cathodes.

2. The idea of the "work function" of electrodes has been developed as applied to electrolytic action, and the variation of its value with different metals has been explained.

3. The "electron affinity" of depolarizers has been defined and its function discussed.

4. A new view of "overvoltage" has been developed along the lines indicated by our theory.

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EQUILIBRIUM DISTRIBUTION OF ACETIC ACID BETWEEN ISOPROPYL ETHER AND WATER

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The removal of undesirable constituents or the recovery of valuable components from solution by selective extraction with non-miscible solvents is a potentially important chemical engineering operation for which few significant quantitative data are available. In the course of experimental studies of the rate of extraction of acetic acid from aqueous solution by isopropyl ether, comprising one phase of an extensive program of investigation of the rates of liquid-liquid extraction processes in progress in the Department of Chemical Engineering of Princeton University, it became necessary to have available distribution data for this system. Inasmuch as the literature apparently reveals no published measurements of this distribution equilibrium, our data on it are presented in this paper. As this system is the basis of a commercial process for the recovery of acetic acid from aqueous solution by extraction, these results are of industrial as well as academic interest.

EXPERIMENTAL TECHNIQUE

Material. The measurements were made with purified isopropyl ether from the Eastman Kodak Company and with distilled water as the solvents, and also with technical isopropyl ether obtained directly from the Carbide and Carbon Chemicals Corporation and with the local tap water. The technical ether was dry to anhydrous copper sulfate, contained an acidity less than 0.01 per cent, and less than 3 per cent by weight of isopropyl alcohol. The acetic acid was glacial (99.5 per cent) acid of the U.S.P. grade.

Analytical method. Acetic acid concentrations in both water and ether phases were determined volumetrically by titration of 10-cc. to 25-cc. samples with a standard alcohol solution of sodium hydroxide. This was prepared by dissolving the usual purified stick caustic in 95 per cent ethyl alcohol, standardized against constant-boiling hydrochloric acid, and employed in concentrations of 0.1 *N*, 0.5 *N*, and 1.0 *N* according to the concentration range in the system under investigation. Prior to titration the samples were diluted to three times the original volume to insure complete miscibility with the titrating solution, alcohol acting as a common solvent. The indicator was phenolphthalein.

Procedure. The distribution measurements were carried out by the ordinary laboratory method usually employed for this purpose. The two solvents, water and isopropyl ether, one containing a sufficient quantity of acetic acid to produce the final acid concentration range desired, were placed in 250-cc. glass-stoppered bottles. The volume of each solvent was usually 100 cc. In order to approach the equilibrium from both sides and thus minimize possible error due to failure to attain equilibrium, independent series of experiments were conducted with acetic acid initially in the water phase and in the ether phase, respectively. After sealing, the bottles were vigorously agitated, placed in a thermostat at 20 ± 0.5°C., and allowed to remain for a period of 170 hours with vigorous agitation at frequent intervals. Ten-cc. samples from each layer were analyzed for acid after 48 hours and 25-cc. samples at the end of 170 hours. Inasmuch as the analyses of the two sets of samples checked closely, it was assumed that equilibrium had been attained. Precaution was taken to prevent evaporation of ether from the samples, these being run directly into alcohol in stoppered flasks. As a check, the sum of the quantities of acid found in each layer by the analyses was compared with the known total quantity of acid originally added to the system. Duplicate experiments were performed for the majority of concentrations.

EXPERIMENTAL RESULTS

The results of the measurements for various acid concentrations are listed in table 1. In this table equilibrium concentrations, expressed in gram-moles per liter of solution, for the water, C_w, and ether, C_e, phases are given in columns 1 and 2, respectively. Corresponding values of the apparent distribution coefficient, $D_{\text{obsd.}} = C_e/C_w$, calculated from the observed concentration on the assumption that the simple ideal distribution law for single undissociated molecules is obeyed, are given in column 3.

It is evident from the data of table 1 that the ideal distribution law is only approximately obeyed, inasmuch as the apparent distribution coefficient calculated from the ratio C_e/C_w slowly increases with total acid concentration. This is an expected result, since one is undoubtedly not dealing with a single molecular species in both phases, acetic acid probably undergoing increasing dissociation in the aqueous phase with increasing dilution and association in the ether phase.

Especially at the higher concentrations the apparent values of the coefficient where the acid was initially in the ether phase are consistently somewhat higher than for corresponding concentrations where the acid was present initially in the water phase. This apparently indicates that true equilibrium was not entirely attained. However, analyses of both phases in each experiment over a 170-hour period with frequent agitation gave no further detectable change in observed concentrations; consequently, further possible change toward equilibrium would be infinitely slow. The apparent variation from true equilibrium is less significant than at first appears, and is probably within the limits of possible analytical error. A deviation in the observed concentrations from the true equilibrium values is multiplied twofold in the calculation of the distribution ratio, and, furthermore, an average error of 0.02 to 0.05 cc. in the titration value could account for the minor discrepancies obtained.

TABLE 1

Distribution of acetic acid between water and isopropyl ether at 20°C.

EQUILIBRIUM CONCENTRATION IN GRAM-MOLES PER LITER		DISTRIBUTION COEFFICIENT, $D = C_e/C_w$	
Ether, C_e	Water, C_w	Observed	Calculated from equation 3
(a) Pure ether and distilled water			
0.0136	0.0732	0.185	0.180
0.0140*	0.0785	0.178	0.180
0.0254	0.1450	0.177	0.182
0.0560*	0.2980	0.188	0.186
0.0577	0.3030	0.190	0.187
0.1186	0.6025	0.196	0.194
0.1430*	0.6925	0.206	0.197
0.1733	0.8900	0.196	0.202
0.2290*	1.1070	0.207	0.208
0.2803	1.3600	0.206	0.215
0.3260*	1.4300	0.228	0.217
0.3994	1.7970	0.222	0.226
0.6740	2.7800	0.242	0.253
(b) Technical ether and tap water			
0.0543	0.2960	0.200	
0.1480	0.7720	0.192	
0.2740	1.3450	0.232	

* In these experiments acid was added initially to the ether.

The results with tap water and technical isopropyl ether are slightly higher than those for the pure solvents. This is probably to be accounted for mainly on the basis of the isopropyl alcohol present in the technical ether.

In figure 1 is plotted the actual distribution equilibrium curve for the range investigated. Distribution data have usually been represented by an empirical equation of the form

$$D' = C_e/C_w^a$$

The present equilibrium curve may be approximately represented over the concentration range investigated by such a parabolic equation, since a satisfactory straight line is obtained in a log-log plot of C_e against C_w. The slope of this line is $a = 1.09$, and its intercept, $D' = 0.148$. Therefore

$$C_e/C_w^{1.09} = 0.148 \qquad (1)$$

which equation may be employed for the approximate calculation of the distribution of acetic acid between water and isopropyl ether over the present concentration range.

DISCUSSION

It has been pointed out by Almquist (1) that the apparent distribution coefficient may frequently be expressed most accurately as a function of the concentration in the water phase by a simple linear equation of the form

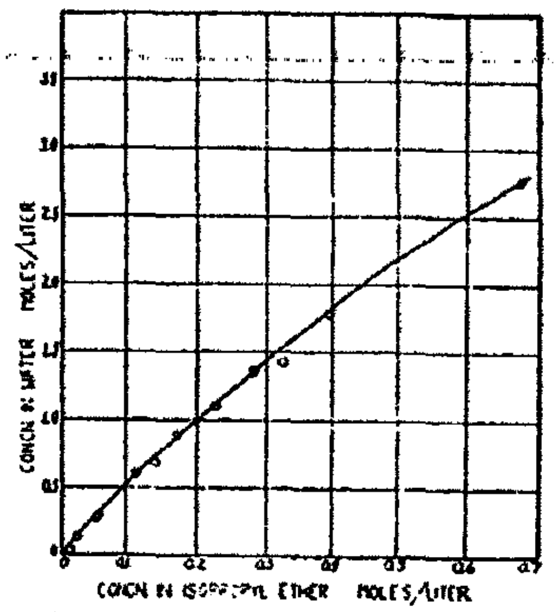

FIG. 1

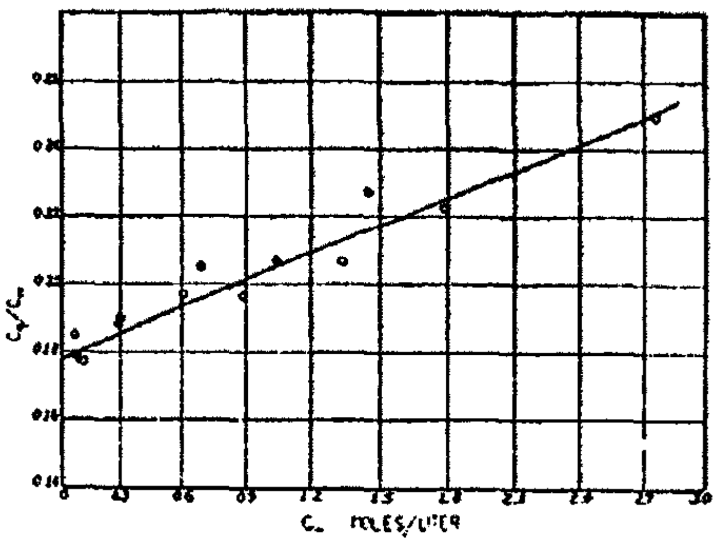

FIG. 2

FIG. 1. EQUILIBRIUM CURVE FOR THE DISTRIBUTION OF ACETIC ACID BETWEEN ISOPROPYL ETHER AND WATER

FIG. 2. VARIATION OF THE APPARENT DISTRIBUTION COEFFICIENT WITH CONCENTRATION IN THE AQUEOUS PHASE

○, acid added initially to the water; ◐, acid added initially to the isopropyl ether.

$$D_{\text{apparent}} = C_e/C_w = D_s C_w + D_i \qquad (2)$$

where D_s is the slope and D_i the intercept. Such an equation possesses theoretical significance and supplies an accurate and useful means of recording, testing, and interpolating distribution data. That the data for the present case conform to such an equation may be seen from figure 2, in which a straight line results from a plot of the ratio C_e/C_w against C_w. The slope of this line is 0.027 and its intercept is 0.178. Hence, its equation is

$$D_{\text{apparent}} = C_e/C_w = 0.027C_w + 0.178 \qquad (3)$$

This equation may be employed with considerable accuracy for distribution calculations for acetic acid between water and isopropyl ether and is recommended for this purpose. In column 4 of table 1 values of the apparent coefficient calculated from the concentrations in the water phase by means of equation 3 are given. Since equation 3 is based on the measurements approaching the equilibrium from both sides, thus representing average values, it is probable that the calculated values in column 4 represent the true distribution ratio more accurately than do the individually observed values in column 3.

Based on theoretical considerations involving the possible distribution and association equilibria existing in such a case and assuming no association in the water phase, Almquist (1) has derived, as a general theoretical relation for the distribution of an organic solute between water and an organic solvent, the equation:

$$C_x/C_w = nK_3K_2^nC_w^{n-1} + K_2 \tag{4}$$

In this equation

n = number of molecules in the polymer in the non-aqueous phase.

$K_3 = (A'_n)/(A')^n$ = association constant in the non-aqueous phase, i.e., the equilibrium constant for the reaction $nA' = A'_n$.

$K_2 = A'/A$ = distribution constant for single molecules between the two phases.

A' and A = concentrations of single molecules in the non-aqueous phase x and the water phase w, respectively.

If the solute is mainly associated only into double molecules in the non-aqueous phase, then $n = 2$, equation 4 reduces to

$$C_x/C_w = 2K_3K_2^2C_w + K_2 \tag{5}$$

and the apparent distribution coefficient is a linear function of C_w. Since this is the case for acetic acid between the present solvents, it is evident that acetic acid is associated into double molecules in isopropyl ether over the concentration range investigated. In the present case the slope of equation 3, 0.027, is identical with $2K_3K_2^2$, the slope of equation 5, and the intercept, 0.178, corresponds to K_2. It therefore follows that the value of the distribution constant for single molecules of acetic acid between water and isopropyl ether is $K_2 = 0.178$, and the value of the association constant for acetic acid in isopropyl ether is $K_3 = 0.43$, concentrations being expressed in moles per liter.

At very low concentrations, owing to dissociation in the water phase, and at very high concentrations where association in the water phase may become appreciable, simple relations of the above form may be expected to be no longer valid.

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STUDIES ON SILICIC ACID GELS. V

THE DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF THE GEL MIXTURES

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INTRODUCTION

In a recent study in this laboratory, on the time of set of gels of silicic acid, Hurd and Carver (1) have emphasized the importance of the pH of the mixture. The quinhydrone method was used to determine the pH. In the special study of the effect of the pH upon the time of set of these gels, Hurd, Raymond, and Miller (2) have used the quinhydrone method also. In view of the apparent importance of this factor, we have considered it essential to make a very careful study of the applicability and reliability of the quinhydrone method in solutions containing silicic acid.

HISTORICAL

The determination of the pH of a solution containing colloidal material is always attended by a certain amount of uncertainty. When one considers the adsorptive powers possessed by colloidal silicic acid, any method for the determination of the pH may be viewed with considerable suspicion.

The indicator method has been used by several investigators, in particular Prasad and Hattiangadi (3). Their difficulties with this method were that the turbidity of the gel mixture caused difficulty in the determination of the color of the indicator. The alcohol in their indicator solution affected the setting of the gel. Our experiments with the indicator method have substantiated these results, and led us to discard the method where the quinhydrone method could be used, that is, in acid gel mixtures.

The glass electrode–vacuum tube potentiometer method has been used, so far as we know, only to check the quinhydrone method, as mentioned by Hurd and Carver (1). It was used only in acid gels. The results by both methods checked satisfactorily.

The quinhydrone method has been used in the studies made in this laboratory, as mentioned. This method depends upon the fact that quinhydrone introduces equal concentrations of quinone and hydroquinone into the solution. If, in these gel mixtures, the colloidal material present should adsorb or render inactive any appreciable quantity of either the quinone or the hydroquinone, the method would not yield satisfactory results for the pH. On the other hand, if the colloidal material should adsorb only a portion of the quinone and the hydroquinone, but in equimolecular amounts, the method should give reliable results. Also, if the colloidal material should not adsorb any of the quinone or hydroquinone, the results should be accurate. Lastly, there is a possibility that some colloidal silicic acid may be adsorbed onto the platinum wire electrode and so cause an error in the determination.

EXPERIMENTAL

The method of investigation devised was as follows. Standard buffer solutions were prepared, using potassium acid phthalate and sodium hydroxide. Six different gel mixtures were prepared. The gel was washed free from soluble materials, namely the sodium acetate and the acid or base which is in excess. The pH of the buffer solution was determined before and after the addition of different amounts of a suspension of the washed and finely suspended gel in water. No evidence of any change in pH was noted. Blanks were also run, using the same volume of distilled water as was used of the gel suspension. No change in pH was noted.

In each determination, 50 cc. of the buffer solution was used. Solid quinhydrone was added until a slight excess remained undissolved. The pH was measured with a Leeds and Northrup quinhydrone pH indicator #7654. A saturated calomel electrode was used. For the quinhydrone electrode we have used a bright platinum wire in a coil. Such an electrode has given us good results, and is easier to clean than the conventional gold wire electrode. The maximum amount of gel suspension or distilled water added was 20 cc.

The preparation of a washed gel, free from electrolytes, presented considerable difficulty. The method of extracting lumps of the gel with distilled water in several extractions was discarded as being uncertain and requiring too much time. Various filtration methods proved unsatisfactory. The method finally developed was as follows. The solutions of sodium silicate and acetic acid were mixed in a beaker and allowed to set. About three times the volume of distilled water was added and the gel broken into coarse lumps. A small, thin stirrer, driven by a very high speed motor, was used to break up the gel into very fine pieces and mix it completely with the distilled water. The gel was allowed to settle and the supernatant liquid was poured away. This could be done very completely, since after standing for a short time the settled gel seemed to knit itself together into a reasonably firm mass. This fact is interesting and is receiving further study. After this process had been repeated several times, the gel was found to be neutral and free from impurities. It was very essential in this problem that the gel should be entirely free from acid or base. The gel was resuspended in about three times its volume of distilled water before being used.

The data are shown in tables 1 and 2.

The concentration of sodium silicate is expressed as normality in terms of its equivalent of sodium hydroxide. The silicate used was E brand, produced by the Philadelphia Quartz Co[1]. The Na_2O/SiO_2 ratio by weight is 1/3.25.

TABLE 1

Composition of the silicic acid gels

NUMBER OF GEL	0.611 *N* SODIUM SILICATE	3.05 *N* ACETIC ACID
	cc.	*cc.*
1	50	20
2	65	20
3	45	20
4	70	20
5	50	25
6	50	10

TABLE 2

Data for buffer solutions

SOLUTION	0.1 *N* SODIUM HYDROXIDE	0.1 *N* POTASSIUM ACID PHTHALATE	DISTILLED WATER	pH
	cc.	*cc.*	*cc.*	
A	0.40	50.0	100.0	3.99
B	17.70	50.0	100.0	4.52
C	29.95	50.0	100.0	5.09
D	39.85	50.0	100.0	5.67
E	45.45	50.0	100.0	5.98

The following combinations were tried, using 50 cc. of the buffer solution and from 0 to 20 cc. of the washed gel or distilled water: A5, A6, B1, B4, B5, C1, C2, C3, C4, D1, D2, D4, E5, and E6. In no case was any change in pH observed. Repetition gave identical results.

We may state, therefore, that silicic acid gel in moderate quantities has no measurable effect upon the pH of phthalate buffer solutions from pH = 4.0 to pH = 6.0 as measured by the quinhydrone method. It would therefore seem reasonable to believe that the silicic acid gel present in gel mixtures will have no measurable effect upon the pH determination by the

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[1] The writers wish to thank the Philadelphia Quartz Co. for the silicate used in this research.

quinhydrone method, the buffering being accomplished by the acetic acid and sodium acetate present.

To determine whether or not the platinum electrode used in the quinhydrone determination is affected by usage in these silicic acid gel mixtures, a large number of trials were made. Determinations were made in mixtures of known pH, before and after using the electrode in a silicic acid gel mixture. Various methods of cleaning the electrode were used. The electrode always requires a fraction of a minute to come to equilibrium. No evidence of any effect of the silicic acid on the platinum was found. The electrode may be cleaned with filter paper, or any coating of silica may be loosened by treatment with dilute sodium hydroxide without apparently affecting the electrode.

THE EFFECT OF SETTING OF THE GEL UPON THE pH

Because of the accuracy developed here in the use of the quinhydrone method, we have thought it worth while to ascertain again whether any change occurs, during setting, in the value of the pH. Very careful determinations were run on three gel mixtures, one of pH 4.64, one of 5.01, and the third 5.92. Readings were obtained as soon as possible after mixing and were continued until long after the gel had set. No observable change could be detected in the pH. This agrees with observations in this laboratory, as mentioned by Hurd and Carver (1), and agrees with the observations of Prasad and Hattiangadi (3), who determined the pH with indicators.

THE EFFECT OF QUINHYDRONE ON THE TIME OF SET

It has been our practice to determine the time of set and the pH in two different portions of the same mixture. This practice obviates the possibility that the quinhydrone might affect the time of set indicated for the mixture. It would not be expected, from the results shown by Hurd and Carver (1), that such small amounts of a sparingly soluble organic compound of this type would have any appreciable effect upon the time of set, as determined by the tilted rod method.

A number of determinations have been carried out in acid mixtures over the pH range given in this and other papers of the series, to detect any effect on time of set caused by the introduction of the same amount of quinhydrone as is used in a pH determination. The data are omitted in the interest of economy. The effect can be considered negligible.

SUMMARY

A study has been made of the quinhydrone method for the determination of the pH in silicic acid gel mixtures prepared by mixing solutions of sodium silicate and acetic acid. All gel mixtures were acid. The quinhydrone method was found to give reliable results.

It does not appear that the platinum electrode is affected by the colloidal silicic acid.

A method of preparing washed gel, free from electrolytes, is described.

No change in pH during and for some time after setting could be detected in gel mixtures with pH from 4.62 to 5.92.

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NEW BOOKS

Kolloidchemisches Praktikum. By E. SAUER. 21 x 14 cm.; ix + 112 pp. Berlin: Julius Springer, 1935. Price: 4.50 RM.

This laboratory manual gives detailed directions for 140 experiments illustrating the preparation of colloidal solutions, the investigation of their mechanical, electrical, and optical properties, phenomena at boundaries, the properties of gels and jellies, and the analysis of particle sizes chiefly by elutriation.

The majority of the examples chosen are what may be called standard or classical; a few—e.g., the preparation of cadmium sulfide from the cyanide—are drawn from less familiar sources, while a number of experiments have been devised by the author himself. The directions are concise but clear, and students of average attainments should find no difficulty in carrying them out and in acquiring a fair knowledge of colloidal technique. The intelligent student will also notice the only serious error overlooked by the proof reader: to prepare colloidal sulfur according to Raffo's method he is instructed to drop a solution of sodium *sulfate* into concentrated sulfuric acid; it should of course be sodium thiosulfate.

The author says in the preface: "Only in rare cases will sufficient time be available at the universities for a practical course in colloids extending over a whole semester. It is, however, possible to give a survey of colloid chemistry by using one or two afternoons only during one semester."

EMIL HATSCHEK.

Lehrbuch der physikalischen Chemie. By K. JELLINEK. Band V, Bogen 1-18. 25 x 16 cm.; 288 pp. Stuttgart: F. Enke, 1935. Price: 27 marks.

The first part of the fifth and final volume of this well-known treatise consists, broadly speaking, of three sections with the beginning of a fourth. The first section deals with surface phenomena and colloids, including electroendosmose, cataphoresis, electrocapillary phenomena, and the Brownian movement. Since only eighty pages are devoted to this section, the treatment is often brief, but the mathematical deductions are clearly given and such typical experimental results are quoted as are necessary to illustrate the applications of the theory. The second section (pp. 81-204) deals with homogeneous and heterogeneous reaction velocity, and modern aspects are represented by discussions of the work of Hinshelwood, Moelwyn-Hughes, and Brönsted. A good feature is the detailed consideration of typical cases, and the rather involved theory is carefully explained. The section on heterogeneous systems includes activated adsorption. The theory of supersaturated solutions on p. 160 is given without mentioning the names of the authors, Jones and Partington. The third section deals with aspects of electrolysis falling within the range of the volume and includes a discussion of modern research on overvoltage. The section on the structure of matter, with which the fifth volume will mainly be concerned, is introduced by eighteen pages on the determination of the electronic charge.

The present volume, although perhaps less detailed than the preceding ones, is planned and executed on the same lines, and it may be recommended as a clear and able exposition of the subjects dealt with.

J. R. PARTINGTON.

Auer von Welsbach. By F. Sedlacek. 25 x 18 cm.; viii + 85 pp.; 30 illustrations. Berlin: Julius Springer, 1934. Price: 3.60 RM.

The present volume constitutes the second part of the larger book *Blätter für die Geschichte der Technik* edited by L. Erhard. The book opens with an interesting account of the parentage and family of Carl Auer von Welsbach from the early seventeenth century, and this is followed by an equally interesting account of his youth and studies. A brief survey of the development of the study of the rare earths leads to a description of the separation of the didymium of Mosander into the two elements praseodymium and neodymium by Auer. The three important contributions of Auer to the general amenities of the world, namely the incandescent gas mantle, the osmium lamp, and the cerium-iron alloys, used in the manufacture of automatic lighters, are considered at length in a manner which is intelligible to the non-scientific. The separation of the ytterbium of Marignac into aldebaranium and cassiopeium by Auer is described, and the whole question of his priority over Urbain is once more explored. The concluding chapter contains a fascinating account of the personality of Auer, who is here named the "Austrian Edison," his activities in the autumn of his life, and his death in 1929 at the age of 71.

This most interesting book is written in a very pleasant manner, and portraits of Auer at seven periods of his life are included. A list of references to the published works of Alois Auer von Welsbach, Carl Auer von Welsbach, and other writers on the subjects in which Auer was active is appended to the book.

The book is the story of a great Austrian, who was both a great man and a great chemist, his scientific investigations, and the development of some of these into vast industrial undertakings. It is a book well worth reading, and it can be recommended without reserve.

James F. Spence.

Acta Physicochimica U. S. S. R. Published in Moscow. Volume 1, 990 pages. Six issues, beginning September 1934. Amkniga Corporation, 258 Fifth Ave., New York; or Knige, Ltd., Aldwych, London, W. C. 2. Price: $4.00 per volume.

Another new journal in the field of physical chemistry has made its appearance, and takes its place as an important scientific publication, access to which promises to be indispensable to those interested in mathematical, theoretical, or general physical chemistry, kinetics, catalysis, photochemistry, electrochemistry, and especially colloids and sorption,—the whole range of physical chemistry and chemical physics.

The board of editors consists of a dozen internationally known investigators. There are some forty permanent contributors distributed over seven cities of the U. S. S. R. The papers in Volume 1 are published in English, German, and occasionally French. Most of them are from the U. S. S. R., but a number are from other countries. Issues 3-4 contain the papers given at the Tenth Six-day Physico-Chemical Conference on Heterogeneous Catalysis, including one paper each from I. Langmuir and H. S. Taylor.

In a country which frankly recognizes scientific progress as a vital necessity and offers every inducement in its power for the pursuit of pure and applied science, it is inevitable that there should be enormous activity in every scientific field. The high quality of this journal in the selected field of physical chemistry commands our congratulations.

James W. McBain.

ERRATUM

Vol. 38, p. 1213. Equation 1 should read

$$X - X_0 = (X_m - X_0)e^{-k(t - t_0)}$$

where the symbols have the meaning given in the article. The theoretical curve in figure 1 was calculated on the basis of the correct equation.

MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. V

SULFUR SOL

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A mechanism of the coagulation of sols by electrolytes based on adsorption and potentiometric measurements on hydrous oxide sols and arsenic trisulfide sol has been proposed in earlier papers (11, 13). While these papers were being prepared Bassett and Durrant (1) carried out experiments on Raffo's sulfur sol which indicated that the precipitating cation carried down by the coagulum was always exactly equivalent to the stabilizing polythionate ion originally held by the sulfur micelles. From this it was concluded that the coagulation is the result of a stoichiometric reaction between the soluble sodium salt of a sulfur polythionate complex and the precipitating electrolyte. Somewhat later Bolam and Bowden (2) and Bolam and Muir (4) determined the change in hydrogen-ion concentration on adding electrolytes to sulfur sol, using the same procedure as we employed with arsenic trisulfide sol. These observations led to the conclusion that the same fraction of hydrogen ion is liberated from the micelles of a given sulfur sol at the coagulation point, whatever the nature of the cation of the coagulating salt.

Since neither of the above conclusions reported by the English workers would be predicted from the mechanism of the coagulation process proposed by us, we have extended our observations on the nature of electrolyte coagulation to sulfur sols.

ADSORPTION EXPERIMENTS

Since the observations of Bassett and Durrant with the various cations were carried out on different sols, it was not possible to compare directly the amounts of the several cations taken up at the precipitation concentration. In order to make such a comparison the adsorption of a series of cations of varying valence was determined on samples of the same sol.

Preparation of sol

Raffo (8) sulfur sols were prepared according to the procedure of Bassett and Durrant: 83.6 g. of sodium thiosulfate crystals was dissolved in 50 cc.

of water and added to 65.5 cc. of concentrated sulfuric acid, keeping the temperature below 25°C. After adding 50 cc. of water, the mixture was heated to 85°C. until all sulfur dioxide was driven off. The mixture was allowed to stand at room temperature for three hours, the coagulated sulfur collected on a Buchner funnel, repeptized in cold water, and coagulated with 5 N sodium nitrate solution; the repeptization and coagulation were repeated three times. Since two or three liters of sol were required for each series of experiments, several portions were prepared and mixed after the first coagulation with sodium nitrate, subsequent coagulations and peptizations being carried out on the whole sol. After the second precipitation with sodium nitrate, the coagulated sulfur was peptized in a small amount of water and about one-fifth of this sol was used to wash the coagulum obtained by the next precipitation with sodium nitrate. In this way the amount of sodium nitrate retained by the sulfur was reduced. Four samples of sol of varying concentrations and ages were used in the following experiments:

TABLE 1

Adsorption by sulfur sol of cations at the precipitation concentration

NO. OF SOL	CC. OF SOL	CATION ADDED	CATION CONCENTRATIONS MILLIEQ PER LITER		ADSORPTION MILLIEQ. PER GRAM OF SULFUR
			Original	Final	
I. 5.4 g. per liter; age 50 days	150	Sr	5.87	2.00	0.73
	150	Ba	5.32	1.66	0.71
	150	Nd	3.68	0.20	0.68
II. 2.75 g. per liter; age 60 days	200	Ba	2.30	0.45	0.74
	175	Sr	3.07	1.30	0.72
	175	Ca	5.28	3.73	0.64
	400	Al	1.60	0.15	0.59
	400	Nd	1.34	0.08	0.52
	400	Th	1.39	0.38	0.41

Adsorption at the precipitation concentration

The precipitation concentration of electrolyte for the sulfur sol was taken as that concentration which was just sufficient to give a clear supernatant solution after the mixture of sol and electrolyte had stood for twenty-four hours. For each trial a 10-cc. portion of sol was employed. The electrolytes were the chlorides of the respective metals. The precipitation concentrations in milliequivalents per liter are given in the fourth column of table 1.

The adsorption measurements were made as follows: To a definite volume of sol contained in a wide-mouthed bottle, varying amounts of water and electrolyte were added to bring the mixture to some constant volume. The mixtures were stoppered, shaken, and allowed to stand for twenty-four hours. The coagulated sulfur was matted down by centrifuging, and the supernatant liquid filtered through a small filter paper to remove any suspended sulfur. The concentration of the cation in the filtrate was then determined. For standardization, samples in which water was substituted for the sol were subjected to the same treatment. Barium and strontium were determined as sulfates; the calcium was precipitated as oxalate and weighed as oxide; and the neodymium, aluminum, iron, and thorium were determined as oxides. All experiments were carried out in duplicate and the average is reported.

TABLE 2

Adsorption by sulfur sol of cations at concentrations above the precipitation values

NO. OF SOL	CC. OF SOL	CATION ADDED	CATION CONCENTRATIONS MILLIEQ. PER LITER		ADSORPTION MILLIEQ. PER GRAM OF SULFUR
			Original	Final	
III. 7.3 g. per liter; age 5 days	50	Sr	10.12	6.12	0.56
	50	Al	7.73	3.31	0.66
	50	Nd	8.32	3.72	0.68
	50	Th	9.46	4.72	0.74
IV. 2.5 g. per liter; age 80 days	100	Ca	4.00	2.68	0.48
	100	Sr	4.00	2.42	0.58
	100	Ba	4.00	2.04	0.71
	100	Al	4.00	1.88	0.77
	100	Nd	4.00	0.82	1.16
	100	Th	4.00	0.68	1.21

The adsorption data at the precipitation values of the respective electrolytes are summarized in table 1.

Adsorption above the precipitation concentration

Observations similar to those described above were made (1) on a freshly formed sol with electrolyte concentrations approximately twice the respective precipitation values, and (2) on an aged sol with the respective electrolytes in equal concentrations well above the precipitation value. The results are summarized in table 2.

Discussion of results

Contrary to the belief of Bassett and Durrant, it is quite evident from the above results that the amounts of the several cations taken up by the particles of sulfur sol are not equivalent either at, or above, the respective precipitation concentrations. The order of precipitating power for sol I was found to be Nd > Ba > Sr, and the adsorption (at the precipitation value) in milliequivalents per gram of sulfur is in the order Sr > Ba > Nd. However, if we compare the relative amounts adsorbed we find that 94 per cent of the added neodymium is adsorbed as compared with 69 per cent of barium and 65 per cent of strontium.

In the case of sol II we find the order of precipitation to be Nd > Th > Al > Ba > Sr > Ca. The occurrence of the lyotropic sequence in the coagulation of sulfur sols has been pointed out by a number of investigators (12, 2, 5). The adsorption is in the order Ba > Sr > Ca > Al > Nd > Th. Again if we compare the percentage amounts of the added cations adsorbed, we find the order to be the same as that of the precipitating power, namely, Th > Nd > Al > Ba > Sr > Ca. As will be observed, tetravalent thorium does not precipitate in lower concentration than trivalent neodymium and the relative adsorption is less. Thorium chloride solution is hydrolyzed to a considerable degree, and we are dealing in this case with mutual coagulation of thorium oxide sol and sulfur sol as well as ionic interchange.

The order of adsorption well above the precipitation concentration, as shown in table 2, is the same as the order of precipitating power, namely, Th > Nd > Al > Ba > Sr > Ca. As will be shown in the subsequent experiments on hydrogen-ion displacement, cationic interchange is completed at or somewhat above the coagulation concentration. Further adsorption occurs, however, and may even lead to a reversal of charge and peptization in the case of thorium. The percentage adsorption from mixtures having the same electrolyte concentration is in the same order as the precipitating power. Thus in sol IV the relative amounts taken up are: thorium, 83 per cent; neodymium, 80 per cent; aluminum, 53 per cent; barium, 49 per cent; strontium, 40 per cent; and calcium, 33 per cent.

Similar observations were made on a Selmi (9) sol prepared by the interaction of hydrogen sulfide and sulfur dioxide (see page 1168); but the adsorption values with the more hydrophobic Selmi sol were smaller than with the Raffo sol.

Summarizing briefly, we note that the adsorption values of the precipitating ions are not equivalent at the precipitation concentration. The relatively more marked adsorption of the cations of higher valence brings about precipitation at lower concentrations.

TITRATION EXPERIMENTS

Preparation of sols

The displacement of hydrogen ion from the colloidal particles by the stepwise addition of various metallic chlorides was observed with both a

Raffo and a Selmi sol. The former was prepared by a method similar to that used by Bolam and Bowden: 25 cc. of concentrated sulfuric acid was added slowly from a dropping funnel to 100 cc. of saturated sodium thiosulfate. The mixture was stirred vigorously with a mechanical stirrer and the temperature was maintained between 20 and 25°C. by surrounding with ice water. After the reaction was complete the mixture was cooled to 0°C. and treated with 100 cc. of saturated sodium chloride solution. The coagulated sulfur was separated by centrifuging and heating to 85°C. with 100 cc. of water. Coagulation and repeptization were then repeated until the supernatant liquid after coagulation was neutral to litmus. Several portions having been prepared in this way, the whole was mixed and freed from sodium chloride by coagulating with concentrated hydrochloric acid and repeptizing by washing, the process being repeated several times. The sol was then dialyzed in a Neidle (7) dialyzer, using a cellophane bag, for three weeks at the rate of 500 cc. of water per hour. No chloride was detected in 100 cc. of dialysate evaporated to 10 cc. Sulfur which had settled out in the course of dialysis was removed by filtration. The sol contained 2.9 g. of sulfur per liter.

TABLE 3

Titration of a Raffo sulfur sol with alkali halides

ELECTROLYTE	AMOUNT ADDED IN EQUIVALENTS × 10^6	ΔE IN MILLIVOLTS	pH	$[H] \times 10^4$ IN SOLUTION	$[H] \times 10^4$ DISPLACED
None	0	53	3.08	8.3	0
KCl	38.4	59	2.98	10.5	2.2
	76.8	60.5	2.96	11.0	2.7
	115.2	61.0	2.95	11.2	2.9
	153.6	64.0	2.90	12.6	4.3
	192.0	65.5	2.87	13.5	5.2
NaCl	38.4	57.5	3.00	10.0	1.7
	76.8	61.0	2.95	11.2	2.9
	115.2	62.5	2.92	12.0	3.7
	153.6	63.5	2.91	12.3	4.0
	192.0	64.5	2.89	12.9	4.6
LiCl	38.4	57.0	3.01	9.8	1.5
	76.8	60.0	2.96	11.0	2.7
	115.2	61.5	2.94	11.5	3.2
	153.6	62.5	2.92	12.0	3.7
	192.0	63.5	2.91	12.3	4.0

The Selmi sol was prepared by the method of Weiser and Cunningham (12, 2, 5). Hydrogen sulfide and sulfur dioxide were passed simultaneously into water previously saturated with sulfur dioxide. Hydrogen was used to wash out the excess gases. After standing thirty days, the sol was filtered and the titration experiments carried out. The sol contained 10.8 g. of sulfur per liter.

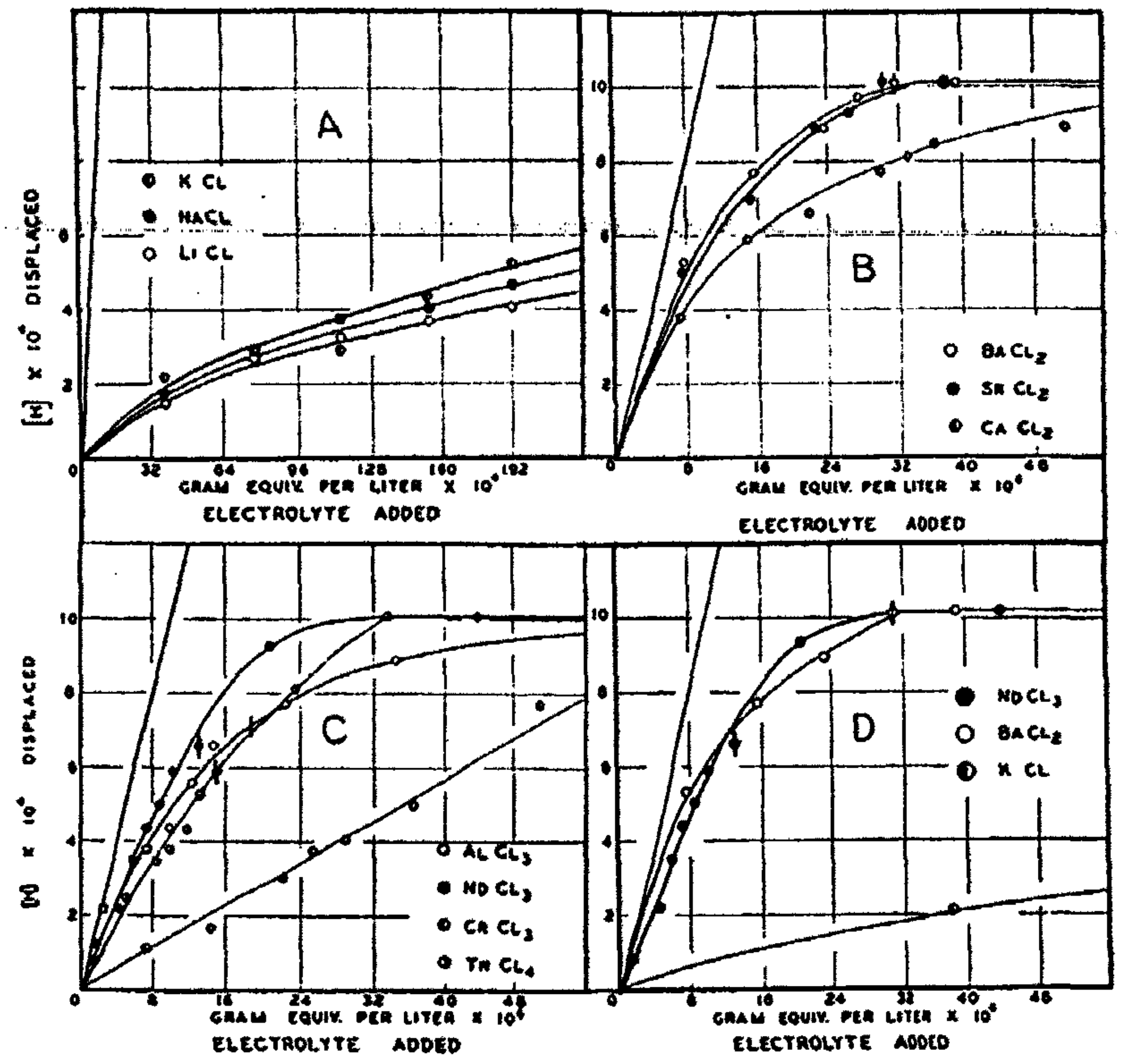

FIG. 1. TITRATION OF RAFFO SOL WITH ELECTROLYTES

Potentiometric titrations on the Raffo sol

To 5-cc. portions of sol contained in small weighing bottles were added varying amounts of water and precipitating electrolyte, bringing the final volume in each case to 5.1 cc. A microburet graduated in 0.01 cc. was used to deliver the water and solutions. After thorough mixing the samples were allowed to stand in a thermostat for eighteen hours before making the potentiometric measurements.

The glass electrode used to determine the pH value was of the MacInnes and Dole type (6). A bulb was blown on the end of a glass tube (Corning No. 015) until the resulting film was thin enough to show interference colors. The end of a tube of the same glass, one-half inch in diameter, was heated to low red heat and placed against the bulb. The adhering film was fused on by careful heating. The tube, except for the lower one-half inch, was covered with paraffin. After the tube had soaked for two days in 0.01 *N* hydrochloric acid, it was rinsed and filled almost to the level of the paraffin with 0.01 *N* hydrochloric acid saturated with quinhydrone, thus forming a quinhydrone half-cell. This electrode was suspended in the weighing bottle containing the sol–electrolyte mixture. The other half-cell was a 0.01 *N* calomel electrode, the tip of the salt bridge making contact with the liquid in the weighing bottle. Such dilute potassium chloride shows no coagulating action on the sol. The Youden glass electrode hydrogen-ion apparatus manufactured by the W. M. Welch Company was employed in measuring the E.M.F. The null-point instrument used in this apparatus is the Lindemann electrometer.

TABLE 4

Titration of a Raffo sulfur sol with alkaline earth halides

ELECTROLYTE	AMOUNT ADDED IN EQUIVALENTS × 10^6	*E* IN MILLIVOLTS	pH	[H] × 10^4 IN SOLUTION	[H] × 10^4 DISPLACED
None	0	53.5	3.07	8.5	0
$BaCl_2$	7.88	66.0	2.86	13.8	5.3
	15.76	70.0	2.79	16.2	7.7
	23.64	72.0	2.76	17.4	8.9
	27.58	73.0	2.74	18.2	9.7
	31.52	74.0	2.73	18.6	10.1
	39.4	74.0	2.73	18.6	10.1
$SrCl_2$	7.60	65.5	2.87	13.5	5.0
	15.20	69.0	2.81	15.5	7.0
	22.80	72.0	2.76	17.4	8.9
	26.60	72.5	2.75	17.8	9.3
	30.40	74.0	2.73	18.6	10.1
	38.0	73.5	2.73	18.6	10.1
$CaCl_2$	7.38	63.0	2.91	12.3	3.8
	14.76	67.0	2.84	14.4	5.9
	22.14	68.5	2.82	15.1	6.6
	29.52	70.0	2.79	16.2	7.7
	33.21	70.5	2.78	16.6	8.1
	36.90	71.5	2.77	17.0	8.5
	51.66	72.0	2.76	17.4	8.9

The glass electrode was standardized with *M*/20 potassium acid phthalate. Other standard buffers of lower pH were frequently run as controls.

The sol was titrated with the chlorides of potassium, sodium, lithium, barium, strontium, calcium, neodymium, aluminum, chromium, and

TABLE 5

Titration of a Raffo sol with $NdCl_3$, $AlCl_3$, $CrCl_3$, *and* $ThCl_4$

ELECTROLYTE	AMOUNT ADDED IN EQUIVALENTS × 10^4	*E* IN MILLIVOLTS	pH	[H] × 10^4 IN SOLUTION	[H] × 10^4 DISPLACED
None	0	53.5	3.07	8.5	0
$NdCl_3$	1.47	56.0	3.03	9.3	0.8
	4.41	59.5	2.97	10.7	2.2
	5.88	62.5	2.92	12.0	3.5
	7.35	64.5	2.89	12.9	4.4
	8.82	65.5	2.87	13.5	5.0
	10.29	67.0	2.84	14.4	5.9
	13.23	68.5	2.85	15.1	6.6
	20.58	72.5	2.75	17.8	9.3
	44.10	74.0	2.73	18.6	10.1
$AlCl_3$	2.48	59.5	2.97	10.7	2.2
	7.44	63.5	2.91	12.3	3.8
	9.92	64.5	2.89	12.9	4.4
	12.40	66.5	2.85	14.1	5.6
	14.88	68.5	2.82	15.1	6.6
	22.32	70.5	2.79	16.2	7.7
	34.72	72.0	2.76	17.4	8.9
$CrCl_3$	7.32	56.5	3.02	9.6	1.1
	14.64	58.5	2.99	10.2	1.7
	21.96	61.5	2.94	11.5	3.0
	25.62	63.0	2.91	12.3	3.8
	29.28	64.0	2.90	12.6	4.1
	36.60	65.5	2.87	13.5	5.0
	51.24	70.0	2.79	16.2	7.7
$ThCl_4$	1.68	57.5	3.01	9.8	1.3
	5.04	60.0	2.96	11.0	2.5
	8.40	62.5	2.92	12.0	3.5
	10.08	63.5	2.91	12.3	3.8
	11.76	64.5	2.89	12.9	4.4
	13.44	66.0	2.86	13.8	5.3
	15.12	67.5	2.84	14.4	5.9
	23.52	71.0	2.78	16.6	8.1
	33.60	74.0	2.73	18.6	10.1

thorium. The data for the alkali chlorides are recorded in table 3 and shown graphically in figure 1A. Since a relatively high concentration of the alkali cations is necessary to cause coagulation, the titrations were not carried to the precipitation value on account of the possibility of serious error in the pH measurements at the higher concentrations.

The results of the titration of the sol with the alkaline earth halides are given in table 4 and shown graphically in figure 1B. The precipitation concentration is indicated by a short vertical line cutting the curve for hydrogen displacement.

The titration data for the cations of higher valence are shown in table 5 and figure 1C.

Referring to figure 1A it will be seen that the displacement curves for the monovalent ions are similar in form. The hydrogen ion displaced is markedly less than equivalent to the cation added (straight line). The displacing power of the cations is in the same order as their precipitating power: K > Na > Li. A similar lyotropic sequence is observed in the case of the divalent ions (figure 1B). Although the displacing powers of barium and strontium are almost the same as are the precipitation values, that of calcium is distinctly lower. Comparing the displacement curves with the straight line representing the cation added, it will be noted that at low concentrations about 60 per cent of the cation added is effective in displacing hydrogen ion, the effectiveness falling off with increasing concentration until the coagulation value is reached, above which no further displacement occurs. With the cations of higher valence, figure 1C, the order of displacing power and coagulating power is the same: Nd > Th > Al > Cr. The reason thorium is less effective than neodymium has been discussed in connection with the adsorption experiments. In contrast to the behavior of the alkaline earth cations, thorium, neodymium, and aluminum coagulate the sol before the maximum displacement of hydrogen ion is attained, indicating further ionic interchange after the charge on the particles has been reduced to the point of coagulation.

Contrary to the view of Bolam and Muir, the displacement of hydrogen ion is not the same at the coagulation point. This is emphasized in figure 1D, which shows that much less hydrogen is displaced at the precipitation value of neodymium than at the precipitation value of barium. Less neodymium ion needs to be adsorbed to lower the charge to the critical coagulation value and accordingly less hydrogen is displaced at the precipitation value of neodymium than of barium.

Potentiometric titrations on the Selmi sol

Observations were made on the more hydrophobic Selmi sol similar to those on the Raffo sol. To conserve space the tables of titration data are omitted, the results being shown graphically in figure 2.

The displacement curves with the monovalent ions, figure 2A, are the same in form as those obtained with the Raffo sol. With the divalent ions the order of displacing power and coagulating power is: Ba > Sr > Ca. The difference in displacing power is slight at lower concentrations, becoming more marked as the precipitation concentration is approached. With the ions of higher valence the curves are quite similar in form, the order of displacing power being: Th > Nd > Cr > Al. This is the same as the order of precipitating power, with the exception that the chlorides of chromium and aluminum precipitate in almost the same concentration. It will be noted that at low concentrations of thorium and neodymium the hydrogen ion displaced is almost equivalent to the cation added

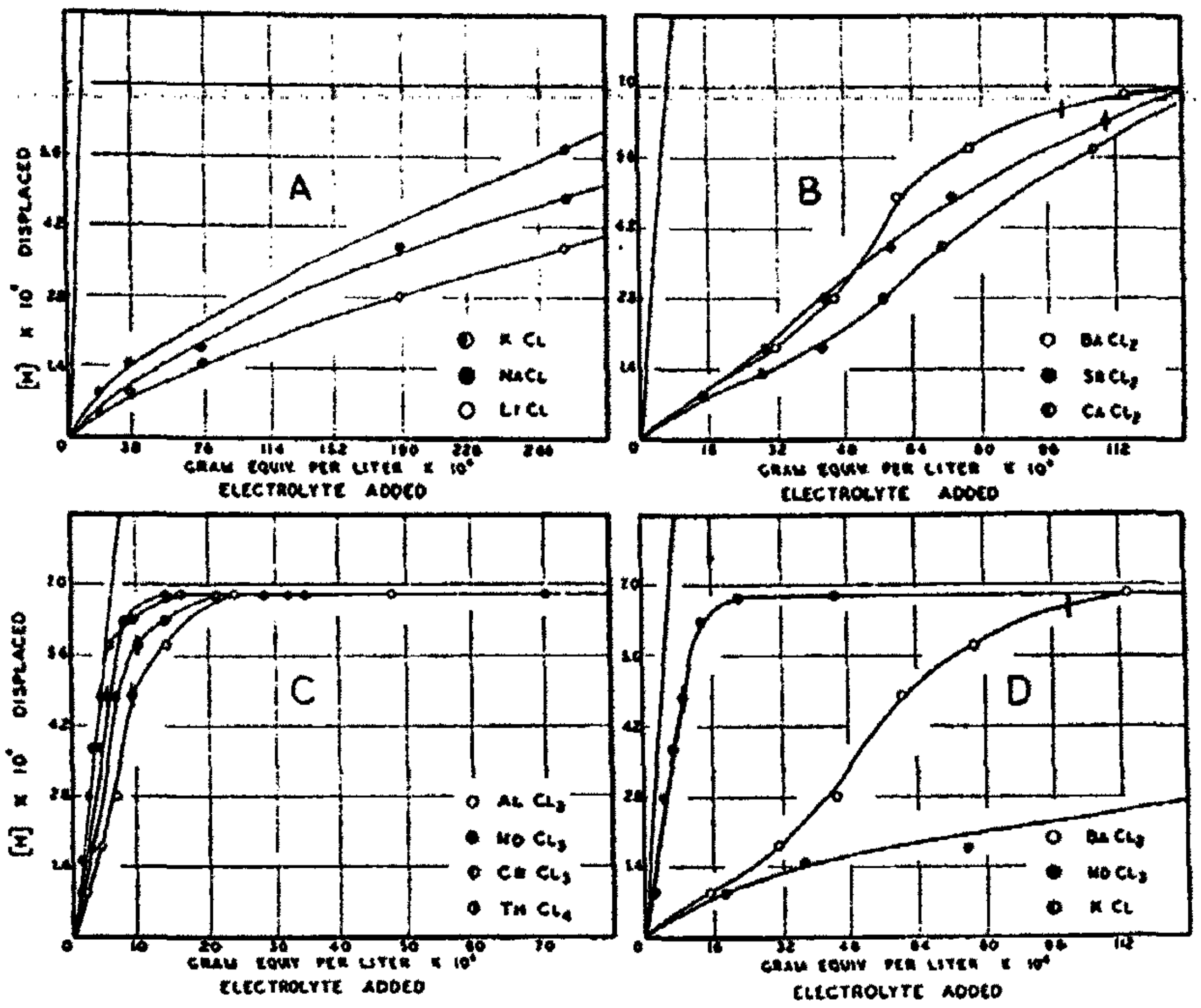

FIG. 2. TITRATION OF SELMI SOL WITH ELECTROLYTES

(straight line). As in the case of the Raffo sol, the displacement of hydrogen ion is far from complete at the precipitation concentration of the strongly adsorbed multivalent ions. For these ions which precipitate in low concentrations that are not far apart, the displacement of hydrogen at the precipitation value of the several ions approaches equivalence in accord with the observations of Bolam and Muir. On the other hand, with ions whose precipitation values are not close together, such as barium and neodymium, the displacement of hydrogen at the precipitation value of the former is much greater than at the precipitation value of the latter (cf. figure 2B), just as was found in the case of the Raffo sol, and for the same reason.

Comparing the observations on the two sols we find the hydrogen-ion concentration of the original Selmi sol to be over four times that of the Raffo sol, whereas after coagulation the ratio in the supernatant solution was reduced to 5:2. Moreover, the effect of the valence of the cation is more marked in the aged Selmi sol than in the Raffo sol. The aging of the former causes it to assume the properties of a typical hydrophobic sol in which the valence and lyotropic influence of the cations is more marked than in the more hydrophilic Raffo sol.

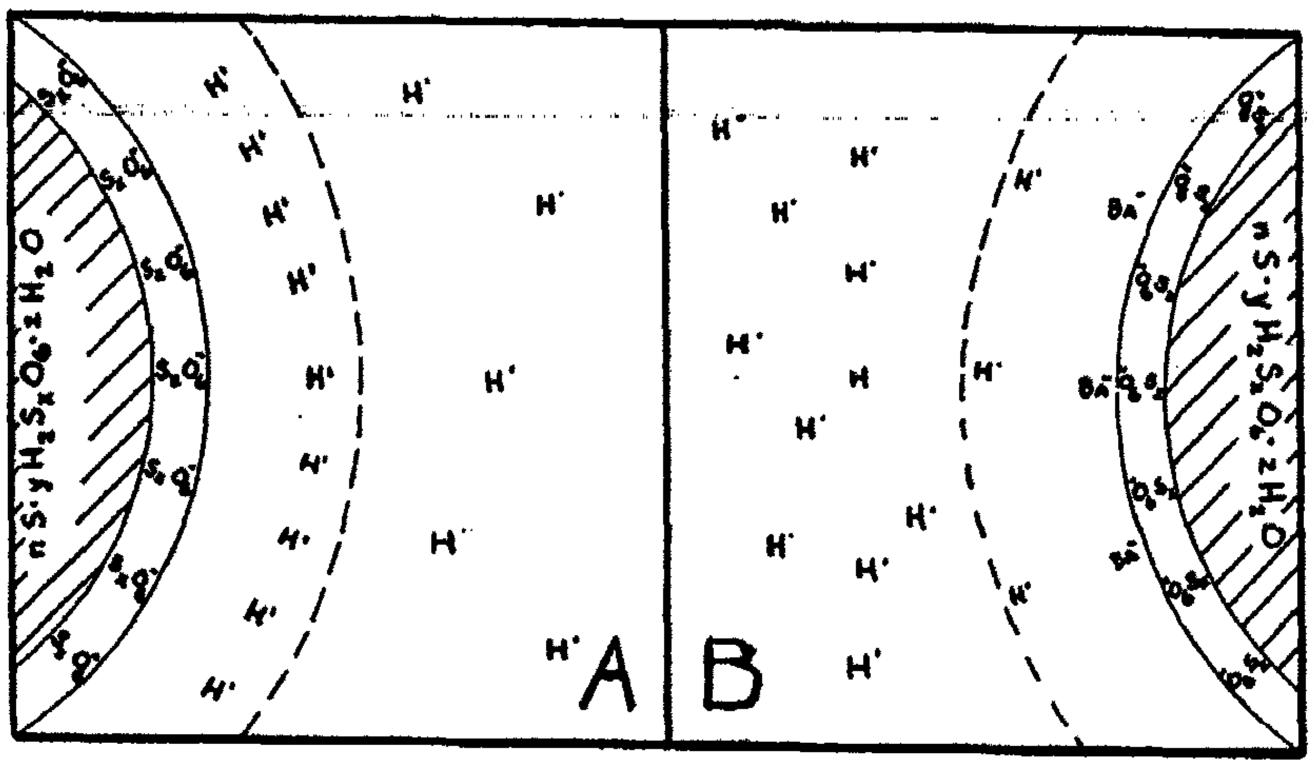

FIG. 3. DIAGRAMMATIC REPRESENTATION OF THE CONSTITUTION OF A PARTICLE OF COLLOIDAL SULFUR BEFORE AND AFTER THE ADDITION OF BARIUM CHLORIDE

MECHANISM OF THE COAGULATION

In sulfur sols prepared by the decomposition of sulfur compounds, the stabilizing electrolytes are polythionic acids, such as pentathionic and hexathionic, which may be represented by the general formula $H_2S_xO_6$. The colloidal particles consist essentially of a nucleus of colloidal sulfur which adsorbs the polythionate ions so strongly that the latter constitute the inner portion of the double layer surrounding the particles and give the particles a negative charge. The outer layer is a diffuse layer of hydrogen ions. The constitution may be represented diagrammatically as shown in figure 3A. The hydrogen ions of the outer layer are osmotically active and have a range of movement determined by the electrostatic field due to the residual $S_xO_6^{--}$ on the surface. Some of the hydrogen ions, shown beyond the dotted line, have sufficient osmotic pressure so that they can be measured potentiometrically. Others are so firmly held by the $S_xO_6^{--}$ layer that they do not influence the hydrogen electrode.

On the addition of an electrolyte, an exchange takes place between some of the hydrogen ions held by the $S_xO_6^{--}$ and the cations in the external liquid. The theory of the diffuse double layer indicates that coagulation occurs when the potential on the particles has fallen below a critical value, as a consequence of the contraction of the double layer by the coagulating ion. The more strongly adsorbed metal ions displace hydrogen ions and take up a position relatively closer to the inner layer, as indicated with barium ion in figure 3B. Monovalent cations are weakly adsorbed and bring about a much smaller displacement of hydrogen ions than an equivalent amount of multivalent ions. Trivalent cations are more effective than divalent, for example, less Nd^{+++} than Ba^{++} needs to be adsorbed to reduce the potential to the coagulation point, and precipitation takes place with lower concentration of neodymium salts than with barium salts. Since less neodymium than barium needs to be adsorbed to reduce the potential to the coagulation point, less hydrogen is displaced from the outer layer at the precipitation value of neodymium than of barium ion. The displacement of hydrogen by cations at the precipitation value approaches equivalence only in case the respective precipitation values are relatively close together.

For cations of the same valence, a definite sequence is shown in the flocculating power; thus the order is $K > Na > Li$, and $Ba > Sr > Ca$. Voet and Balkema (10) showed that when different ions of the same valence have the same concentration in the medium, the smaller ions have the smaller concentration in the double layer. As the magnitude of the contraction of the double layer depends on the concentration of the cations, it is evident that the larger ions have the greater effect and show therefore the greater decrease in the electrokinetic potential and the greater flocculating power.

SUMMARY

The following is a brief summary of the results of this investigation:

1. The adsorption of thorium, neodymium, aluminum, barium, strontium, and calcium during the coagulation of Raffo sulfur sols has been determined at the coagulation concentration and at higher concentrations. Contrary to the results of Bassett and Durrant, the adsorption values of the various cations are not equivalent at the respective precipitation concentrations.

2. At the precipitation concentration, the order of adsorption of the several cations expressed in milliequivalents per gram of sulfur is in inverse order to the precipitating power. However, if one compares the fraction of the precipitation value adsorbed, the adsorption is in the same order as the coagulating power.

3. The order of adsorption above the precipitation value is the same as that of the precipitating power: Th > Nd > Al > Ba > Sr > Ca.

4. The displacement of hydrogen ions during the stepwise addition of electrolytes to both Raffo and Selmi sols has been followed potentiometrically, using the glass electrode.

5. The hydrogen-ion displacement by the several cations is in the same order as the coagulating power.

6. Equivalent amounts of hydrogen ion are not displaced at the precipitation value of the several cations, as claimed by Bolam and Muir. The displacement approaches equivalence only when the precipitation values are of the same order of magnitude.

7. With cations of the same valence, the order of hydrogen-ion displacement as well as coagulating power is related to the size of the ions. At the same concentration, the largest ion produces the greatest displacement. Thus we find the order to be as follows: K > Na > Li, and Ba > Sr > Ca.

8. A mechanism has been proposed to account for the above-mentioned phenomena of adsorption and displacement of hydrogen ion which accompany the processes of potential reduction and coagulation.

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A STUDY OF THE DILATOMETRIC METHOD FOR FOLLOWING THE HYDROLYSIS OF SUCROSE

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INTRODUCTION

Dilatometers have been successfully used by Åkerlöf (1) and Brönsted (4), among others, in precise studies of the kinetics of catalyzed reactions. More recently, dilatometers have been applied by Sreenivasaya (15) and Rona (14) to the study of the hydrolysis of sucrose in the presence of invertase. These workers reported that the change in volume was proportional to the change in rotation, and that the total contraction accompanying the hydrolysis varied only with the amount of sucrose present, being 6 cc. per mole.

The figures averaged by Rona (14) to obtain this value showed considerable scattering, and were not obtained by direct observation of the total volume change from the beginning to end of the hydrolysis, but by calculation from the known changes in rotation and the proportionality between changes in volume and in rotation. Sreenivasaya (15) stated that he had confirmed Rona's figure by direct observation in a special dilatometer in which the reaction could be started as well as finished, but he gave no detailed data for his experiments with invertase. Since Riiber (13) had found that the mutarotation of glucose and fructose was accompanied by a small increase in volume, it seemed unlikely that the kinetics of the volume change could be exactly the same as that of the hydrolysis itself. This effect of mutarotation is avoided in the best polarimetric technique by the addition of alkali before the rotation is measured, but it does not seem possible to avoid it in a dilatometer. Yet, if the dilatometric method could be shown to be reliable, it would make possible the study of this important enzyme in a laboratory not provided with an expensive polarimeter.

The object of the present work, therefore, was to find out how well the dilatometric method would reproduce the known characteristics of invertase action, as well as those of the hydrolysis of sucrose under the influence of hydrochloric acid.

EXPERIMENTAL

Materials

Invertase was prepared from baker's yeast by the method of Nelson and Born (10), with the omission of the precipitations by alcohol and the treatment with kaolin. A very similar method has been included in those of the Association of Official Agricultural Chemists (2). The solution was dialyzed to a specific conductivity of about 10^{-6}. Its solid content was 0.95 per cent, and the dry matter contained 1.56 per cent of nitrogen. This solution was diluted to one-tenth of the above concentration with distilled water, and the invertase concentrations mentioned below refer to cubic centimeters of this diluted solution in 100 cc. of the reacting mixture.

The sucrose used was granulated table sugar, of a brand sold in sealed cartons. Its ash and moisture contents were found to be negligible, 0.0075 and 0.02 per cent, respectively. It was not further purified because one of us had previously found the specific rotation of other samples of the same brand to agree with the accepted value within 0.1 per cent.

The acidity of the sucrose-invertase solutions was regulated by acetate buffers prepared from standardized solutions of C.P. acetic acid and sodium hydroxide. The concentration of both acid and salt in each reaction mixture was 0.01 *M*. The acidity of the reaction mixtures was measured electrometrically at 25°C., using hydrogen electrodes with a saturated potassium chloride junction. The pH values are based on 0.1 *M* hydrochloric acid as standard, its pH being taken as 1.075. Hydrochloric acid solutions were prepared by diluting weighed amounts of the constant-boiling mixture, the concentrations being checked by weighing silver chloride.

Apparatus and method

The dilatometers were constructed of Pyrex glass and were like that depicted by Åkerlöf (1), without a water jacket around the capillary tube.[1] Two instruments were used, of such dimensions that the total change observed was always between 10 and 50 cm., in most cases about 25 cm. The larger dilatometer had a capacity of 182.6 cc., and a fall of 1 cm. in its tube corresponded to a contraction of 2.56 cu. mm. The corresponding figures for the smaller dilatometer were 92.8 cc. and 3.67 cu. mm. per centimeter. The height of the meniscus in the capillary was read to 0.01 cm. by means of a scale of millimeter paper and a hand lens. The temperature of the dilatometers was controlled by a well-stirred bath containing about 300 l. of water, maintained at 25° ± 0.003°C. During some of the experiments which were done in hot weather, it was necessary to cool the surface of the bath by an electric fan, but the regulation was just as good

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[1] The writers are indebted to Dr. G. Åkerlöf for several pieces of selected capillary tubing.

as in cooler weather. Each dilatometer was supported in a brass rack and immersed to a level a few millimeters above the base of the capillary tube.

Before each experiment the dilatometer was cleaned with chromic acid solution, washed with water and alcohol, and dried by a current of air. It was then kept in the bath at least fifteen minutes before being filled. In filling the dilatometer, solution was transferred from an Erlenmeyer flask in the bath through a delivery tube connected by a short piece of rubber tubing to the side arm of the dilatometer. The solution was driven over by air pressure applied above the surface of the liquid in the flask. Air bubbles were removed by alternately applying and releasing the pressure during the filling. When the meniscus had risen to the desired part of the capillary, the stopcock was tightly closed and readings were begun, without the introduction of a mercury column. Control experiments with water, or sugar solution without a catalyst, showed constancy of level only after eight or ten minutes, because of temperature changes during the passage of the solution through the delivery tube and side arm, which were not immersed in the bath. After this initial period the level in the control experiments remained constant within 0.02 cm. for many days, proving the absence of leakage and the adequacy of the temperature control.

In the enzyme experiments, the reaction was started by adding invertase solution from a volumetric pipet to a measured volume of buffered sugar solution. Each pipet was calibrated at 25°C., after part of its tip had been cut off to allow it to deliver completely within five to ten seconds. Complete mixing was assured by shaking within ten seconds of the start, which was taken as the time when half of the enzyme solution had left the pipet. Experiments with 0.1 *M* hydrochloric acid as catalyst were started in the same way. In the case of the more concentrated acid solutions, equal volumes of double strength acid and sugar solutions were brought to 25°C. in separate flasks, and mixed by pouring rapidly from one flask into the other and back again. Titrations of the acid solutions showed that when 2.0 *M* hydrochloric acid was mixed in this way with an equal volume of 20 per cent sugar, the acid concentration of the resulting solution was only 0.25 per cent greater than 1.0 *M*. In reporting the results, this slight deviation from simple proportionality on dilution has been neglected.

Final readings, after the completion of the hydrolysis, were constant (± 0.01 cm.) after one to three days in the invertase experiments. With 0.1 *M* hydrochloric acid, the level was constant from the sixth or seventh to at least the tenth or twelfth day. With 0.5 *M* acid, the level remained constant during the second day, but in some cases rose gradually after that. With 1.0 *M* acid, the level always passed through a minimum and then rose gradually, the minimum occurring after about ten hours with 10 per cent sugar and after about twenty-four hours with the more dilute solutions. Since this slow increase in volume was presumably due to some secondary action of the strong acid on invert sugar, the lowest observed value was taken as the final reading with respect to the hydrolysis.

Calculation of reaction velocities

Since the method used in these experiments does not give directly a value for the initial reading at the time of starting the reaction, the attempt was made to express the reaction velocity in such a way as to avoid the use of an initial reading. This could easily be done in the case of the experiments with acid, because it was found that the volume change followed the unimolecular law. The unimolecular velocity constant was calculated by the short interval formula,

$$k = \frac{1}{t_2 - t_1} \log \frac{R_1 - R_\infty}{R_2 - R_\infty} \qquad (1)$$

where t is time in minutes and R is the corresponding reading of the dilatometer, in centimeters measured upwards along the capillary from an arbitrary zero point. The velocity constants so calculated, from points corresponding to five or six equally spaced readings of volume, were fully as constant as those recorded by others in polarimetric experiments, and the average of four or five such values was taken as the best measure of the reaction velocity in each experiment. To obtain a value for the total volume change corresponding to complete hydrolysis, the average value of k from equation 1 was put into the unimolecular equation in the long interval form,

$$k = \frac{1}{t} \log \frac{R_0 - R_\infty}{R - R_\infty} \qquad (2)$$

which was solved for $R_0 - R_\infty$, the distance in centimeters corresponding to the total volume change. For comparison with the invertase experiments, the velocities were also expressed in terms of the half period, $t_{0.5}$, which is the time in minutes required for one-half of the total change in volume. These values were likewise obtained from the average values of k from equation 1, by the use of equation 2 in the form,

$$t_{0.5} = \frac{1}{k} \log 2 = \frac{0.3010}{k} \qquad (3)$$

In the case of the invertase experiments the problem was more difficult, because the course of the reaction does not follow any theoretical velocity equation. If the dilatometer readings are plotted against time, the curve obtained is concave upwards, the volume decreasing less and less rapidly as the reaction proceeds. During the first 10 or 20 per cent of the change the curve is practically a straight line, just as in polarimetric experiments. With the polarimeter, these linear initial velocities can be used as a reliable measure of the reaction velocity (7, 8, 9). With this dilatometric method, the points obtained during the first ten minutes could not be used. However, when the readings obtained after ten minutes were plotted against time on a large scale, they appeared to fall on straight lines for a considerable further interval. These lines were extrapolated back to zero time to give an initial reading, which was recorded as a minimum value, since, if the line is not really straight, it must be concave upwards.

When the logarithms of the experimental values of $R - R_\infty$ were plotted against time, curves were obtained which were concave downwards, at least up to about 90 per cent completion. This is an indication of the established fact that the unimolecular velocity coefficient increases with time in invertase experiments (8, 12). The curves could be extrapolated back to zero time by the use of a flexible spline, giving values of log $(R_0 - R_\infty)$. These values are likely to be too high, because in extrapolating a curve the tendency is to approach a straight line rather than to increase the curvature. Hence the two methods of extrapolation should give a minimum and a maximum value, respectively, for the total volume change in each experiment. These extrapolations were made from large scale plots of the data obtained in all of the invertase experiments, and the semi-logarithmic plot did, in fact, give somewhat higher values for the total change than the direct plot in twenty out of twenty-three cases. Since the two sets of values did not differ by more than 1.1 per cent in the extreme case, and their average difference was less than 0.5 per cent, it was considered that the average of the two extrapolated values would give a reliable value for the total volume change in each experiment.

These average values for the total change were used to obtain the half-period from the large scale semi-logarithmic plots. It was considered that the reciprocal of the half-period was a better measure of the reaction velocity than the apparent initial slope of the direct plot, since in obtaining the latter there was always uncertainty as to whether the points used were really on the straight part of the curve.

The half-period may be translated into a unimolecular velocity coefficient by the use of equation 3, but such coefficients are without theoretical significance in the case of invertase experiments because the reaction does not follow the unimolecular law.

RESULTS AND DISCUSSION

The results of the principal experiments are summarized in tables 1 and 2. Each figure is the mean of those obtained from concordant duplicate experiments.

Hydrolysis by acid

The data of table 1 indicate that for each concentration of sucrose the velocity constant increases with the acid concentration, but that the increase is more than proportional. This variation is exhibited in figure 1, in which the ratios of velocity constant to acid concentration are plotted as functions of the acid concentration. Each curve is marked with the initial sucrose concentration in grams per 100 cc. The points indicated as half-inked circles represent the polarimetric data of Lamble and Lewis (6) for 10 per cent sucrose solutions at 25°C. The agreement of their data with ours is a satisfactory indication that the two methods measure the velocity of the same reaction.

TABLE 1

Rate and extent of contraction in volume of sucrose-hydrochloric acid solutions at 25°C.

SUCROSE PER 100 CC. OF SOLUTION	HCl PER LITER OF SOLUTION	VELOCITY CONSTANT (BASE 10) × 1000	HALF-PERIOD	TOTAL CONTRACTION PER MOLE OF SUCROSE
grams	*moles*	*1000/minutes*	*minutes*	*cc.*
2	0.0972	0.325	926	6.77
2	0.486	1.95	154.4	6.63
2	0.972	4.95	60.8	6.44
5	0.0953	0.330	912	6.62
5	0.486	2.04	147.5	6.45
5	0.972	5.15	58.4	6.25
10*	0.0952	0.343	877	6.49
10	0.486	2.15	139.8	6.31
10	0.952	5.26	57.2	6.14

* Not done in duplicate.

TABLE 2

Rate and extent of contraction in volume of sucrose–invertase solutions at 25°C.

SUCROSE PER 100 CC. OF SOLUTION	INVERTASE PER 100 CC. OF SOLUTION	ACIDITY	HALF-PERIOD	TOTAL CONTRACTION PER MOLE OF SUCROSE
grams	*cc. of stock solution*	pH	*minutes*	*cc.*
2	0.4	4.67–4.70	344	6.82
2	1.0	4.67–4.70	138.7	6.85
2	2.0	4.67–4.70	68.7	6.91
5	1.0	4.67–4.70	296	6.67
5	2.5	4.67–4.70	117.1	6.70
5	5.0	4.67–4.70	58.5	6.76
10	2.0	4.67–4.70	316	6.52
10	5.0	4.67–4.70	125.2	6.58
10	10.0	4.67–4.70	62.8	6.59

Figure 2 shows the constancy of the unimolecular velocity coefficient throughout the course of the volume change in individual experiments. The abscissas represent the percentage of the total contraction occurring in the time t, and the ordinates are the values of $1000\,k$, calculated from the unimolecular law, equation 2. It is evident from figure 2 that there is no trend in the successive values of k, and that they are constant within 0.5 per cent or better.

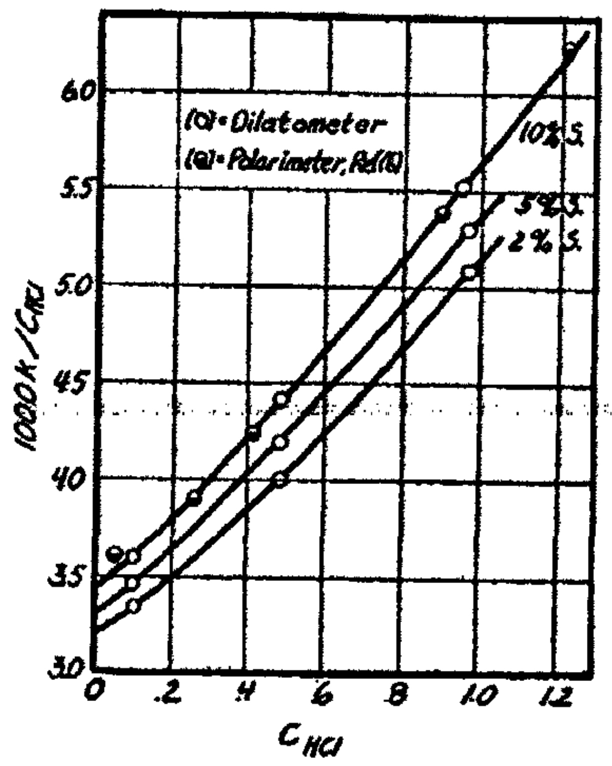

FIG. 1. EFFECT OF ACID CONCENTRATION ON THE RATE OF CONTRACTION OF SUCROSE-HYDROCHLORIC ACID SOLUTIONS

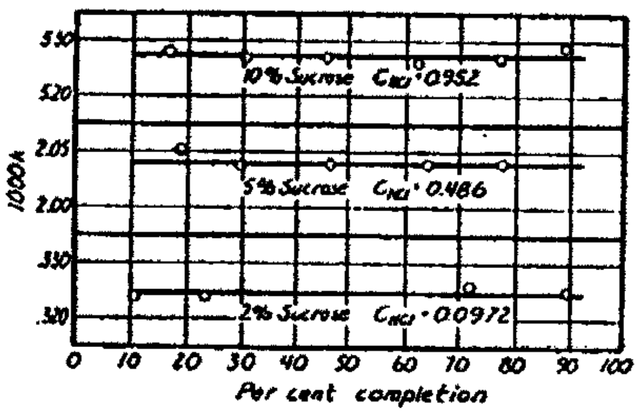

FIG. 2

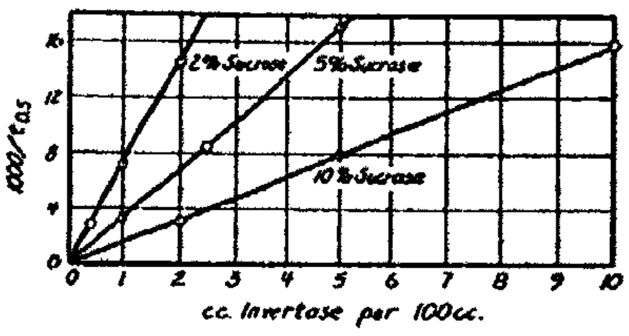

FIG. 3

FIG. 2. APPLICABILITY OF THE UNIMOLECULAR LAW TO THE KINETICS OF THE CONTRACTION OF SUCROSE-HYDROCHLORIC ACID SOLUTIONS

FIG. 3. EFFECT OF INVERTASE CONCENTRATION ON THE RATE OF CONTRACTION OF SUCROSE-INVERTASE SOLUTIONS

Hydrolysis by invertase

When the hydrolysis of sucrose is catalyzed by invertase, it has been found in polarimetric experiments that the reaction velocity is closely proportional to the concentration of the enzyme (7, 12, 11). The data in table 1 and figure 3 show that this simple relation is also true for the rate of the volume change, if the rate is taken as proportional to the reciprocal of the half-period. Such exact proportionality could not be obtained, however, by using the apparent initial slopes as a measure of the reaction velocity. On this basis the velocity of the faster reactions appeared to fall below the line of proportionality, which indicates that the slopes used were too small.

The effect of the initial sucrose concentration on the velocity of hydrolysis by invertase has usually been expressed by plotting the actual velocity, in degrees of change in rotation or amount of sucrose hydrolyzed in unit time, against the initial concentration. The curves so obtained show that the velocity at first increases rapidly with the concentration, but reaches a rather flat maximum at concentrations of about 5 to 10 g. of sucrose per 100 cc. (8, 12, 9). The data for each experiment in table 2 were translated into similar units by dividing the initial sucrose concentration by the product of the half-period and the invertase concentration, and then reduced to relative velocities by dividing by the maximum velocity. The effect of the initial sucrose concentration on the relative velocity is shown in figure 4, in which the full circles represent the dilatometric data and the half-inked circles represent the polarimetric experiments of Nelson and coworkers[2] (12, 9). Except for the point for 10 per cent sucrose, the dilatometric data agree with the polarimetric fully as well as the two sets of polarimetric data agree with each other.

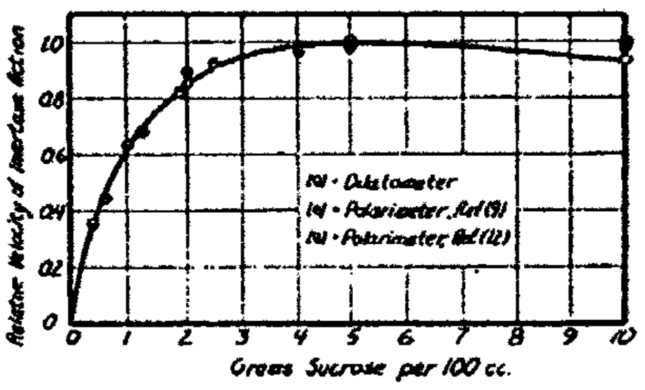

FIG. 4

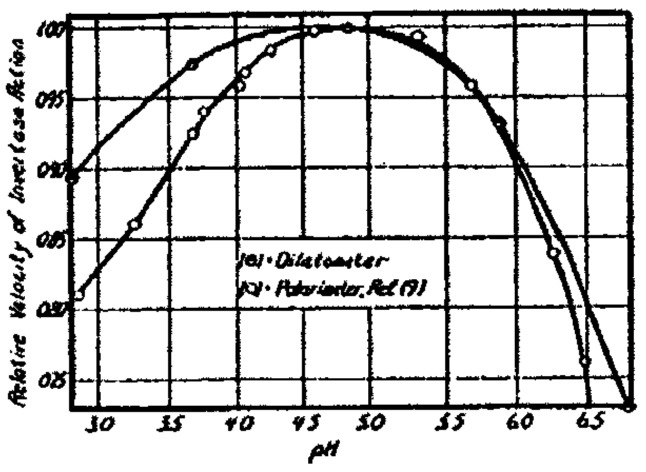

FIG. 5

FIG. 4. EFFECT OF INITIAL SUCROSE CONCENTRATION ON THE RELATIVE RATE OF CONTRACTION OF SUCROSE-INVERTASE SOLUTIONS

FIG. 5. EFFECT OF pH ON THE RELATIVE RATE OF CONTRACTION OF SUCROSE-INVERTASE SOLUTIONS

The effect of pH on the velocity of the volume change during the hydrol-

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[2] In Nelson and Bloomfield's table 1 (ref. 9, p. 1027), the third figure in the fourth column should be 0.985 instead of 0.085. In Nelson and Vosburgh's table 5 (ref. 12, p. 803), the last figure in the last column should be 0.0118 instead of 0.0085.

ysis by invertase was studied by additional experiments not shown in table 2. The pH was varied by the use of buffers of secondary sodium citrate and hydrochloric acid or sodium hydroxide, the total citrate concentration being 0.01 M in each reaction mixture. The sucrose concentration was 5 g. per 100 cc., and the invertase concentration was 5 cc. per 100 cc. The reaction velocities were expressed as reciprocals of the half-period, and reduced to relative velocities by dividing by the maximum velocity. Figure 5 shows the effect of pH on the relative velocity. Here the half-inked circles represent the dilatometric data, while the full circles represent polarimetric data of Nelson and Bloomfield (9). The two methods give the same optimum zone of pH values, about 4.5 to 5.0, but the velocities of the volume change appear to fall off less sharply with changes in acidity than those obtained by the polarimeter. This may be a real difference in the results of the two methods, or it may conceivably be due to peculiarities of the different invertase preparations. It is not due to the fact that Nelson and Bloomfield's experiments were done with 10 per cent sucrose solutions, for an additional set of dilatometric experiments with this concentration gave results very similar to those shown for the 5 per cent solutions.[3]

The kinetics of the volume change in the individual experiments were found to be like that of the chemical change, as determined by the polarimeter, in that the unimolecular velocity coefficients increased with time throughout the greater part of the reaction. It was possible also to reproduce with the dilatometer the peculiarity recently described by White (16), who found in polarimetric experiments with invertase that the unimolecular velocity coefficient passed through a maximum and decreased after the reaction was 90 to 96 per cent complete.

Several equations which have been proposed by various workers (5, 8, 11, 3, 16) to represent the kinetics of invertase action were applied to the dilatometric data, but none of them was found to give an accurate description of the whole course of the volume change. This was not surprising, for even if an equation did represent the true course of the hydrolysis, it would probably not fit the course of the volume change, because the latter includes the effect of mutarotation.

Variations in the total volume change

One unexpected result of the present investigation was that the total decrease in volume during the hydrolysis of a given amount of sucrose

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[3] Professor J. M. Nelson (private communication) writes that the difference between the two curves of figure 5 in the more acid region is to be expected, since Dr. E. L. Saul, working at Columbia University, has been able to vary this branch of the curve at will by dilution of certain invertase solutions or by adding extraneous material.

appeared to vary with the concentration of the catalyst. Moreover, the total volume change was not exactly proportional to the initial sucrose concentration. This is contrary to the conclusions of previous workers (15, 14). The last columns in tables 1 and 2 give the extent of the total decrease in volume observed from the beginning to the end of each reaction, expressed as cubic centimeters per mole of sucrose initially present. These data are plotted against the concentrations of catalyst in figure 6. It will be observed that the total change is practically a linear function of the concentration of the catalyst, and that it increases with the concentration of invertase, but decreases with the concentration of hydrochloric acid. This decrease may possibly be connected with the onset of the secondary reaction, which was inferred from the slow ultimate increase in volume observed in the experiments with 0.5 and 1.0 M acid. No explanation has been found for the less marked increase in the total change observed as the concentration of invertase was increased. The constancy of the end point in these experiments left nothing to be desired, and the extrapolated values for the initial readings are believed to be reliable, for the reasons already given. In polarimetric experiments, it has always been found that the total change in rotation is independent of the invertase concentration, and it is generally believed that the hydrolysis always proceeds to completion.

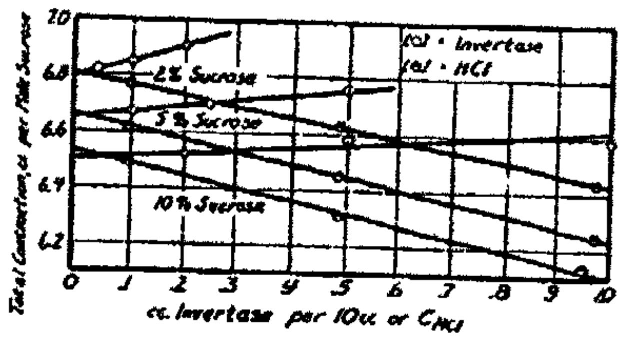

FIG. 6

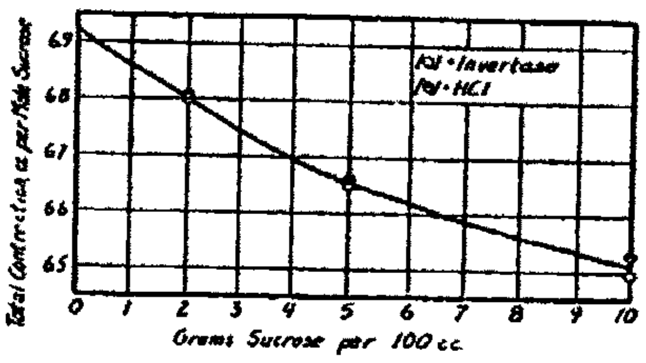

FIG. 7

FIG. 6. VARIATION OF THE TOTAL EXTENT OF CONTRACTION WITH THE CONCENTRATION OF THE CATALYST IN SUCROSE SOLUTIONS CONTAINING INVERTASE OR HYDROCHLORIC ACID

FIG. 7. VARIATION OF THE TOTAL CONTRACTION, EXTRAPOLATED TO ZERO CONCENTRATION OF CATALYST, WITH THE INITIAL SUCROSE CONCENTRATION

The trend of the points plotted in figure 6, however, lends support to a belief in the reality of the variation of the total volume change, because for each sugar concentration the line for acid hydrolysis and that for invertase hydrolysis give nearly the same extrapolated value for the total volume change per mole of sucrose at zero concentration of catalyst. Moreover, these extrapolated values show a regular trend with changes in the initial sucrose concentration, as shown in figure 7. This figure indicates that the volume change accompanying the complete hydrolysis of 1 mole of sucrose in an infinitely dilute solution, with an infinitely small concentration of catalyst, would be about 6.92 cc. This value should correspond to the difference in volume, under these ideal limiting conditions, between 1 mole of sucrose plus 1 mole of water, and 1 mole each of glucose and fructose, after complete mutarotation, at 25°C.

This figure for the volume change at infinite dilution is supported by the following calculations. Riiber (13) found the apparent molar volume of equilibrium glucose at infinite dilution to be 111.06 cc. at 20°C., and that of fructose to be 110.03 cc. The corresponding figure for sucrose has been determined from the density data, also for 20°C., given in the International Critical Tables. A plot of the apparent molar volumes against concentration showed considerable curvature at concentrations below 5 per cent, with a point of inflection at about 1.5 per cent. If the curve is extrapolated from the points for 5 to 25 per cent sucrose, the molar volume at infinite dilution appears to be 210.2 cc., while if the curve is drawn through points for concentrations as low as 0.5 per cent, it appears to be 209.8 cc. Hence this figure may be taken as 210.0 ± 0.2 cc. Since 1 mole of water at 20°C. occupies 18.05 cc., the contraction on the complete hydrolysis of 1 mole of sucrose at 20°C. and at infinite dilution is calculated to be 210.0 (±0.2) + 18.05 − 111.06 − 110.03, or 6.96 ± 0.2 cc. This agrees much better with the figure found in the present investigation, 6.92 cc. for 25°C., than does the earlier figure of 6.0 cc. for 30°C., reported by Rona (14) and by Sreenivasaya (15). It should be added that the latter authors did not extrapolate to infinite dilution, as they found no definite change of the contraction per mole with changes in concentration.

SUMMARY AND CONCLUSIONS

The rate and extent of the contraction in volume accompanying the hydrolysis of sucrose in solutions containing yeast invertase or hydrochloric acid were measured in dilatometers at 25°C. The volume change in the sucrose-hydrochloric acid solutions was strictly unimolecular, and the velocity constants agreed with those obtained polarimetrically by others. The rate of the volume change in sucrose-invertase solutions, as measured by the reciprocal of the half-period, was directly proportional to the concentration of invertase. The characteristic effects of sucrose concentration and pH on the velocity of invertase action were approximately the same in the dilatometric experiments as in the polarimetric experiments of earlier workers.

The total contraction per mole of sucrose, when the hydrolysis was allowed to go to completion, varied regularly with the concentrations of catalyst and of sucrose, the extreme values observed being about 6.1 and 6.9 cc. From an extrapolation of these values, it was inferred that the complete hydrolysis of 1 mole of sucrose at infinite dilution, to form glucose and fructose in mutarotation equilibrium, would be accompanied by a decrease in volume of about 6.92 cc. at 25°C.

It is concluded that the dilatometric method may be used with confidence in place of the polarimetric method in studying the hydrolysis of sucrose in acid solutions, and that it may also be used in studying invertase action to get a measure of the activity, under optimum conditions, of preparations of yeast invertase.

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THE JOULE-THOMSON EFFECT OF METHANE, NITROGEN, AND MIXTURES OF THESE GASES

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INTRODUCTION

The experimental difficulties of measuring Joule-Thomson coefficients are great and, until fairly recently, too few thermodynamic data (*P-V-T* and specific heat) of mixtures of gases were available to calculate these coefficients. Although such calculations are tedious, there is little doubt but that the results obtained are certainly as accurate as engineering calculations of design require, and, in many cases, the accuracy of such calculations compares favorably with that of experimentally measured values.

It is the purpose of this paper to present the results of some calculations of the Joule-Thomson coefficients of methane, nitrogen, and mixtures of these gases. The calculations were made originally because of the small amount of actual experimental data available in this field. For the same reason the method will become increasingly important as the liquefaction of gases plays a continually greater rôle in industry. This is particularly true because of the large number of gases to which it may be applied.

THEORETICAL

It is well known that the Joule-Thomson effect, or any other thermodynamic property of a substance, can be readily evaluated if, first, an accurate equation of state representing the pressure-volume-temperature data of the substance is available, and second, if the variation of a pertinent thermal property with temperature is known.

Probably the most accurate and widely applicable equation of state proposed to date is that of Beattie and Bridgeman (3), which reproduces the experimental data of fourteen gases to within 0.1 to 0.2 per cent over a wide range of temperature and pressure. This equation is:

$$P = \frac{RT\,(1 - \epsilon)}{V^2}\,(V + B) - \frac{A}{V^2}$$

where $A = A_0\left(1 - \frac{a}{v}\right)$, $B = B_0\left(1 - \frac{b}{v}\right)$, $\epsilon = \frac{c}{vT^3}$, and A_0, a, B_0, b, and c

are constants specific for each gas, V is volume, P is the pressure, T is the temperature, and R is the gas constant.

In this equation, as in the rest of this paper, the units used are: volume in liters per mole, pressure in atmospheres, and temperature in degrees Kelvin.

Bridgeman (6) utilized this equation of state in deriving an expression for the Joule–Thomson effect based on the thermodynamic relationship

$$\mu C_p = \left(\frac{\partial v}{\partial T}\right)_p - V$$

As a check of this equation he calculated the values for air, and showed that the agreement with the observed values was excellent.

However, this equation was unwieldy and calculations with it were tedious. This led Beattie (2) to attempt several approximations which simplified considerably the final equation without impairing appreciably the accuracy, as was proved by recalculating the values of μ for air.

This latter equation is that used in this paper, since it was sufficiently accurate and was much more convenient to use. The equation is:

$$\mu C_p = \left(-B_0 + \frac{2A_0}{RT} + \frac{4c}{T^3}\right) - \left(\frac{2B_0 b}{RT} - \frac{3A_0 a}{R^2T^2} + \frac{5B_0 c}{RT^4}\right)P$$

where μ is the Joule-Thomson coefficient, C_p is the specific heat at constant pressure, and A_0, a, B_0, b, c, R, T, and P are as in the Beattie–Bridgeman equation of state.

CALCULATIONS

The constants A_0, a, B_0, b, and c were calculated for methane and nitrogen by Beattie and Bridgeman and presented in one of their original articles (4). A method of obtaining these constants for mixtures of gases from the constants for the pure gases has been evolved by Beattie (1) and Beattie and Ikehara (5). This is quite simple and merely involves the linear combination of the a's, b's, c's, and B_0's, and squaring the linear combination of the square root of the A_0's.

The constants calculated in this way are as given in table 1.

The constants for the pure gases are those used by Beattie (1) when he showed that the above method of combining constants held for the nitrogen–methane mixtures. Beattie and Bridgeman had also proposed another set of values for nitrogen. Several calculations showed that either set would have been sufficiently exact for the present purpose.

The equation of state for methane reproduced the observed pressures with an average difference of 0.05 per cent over a range of 0 to 200°C. and up to 243 atmospheres. That for nitrogen gave an average deviation of 0.04 per cent in the same temperature range and up to 213 atmospheres.

The sole remaining requirement for the calculation of the Joule–Thomson coefficients is a knowledge of the value of C_p for the pure gases and for the mixture of gases.

Eastman (7) has collected the specific heat data for a number of gases and formulated empirical equations of the form,

$$C_p = \alpha + \beta T + \gamma T^2 + \ldots.$$

to reproduce these data. For methane and nitrogen they are as follows: for methane, $C_p = 5.90 + 0.0096T$; for nitrogen, $C_p = 6.76 + 0.000606T + 0.00000013T^2$. The equation for methane is accurate to only about 5 per cent in the range 150 to 400°K.; and that for nitrogen to about 1.5 per cent in the range 300 to 2500°K.

TABLE 1

Constants calculated for mixtures of methane and nitrogen

Mole per cent CH_4 ……… Mole per cent N_2.	100 0	75 25	50 50	25 75	0 100
A …………	2.2769	1.9575	1.6622	1.3910	1.1440
a …………	0.01855	0.01838	0.01822	0.01805	0.01788
B …………	0.05587	0.05269	0.04951	0.04633	0.04314
b …………	−0.01587	0.01592	0.01598	0.01603	0.01608
c …………	12.8×10^4	11.02×10^4	9.22×10^4	7.41×10^4	5.60×10^4
R …………	0.08206	0.08206	0.08206	0.08206	0.08206

C_p, calculated by these equations, is expressed in calories per mole. The factor, 0.0413 liter-atmospheres per calorie, was used to express C_p in liter-atmospheres. The final equations are then:

$$\text{Methane: } C_p = 0.244 + 0.000396T$$
$$\text{Nitrogen: } C_p = 0.279 + 0.0000250T + 0.0000000054T^2$$

By means of linear combination of the coefficients in these equations similar equations for the gas mixtures can easily be obtained.

The calculation of the Joule–Thomson coefficients at atmospheric pressure then becomes relatively simple. However, to calculate the coefficients at other pressures it is necessary to evaluate C_p at these pressures. This can be done by means of another equation derived by Beattie (1a) from thermodynamic relations and the Beattie–Bridgeman equation of state. This equation is:

$$C_p = C_p^* + \left[\frac{2A_0}{RT^2} + \frac{12c}{T^4}\right]P$$

where C_p is the specific heat at absolute temperature T and at pressure P, A_0, c, and R are as in the Beattie–Bridgeman equation of state, and C_p^* is a constant for the given temperature.

C_p^* must be calculated for each temperature at which it is desired to evaluate C_p. This is easily done, since C_p can be calculated from the usual equations at 1 atmosphere, after which substitution will permit solving for C_p^*. With C_p^* known for a certain temperature, C_p can be evaluated for any pressure at this temperature. This same method applies to gas mixtures if the constants for the Beattie–Bridgeman equation of state and the C_p equations are known.

These calculations of the Joule–Thomson coefficients can be systematized so that the process is not so long and tedious as it would at first appear to be.

DISCUSSION OF RESULTS

The results with the pure gases and the three mixtures are given in table 2. The lower temperatures are outside the range for which the original equations were derived, but it is believed that because of the excellent agreement between the observed and the calculated P–V–T data in the given range the extrapolation does not introduce serious error when taking into account the accuracy of the calculations as a whole.

The original calculations were made principally for engineering purposes, so that the accuracy of the calculated values did not have to be of an extremely high order. The accuracy in the calculations was limited by the accuracy of the available specific heat equations, which, in the case of methane, was not very great.

Pure gases

For the purpose of comparison, the few available data on the Joule–Thomson effect for methane and nitrogen are given below. The agreement between the observed and calculated data for methane is quite good, but that for nitrogen is very poor. Inasmuch as the equation of state for nitrogen fitted the P–V–T data so well and gave such good results in the calculations of the equations of state of mixtures, it is believed that the older observed data are probably at fault. Because of the difficulty of the experimental determinations of Joule–Thomson coefficients this is not surprising.

Gas mixtures

An examination of the equations for the Joule–Thomson coefficients will reveal the fact that with the given method of combining constants the coefficients for gas mixtures should be obtainable for most purposes by a linear combination of the coefficients of the pure gases. An examination of table 2 will indicate that this is true within the accuracy of the calculations.

USE OF FIGURES 1 AND 2

The isotherms for the pure gases are given in figures 1 and 2. To estimate the Joule–Thomson coefficients for any mixture, it is only necessary

TABLE 2

Joule-Thomson coefficients of nitrogen-methane mixtures

PRESSURE IN ATMOSPHERES	JOULE-THOMSON COEFFICIENTS				
	200°K.	250°K.	300°K.	350°K.	400°K.
	(a) 100 per cent CH_4				
1	0.88	0.58	0.41	0.30	0.23
5	0.85	0.57	0.40	0.30	0.22
25	0.73	0.51	0.37	0.28	0.21
50	0.62	0.46	0.34	0.26	0.20
100	0.46	0.37	0.28	0.22	0.17
	(b) 75 per cent CH_4 and 25 per cent N_2				
1	0.77	0.50	0.36	0.26	0.20
5	0.74	0.49	0.35	0.26	0.19
25	0.65	0.45	0.33	0.24	0.18
50	0.55	0.40	0.30	0.22	0.17
100	0.41	0.34	0.25	0.19	0.15
	(c) 50 per cent CH_4 and 50 per cent N_2				
1	0.65	0.43	0.31	0.22	0.17
5	0.64	0.42	0.30	0.22	0.16
25	0.56	0.39	0.26	0.21	0.15
50	0.48	0.35	0.26	0.19	0.14
100	0.37	0.28	0.21	0.16	0.12
	(d) 25 per cent CH_4 and 75 per cent N_2				
1	0.54	0.36	0.25	0.18	0.14
5	0.53	0.35	0.25	0.18	0.13
25	0.47	0.33	0.23	0.17	0.13
50	0.41	0.29	0.21	0.16	0.11
100	0.32	0.24	0.17	0.13	0.09
	(e) 100 per cent N_2				
1	0.44	0.29	0.20	0.15	0.10
5	0.43	0.28	0.20	0.14	0.10
25	0.38	0.26	0.18	0.13	0.09
50	0.33	0.23	0.17	0.12	0.08
100	0.26	0.19	0.14	0.10	0.07

Joule-Thomson effect data from International Critical Tables, Vol. V, pp. 144–6

For CH_4, $\mu = t_1 - t_0/p - 1$ in °C. per atmosphere ± ca. 0.05

p	25	17	14.6	27	55
t_1 in °C.	−77	−78	−78	−10	10
μ	0.75	0.75	0.74	0.35	0.40

For N_2, μ in °C. per atmosphere

°C.	0	20	40	60	80	100
μ	0.333	0.291	0.250	0.215	0.187	0.159

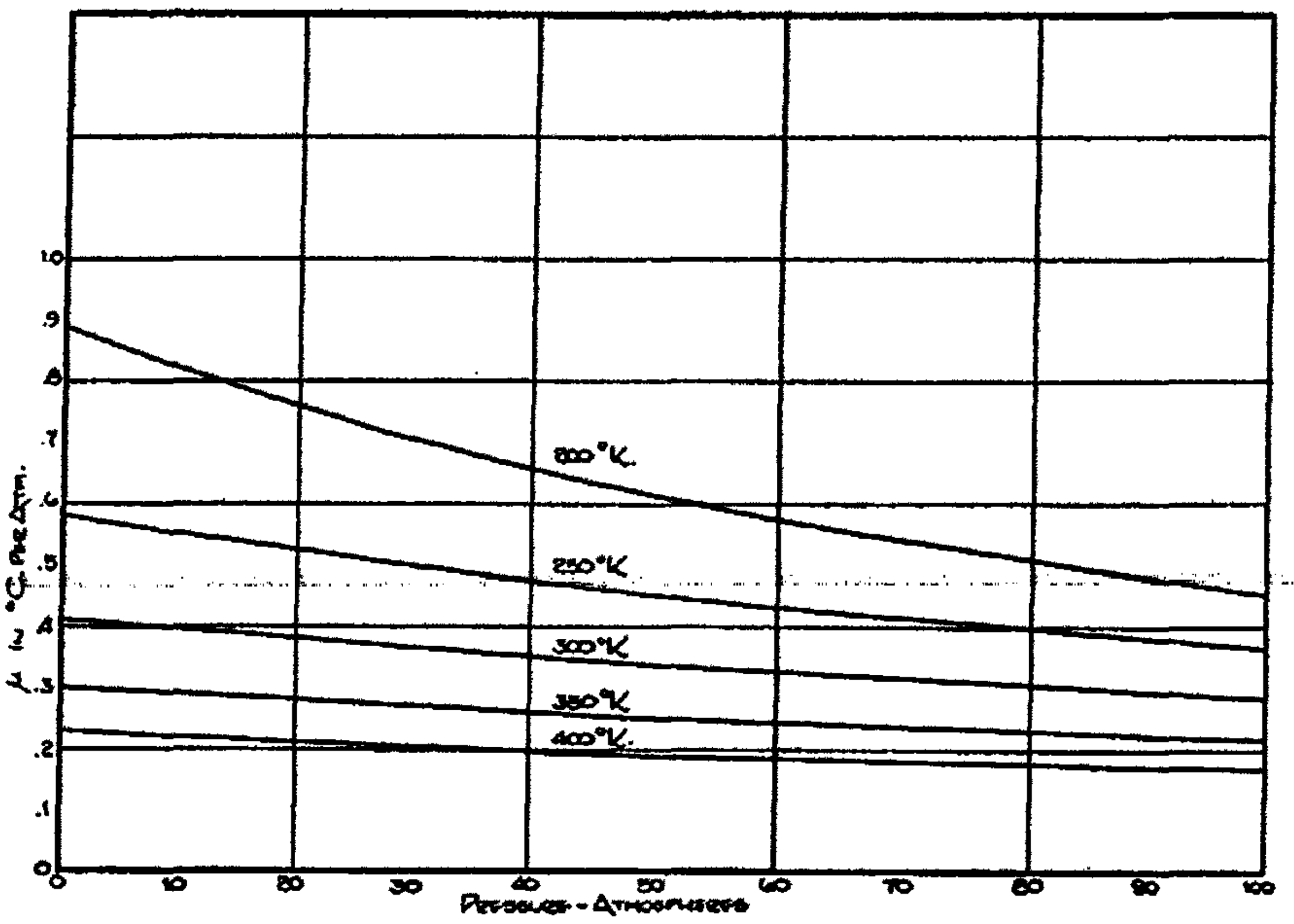

FIG. 1. THE JOULE-THOMSON EFFECT FOR METHANE

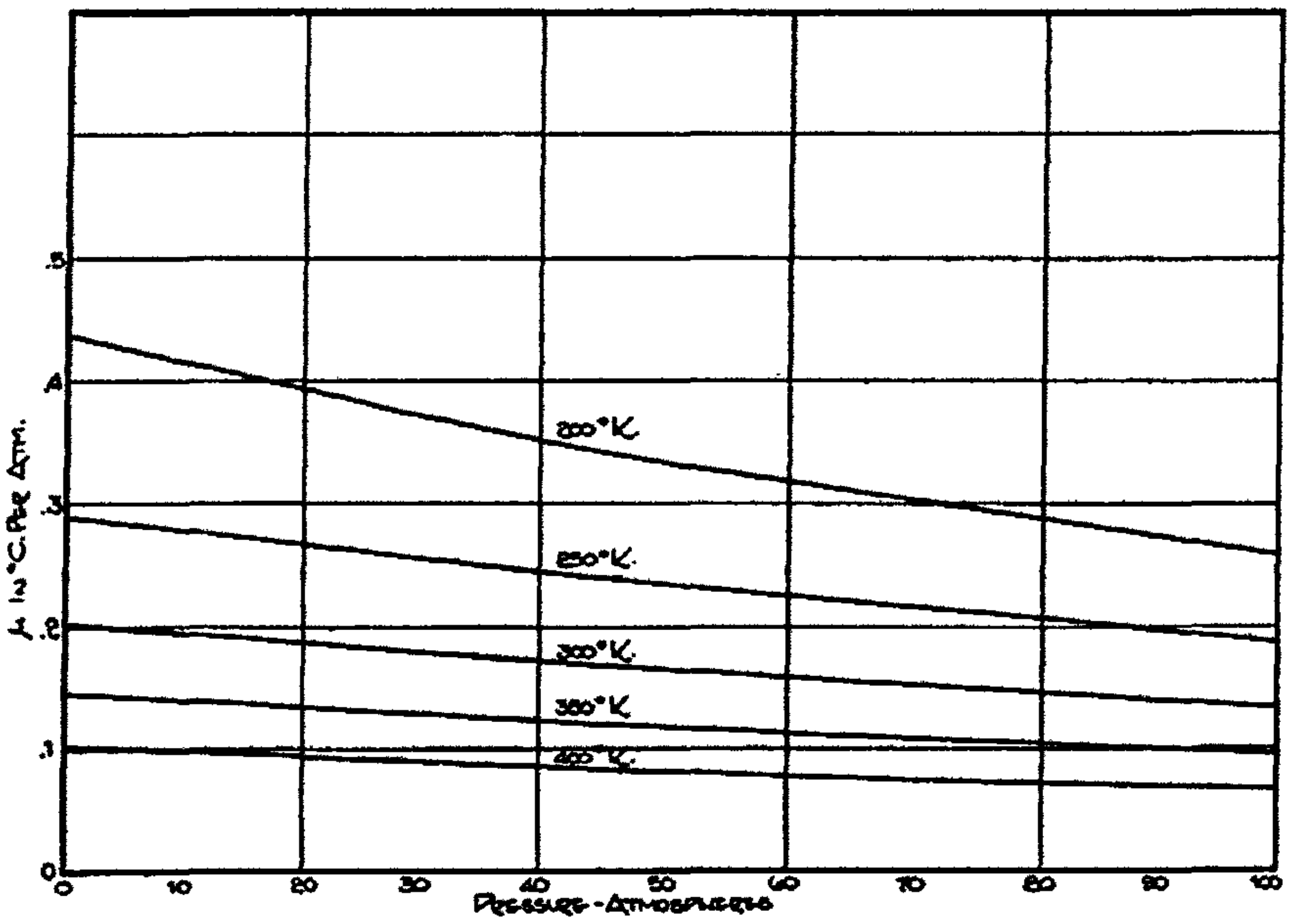

FIG. 2. THE JOULE-THOMSON EFFECT FOR NITROGEN

to combine linearly the values for the pure gases as obtained from these curves. Since μ is the change of temperature with pressure, a positive sign indicates that a decrease in pressure will be accompanied by a decrease in temperature.

CONCLUSIONS

The Joule–Thomson coefficients of methane and nitrogen have been calculated at the temperatures 200, 250, 300, 350, and 400°K. and pressures of 1, 5, 25, 50, and 100 atmospheres, using the Beattie-Bridgeman equation of state. A method of obtaining the coefficients for mixtures of these gases from those of pure gases has been indicated, and data for three mixtures of these gases have been calculated and tabulated.

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THE COMPARATIVE ACTION OF MIXED CATALYSTS WHEN USED FOR THE JOINT DEHYDRATION OF ETHYL ALCOHOL AND AMMONIA. I

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Sabatier and Mailhe (8) were the first to indicate the possibility of obtaining alkylamines by the interaction of alcohol and ammonia in the presence of such dehydrating catalysts as thoria or alumina. Subsequently, many investigators studied quantitatively the process of the catalytic alkylation of ammonia.

Eug. and Kaz. Smolensky (9) passed ammonia gas and vapors of ethyl alcohol over alumina at temperatures of 330–350°C. and obtained a mixture of three amines with a yield of 53 per cent, based on the ethyl alcohol that had entered the reaction, and, as by-products, ethyl ether and ethylene. When the molecular ratio $NH_3:C_2H_5OH$ was 1:2, the mixture consisted of 15 per cent of mono-, 70 per cent of di-, and 15 per cent of trimethylamine.

Brown and Reid (3) studied the joint catalytic dehydration of ammonia and methyl, ethyl, *n*-propyl, and *n*-butyl alcohols. These authors tried not only individual catalysts, such as blue tungsten oxide and silica gel, but also mixed catalysts, such as the following: alumina on pumice, mixtures of silica gel and nickel oxide, cerium oxide on pumice, and mixtures of silica gel and thorium oxide. The best catalyst among those mentioned above proved to be a silica gel prepared in a special way. At 465°C., with this catalyst, 39.5 per cent of ethyl alcohol was converted into a mixture of amines in the ratio 2:5:3.

Dorrell (4) studied the influence of temperature, contact time, and ratio of ethyl alcohol to ammonia in the presence of alumina. The best yield was obtained at 344°C. In runs where a relatively large amount of alcohol was taken, there was an increase in the yield of the secondary amine. A decrease in the velocity of the initial products (an increase of the contact time) led to a decomposition of the amines into ammonia and ethylene.

A similar investigation was carried out with methyl alcohol by Briner and Gandillon (2). The authors studied the catalytic activity of alumina, thoria, silica gel, kaolin, and blue tungsten oxide. The catalysts are reported in the order of their decreasing activity in the reaction of the methylation of ammonia. In the presence of alumina at 405°C., with a volume ratio $NH_3:CH_3OH = 2.25:1$, a mixture of amines was obtained with a yield of 52.7 per cent. The content of the different amines in the mixture was as follows: methylamine, 43 per cent; dimethylamine, 36 per cent; and trimethylamine, 31 per cent. A decrease in the contact time led to an increased yield of the primary amine and to the decomposition of the secondary and tertiary compounds.

All the authors quoted above have investigated only the action of individual catalysts. Only in a few separate runs by Brown and Reid (3) have mixed catalysts been tried. The most effective one proved to be a mixture of silica gel and thoria. Up to now there have been no investigations dealing with the comparative action of mixed catalysts in the alkylation reaction of ammonia by means of alcohols.

The present investigation had for its purpose the study of the dehydrating action of mixtures, consisting of alumina and of iron, chromium, tin, and zinc oxides, and the comparison of the activity of these mixtures with that of pure alumina, which has proved to be, according to former investigations, a highly active catalyst for the dehydration of the system alcohol–ammonia.

It seemed interesting also to find out how catalysts consisting of alumina and of tin or zinc oxide would behave in this case, taking into consideration that the latter two substances in a pure state are catalysts of complex action, with a considerable predominance of dehydrogenating over dehydrating properties.

In the present paper, the following catalysts were investigated:[1] (1) alumina; (2) Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent); (3) Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent); (4) Al_2O_3 (90 per cent) + SnO (10 per cent); (5) Al_2O_3 (90 per cent) + ZnO (10 per cent).

In our former investigation, dealing with the hydration of diethyl ether under pressure (1), mixtures of zinc and iron oxides with alumina proved to be more active than pure alumina.

EXPERIMENTAL PART

A. Preparation of catalysts

Aluminum hydroxide and the mixture consisting of aluminum hydroxide (90 per cent) and iron hydroxide (10 per cent) were prepared as described in a previous paper dealing with the hydrolysis of diethyl ether (1). The catalyst, consisting of Al_2O_3 (80 per cent) and Cr_2O_3 (20 per cent), was prepared by precipitating a solution containing 750.3 g. of $Al(NO_3)_3 \cdot 9H_2O$

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[1] All the oxides used were hydrated oxides.

and 134.2 g. of $Cr(NO_3)_3 \cdot 9H_2O$ with a 25 per cent solution of ammonium hydroxide, the mixture being vigorously stirred all the time.

The catalyst containing Al_2O_3 (90 per cent) and SnO (10 per cent) was prepared as follows: To a solution of 664.4 g. of $Al_2(SO_4)_3 \cdot 18H_2O$ and 18.1 g. of $SnSO_4$, sodium hydroxide was added with stirring until the dissolution of the hydroxides that appeared at first. Then sulfuric acid was added until the disappearance of the alkaline reaction to litmus.

In order to obtain the catalyst consisting of Al_2O_3 (90 per cent) and ZnO (10 per cent), two separate solutions were prepared, one containing 750.3 g. of $Al(NO_3)_3 \cdot 9H_2O$, and the other 41.4 g. of $Zn(NO_3)_2 \cdot 6H_2O$. These two solutions were added separately to a concentrated solution of sodium hydroxide until the precipitates completely disappeared. The aluminate and zincate solutions were then mixed together and nitric acid added to the mixture until the alkaline reaction to litmus disappeared.

In the preparation of all of these catalysts, the precipitates were carefully washed with hot water until a negative test for the corresponding anion was obtained, then they were dried at 150°C. and fragments of the size of an average pea were used.

B. Experiments on joint dehydration of ammonia and ethyl alcohol

These experiments were carried out at temperatures of 300, 330, 360, and 400°C. The apparatus consisted of a glass reaction tube, having a diameter of 15 mm., and placed in an electric furnace. The catalyst, dried at 150°C., was packed in a 30-cm. section of the tube.

The alcohol was added from a graduated buret, and the ammonia (Schering-Kahlbaum) was taken from a bomb and passed first through a flask filled with lumps of sodium hydroxide for drying purposes. The rate at which the ammonia was added was measured by a flowmeter filled with alcohol. In different runs this rate varied from 55 to 60 cc. per minute. The alcohol was added in all runs at a rate of 1.6 cc. per 10 minutes. Twenty cubic centimeters of alcohol was passed over the catalyst in each run. The molecular ratio $NH_3:C_2H_5OH$ was about equal to 1.

The condensate was collected in three consecutive receivers. The last two were provided with coils and placed in a cooling mixture. The gases, after passing the last receiver, were collected in a graduated gasometer over water, where their volume could be measured with a precision up to 5 cc. The largest amount of condensate was collected in the first receiver.

Products obtained in the experiments with the catalysts $Al_2O_3 + Cr_2O_3$ and $Al_2O_3 + ZnO$ at 360 and 400°C., had a characteristic odor of pyridine bases. Probably in the above experiments there was a side reaction consisting in the dehydrogenation of alcohol with the formation of the corresponding aldehyde, and this aldehyde condensed with ammonia giving α- or β-picolines. These products were obtained under similar conditions by Tschitschibabin (10).

C. *The analysis of reaction products*

The analysis of the reaction products was effected by using a modification of the methods of François (6) and Erdmann (5). All the condensate was neutralized with dilute (1:1) hydrochloric acid under cooling. The condensate from those receivers that had been cooled during the experiment was distilled into a flask containing dilute acid (figure 1), first by heating each receiver with the hand and then by heating on a warm water bath. The liquid that did not distil under these conditions was neutralized in the receiver.

The solution of amine hydrochloride was placed in a citrate bottle of 400-cc. capacity, and a mixture consisting of equal volumes of a saturated soda solution and a 20 per cent sodium hydroxide solution was added in excess. Then 70 g. of ground yellow mercuric oxide was also added to the mixture. The mixture was shaken on a mechanical shaker for one hour and then was left standing for twenty hours. The solution was filtered from the precipitate and the latter was washed three times with small quantities of water.

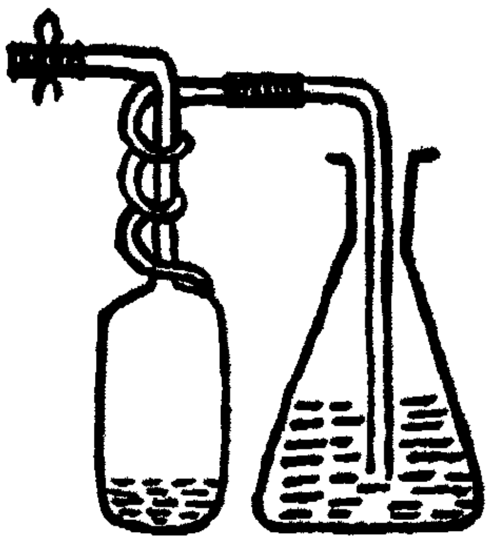


Fig. 1

The mixture of amines was distilled and collected in a 0.2 *N* hydrochloric acid solution; the excess of acid was titrated with a 0.1 *N* sodium hydroxide solution in the presence of methyl red.

In all experiments only the total amine content was determined. The catalyst was heated before the experiment to 400°C. until the elimination of water ceased, and then before every experiment ammonia was passed over the catalyst for thirty to forty minutes.

DISCUSSION OF RESULTS

The results of our experiments on the joint catalytic dehydration of ethyl alcohol and ammonia are reported in table 1. The catalysts are given in the first column in the order of their decreasing activities for this process at 400°C. In the second column the temperature of the experiments is reported. In the third the yields of the amines, expressed in cubic centimeters of a 0.1 *N* hydrochloric acid solution that was used for the neutralization of these amines. In the fourth column the decomposition of the alcohol is expressed in percentage calculated on the basis of the gas collected in the gasometer.

TABLE 1

Catalytic dehydration of ethyl alcohol and ammonia

CATALYST	TEMPERATURE OF THE EXPERIMENT	AMOUNT OF 0.1 *N* HCl USED FOR THE NEUTRALIZATION OF THE AMINES	ALCOHOL DECOMPOSED
	°C.	*cc.*	*per cent*
Al_2O_3	300	516.7	8.9
	330	520.9	12.6
	360	570.3	15.9
	400	727.7	23.5
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent)	300	82.0	1.8
	330	215.5	2.6
	360	579.0	3.9
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent)	400	725.8	12.5
Al_2O_3 (90 per cent) + ZnO (10 per cent)	300	90.3	2.0
	330	96.0	4.3
	360	247.4	9.6
	400	319.2	27.1
Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent)	300	219.2	4.0
	330	287.7	12.3
	360	275.9	46.6
	400	195.4	70.2
Al_2O_3 (90 per cent) + SnO (10 per cent)	300	283.7	1.5
	330	300.9	4.0
	360	408.6	11.6
	400	141.6	41.1

From table 1 we may see that the mixed catalysts used by us, if compared with pure alumina, do not seem to accelerate the reaction of ethylation of ammonia with ethyl alcohol. The only exception is the mixture $Al_2O_3 + Fe_2O_3$, which at 360°C. as well as at 400°C. gives practically the same yield as pure alumina. Besides, it is necessary to note the small activity of this catalyst in the decomposition of alcohol. This fact distinguishes it in the process from all other catalysts.

In the case of pure alumina and a mixture of the latter with ferric oxide and zinc oxide, the yield of amines in the interval between 300 and 400°C. increases with the rise of temperature, whereas in the case of the catalyst $Al_2O_3 + SnO$ a maximum yield was obtained at 360°C., and in the case of $Al_2O_3 + Cr_2O_3$ at 330°C. The latter catalyst showed at 360 and 400°C. an extremely high activity in the direction of alcohol decomposition, and a small activity in the ethylation of ammonia.

The catalysts can be arranged as follows in order of their decreasing activity in the reaction of the decomposition of alcohol at 400°C.: $Al_2O_3 + Cr_2O_3$; $Al_2O_3 + SnO$; $Al_2O_3 + ZnO$; Al_2O_3; $Al_2O_3 + Fe_2O_3$.

As we should have expected, the percentage of alcohol decomposition increases with the rise of temperature. In the case of alumina this increase is almost a linear function.

According to Sabatier (8; cf. ref. 7), if we have pure alumina or pure chromium oxide and pass over them ethyl alcohol and ammonia, these catalysts will decompose ethyl alcohol only slightly with the formation of ethylene and water, because the chief reaction would be the formation of an amine. But when in our case we added to alumina 20 per cent of chromium oxide, the chief reaction was already the decomposition of the alcohol (at 360°C., 46.6 per cent; at 400°C., 70.2 per cent).

Likewise, a catalyst consisting of alumina and 10 per cent of tin suboxide decreases the rate of the reaction of ethylation of ammonia fivefold at 400°C., and increases the decomposition rate of the alcohol nearly twice.

Alumina to which 10 per cent of zinc oxide has been added lowers considerably the rate of both possible processes,—the ethylation of ammonia as well as the decomposition of the alcohol—particularly in the interval 300–330°C.

The catalyst consisting of alumina to which 10 per cent of iron oxide has been added influences the reaction of the ethylation of ammonia in the 360–400°C. range, in the same way as pure alumina, considerably decreasing the process of alcohol decomposition (at 360°C., four times; at 400°C., nearly twice).

The catalytic action of these mixed catalysts shows that their properties are different from the properties of oxides of which these mixtures are made, and also that apparently they can even change the direction of the reaction.

The results thus obtained are of interest from still another point of view.

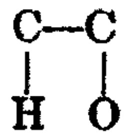
In a previous paper[2] it was shown that a great number of reactions could be expressed by means of structural matrices:

$$\Phi_3 = \begin{Vmatrix} \varphi_{11} & \varphi_{12} & \varphi_{13} \\ \varphi_{21} & \varphi_{22} & \varphi_{23} \\ \varphi_{31} & \varphi_{32} & \varphi_{33} \end{Vmatrix}$$

where φ_{11}, φ_{31}, φ_{33}, and φ_{13} correspond to atoms in the molecule that come in contact with the catalyst, φ_{12}, φ_{21}, φ_{32}, and φ_{23} correspond to bonds, and $\varphi_{22} = 0$.

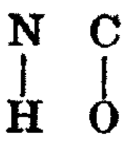
In a study of catalysis, one of the chief problems is to find a relation between these matrices (indexes) and the nature of the catalyst.

Such a relation may really be observed, but it has been but very poorly traced in the case of a systematic change of separate elements. In our case we can select the following elements for comparison. These elements are separate members of the complete system that was found previously:



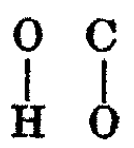
$$\begin{array}{cc} C\!-\!C \\ | \quad | \\ H \quad O \end{array}$$

II K^2_{17} 3



$$\begin{array}{cc} N & C \\ | & | \\ H & O \end{array}$$

U(II K^2_1 1)[3]

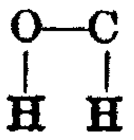


$$\begin{array}{cc} O & C \\ | & | \\ H & O \end{array}$$

II K^3_{43} 1

As may be seen, the difference consists only in the elements φ_{11} (C, N, and O), which change according to the order of their atomic numbers (the difference in φ_{12} has only a subordinate significance).

For catalysts to be compared we take the type of mixed catalysts where one of the components is aluminum hydroxide, which, as is already known, facilitates the reaction having the index II K^2_{17} 3, and the other component is such a metallic oxide as catalyzes the dehydrogenation of alcohols:



$$\begin{array}{c} O\!-\!C \\ | \quad | \\ H \quad H \end{array}$$

U(II K^2_3 2)U

The latter index differs from index II K^3_{43} 1 by the elements φ_{33}: in II K^3_{43} 1, φ_{33} corresponds to an oxygen atom, and in the case of dehydrogenation φ_{33} corresponds to a hydrogen atom.

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[2] The terminology in the present paper is taken from the article referred to (see Balandin: J. Phys. Chem. U. S. S. R. 5, 679–706 (1934).

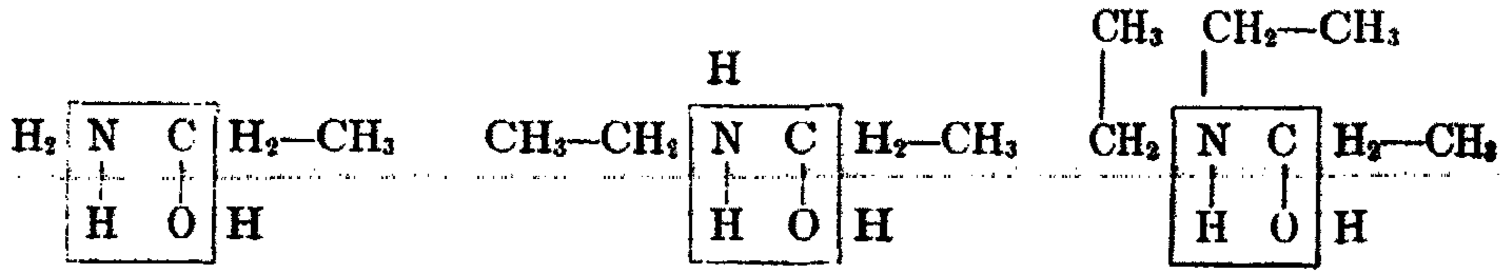
[3] Below the index its symbol is given; when multiplied by matrix

$$U = \begin{Vmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{Vmatrix}$$

the index does not change, but only turns.

Experiments (1) have shown that such mixed catalysts accelerate considerably reactions belonging to class II K_{43} 1 (ether hydrolysis). The reaction II K^2_{17} 3 (alcohol dehydration), it seems, is not sensitive towards the addition of dehydrogenating oxides to alumina.

The reaction studied in the present paper, the joint dehydration of ethyl alcohol and ammonia, is one of the cases of index $U(\mathrm{I}\ K^2_1\ 1)$, which occupies a middle position in the above-mentioned series. This applies not only to the first stage, the formation of a primary amine, but also to subsequent reactions,—to the formation of a secondary and tertiary amine:

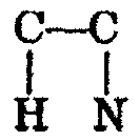


$$H_2\begin{array}{|cc|}\hline N & C \\ H & O \\ \hline\end{array}\begin{array}{l} H_2{-}CH_3 \\ H \end{array} \qquad CH_3{-}CH_2\overset{H}{\begin{array}{|cc|}\hline N & C \\ H & O \\ \hline\end{array}}\begin{array}{l} H_2{-}CH_3 \\ H \end{array} \qquad \overset{CH_3}{CH_2}\overset{CH_2-CH_3}{\begin{array}{|cc|}\hline N & C \\ H & O \\ \hline\end{array}}\begin{array}{l} H_2{-}CH_3 \\ H \end{array}$$

In order that such a reaction may take place upon the same active centers of the catalysts on which the alcohol dehydration reaction took place, it is necessary for the alcohol molecule to turn somewhat, i.e., to be oriented in a different way, so that the places previously occupied by atoms $\overset{C}{\underset{H}{|}}$ and now left free in the left part of the index, should be occupied by the group $\overset{N}{\underset{H}{|}}$. It appears that in such a case the addition of dehydrogenating oxides to alumina decreases the rate of the reaction, in contrast to the case of ether hydrolysis. In that instance we can see how profoundly specific is the action of a catalyst, even when the reactions are very similar. The introduction of a nitrogen atom instead of oxygen into the index already produces a perturbation in the catalytic activity.

According to previous theories, the reactions of ether hydrolysis as well as of the amination of an alcohol were considered as representing one and the same type of reaction, namely, the reaction of addition or removal of water. It was considered that only the elements of water come into a temporary contact with the catalyst. From the point of view of these old theories it was not possible to expect a difference in the catalyst action. From the point of view of the new theory, where the interaction of *all* the atoms participating in the reaction is taken into consideration, such a difference cannot readily be unexpected.

We should remark still further that the addition of iron oxide decreases the rate not only of reactions II K^2_{17} 3, but also of an analogous reaction,—the splitting of the amine that was formed,



$$\begin{matrix}\mathrm{C} & - & \mathrm{C}\\ | & & | \\ \mathrm{H} & & \mathrm{N}\end{matrix}$$

II K$^2_{16}$ 4

which differs from the former reaction only by φ_{33} (φ_{33} corresponds to an oxygen atom in II K$^2_{17}$ 3, and to a nitrogen atom in II K$^2_{16}$ 4). The specific action of the catalyst in this case is manifested just as sharply as in previous cases.

CONCLUSIONS

1. Mixed catalysts studied by us (except $Al_2O_3 + Fe_2O_3$ at 360°C. and 400°C.), when compared to pure alumina, under the conditions of our experiments, decrease the reaction rate of the formation of amines from ethyl alcohol and ammonia.
2. Among the mixed catalysts that we tried, the most effective one proved to be a catalyst consisting of 90 per cent Al_2O_3 and 10 per cent Fe_2O_3. The advantage of this catalyst over pure alumina consists in a smaller decomposition of the alcohol in its presence.
3. The action of mixed catalysts in this case is not an additive one.
4. The facts observed are interpreted from the point of view of the multiplet theory.

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COMPARATIVE ACTION OF MIXED CATALYSTS WHEN USED FOR THE JOINT DEHYDRATION OF ETHYL ALCOHOL AND ANILINE. II

CATALYTIC PREPARATION OF MONOETHYLANILINE

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In our former paper (9) we have investigated the action of mixed catalysts in the joint dehydration of ethyl alcohol and ammonia with the formation of corresponding amines. In connection with this it appeared interesting to test the efficiency of the same catalysts (see below) in the joint dehydration of aniline and ethyl alcohol with the formation of mono- and diethylaniline and to compare their action with the activity in this process of pure alumina. We have also tested a catalyst consisting of 95 per cent alumina and 5 per cent nickel oxide, which had proved to be very active in the hydrolysis of diethyl ether under pressure (2).

The possibility of obtaining alkylanilines by means of heterogeneous catalysis under ordinary pressure was for the first time established by Mailhe and de Godon (7). These authors passed methyl alcohol and aniline over alumina at 400–430°C. and obtained methylaniline and from it, by a further action of methyl alcohol, dimethylaniline. In the presence of the same catalyst, from *o*-, *m*-, and *p*-toluidines and methyl alcohol at 350–400°C., they obtained (8) a mixture of nearly equal amounts of the corresponding secondary and tertiary amines.

Mailhe in his patent (6) concerning the preparation of a series of arylamines, among them ethyl- and diethyl-aniline, recommends the following catalysts: Al_2O_3, ThO_2, and ZrO_2. For the reaction between ethyl alcohol and aniline he proposes alumina at a temperature of 350–400°C.

E. and K. Smolensky (10) claim that by passing twice a mixture of methylaniline with methyl alcohol over alumina at 300°C. they obtained dimethylaniline with a yield of 95 per cent. By passing aniline and methyl alcohol over silicon dioxide at 300–320°C., monomethylaniline could be obtained.

Brown and Reid (3) have investigated the catalytic action of silica gel in the reaction of the ethylation of aniline with alcohol. They found that at a temperature of 385°C. (using a molar ratio aniline:alcohol = 1:1.05) a mixture of secondary and tertiary amines was obtained with a ratio of 5:1 and a yield of 41.5 per cent. Using the same temperature but a molar ratio aniline:alcohol = 1:2.05 they obtained 46.6 per cent of ethylaniline and 13.3 per cent of diethylaniline (ethylaniline:diethylaniline = 77:2); the catalyst rapidly lost its activity.

In later papers the joint dehydration of methyl alcohol and aniline was investigated only in the presence of "Japanese acid earth" (5) (its composition after washing with water and drying in the air: SiO_2, 61.67 per cent; Al_2O_3, 12.28 per cent; Fe_2O_3, 1.87 per cent; CaO, 0.16 per cent; MgO, 3.44 per cent; loss after drying at 110°C., 15.66 per cent; loss after heating to incandescence, 4.64 per cent) and in the presence of thorium oxide (4).

The joint dehydration of ethyl alcohol and aniline in the presence of mixed catalysts has not as yet been investigated.

It must be remarked that the study of mixed catalysts used for the alkylation of aromatic amines has not only a purely theoretical interest, but also a practical one, because it gives the necessary data concerning the influence of impurities upon the action of catalysts in industrial processes.

The following catalysts have been tested in our experiments:[1] (1) Al_2O_3; (2) Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent); (3) Al_2O_3 (90 per cent) + SnO (10 per cent); (4) Al_2O_3 (90 per cent) + ZnO (10 per cent); (5) Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent); (6) Al_2O_3 (95 per cent) + NiO (5 per cent).[2]

EXPERIMENTAL PART

Experiments on the joint catalytic dehydration of aniline and ethyl alcohol were performed with each of the above-mentioned catalysts at temperatures of 350, 375, and 400°C.

The apparatus consisted of a tube of hard glass having a 15 mm. interior diameter into which the catalyst was placed. The catalyst was in the form of small lumps dried at 150°C. The tube was placed in an electric furnace and was provided at its front end with a special buret (1) for a regular introduction of a mixture of alcohol and aniline, and at the rear end with a receiver that was cooled with ice. The length of the catalyst layer in all experiments was 48 cm.

In every experiment the same mixture was used, consisting of 86 g. of pure, freshly distilled aniline (b.p. 182.5–183.5°C., $n_D^{20°}$ 1.5864) and 64 g. of 96 per cent rectified ethyl alcohol ($d_4^{15°}$ 0.8056).

The molecular ratio aniline:alcohol was about 2:2.9. The mixture of aniline and alcohol was introduced into the reaction tube regularly, at a rate of 12 cc. per hour, and was passed over the catalyst once. As all the

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[1] The description of their preparation is given in the preceding paper by Shuykin, Balandin, and Plotkin (9). All the catalysts were actually hydroxides.

[2] For the preparation of this catalyst see reference 9.

experiments were of a comparative nature, the same conditions were maintained in all cases where this was possible.

In all the experiments at a temperature of 300°C. the color of the condensate was light yellow; with the rise of the temperature a change of color to orange-yellow was observed.

The condensates obtained were separated from the water-alcohol layer and dried over melted sodium hydroxide. The product was fractionated twice with a Vigreux column (sixteen sections, length 58 cm.), which was heated by means of electricity to a constant temperature. An insignificant quantity of the product which distilled up to 160°C. consisted of ether, of alcohol that had not entered into the reaction, of water, and of traces of aniline. This fore-run was not taken into account.

TABLE 1

Indices of refraction of mixtures

ANILINE	ETHYLANILINE	$n_D^{20°}$ OF THE MIXTURE	ETHYLANILINE	DIETHYLANILINE	$n_D^{20°}$ OF THE MIXTURE
per cent	*per cent*		*per cent*	*per cent*	
100	0	1.5864	100	0	1.5557
90	10	1.5812	90	10	1.5543
80	20	1.5781	80	20	1.5528
70	30	1.5753	70	30	1.5516
60	40	1.5722	60	40	1.5503
50	50	1.5693	50	50	1.5490
40	60	1.5663	40	60	1.5477
30	70	1.5637	30	70	1.5466
20	80	1.5607	20	80	1.5453
10	90	1.5580	10	90	1.5440
0	100	1.5557	0	100	1.5424

The following fractions were collected: I, 160–195°C.; II, 195–210°C.; and III, 210–230°C. In the flask there remained a small quantity of a liquid, boiling above 230°C., which was not investigated further.[3] Fraction I (160–195°C.) consisted of a mixture of aniline and ethylaniline; fraction II (195–210°C.) of aniline, ethylaniline, and traces of diethylaniline; fraction III (210–230°C.) of ethylaniline and diethylaniline.

For each fraction the indices of refraction were determined. In order to determine the composition of these fractions by the indices of refraction, two series of synthetic mixtures were prepared consisting (a) of aniline and ethylaniline and (b) of ethylaniline and diethylaniline, taken in different percentages by weight (see table 1). The initial substances (Kahl-

[3] The residues from all experiments were collected and fractionated. The product boiled from 230 to 271°C. and gave a negative reaction for the presence of diphenylamine.

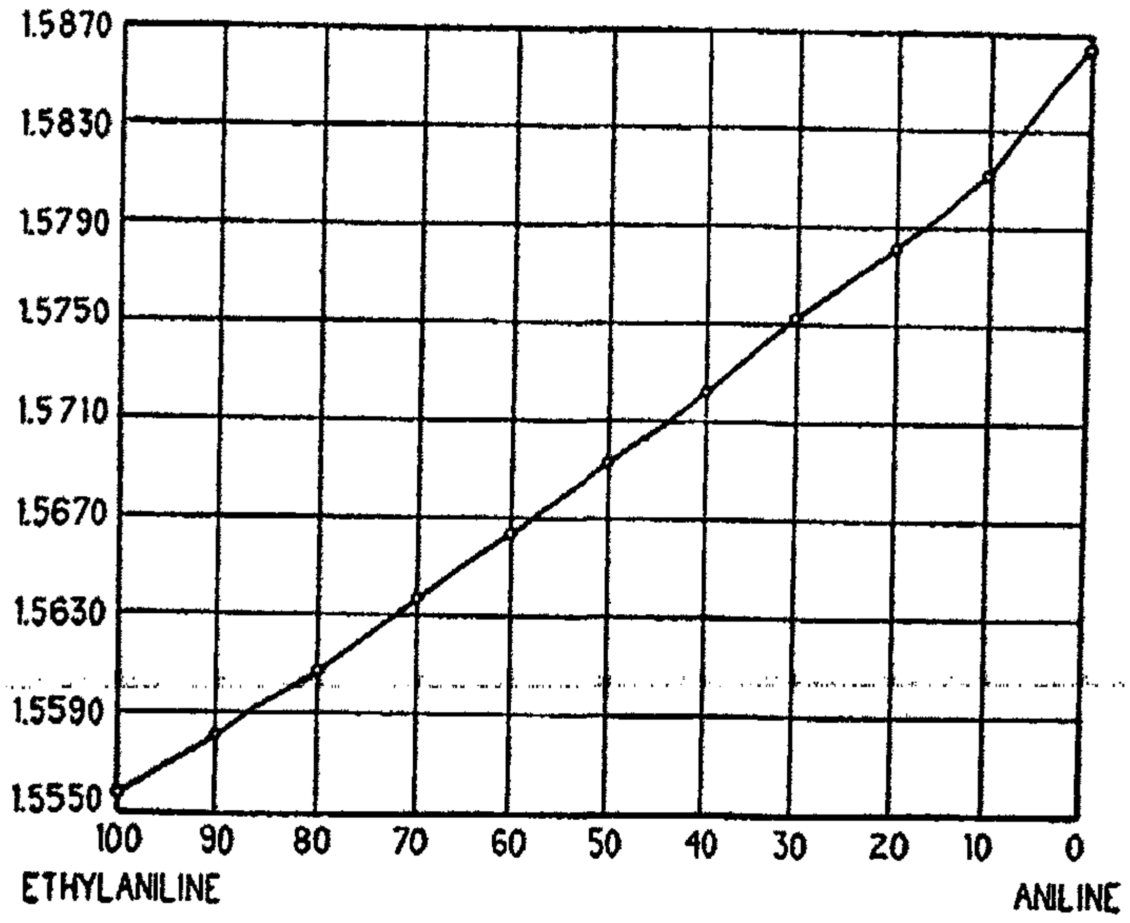

FIG. 1. DEPENDENCE OF INDEX OF REFRACTION ON THE COMPOSITION OF THE MIXTURE

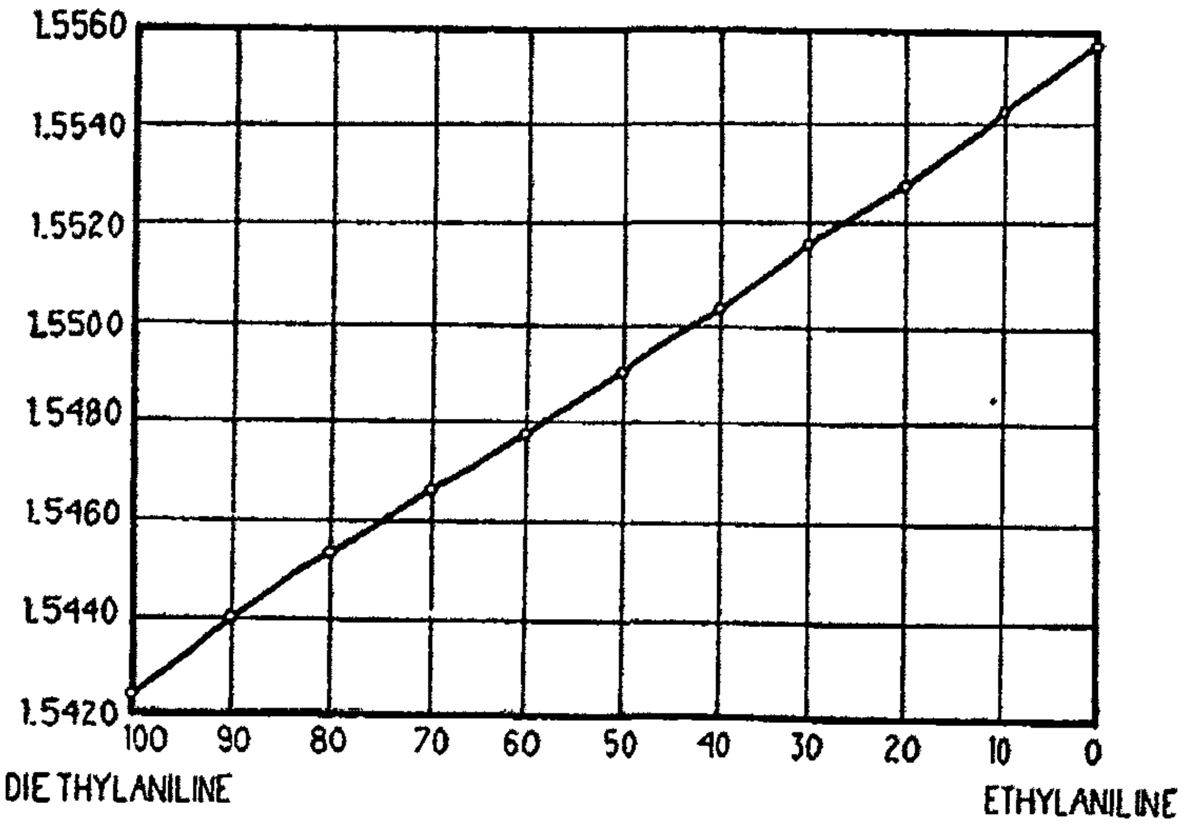

FIG. 2. DEPENDENCE OF INDEX OF REFRACTION ON THE COMPOSITION OF THE MIXTURE

baum) were previously distilled twice: aniline, b.p. 182.5–183.5° at 751 mm., $n_D^{20°}$ 1.5864; ethylaniline, b.p. 203–204°C. at 754 mm., $n_D^{20°}$ 1.5557; diethylaniline, b.p. 214.5–215.5°C. at 754 mm., $n_D^{20°}$ 1.5424.

TABLE 2

Alkylation of aniline

CATALYSTS	TEMPERATURE OF EXPERIMENT	WEIGHT OF CRUDE CONDENSATE	NO. OF FRACTIONS	WEIGHT OF FRACTIONS	n°_{D} OF FRACTIONS	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF MONOETHYLANILINE	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF DIETHYLANILINE	TOTAL PERCENTAGE OF TRANSFORMED ANILINE	LOSS OF ALCOHOL
	°C.	*grams*		*gm.*		*per cent*	*per cent*	*per cent*	*per cent*
Al_2O_3	350	140	1	30	1.5631	64.3	3.2	67.5	26.7
			2	60	1.5556				
			3	7	1.5474				
	375	136	1	19	1.5679	51.4	3.5	54.9	37.4
			2	50	1.5581				
			3	7	1.5468				
	400	135	1	22	1.5728	41.8	7.1	48.9	40.1
			2	37	1.5581				
			3	15	1.5471				
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent)	350	142	1	28	1.5727	48.0	2.1	50.1	21.4
			2	39	1.5556				
			3	7	1.5502				
	375	140	1	32	1.5700	52.2	0.7	52.9	26.7
			2	42	1.5576				
			3	6	1.5528				
	400	132	1	52	1.5732	39.4		39.4	48.1
			2	25	1.5595				
			3	4	1.5557				
Al_2O_3 (90 per cent) + SnO (10 per cent)	350	137	1	25	1.5748	45.6	2.8	48.4	34.7
			2	39	1.5562				
			3	9	1.5500				
	375	136	1	25	1.5785	48.7	1.5	50.2	37.4
			2	46	1.5550				
			3	4	1.5486				
	400	135	1	40	1.5703	44.0	0.3	44.3	40.1
			2	31	1.5579				
			3	3	1.5540				

TABLE 2—*Concluded*

CATALYSTS	TEMPERATURE OF EXPERIMENT	WEIGHT OF CRUDE CONDENSATE	NO. OF FRACTIONS	WEIGHT OF FRACTIONS	$n_D^{20°}$ OF FRACTIONS	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF MONOETHYLANILINE	PERCENTAGE OF ANILINE USED FOR THE FORMATION OF DIETHYLANILINE	TOTAL PERCENTAGE OF TRANSFORMED ANILINE	LOSS OF ALCOHOL
	°C.	*grams*		*gm.*		*per cent*	*per cent*	*per cent*	*per cent*
Al_2O_3 (90 per cent) + ZnO (10 per cent)	350	141	1	60	1.5750	31.6	Traces	31.6	24.1
			2	18	1.5631				
			3	4	1.5556				
	375	132	1	52	1.5744	29.7		29.7	48.1
			2	14	1.5646				
			3	8	1.5586				
	400	133	1	66	1.5796	18.9		18.9	45.4
			2	14	1.5689				
			3	4	1.5610				
Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent)	350	132	1	58	1.5726	34.9	0.6	35.5	48.1
			2	16	1.5580				
			3	3	1.5518				
	375	136	1	47	1.5726	43.2	Traces	43.2	37.4
			2	31	1.5578				
			3	2	1.5553				
	400	126	1	54	1.5773	24.4		24.4	64.2
			2	16	1.5620				
			3	3	1.5571				
Al_2O_3 (95 per cent) + NiO (5 per cent)	350	138	1	53	1.5720	38.4	0.1	38.5	32.1
			2	20	1.5600				
			3	5	1.5554				
	375	132	1	55	1.5785	16.3		16.3	48.1
			2	6	1.5590				
			3	3	1.5564				
	400	131	1	63	1.5779	15.3		15.3	50.8
			2	5	1.5646				
			3	1	1.5605				

On the basis of the refractometric data obtained, two curves were plotted (figures 1 and 2), showing the dependence of the index of refraction on the composition of the mixture expressed in per cent. By means of these curves the content of amines in the fractions was determined (with a certain approximation). When calculating we did not take into consideration the possible presence in every fraction of small amounts of a third component. Such an arbitrary supposition in the determination of the composition of the mixture leads to an error not exceeding 2 to 3 per cent. We used the refractometric curves in order to calculate for every experiment the percentage of the aniline transformed, so that the efficiency of different catalysts in the reaction of the ethylation of aniline could be compared.

The percentage of the aniline transformed is easily obtained, knowing the composition of the fractions and taking into account that for the formation of 1 g. of monoethylaniline and of diethylaniline, respectively, 93/121 and 93/149 g. of aniline are required.

The results obtained in all experiments are given in table 2. The loss of alcohol, due to decomposition, shown in the last column of the table, is calculated from the difference in weight between the initial mixture and the crude condensate, taking into consideration that the decomposition leads to the formation of ethylene.

DISCUSSION OF RESULTS

Comparing the results obtained, it may be seen that all the mixed catalysts that were tested in the reaction of the ethylation of aniline with alcohol proved to be less efficient compared with pure alumina.

Among the mixed catalysts investigated the most active ones in this process have been found to be $Al_2O_3 + Fe_2O_3$ and $Al_2O_3 + SnO$. As well as in the case of the ethylation of ammonia, the first of these catalysts, used at a temperature of 350 and 375°C., leads to a reaction with a smaller decomposition of alcohol as compared with pure alumina.

It is interesting to note that at a temperature of 400°C. the percentage of aniline transformed is in all cases and with all catalysts considerably smaller than at lower temperatures. In the case of pure Al_2O_3, $Al_2O_3 + NiO$, and $Al_2O_3 + ZnO$ it already attains its maximum value at 350°C.; in the case of other catalysts at 375°C.

As a rule, the loss of alcohol due to decomposition increases with the rise of temperature; an exception is presented by $Al_2O_3 + ZnO$ at 375°C., but these results are within the limits of a possible error in the experiment. The loss of alcohol in the experiment with $Al_2O_3 + Cr_2O_3$ at 375°C. may be explained by a comparatively high yield of the products of the principal reaction of ethylation.

It should be noted that under the conditions of our experiments the mixed catalysts direct the reaction chiefly towards the formation of monoethylaniline. In the presence of pure alumina the relative yield of diethylaniline is considerably higher, which is shown by the determination of the composition of the condensates using the indices of refraction. Thus, for instance, in the case of pure alumina, at 400°C., about 42 per cent of aniline was transformed into monoethylaniline, and 7 per cent into diethylaniline, while at the same temperature, in the presence of $Al_2O_3 + Fe_2O_3$, about 39 per cent was transformed into monoethylaniline, and no transformation whatever into diethylaniline was observed.

An insufficient amount of alcohol in comparison with that required by theory for a complete transformation of aniline into diethylaniline (aniline: alcohol $= \sim 1:1.5$ instead of 1:2) was taken with the purpose of promoting the formation of monoethylaniline. However, as the data of the present paper show, this measure was superfluous, as in the presence of the mixed catalysts that were used the secondary amine is formed almost exclusively.

It follows from all this, as well as from the consideration of the data of table 2, that in this case (as well as in the investigations concerning the ethylation of ammonia by alcohol) no additivity of the properties of oxides entering into the composition of mixed catalysts is observed.

The conclusions we have presented in our preceding paper concerning the specific properties of mixed catalysts when used for similar changes of the systems

$$\begin{array}{ccc} \begin{array}{cc} C & \!\!-\!\! C \\ | & | \\ H & O \end{array} & \begin{array}{cc} N & C \\ | & | \\ H & O \end{array} & \begin{array}{cc} O & C \\ | & | \\ H & O \end{array} \end{array}$$

II K^2_{17} 3 $\quad$ U(I K^2_1 1) $\quad$ II K^3_{43} 1

differing only by the elements φ_{11} (C, N, and O, which change according to the order of their atomic numbers) remain also valid for the case being investigated, with the only difference that in the catalytic ethylation of aniline one must take into account the influence of the phenyl radical, which increases the rate of this reaction in comparison with a similar reaction, the ethylation of ammonia.

The addition to alumina of dehydrogenating oxides investigated by us causes the retardation of the reaction of class I K^2_1 1, contrary to the case of the hydrolysis of diethyl ether (class II K^3_{43} 1). This conclusion applies not only to the formation of monoethylaniline, but also to the retardation of the next stage—the formation of diethylaniline from monoethylaniline—a reaction, which, as one can easily see, requires the same index with the symbol U (I K^2_1 1).

Thus the application of mixed catalysts of the type investigated, decreasing the reaction rate, makes it possible to obtain synthetically monoalkylanilines, which are more difficult to obtain in a pure state than the dialkylsubstituted anilines (exhaustive alkylation).

CONCLUSIONS

1. In the present paper the action of mixed catalysts on the joint dehydration of aniline and ethyl alcohol has been studied; a dehydrating catalyst, alumina, was taken, to which oxides of metals promoting dehydrogenation were added.

2. The alkylating action of the catalysts studied after a single passing of the mixture of aniline with 96 per cent ethyl alcohol having a molecular ratio 1 : 1.45, at a rate of 12 cc. per hour, at 350, 375, and 400°C. may be seen from table 3.

TABLE 3

Alkylating action of the catalysts

CATALYSTS	TEMPERATURE CORRESPONDING TO A MAXIMUM TRANSFORMATION OF ANILINE	TOTAL PERCENTAGE OF TRANSFORMED ANILINE	YIELD OF MONOMETHYLANILINE (RECKONED FROM ANILINE)	YIELD OF DIETHYLANILINE (RECKONED FROM ANILINE)
	°C.	*per cent*		
Al_2O_3	350	67.5	64.3	3.2
Al_2O_3 (90 per cent) + Fe_2O_3 (10 per cent)	375	52.9	52.2	0.7
Al_2O_3 (90 per cent) + SnO (10 per cent)	375	50.2	48.7	1.5
Al_2O_3 (80 per cent) + Cr_2O_3 (20 per cent)	375	43.2	43.2	Traces
Al_2O_3 (95 per cent) + NiO (5 per cent)	350	38.5	38.4	0.1
Al_2O_3 (90 per cent) + ZnO (10 per cent)	350	31.6	31.6	Traces

3. It has been found that the above-mentioned additions decrease the reaction rate as compared with pure alumina.

4. This leads to the formation of monoethylaniline by preference, and this circumstance can be made use of for synthetic purposes.

5. The substitution of hydrogen by the phenyl radical in the molecule of ammonia increases the reaction rate of the joint dehydration with ethyl alcohol.

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THE ACTION OF HYDROGEN SULFIDE ON CHROMATES

Potassium Dichromate

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When a slow stream of hydrogen sulfide, purified by passing through scrubbers containing iodine and sodium sulfide, was passed into a 5 per cent solution of potassium dichromate of tested purity, the color of the solution first changed to a dark brown with the separation of a brown solid. As the current continued, the color changed to dirty brown and, passing through various shades, gave after four hours a whitish-green precipitate. When the color did not change perceptibly, the stream of hydrogen sulfide was stopped and the whitish green precipitate, which settled down, was filtered off. The filtrate was heated to coagulate colloidal chromium hydroxide and filtered. This filtrate was again subjected to the action of the gas but no more green precipitate separated, although there was a further deposit of sulfur.

The green precipitate consisted of chromium hydroxide, thiosulfate, and sulfur, and the filtrate contained thiosulfate and polysulfide of potassium. The observation (4) that sulfate is formed in the early stages of the reaction was due (while testing for sulfur acids) to the development of sulfate from tetrathionate, which is now shown to be an intermediate by-product of the reaction. The precipitate formed by the action of hydrogen sulfide on chromic acid (3) has been shown to contain sulfate also.

The mechanism of the reaction was studied by investigating the products at certain definite stages. Stage I, subsequently called the "intermediate stage": the gas was passed until the brown precipitate was just on the point of changing into green. Stage II—the final stage—when hydrogen sulfide was bubbled through the solution until precipitation was complete.

The intermediate stage

Hydrogen sulfide was passed into potassium dichromate solution (19–20°C.) with continual stirring for about half an hour until the green precipitate just began to form and the color of the reaction mixture was a dirty brown.

The reaction mixture was allowed to stand overnight in a stoppered flask and then filtered. An alkaline yellow filtrate was obtained, which contained potassium chromate and thiosulfate, but neither sulfide nor sulfate. Sulfate, in the presence of thiosulfate and chromate, was tested for by adding a 3 per cent solution of barium chloride to the alkaline filtrate in order to precipitate chromate and sulfate (if any). The washed precipitate was treated with dilute hydrochloric acid. The solid was completely dissolved, leaving no turbidity, showing the absence of sulfate, which is not formed if the concentration of hydroxyl ions is above a certain critical value.

The brown solid was insoluble in cold and hot water but dissolved in hydrochloric acid with evolution of sulfur dioxide and chlorine, giving a green solution containing free sulfur. Potassium was absent from the intermediate precipitate.

When treated with 0.3 *N* potassium hydroxide, a green solid remained which contained neither thiosulfate nor chromate. The alkali extract, however, contained both thiosulfate and chromate, showing that the coördinated complex was broken up by alkali treatment.

The molecular ratio of the chromium sesquioxide (Cr_2O_3) to chromic acid (CrO_3), calculated from chromate obtained by treatment of the brown solid with potassium hydroxide, was roughly constant. The mean of four determinations was $Cr:O_{1.93}$, which corresponds approximately to chromium dioxide (CrO_2) or chromium chromate ($Cr_2O_3 \cdot CrO_3$). Thus the brown solid is the same as that obtained by the action of hydrogen sulfide on chromic acid (3) and hence is different from the brown compound produced by the action of chromic acid on chromic sulfate.

Chromate in the presence of thiosulfate was estimated as follows: The alkaline liquid was carefully neutralized with dilute acetic acid, and the chromate precipitated with barium acetate from a boiling solution. After heating for some time to make the precipitate granular, it was filtered and washed in a sintered glass crucible, dried at 100–105°C., and weighed.

The brown product was thoroughly washed, suspended in water, and a current of hydrogen sulfide passed until a green precipitate was obtained. This was filtered off, washed, and found to contain sulfate.

The brown precipitate must be washed quite free from traces of both chromate and potassium, otherwise the reaction mixture develops alkalinity through the hydrolysis of KHS or K_2S_x, and no sulfate is formed. This shows that the oxidation of thiosulfate to sulfate does not take place in the presence of hydroxyl ions above a certain concentration.

The properties of the brown substance were compared with those of chromium dioxide, obtained by the action of sodium thiosulfate on potassium dichromate (9).

$$2K_2Cr_2O_7 + Na_2S_2O_3 \rightarrow K_2CrO_4 + K_2SO_4 + Na_2SO_3 + 3CrO_2 \qquad (1)$$

The solid was washed free from chromate, sulfite, and sulfate. It gave chlorine with hydrochloric acid, and chromate and chromium hydroxide with potassium hydroxide. The dark brown chromium dioxide was suspended in water and hydrogen sulfide passed until a green precipitate was obtained. This contained coördinated sulfate, chromium hydroxide, and sulfur. Thiosulfate was absent because the chromium dioxide contained no coprecipitated chromium hydroxide and sulfur (3).

The chromium dioxide in the precipitate from potassium dichromate was reduced in an alkaline medium and hence thiosulfate but no sulfate was formed.

TABLE 1

Examination of the products at the intermediate stage

Values are shown in mg. for 1 g. of potassium dichromate

EXPERIMENT	TIME FOR WHICH ALLOWED TO STAND	FILTRATE		PRECIPITATE				TOTAL $K_2Cr_2O_7$ ACCOUNTED FOR	TOTAL THIOSULFATE
		*Unused $K_2Cr_2O_7$	Thiosulfate	*Unused $K_2Cr_2O_7$	Cr_2O_3 in the ppt.	Corresponding $K_2Cr_2O_7$	Thiosulfate		
		mg.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*
(a)......	Filtered immediately	313	58	79	303	586	11	978	69
(b)......	1 hour	316	56	75	309	598	13	989	69
(c)......	1 hour	295	54	72	319	616	12	983	69
(d)......	4 hours	292	52	62	326	631	13	986	65
(e)......	4 hours	300	59	68	326	631	15	984	74
(f)......	12 hours	304	63	65	319	618	14	987	77
(g)......	12 hours	312	68	67	318	615	14	995	82

* Calculated from chromate.

The following determinations were carried out at the intermediate stage (table 1): (1) The brown solid was extracted with potassium hydroxide (0.3 *N*) and the chromate and thiosulfate determined in solution. (2) The residual green solid was dissolved in hydrochloric acid and the chromium precipitated as hydroxide, which was weighed as Cr_2O_3. (3) Chromate and thiosulfate were also estimated in the filtrate, which does not contain any sulfide.

The lack of uniformity in the results is not surprising, as it is impossible to arrest the reaction at exactly the same point in each case. The values represent intermediate stages of a continuous reaction.

Experiments b and c, d and e, and f and g were carried out under exactly similar conditions and show that the reaction proceeds systematically.

Since the filtrate is alkaline and potassium hydroxide extracts chromate from chromium dioxide, one would expect that no sulfide of potassium is formed in the filtrate until all the chromium dioxide is removed from the solid phase. Careful investigation showed that, so long as chromate is present in the reaction mixture, potassium sulfide does not form. This was established by examining the action of hydrogen sulfide on potassium chromate, stopping the reaction at different stages, and testing for chromate and sulfide. As soon as chromate disappears from the liquid phase, sulfide makes its appearance.

The final stage

Hydrogen sulfide was passed until the precipitation was complete. On filtering, a whitish-green precipitate and a strongly alkaline, golden-yellow filtrate were obtained.

TABLE 2

The final green precipitate

EXPT. NO.	CONCENTRATION OF $K_2Cr_2O_7$ SOLUTION	AMOUNT TAKEN	Cr_2O_3	(S_2O_3) Iodometric method	(S_2O_3) $BaSO_4$ method	SULFUR FROM (S_2O_3)	TOTAL SULFUR	FREE SULFUR (BY DIFFERENCE)
	per cent	*cc.*	*grams*	*grams*	*grams*	*grams*	*grams*	*grams*
1	2	50	0.5144[a]	0.0212	0.0208	0.0059	0.0524	0.0475
2	2	50	0.5128	0.0214	0.0200	0.0061	0.0522	0.0461
3	3	50	0.7708[b]	0.0322	0.0316	0.0094	0.0781	0.0687
4	3	50	0.7712	0.0321	0.0312	0.0089	0.0766	0.0677
5	5	50	1.2892[c]	0.0532	0.0522	0.0150	0.1260	0.1110
6	5	50	1.2906	0.0529	0.0514	0.0142	0.1245	0.1103
7	5	50	1.2902	0.0531	0.0524	0.0149	0.1264	0.1115

Theory: a = 0.517 g.; b = 0.776 g.; c = 1.292 g.

The green solid was insoluble in water. With hydrochloric acid it gave sulfur dioxide and a green solution containing suspended sulfur. Thiosulfate was present, but neither sulfate nor polythionates. All the thiosulfate was extracted by treatment with potassium hydroxide and estimated in the filtered solution. The residue contained chromium hydroxide and free sulfur. The statement (4) that sulfate is produced in the reaction was especially investigated (see p. 1224) and found to be incorrect.

Sulfate is an important product in the action of hydrogen sulfide on chromic acid (3) and the fact that the final stage in the present case does not contain sulfate sets a limit to the oxidizing power of potassium dichromate. As already stated (p. 1218) the development of a considerable concentration of hydroxyl ions prevents the formation of sulfate in this case.

The strongly alkaline, final filtrate contained only thiosulfate and polysulfide of potassium.

Chromium hydroxide, thiosulfate, and free sulfur were estimated in the precipitate as described by Dunnicliff and Kotwani (3), in an attempt to define its composition (table 2).

Kurtenacker and Wollak's method (8) for the removal of sulfide in the presence of thiosulfate was also used, but it was observed that in the absence of sulfite the cadmium carbonate method gives accurate results.

Even when special precautions are taken (1), the free sulfur is invariably higher than theory, owing to dissolved oxygen in water, air contact, and, to some degree, the action of light.

The values for thiosulfate (column 5) obtained by titration agreed closely with those calculated from barium sulfate obtained by oxidation with bromine water. The latter value was not higher than the former in any instance, as would have been the case if a thionate had been present. The absence of a polythionate in the final stage was thus confirmed, and the only sulfur compound in the precipitate was thiosulfate. The existence of a trithionate was thus ruled out since, if formed, it should persist in the final stage (7), being the only thionate stable in the presence of hydrogen sulfide.

Coördinated and ionic thiosulfate

While trying to oxidize the sulfur and thiosulfate in the precipitate to sulfate with bromine water, it was observed that, even after refluxing for two hours, the remaining solid still contained thiosulfate. This slow attack of the thiosulfate by bromine suggested a method for distinguishing between ionic and coördinated thiosulfate groups in the complex molecule.

Portions of the precipitate were shaken with bromine water of various concentrations in the cold and filtered. The ratio A/B, between A, the thiosulfate estimated directly in the residue thus obtained, and B, that calculated from sulfate in the filtrate, shows very wide variations (table 3).

The inference is that bromine attacks both the ionic and coördinated thiosulfate. It is probable that, as the ionic thiosulfate is removed, the equilibrium between coördinated and ionic thiosulfate is disturbed and more ionic thiosulfate is formed. Possibly bromine is catalytic in this sense.

A series of experiments was tried using iodine. (1) The washed precipitates from a number of samples of 50 cc. of 5 per cent dichromate solution were treated with excess of different strengths of iodine solution and allowed to stand. The iodine disappeared entirely after times which increased with the strength of the solution. This was due to the adsorption of iodine by the solid particles. Hence methods involving excess of iodine solution were rejected. (2) After first making acid with dilute acetic acid, direct titrations with iodine of various strengths (0.1 *N* to 0.01 *N*) against a fine suspension were then performed (titer *a* cc.) in the hope that, when the ionic thiosulfate had all been attacked, a momentary end point might be obtained with starch used as an external indicator. After filtration, the precipitate was treated with potassium hydroxide and the acidified extract titrated against iodine (titer *b* cc.). It was found that *N*/40 to *N*/60 iodine gave $a/b = 2$ (approximately) (see table 4).

TABLE 3

Ionic and coördinated thiosulfate in the precipitate (bromine method)

TIME OF CONTACT	$BaSO_4$ FROM FILTRATE	A (S_2O_3) CALCULATED FROM $BaSO_4$	B (S_2O_3) IN THE PPT.	A/B
hours	*grams*	*grams*	*grams*	
1	0.0242	0.0058	0.0026	2.24
1	0.0366	0.0088	0.0051	1.17
1	0.0624	0.0149	0.0072	2.07
2	0.0532	0.0127	0.0040	3.17
2	0.0746	0.0179	0.0058	3.09
4	0.0382	0.0092	0.0024	3.83
4	0.0522	0.0125	0.0042	2.97
4	0.0388	0.0093	0.0038	2.46
12	0.0524	0.0125	0.0026	4.81
12	0.0692	0.0166	0.0031	5.35

TABLE 4

Titration of suspensions with iodine solutions

a	*b*	*a/b*	*a*	*b*	*a/b*	*a*	*b*	*a/b*
cc.	*cc.*		*cc.*	*cc.*		*cc.*	*cc.*	
2.30	1.05	2.19	1.95	0.90	2.17	2.85	1.30	2.19
3.80	1.70	2.23	2.10	1.15	1.83	3.20	1.55	2.07
2.30	1.20	1.92	2.60	1.20	2.17	2.45	1.05	2.33
2.45	1.15	2.15	2.50	1.25	2.00	1.80	0.85	2.11
2.60	1.10	2.36	3.30	1.55	2.13	2.30	1.05	2.19

Mean of 15 determinations = 2.14

Considering the small titration volume and the presence of solid, which in any case adsorbs a little iodine, the agreement is significant and the ratio of the ionic to coördinated thiosulfate is probably of the order 2:1.

Composition of the final filtrate

Although the final filtrate is alkaline, it does not extract the whole of the thiosulfate from the precipitate as it does in the case of potassium chromate (4). Table 2 shows that the percentage of thiosulfate in the precipitate varies directly with the concentration of the solution used, and the constant values for experiments 1 and 2, 3 and 4, and 5, 6, 7 show that an equilibrium is set up between the thiosulfate (total) content of the precipitate and the concentration of thiosulfate in the solution.

After the removal of colloidal chromium hydroxide under reduced pressure the final alkaline filtrate contained only polysulfide and thiosulfate of potassium. The color varied between yellow and orange, with the amount of hydrogen sulfide passed and the temperature of the reaction.

The whole of the potassium was in the filtrate. Potassium from 50 cc. of 5 per cent potassium dichromate: found 0.6605, 0.6614, 0.6612, and 0.6616 g.; theoretical value = 0.6633 g.

TABLE 5

Thiosulfate in filtrate (5 per cent solution of potassium dichromate)

g. S_2O_3 (by titration) × 10^4 (actual)	3321	3256	3241	3186	3146	3283	3132	3374	3125	3286
Calculated per 100 g. of $K_2Cr_2O_7$	13.28	13.02	12.97	12.74	12.58	13.13	12.53	13.49	12.50	13.14

Mean = 12.93

TABLE 6

Values in grams per 100 grams of the polysulfide

NO.	(a) TOTAL POTASSIUM	(b) TOTAL SULFUR	(c) POTASSIUM THIOSULFATE $K_2S_2O_3 \cdot 5H_2O$	(d) POTASSIUM PRESENT AS THIOSULFATE CALCULATED FROM (c)	(e) SULFUR PRESENT AS THIOSULFATE CALCULATED FROM (c)	(f) POTASSIUM PRESENT AS POLYSULFIDE (a) − (d)	(g) SULFUR PRESENT AS POLYSULFIDE (b) − (e)	CALCULATED FORMULA K_2S_y
	grams	*grams*	*grams*	*grams*	*grams*	*grams*	*grams*	
I	28.45	31.63	78.46	21.85	17.93	6.60	13.70	$K_2S_{5.06}$
II	27.72	29.60	84.35	23.50	19.30	4.22	10.30	$K_2S_{5.96}$
III	28.43	32.42	76.52	21.31	17.49	7.12	14.93	$K_2S_{5.12}$
IV	21.75	23.75	61.21	17.05	14.00	4.70	9.75	$K_2S_{5.06}$

Thiosulfate in the filtrate was estimated after removing the polysulfide by means of cadmium carbonate. The filtrate was acidified with dilute acetic acid and titrated against iodine. These values (table 5) varied slightly. Probably this was due to the conversion of some of the polysulfide into thiosulfate by contact with air (10). The determination had, therefore, always to be made in fresh filtrate.

When the reaction was allowed to proceed at the laboratory temperature (19–20°C.), the formula of the polysulfide worked out to K_2S_3 (mean of three determinations = $K_2S_{3.1}$).

In addition to the method of estimating the polysulfide sulfur given below, that of Kurtenacker and Bittner (6) was found to give satisfactory results, but the modified procedure of Szeberenyl (12) was found to be more convenient, as it avoids the necessity for tedious corrections.

In order to get the most polysulfide and to accelerate the otherwise slow reaction, hydrogen sulfide was passed into a 10 per cent solution of potassium dichromate at 80–85°C. for nearly ten hours. The chromium hydroxide which separated when the filtrate was concentrated under reduced pressure was filtered off, and the polysulfide allowed to crystallize out under reduced pressure at about 50°C. The crystals were pressed between folds of filter paper, keeping them, as far as possible, out of air contact. Potassium, "sulfide," and thiosulfate were determined in a weighed amount of the dried polysulfide (4).

Table 6 shows that the molecular ratio $K_2S_2O_3:K_2S_x$ is not constant. Possibly, under ideal conditions, potassium thiosulfate and pentasulfide are formed in equimolecular proportions.

With the exception of the potassium hydrosulfide, the analyses in tables 2 and 4 can be represented approximately by the following equation:

$$56(K_2Cr_2O_7 + 3H_2S + H_2O) \rightarrow Cr_2(S_2O_3)_3 + 110Cr(OH)_3 + 20(K_2S_2O_3 + KHS) + 26K_2S_5 + 24S + 49H_2O \quad (2)$$

Note on the observation (4) that sulfate is formed in the action of hydrogen sulfide on potassium dichromate

If the intermediate filtrate *is acidified* and then treated with barium chloride solution a white precipitate of barium sulfate is produced, but the final stage contains no sulfate. Since sulfate is not found in the final products and it is not decomposed by hydrogen sulfide, it is obvious that it was developed in testing, and the only source of such sulfate would be by the action of hydrochloric acid on a polythionate.

The reaction was studied in order to determine the exact stage at which the formation of sulfate *on acidification* is suppressed, i.e., when polythionate ceases to be a by-product, and the following procedure was adopted: A saturated solution of hydrogen sulfide was mixed in small but increasing quantities (10 cc. at a time) with 20 cc. of 5 per cent potassium dichromate and the products analyzed next day. The reaction was divided into three stages: (a) When up to 40 cc. of saturated hydrogen sulfide solution was added. A brown solid and a golden-yellow, slightly acidic filtrate were obtained. (b) On the addition of from 50 to 130 cc. of hydrogen sulfide solution, the precipitate was green and chromate was present in the filtrate. (c) When more than 130 cc. of hydrogen sulfide was added, the polysulfide made its appearance and the composition of the final precipitate (expt. 16, table 6) was almost the same as given in table 2, p. 1220.

Tables 7a, 7b, and 7c give results in which sulfate was precipitated by previous *acidification* and addition of barium chloride. The scheme for the analysis of all other radicals is as given previously.

The results show that (a) the amount of sulfate formed from 1 g. of potassium dichromate remains practically constant up to experiment 8; (b) so long as the solution is acidic, thiosulfate is not formed; (c) at a certain stage the sulfate entirely disappears, the disappearance being first apparent in the precipitate; and (d) so long as chromate is present in the filtrate or precipitate, a test for sulfate is given on acidification, but as soon as chromate disappears (expt. 12) the test for sulfate is negative.

TABLE 7a

Precipitates

Values are shown in mg. for 1 g. of potassium dichromate

(1) EXPT. NO.	(2) COLOR OF PPT. AND REACTION	(3) VOLUME OF H_2S USED	(4) CHROMATE IN TERMS OF $K_2Cr_2O_7$	(5) Cr_2O_3 IN PPT.	(6) CORRESPONDING $K_2Cr_2O_7$	(7) (SO_4) FROM THIONATE	(8) (S_2O_3)	(9) $K_2Cr_2O_7$ ACCOUNTED FOR IN PPT.
		cc.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*
1	Brown, acidic	30	62	120	233	14		295
2	Brown, acidic	40	64	158	306	14		370
3	Brown, neutral	50	62	302	584	11	13	646
4	Brown, alkaline	60	64	305	593	12	12	657
5	Dirty-brown, alkaline	70	22	342	663	4	13	685
6	Green, alkaline	80		352	681		12	681
7	Green, alkaline	90		359	695		16	695
8	Green, alkaline	100		351	679		12	679
9	Green, alkaline	110		363	699		11	699
10	Green, alkaline	120		478	925		14	925
11	Green, alkaline	130		491	950		16	950
12	Green, alkaline	140		513	993		16	993
13	Green, alkaline	150		516	999		16	999
14	Green, alkaline	160		514	995		16	995
15	Green, alkaline	170		512	990		18	990
16	Green, alkaline	180		514	995		18	995

The explanation is that sulfate is not present as such but is formed owing to the oxidation (by the chromic acid produced on acidification) of some thiosulfate or a thionate. Since, however, the values for thiosulfate show the same regular increase (expts. 11 and 12) without any abrupt change, the formation of sulfate is clearly due to the decomposition of a thionate.

TABLE 7b

*Filtrates**

(1) EXPT. NO.	(2) CHROMATE IN TERMS OF $K_2Cr_2O_7$	(3) $K_2Cr_2O_7$ CORRESPONDING TO COLLOIDAL $Cr(OH)_3$	(4) (SO_4) FROM THIONATE	(5) (S_2O_3)	(6) $K_2Cr_2O_7$ ACCOUNTED FOR IN THE FILTRATE
	mg.	*mg.*	*mg.*	*mg.*	*mg.*
1	625	54	59		679
2	578	22	61		600
3	306	21	62	58	327
4	299	18	61	59	317
5	292		59	60	292
6	293		61	55	293
7	290		69	61	290
8	294		73	68	294
9	266		19	70	266
10	49		19	83	49
11	15		8	94	15
12				98	
13				110	
14				117	
15				121	
16				121	

* The filtrates correspond to the precipitates in table 7a.

TABLE 7c

Total potassium dichromate accounted for and total sulfate and thiosulfate formed in precipitate and filtrate

EXPT. NO.	$K_2Cr_2O_7$ (TOTAL OF COLUMN 9 IN TABLE 7a AND COLUMN 6 IN TABLE 7b)	SULFATE (SO_4) (COLUMN 7 IN TABLE 7a AND COLUMN 4 IN TABLE 7b)	THIOSULFATE (S_2O_3) (COLUMN 8 IN TABLE 7a AND COLUMN 5 IN TABLE 7b)
	mg.	*mg.*	*mg.*
1	974	73	
2	970	75	
3	973	73	71
4	974	73	71
5	977	63	73
6	974	61	77
7	975	69	77
8	973	73	80
9	965	19	81
10	974	19	97
11	965	8	110
12	993		114
13	999		126
14	995		133
15	990		139
16	995		139

That sulfate is not a product of the reaction under consideration was shown as follows: The intermediate filtrate (and the alkali extract from the precipitate) were treated separately with barium chloride *without acidifying.* The precipitates were filtered. On treatment with hydrochloric acid the barium chromate dissolved out and no cloudiness or precipitate remained in solution. This was confirmed by determining sulfate by the old and new methods (see table 8).

Direct proof of the existence of a thionate

The alkaline filtrate from the intermediate stage was treated with barium chloride to remove chromate, and the filtrate made up to a known volume. An aliquot portion, after acidification with dilute acetic acid, was titrated against iodine. This gave the titer for thiosulfate existing normally in the filtrate.

TABLE 8

NO.	VOLUME OF H_2S USED	WEIGHT OF $K_2Cr_2O_7$	$BaSO_4$ ON ACIDIFYING	$BaSO_4$ WITHOUT ACIDIFYING
	cc.	*grams*	*grams*	*grams*
1	70	1.00	0.0875	0.0012
2	80	1.00	0.0768	0.0009
3	90	1.00	0.0764	0.0014
4	100	1.00	0.0787	0.0011

Another portion of the filtrate was treated with sodium sulfide; the white precipitate which formed was filtered off and the sulfide removed with cadmium carbonate. The filtrate from this when titrated with iodine gave a titer almost three times as large as that obtained before.

This is conclusive evidence of the existence of a thionate.

The existence of trithionate is ruled out since, if formed, it should persist in the final stages (7) (p. 1221). The polythionates which are possible under the existing conditions are the di- and tetra-thionates. Quantitative results show that a tetrathionate, which is easily converted into thiosulfate by an alkaline sulfide (11, 2), is present.

$$K_2S_4O_6 + Na_2S \rightarrow K_2S_2O_3 + Na_2S_2O_3 + S \qquad (4)$$

This would account for the fact that no potassium sulfide is present so long as tetrathionate exists. It also explains the regular increase in the thiosulfate content and the ultimate elimination of tetrathionate.

M. J. Fordos and A. Gellis (5) state that mild oxidizing agents like ferric chloride react with sodium thiosulfate to give tetrathionate.

$$2Na_2S_2O_3 + 2FeCl_3 \rightarrow Na_2S_4O_6 + 2NaCl + 2FeCl_2$$

Thus the tetrathionate is formed due to the oxidation of thiosulfate by the very weak chromic acid present in the initial stages. This reaction accounts for the fact that no test for tetrathionate is obtained when chromate is absent.

Direct estimation of tetrathionate was found to be cumbersome, and therefore the values for sulfate found by the acidification method have been given in tables 7a, 7b, and 7c.

SUMMARY AND DISCUSSION

The brown solid formed in the intermediate stages of the reduction of 5 per cent potassium dichromate by hydrogen sulfide consists of chromium dioxide and hydroxide, a coördinated chromium thiosulfate, chromium ~~tetrathionate, and free sulfur, while the filtrate contains unattacked potas~~sium dichromate together with potassium thiosulfate and tetrathionate.

The amount of tetrathionate decreases with the amount of chromate present, until eventually both disappear simultaneously.

So long as chromate remains sulfide is not present, and the dichromate accounted for as thiosulfate is less than theory by the amount of tetrathionate formed.

Accepting views previously advanced (3, 4) for the development of thiosulfate in these reactions, it has been shown that thiosulfate is the source of the tetrathionate formed in a side reaction, owing to the mild oxidation of part of the thiosulfate by chromate.

The tetrathionate is ultimately reduced to thiosulfate by the alkaline sulfide.

Sulfate is not formed in these reductions if the concentration of hydroxyl ions is above a certain critical value.

The final products are (a) a precipitate containing chromium hydroxide, sulfur, and a complex chromium thiosulfate in which the ratio of ionic to coördinated thiosulfate is approximately 2:1, and (b) potassium thiosulfate and polysulfide in solution.

The polysulfide formed depends on the temperature of the reaction, being K_2S_3 at laboratory temperatures and the pentasulfide at temperatures approaching 90°C.

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Editor's Note: Owing to unforeseen circumstances, the publication of this paper has been unavoidably delayed. A private communication from Professor Dunnicliff states that further investigation has proved that, if the reduction of sodium, potassium, or ammonium dichromates is carried out rapidly at 90–95°C., some sulfate appears in the product, but no sulfate is formed after the reaction mixture becomes alkaline. The formation of sulfate is totally suppressed in the alkaline media which result from the reduction of the chromates of sodium, potassium, and ammonium.

A study of the reduction of the insoluble chromates by hydrogen sulfide has also yielded valuable results. Among the reduction products of silver, mercurous, and thallous chromates at medium or low temperatures, sulfite has been found, while the chromates of lead, barium, strontium, etc. give no sulfite in any circumstances.

Evidence is adduced to show that sulfite is the precursor of both thiosulfate and sulfate in the general reaction. Details of this work will be published shortly.

PHOTOCHEMICAL REACTION BETWEEN SODIUM FORMATE AND IODINE AND A RELATION BETWEEN CHEMICAL REACTIVITY AND LIGHT ABSORPTION

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Amongst the photochemical reactions taking place in solutions, the iodine–formate reaction is easy to investigate as it is fairly rapid. N. R. Dhar (24) first showed that the reaction between sodium formate and iodine is markedly photosensitive; he studied the reaction only in visible light with iodine dissolved in an aqueous solution of potassium iodide, which considerably inhibits the reaction velocity. This reaction has now been investigated in detail, using an aqueous solution of iodine without any potassium iodide. In addition to kinetic measurements we have tried to establish a relation between chemical reactivity and light absorption photographically with different concentrations of the reactants.

EXPERIMENTAL PROCEDURE

A tilting-type quartz mercury-vapor lamp working at 220 volts was used in order to obtain ultra-violet radiations, whereas for visible and infra-red radiations, a 1000-watt gas-filled tungsten filament lamp was employed. All materials used were purified by recrystallization. Merck's pure iodine was further purified by resublimation. All solutions were prepared in conductivity water. In order to isolate different regions from the entire spectrum of the light source, solution filters were used. The light transmitted by these filters has been carefully determined and described in previous papers (1). The filters used for infra-red radiations cut off all the visible and ultra-violet light. For measurements of the energy absorbed, a Moll thermopile with a sensitive galvanometer was used. The velocity of the reaction at a particular instant was ascertained by estimating the unchanged iodine against very dilute solutions of sodium thiosulfate.

The reaction is monomolecular in the dark. The expression for a semimolecular reaction velocity is

$$K_{\frac{1}{2}} = \frac{2}{t}\left\{\frac{1}{\sqrt{a-x}} - \frac{1}{\sqrt{a}}\right\}$$

where a denotes the initial concentration of the reactant and x its concentration after a period t. The reaction between sodium formate and iodine follows the semimolecular law when the system is illuminated by radiations of different wave lengths, as is clear from table 1.

KINETICS

The temperature coefficients have been calculated after deducting the dark reaction velocity (see tables 2 and 3).

The results show that Einstein's law of photochemical equivalence is not obeyed. This is true for many exothermal photochemical reactions, and it appears that the energy given out in the transformation of molecules, caused by light absorption, may effect activation or loosening of the binding forces of molecules. The quantum yield increases with temperature and the frequency of the incident radiation.

TABLE 1

The reaction between sodium formate and iodine

CONDITIONS	TIME	HYPO PER 5 CC. OF THE REACTING MIXTURE	REACTION VELOCITY
	minutes	*cc.*	
Dark (T = 20°C.)......................	0 10 20	4.6 3.75 3.05	0.00888 (K_1) 0.00892 (K_1)
Mean K_1..			0.00890
λ = 4295 A.U. (T = 15°C.)............	0 10 20	4.6 3.7 2.9	0.04419 ($K_{\frac{1}{2}}$) 0.04416 ($K_{\frac{1}{2}}$)
Mean $K_{\frac{1}{2}}$..			0.04418

RELATION BETWEEN THE INTENSITY OF LIGHT (AMOUNT OF ENERGY ABSORBED) AND THE VELOCITY OF REACTION

We have investigated the problem of the variation of the relation between intensity and velocity by changing the amounts of potassium iodide (a marked retarder) present in the iodine solution, and thus altering the dark reaction velocity. The results given in table 4 show that the relation between the velocity and intensity in the reaction between sodium formate and iodine at 20°C. can vary from $I^{\frac{1}{4}}$ to $I^{\frac{1}{2}}$.

From the results given in table 4 it is obvious that there are two important factors which are of consequence in the relation between intensity and velocity of the reaction: (1) the amount of absorption of the incident radiation by the reacting system, and (2) the acceleration of the reaction on illumination. A photochemical reaction which follows less than direct

TABLE 2

Reaction between sodium formate and iodine (aqueous without potassium iodide)
N/25 sodium formate; *N*/1125 iodine; *N*/400 borax (used as buffer)

CONDITIONS	TEMPERATURE	K (SEMIMOLECULAR)	TEMPERATURE COEFFICIENTS	QUANTUM YIELD
	°C.			
Dark	15	0.03393	1.77	
	20	0.04166		
	25	0.06012		
λ = 3125 A.U. (range of transmission = 3290–2961 A.U.)	15	0.06101	1.45	32
	20	0.07214		46
	25	0.09921		64
λ = 3340 A.U. (range of transmission = 4063–2618 A.U.	15	0.05282	1.52	31
	20	0.06485		40
	25	0.08835		54
λ = 3452 A.U. (range of transmission = 3307–3598 A.U.)	15	0.04865	1.57	26
	20	0.06120		36
	25	0.08329		42
λ = 3512 A.U. (range of transmission = 3290–2961 A.U., 4023–4063 A.U.)	15	0.04865	1.57	
	20	0.06120		
	25	0.08329		
λ = 4295 A.U. (per cent of transmission = 20.4; range of transmission = 4000–4590 A.U.)	15	0.04418	1.61	
	20	0.05688		
	25	0.07669		
λ = 5700 A.U. (per cent of transmission = 16.2; range of transmission = 5200–6200 A.U.)	15	0.04059	1.66	
	20	0.05187		
	25	0.07119		
λ = 6640 A.U. (per cent of transmission = 58.8; range of transmission = 6280–7000 A.U.)	15	0.03859	1.71	
	20	0.04696		
	25	0.06809		
λ = 8500 A.U. (range of transmission = 8000–9000 A.U.)	15	0.03662	1.75	
	20	0.04417		
	25	0.06483		

relationship, becomes directly proportional or even greater than proportional to the intensity of incident radiation, by increasing the dark reaction velocity and exposing it to radiation, slightly absorbed by the system. On the contrary, a photochemical reaction which is nearly proportional to the square of the incident radiation or is directly proportional can be made to be proportional to the square root of the incident radiation by decreasing the dark reaction velocity. This is certainly one of the many reactions which have been proved by us to show a variable relation between the velocity and the light intensity or amount of energy absorbed (compare reference 4, pp. 340–4).

TABLE 3

Reaction between sodium formate and iodine (aqueous solution containing a little potassium iodide)

N/6.25 sodium formate; *N*/6.7 sodium acetate; *N*/204 iodine; *N*/47.4 potassium iodide

CONDITION	TEMPERATURE	$K_{\frac{1}{2}}$ (SEMI-MOLECULAR	TEMPERATURE COEFFICIENTS
	°C.		
Dark	20	0.00883	4.26
	30	0.03760	4.17
	40	0.15686	
λ = 4295 A.U.	20	0.01216	3.95
	30	0.05076	3.84
	40	0.20736	
λ = 5700 A.U.	20	0.01104	4.14
	30	0.04676	4.04
	40	0.19391	
λ = 6640 A.U.	20	0.010529	4.19
	30	0.04472	4.02
	40	0.18547	
λ = 8500 A.U.	20	0.00928	4.22
	30	0.03948	4.12
	40	0.16461	

Temperature coefficients

The results recorded in table 2 show that the temperature coefficient of the dark reaction velocity has the value 1.77 between 15°C. and 25°C., when aqueous solutions of iodine are employed. On the contrary the temperature coefficient has the value 4.26 between 20°C. and 30°C., and 4.17 between 30°C. and 40°C., when a little potassium iodide (*N*/47.4) is added to the aqueous iodine solution. Potassium iodide markedly retards the reaction. This is in agreement with the observations of N. R. Dhar (3), who showed that the temperature coefficient of a reaction falls off when

TABLE 4

Relation between reaction velocity and light intensity

EXPT.	REACTANTS	SOURCE OF LIGHT	DIAMETER OF THE APERTURE IN CM.	DARK REACTION VELOCITY	K_1 (MONOMOLECULAR AFTER DEDUCTING THE DARK REACTION VELOCITY
A	*N*/6.25 sodium formate; *N*/6.7 sodium acetate; *N*/204 iodine; KI, 1.0464 g. in one liter	Total light from 1000-watt lamp	2.2 0.5 1.0	0.00561	0.00566 I 0.00035 III 0.001293 II
B	*N*/6.25 sodium formate; *N*/6.7 sodium acetate (as buffer); *N*/204 iodine; *N*/47.4 potassium iodide	Total light from 1000-watt lamp	2.2 1.0 0.5	0.00180	0.00472 I 0.00132 II 0.00044 III
C	*N*/25 sodium formate; *N*/1125 iodine without KI; *N*/26.8 sodium acetate	Total light from 1000-watt lamp	2.2 1.0 0.5	0.00826	0.00764 I 0.00166 II 0.00060 III
D	*N*/25 sodium formate; *N*/1125 iodine; *N*/400 borax (as buffer)	Total light from 1000-watt lamp	2.2 1.0	0.00890	0.00483 I 0.00091 II
E	Same as in D	Mercury vapor lamp, λ = 3340 A.U.	2.2 1.0		0.01954 I 0.00288 II
F	Same as in D	λ = 3125 A.U.	2.2 1.0		0.02083 I 0.00372 II

EXPT.	RATIO OF VELOCITIES	IF DIRECTLY PROPORTIONAL TO CHANGE IN INTENSITY	EXPT.	RATIO OF VELOCITIES	IF DIRECTLY PROPORTIONAL TO CHANGE IN INTENSITY
A	I/II = 4.37 II/III = 3.67 I/III = 16.07	4.84 4.0 19.36	C	I/II = 4.6 II/III = 3.8 I/III = 17.5	4.84 4.0 19.36
B	I/II = 3.57	4.84	D	I/II = 5.3	4.84
	II/III = 3.0 I/III = 10.7	4.0 19.36	E	I/II = 6.7	4.84
			F	I/II = 5.6	4.84

it is accelerated and rises when it is retarded. Moreover, it will be observed that the temperature coefficient in ultra-violet light, which markedly accelerates the reaction, varies from 1.45 to 1.57 between 15°C. and 25°C. Hence it is clear that the greater the velocity of the reaction in light, the smaller is the temperature coefficient of the reaction.

When the reaction is accelerated by infra-red radiations of mean wave length 8500 A.U., which affect the velocity much less than ultra-violet light, the difference between the temperature coefficients of the thermal and photochemical velocities is much less. In radiations of wave length 8500 A.U. the temperature coefficient between 25°C. and 15°C. is 1.75. In other words, the greater the acceleration of the reaction by light absorption, the smaller is the temperature coefficient.

CHEMICAL REACTIVITY AND LIGHT ABSORPTION

We have measured the light absorption of the reacting substances separately and in mixtures by photographing their absorption spectra with Hilger quartz spectrographs E_1 and E_3 using a copper arc as the light source. The effect of increase in the concentration of sodium formate on light absorption on the entire spectrum, with a constant concentration of iodine and *vice versa*, has also been investigated photographically. The exposure for taking the photographs was varied from 7 to 45 seconds. The amount of chemical change during the period of exposure was negligible, and hence the products formed as a result of the chemical change from the reacting mixtures did not play any important part in effecting the light absorption. We have tested this by taking the photographs with 20

FIG. 1. VISIBLE AND ULTRA-VIOLET REGION

From 5220 to 3247 A.U. Exposure = 45 seconds. Ilford rapid plates

	Light absorption
(1) Copper arc	
(2) *N*/700 iodine	5220–5105 A.U. 5105–4580 A.U. 4573–4441 A.U. 3577–3426 A.U. 3426–3282 A.U.
(3) *N*/2 sodium formate	No absorption
(4) Mixture of *N*/350 iodine with *N* sodium formate	5220–5105 A.U. 5105–3247 A.U.
(5) *N*/4 sodium formate	No absorption
(6) Mixture of *N*/2 sodium formate with *N*/350 iodine	5105–4850 A.U. 4441–3247 A.U.
(7) *N*/8 sodium formate	No absorption
(8) Mixture of *N*/4 sodium formate with *N*/350 iodine	5105–4441 A.U. 4441–3266 A.U.
(9) *N*/12.5 sodium formate	No absorption
(10) Mixture of *N*/6.25 sodium formate with *N*/350 iodine	5105–4441 A.U. 4441–3266 A.U.

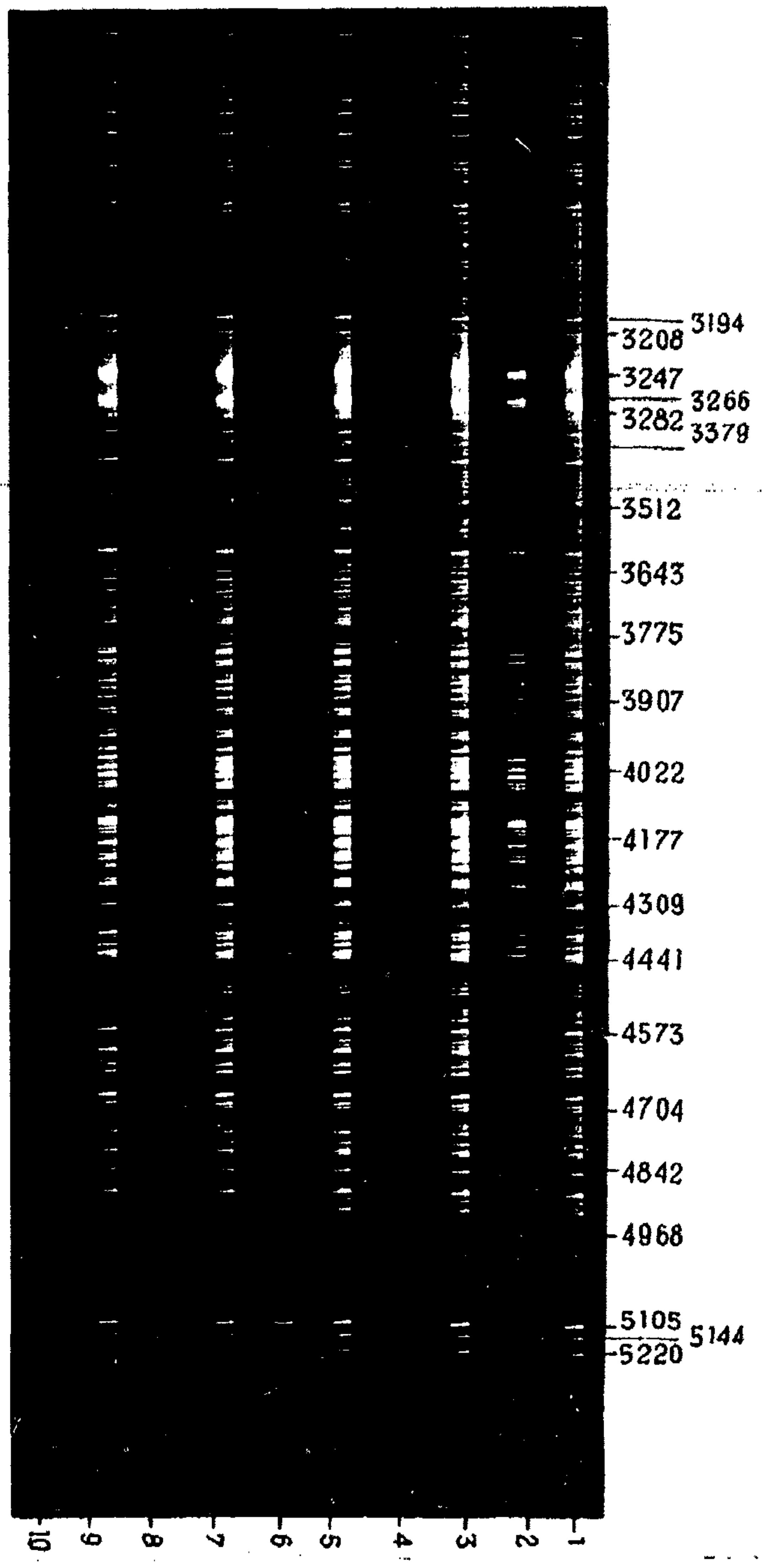
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Fig. 1

seconds and 7 seconds exposure and found no perceptible difference in light absorption.

Figures 1 to 5 are the photographs taken with different concentrations of sodium formate and a constant concentration of iodine (aqueous), separately and with mixtures.

From the photograph taken with $N/2$ sodium formate and $N/700$ iodine separately and their mixtures, it is evident that the iodine solution alone shows complete absorption from 2369 A.U., while with sodium formate complete absorption begins from 2294 A.U., but in the mixture complete absorption starts from 5216 A.U. It appears, therefore, that the presence of sodium formate sensitizes the decomposition of iodine molecules, which becomes reactive in radiations of longer wave lengths on the addition of sodium formate. The addition of sodium formate weakens the binding forces of halogen molecules, which are readily broken up either by increase of temperature or illumination, and thus increased light absorption has been observed with the mixture. Hence the reactivity of a mixture is preceded by the formation of an additive product with the weakening of the binding forces and increased light absorption.

Our experimental observations further show that the increase in the concentration of the reducing agent leads to more light absorption by the mixture. In other words, the higher the concentration of the reducing agent, the greater is the light absorption by the mixture of the reducing agents with the halogens. This may be due to the loosening of the binding forces of more of the iodine molecules, leading to increase in light absorption, especially of *visible and ultra-violet regions*.

It has also been observed by us that the decrease in the concentration of iodine, keeping the concentration of sodium formate constant, leads to a diminution of light absorption by the mixture, as is clear from the above photographs. It is interesting to note that the variation of the concentration of iodine produces more marked effect on light absorption by the mixture than when the concentration of the reducing agent is altered.

FIG. 2. VISIBLE AND ULTRA-VIOLET REGION

From 5220 to 3274 A.U. Exposure = 45 seconds

	Light absorption
(1) Copper arc	
(2) $N/1400$ iodine	5105–4573 A.U. 4573–4441 A.U.
(3) $N/2$ sodium formate	No absorption
(4) Mixture of N sodium formate and $N/700$ iodine	4022–3266 A.U.
(5) $N/4$ sodium formate	No absorption
(6) Mixture of $N/2$ sodium formate and $N/700$ iodine	3907–3379 A.U.
(7) $N/8$ sodium formate	No absorption
(8) Mixture of $N/4$ sodium formate and $N/700$ iodine	3775–3400 A.U.

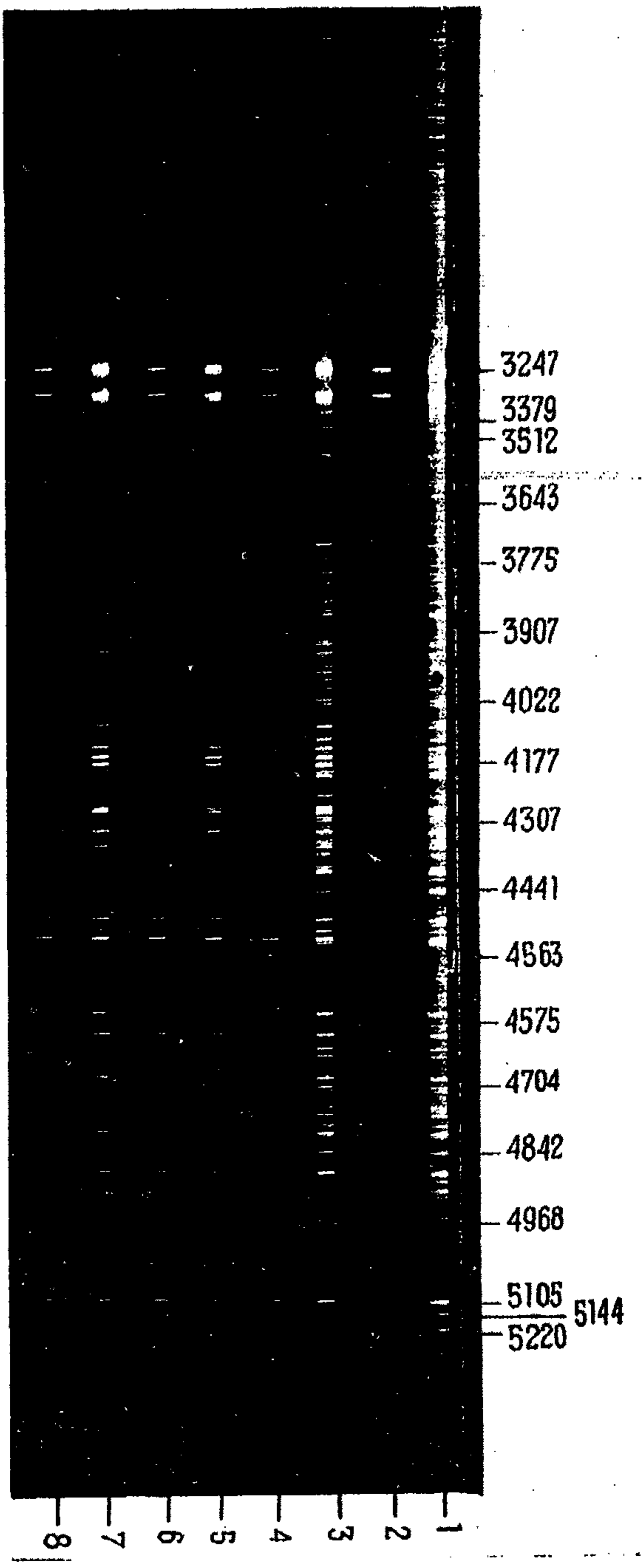
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FIG. 2

The observations of Fajans and Karagunis (5) on increased light absorption by silver halides containing adsorbed silver and those of Weigert and Kellermann (7) on increased light absorption by a mixture of chlorine and hydrogen, and the increased light absorption observed by J. C. Ghosh and collaborators (6) with mixtures of organic substances and solutions of ferric and mercuric chlorides and uranyl nitrate, etc., can be interpreted on the viewpoint that the chemical reactivity of these various systems is associated with the weakening of the binding forces and increased light absorption.

Our conclusions are also supported by the observations of Franck and Victor Henri, who showed that light absorption or increased temperature enhances the reactivity and the power to absorb light of gaseous molecules. Just as the physical agencies like light absorption, increase of temperature, etc., can loosen the binding forces of the molecule, so the introduction of a reactive chemical substance into a light-absorbing system can weaken the

FIG. 3. ULTRA-VIOLET REGION

From 3247 to 2442 A.U. Exposure = 45 seconds

	Light absorption
(1) Copper arc	
(2) $N/700$ iodine	3000–2961 A.U. 2961–2824 A.U. 2824–2766 A.U. 2766–2618 A.U. 2600–2492 A.U. 2492–2442 A.U.
(3) $N/2$ sodium formate	No absorption
(4) Mixture of N sodium formate and $N/350$ iodine	Total absorption
(5) $N/1400$ iodine	2961–2882 A.U. 2880–2824 A.U. 2824–2766 A.U. 2729–2618 A.U.
(6) $N/4$ sodium formate	No absorption
(7) Mixture of $N/2$ sodium formate and $N/350$ iodine	Total absorption
(8) Mixture of $N/2$ sodium formate and $N/700$ iodine	3194–2618 A.U. 2618 onwards total
(9) $N/8$ sodium formate	No absorption
(10) Mixture of $N/4$ sodium formate and $N/350$ iodine	3247–2618 A.U. 2618 onwards complete
(11) Mixture of $N/4$ sodium formate and $N/700$ iodine	3012–2618 A.U. 2610–2492 A.U. 2492 onwards complete

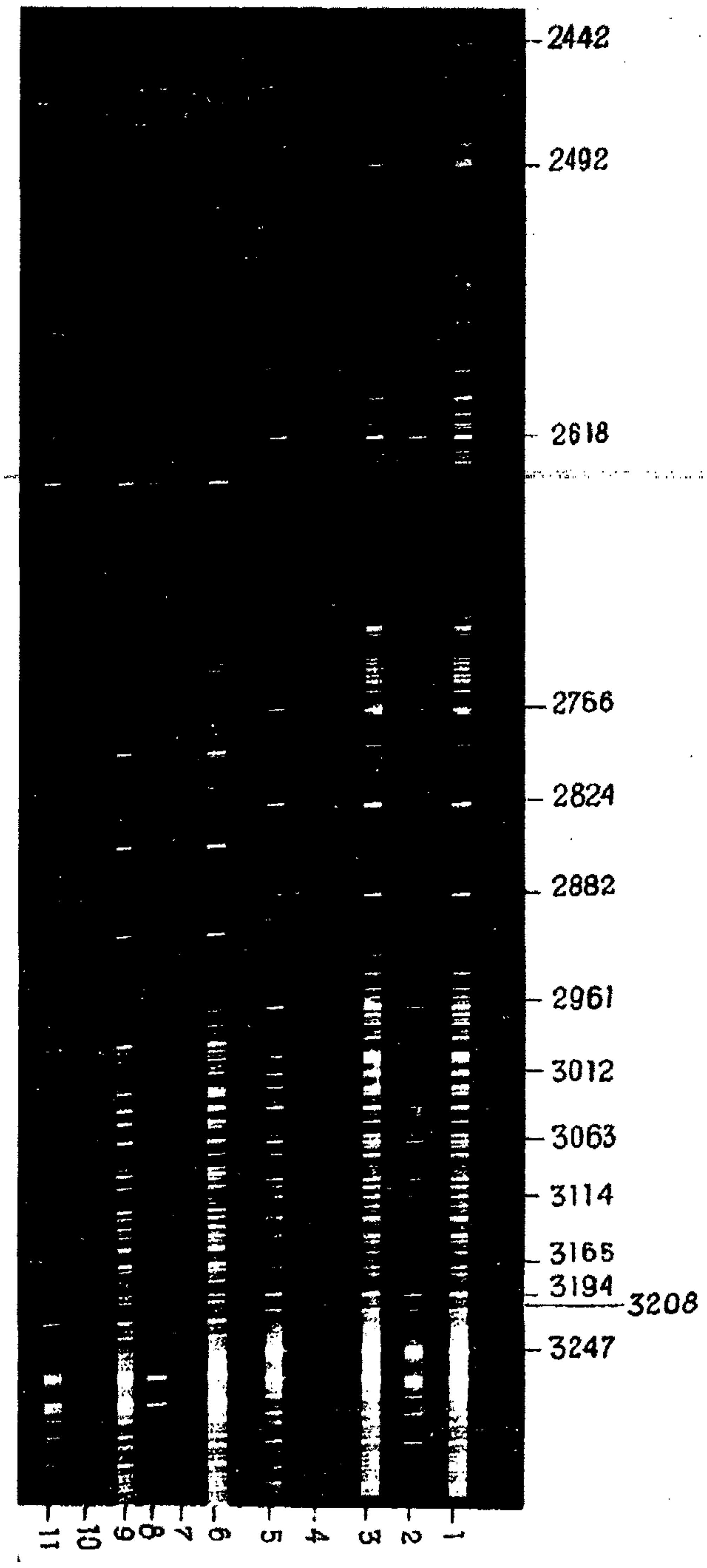
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Fig. 3

FIGS. 4 AND 5. ULTRA-VIOLET REGION
From 2406 to 2104 A.U. Exposure = 45 seconds

	Light absorption
(1) Copper arc	
(2) $N/700$ iodine	2406-2398 A.U. 2398-2392 A.U. 2392-2369 A.U. and onwards complete
(3) $N/2$ sodium formate	2369 onwards complete
(4) Mixture of $N/350$ iodine and N sodium formate	Total absorption
(5) $N/4$ sodium formate	From 2369 total absorption
(6) Mixture of $N/2$ sodium formate and $N/350$ iodine	Total absorption
(7) Copper arc	
(8) $N/1400$ iodine	2369 A.U. onwards complete absorption
(9) Mixture $N/700$ iodine and N sodium formate	Total absorption
(10) Mixture $N/700$ iodine and $N/2$ sodium formate	Total absorption
(11) $N/8$ sodium formate	2369-2303 A.U. 2303 onwards complete absorption
(12) $N/4$ sodium formate and $N/350$ iodine	Total absorption
(13) $N/4$ sodium formate and $N/700$ iodine	Total absorption

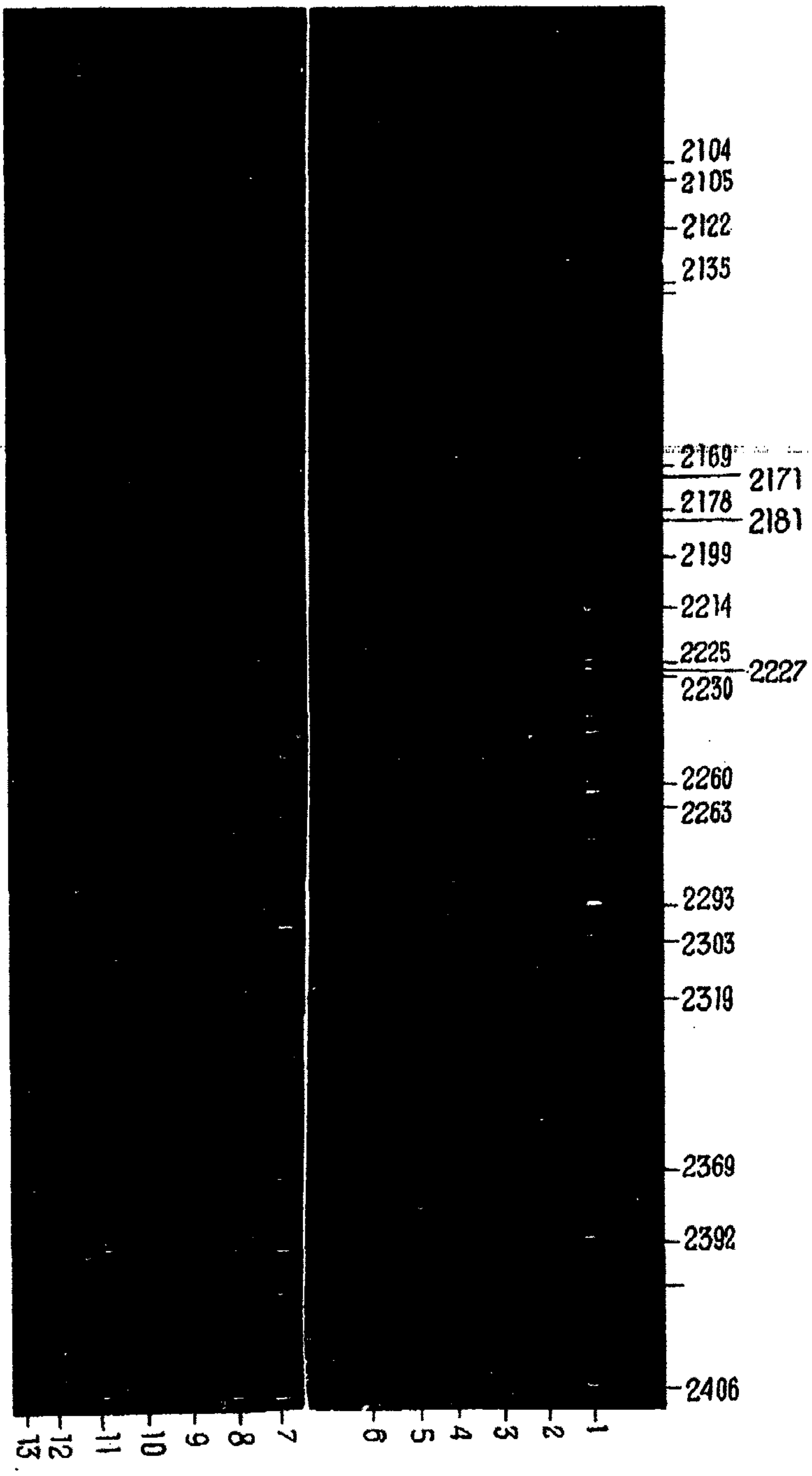
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FIG. 4 AND 5

binding forces of the molecule. In other words, the presence of a reducing agent like sodium formate sensitizes the decomposition of iodine molecules and makes them reactive in radiations of longer wave lengths. It seems that chemical reactivity is associated with increased light absorption.

SUMMARY

1. The reaction between sodium formate and iodine (aqueous) in the absence of potassium iodide is unimolecular in the dark and semimolecular in light.

2. The temperature coefficient of the reaction velocity between 15°C. and 25°C. has the following values: 1.77 (dark), 1.75 (8500 A.U.), 1.71 (6640 A.U.), 1.66 (5700 A.U.), 1.61 (4295 A.U.), 1.57 (3512 A.U.), 1.57 (3452 A.U.), 1.52 (3340 A.U.), and 1.45 (3125 A.U.). The greater the acceleration due to light, the smaller is the temperature coefficient.

3. The relation between light intensity and velocity of the reaction varies from I^1 to $I^{\frac{1}{2}}$.

4. Einstein's law of photochemical equivalence is not obeyed. The quantum yield increases with the temperature and the frequency of the incident radiation.

5. It has been observed that the light absorption by a mixture of sodium formate and iodine is greater than the absorption by the ingredients. The increased absorption appears to be due to the activation of the iodine molecules by the presence of the molecules of the reducing agent. The activation of the molecules is associated with the weakening of the binding forces and consequent increased light absorption.

The increase in the concentration of sodium formate or iodine causes an increase in the light absorption by the mixture of sodium formate and iodine.

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THE ABSORPTION OF CAUSTIC SODA BY CELLULOSE

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In a recent paper by Bancroft and Calkin (1) highly accurate data for the composition of the liquor removed by centrifuging a mass of cellulose impregnated with caustic soda solution are given. These authors make use of the change in concentration of the centrifuged liquor to determine the point where "adsorbed solution" begins to come off, and so to calculate the "true" adsorption as distinct from the "apparent" adsorption calculated from the change-in-titer method. They do not emphasize, however, the importance of the fact that the concentration of the adsorbed solution removed by powerful centrifuging falls steadily as centrifuging proceeds.

There appears to be no *a priori* reason why this should be the case, but it would follow if the concentration of free hydroxyl ion in the adsorbed solution is determined by the Donnan equation, as suggested by the author (2).

The following values derived from the latter half of table 1 of Bancroft and Calkin's paper demonstrate that this fall is very marked.

CENTRIFUGING TIME INTERVAL	GRAMS REMOVED IN INTERVAL		"INTERVAL" CENTRIFUGED LIQUID NaOH PER GRAM OF H_2O
	NaOH	H_2O	
minutes	*grams*	*grams*	*grams*
0–¼	0.1573	0.831	0.1893
¼–½	0.0120	0.070	0.171
½–1	0.0143	0.086	0.166
1–3	0.0064	0.050	0.128

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NEW BOOKS

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Annual Tables of Constants. A.C. and Numerical Data Chemical, Physical, Biological and Technological, published under the patronage of the International Union of Chemistry. Volume X. Two parts, about 1800 pages. New York: McGraw-Hill Book Co., Inc., 1930. Price (for subscribers): cloth, $20.00.

This very useful volume covers the research published in 1930. All texts are given in both French and English.

F. H. MacDougall.

Hochpolymere organische Naturstoffe. By H. Saechtling. 22 x 14 cm.; vi + 125 pp. Braunschweig: Friedr. Vieweg und Sohn, 1935. Price: 8 RM.

This is a neat little book, just the thing one wants nowadays when it is fast becoming almost impossible to attend to one's business and at the same time take an intelligent interest in, let alone make proper use of, other people's work. The structure and properties of the high polymers and condensation products, natural and artificial, is a big subject which daily grows more and more important both for biology and industry, but the gist of it is well set out here, and the author is to be congratulated on his contribution. There are several other, and larger, books available, each authoritative in its way, but Dr. Saechtling has tried to dissociate himself from any particular viewpoint or method of approach, and has concerned himself rather with bringing out as concisely as possible the essential unity of ideas that has now been reached.

After a statement of the problem, the treatment falls into seven chapters, dealing in turn with the general chemical principles underlying the structure of the natural high polymers, microscopic investigations, x-ray investigations, constitutional chemistry, structure and mechanical properties, artificial high polymers as an aid to understanding the natural high polymers, and natural growth structures, the whole being supported by a selection of more specialized textbooks and a list of no fewer than 239 references to original papers. For the most part the argument rests, of course, on cellulose, the proteins, and rubber, but it will be seen that the scheme is eminently reasonable, and there can be no hesitation about recommending this book to anyone looking for a rapid and up-to-date sketch of a field that is not merely of great technical significance but that lies at the very foundation of the science of life itself.

W. T. Astbury.

Molekülspektren und ihre Anwendung auf chemische Probleme. I. Tabellen. By H. Sponer. 21 x 14 cm.; vi + 154 pp. Berlin: Springer, 1935. Price: unbound, 16 RM; bound, 17.60 RM.

Customarily tables of data such as these would form an appendix to the main text of a comprehensive work. The plan here adopted of issuing the tables separately has the double advantage of enabling the author to revise the tables more frequently than the text and readers who so wish to have the tables without the text, which is to follow in volume II. The tables for diatomic molecules contain constants for all the known electronic states and band systems, observed isotope effects, predissociations, alternating intensities and nuclear spins, and electron impact processes. Most of them are based, as Dr. Sponer very generously acknowledges, on the corresponding tables in the reviewer's Report (Physical Society, 1932), supplemented by more recent data and by columns giving electron configurations and dissociation products. For polyatomic molecules the tables, which are entirely new, cover infra-red and Raman spectra (with diagrams showing modes of vibration), electronic bands, and electron impact processes. Data published while the rest of the volume was in the press in 1934 and early 1935 are included in two supplementary tables. A brief explanation and a list of references accompany each group of tables, and the work is well indexed. Remarkably few omissions and numerical errors have been detected. The compilation, which represents a vast amount of careful work, will be invaluable to spectroscopists and chemists.

W. JEVONS.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 53: Molybdän. 25.5 x 17.5 cm.: xi + 393 pp. Verlag Chemie, 1935. Price: 64 marks.

The present volume deals with the ores of molybdenum, the extraction, refining, and physical and chemical properties of the metal and its alloys, and with the chemistry of the compounds of molybdenum, including the heteropolyacids. The treatment is very detailed and physicochemical aspects are well represented. The book contains a wealth of accurate and well-arranged information, and the literature is covered till the end of 1934.

J. R. PARTINGTON.

Kristallplastizität. By E. SCHMID and W. BOAS. 22 x 15 cm.; x + 373 pp. Berlin: Julius Springer, 1935. Price: 32 marks (paper covers), or 33.80 marks (bound).

The study of crystal plasticity has made remarkable progress in recent years; this has been achieved by a number of workers largely independent of each other, and not infrequently approaching the problem with different aims. For example, the plastic nature of the crystalline state is of great importance to the engineer in his search for special alloys; the chemist and physicist, however, are more concerned to extract what they can to shed light upon the nature of the forces acting in the lattice. The authors of the present book have in fact provided an encyclopaedia of all that is at present known about these matters, with special reference to metals.

The volume falls into three parts,—general, special experimental results, and the significance of the effects shown by single crystals. An idea of the scope embraced by the writers can be gathered from the list of references collected at the end, which number over seven hundred entries.

The discussion of hardness in ionic crystals is exceptionally clear. Two points are stressed (which even to-day need underlining), firstly that hardness is not a definite quantity, but only has a meaning when expressed in terms of a particular method of determination, and secondly, that the time is not yet when we can link such observations with crystal strength, and consequently, no doubt, with lattice properties. Scratch-hardness curves for rock salt and fluorite on the (100) and (111) faces are delightful illustrations of the anisotropy of a surface. The same is true of the pendulum method for rock salt on (001), yielding maximum values of about 0.5 with an intervening minimum as low as about 0.2.

The price of the book is very high, but for those wishing to have all the information there is to be had about plasticity in crystals, this book should be invaluable. As in the case of other Springer publications, the format is excellent.

F. I. G. RAWLINS.

The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases. By J. T. RANDALL. 23 x 15 cm.; xii + 290 pp. London: Chapman and Hall, 1934. Price: 21s.

In producing this book Dr. Randall has done a great service to science. Ever since the discovery, in 1912, of diffraction of x-rays by crystals our knowledge of the solid state has gone forward by leaps and bounds. And now, Dr. Randall produces a volume covering the field of diffraction of rays in non-crystalline media. His treatment is admirably logical. He begins with a short summary of the methods of crystal analysis by x-rays and electrons. This introduces the fundamental notion of the diffraction pattern of a crystal consisting of rays of different intensities and the effect on this pattern of decreasing the size of the crystal, as in this way is reached the liquid state, being the limit of infinite diminution of crystal size. Before passing to liquids, however, it is necessary to see what the diffraction effects of individual atoms and molecules are, and this can be determined by the diffraction of electrons and of x-rays in gases where the mutual diffraction of molecules is neglected. A description is given of modern methods of electron molecular analysis. The diffraction of liquids represents the superposition of effects of the individual molecules and their mutual position.

Dr. Randall gives particular attention to the structure of liquid metals, water, and the paraffins. He proceeds from the study of liquids to the consideration of the glasses and gives a careful description of the phenomenon of vitrification.

The remaining chapters are devoted to a discussion of fibers, the structure of surfaces as revealed by electron diffraction, and finally the nature of liquid crystals.

The treatment throughout is admirably clear. There is a full bibliography. The whole of the subject is still in a controversial state, but Dr. Randall is fair and reserved in his conclusions. Anyone who has read this book will have acquired a knowledge of the structure of liquids and glasses which is bound to be of great value in dealing with both the chemical and physical sciences.

J. D. BERNAL.

Principles of Phase Diagrams. By J. S. MARSH. 193 pp. New York: The McGraw-Hill Book Company.

This excellent work purports to provide a "moderately strong grounding in the principles of the phase theory," but it does considerably more than that. It furnishes a skeleton for the study or review of a generous slice of the field of fundamental thermodynamics. It is by no means a book that can be skimmed, as the reviewer soon discovered. In the foreword Dr. John Johnston warns that it is not for the casual reader and "even the studious reader will find that he must himself do a deal of hard thinking."

The book apparently evolved away from the original idea. It is one of the Alloys of Iron Research Series and was originally intended as a utilitarian key to point the way to interpretation of some of the numerous phase diagrams with which metallographists and metallurgists are always struggling. Undoubtedly there is call for a key. As the plan for the work progressed, it soon became evident that a detailed, cook-book sort of explanation for a few diagrams would not fill the bill,—that an exposition of underlying principles was what was needed. Thus the book finally evolved into a "generalized treatment, to appear as a special monograph of the series, which would at once care for the needs of the student, the chemist, the metallurgist, or any other person confronted with a problem of so-called heterogeneous equilibrium, whether his interest be in organic, inorganic salt or metallic systems." The author has undoubtedly succeeded in putting the requisite material in his allotted

187 pages of text material, but if he expects the average "student, chemist or metallurgist" to be able to master it, he has decidedly overshot his mark.

As it stands, it is a book for the experts, though in the preface the author seems to apologize because he did not "enter the field of advanced phase theory or of philosophic argument." Even at that he is working considerably over the heads of those who are going to be the greatest users of the books of the Alloys of Iron Research Series. It is a book for experts, because the material is for the most part presented in the abstract or a generalized form; not as abstractly as Gibbs presentations by any means, but the treatment is usually too general to build up clear physical concepts. That the reader must do for himself, and he must have a considerable background of experience in that sort of thing.

In a few cases the author must have felt that he was throwing out a morsel a little too tough for the intended audience and therefore tried to "write down" to the field; he usually overdid it. For example, he uses almost two pages to explain the very simple items of mass percentage, "often called (erroneously) *weight percentage*," and mole percentage, but in the next chapter he uses only a little over one-half a page to explain a subject fully one hundred times as involved,—the conditions of thermodynamic equilibrium. He also seems to spend a great deal of time in polishing his definitions to the point of fastidiousness.

Though the title of the book and the preparatory intentions may be somewhat misleading, that does not detract from its excellence. For the well-trained physical chemist, well versed in heterogeneous equilibria, it is an excellent review and gives many new viewpoints. For the average person who will be interested in phase diagrams, this book should be labelled as a base camp in a wilderness of considerable complexity. It should be the frame work for a reading course of considerable magnitude, a place to which the explorer can return at frequent intervals to replenish his supplies, but not, it is feared, to rest. The work would be useful to a great many more people if there were more complete and specific references for outside study. This is especially necessary to help build up physical concepts by illustration of known physical phenomena.

The average person who becomes interested in phase diagrams is one who has had a certain amount of physical chemistry and perhaps thermodynamics, but is by no means an expert in heterogeneous equilibrium. He suddenly has good reason to learn more of the significance of the complex labyrinth of some ternary diagram. He soon discovers his shortcomings and decides to study up a bit. Such a person should not be advised to take this book undiluted. The reviewer would recommend that he first brush off some of the dust by reviewing portions of one of the simpler college texts on physical chemistry, Getman's perhaps. Then he should work over the applicable portions of the section on heterogeneous equilibrium in Taylor's *Treatise on Physical Chemistry*. After this "warming up" period, he should take up Marsh's Chapter I, on "Fundamentals." This chapter may then seem very simple, but that is an illusion, for the background study is essential to master all the concepts involved. The student should then jump over the long and meaty Chapter II, "Fundamentals (Continued)", and study the chapter entitled "Systems of One and Two Components." After that it is time to leave Marsh for a while. The student needs some outside work at this point to help build up concepts for the three-component system. Passing over all the pedagogical efforts in this field, there is probably nothing that will help as much in giving a person an understanding of a complicated three-component system as Rankin and Wright's outstanding article on "The Ternary System $CaO-Al_2O_3-SiO_2$" (Am. J. Sci. [4] **39**, 1-79 (1915). A side excursion into Findlay's *Phase Rule* might be interesting but not necessary. After the student has gone this far he can probably interpret most phase diagrams with considerable confidence and facility. If he wishes to go deeper into the subject he should now return to Marsh's Chapters IV and V on ternary systems, provided he is ready to do some serious studying. He may profitably continue into the chapter on "Conclusions," where systems of more than three components are discussed. If by this time the student is interested in the real fundamentals of the subject, he may turn to Chapter II "Fundamentals (Continued)." He will get a good review of parts of his thermodynamics and might find it profitable to refer to portions of Lewis and Randall's *Thermodyncmics* and Planck's *Treatise on Thermodynamics*. In addition to this he will find some interesting discussions on the properties of non-perfect solutions and intermolecular forces. After completing this course of study the student will feel that he has been to places of considerable consequence, but the long journey is necessary if one is to get a real understanding of the material in Marsh's book. The short distance between the covers is deceptive. Do not be misled.

C. C. Furnas.

The Optical Basis of Chemical Valence. By R. de Kronig. Cambridge Physical Chemistry series. 237 pp.; 67 figs. Cambridge University Press.

The modern ideas of atomic and molecular structure are discussed briefly. Most of the mathematical formulas are stated without derivation. Any other procedure is of course impossible in the space of this volume. The book best lends itself therefore to obtaining a general view of modern thought in the fields of structure of atoms and molecules as derived from spectroscopy. The nature of chemical binding and dissociation are dealt with on a modern basis. The beginning student can get a good survey of the field, and the advanced reader will enjoy the clear concise style in which the book is written. That the author has succeeded in covering the field remarkably well is shown by the chapters into which the volume is divided: I. Introduction. II. The investigation of atomic and molecular structure by means of x- and cathode rays. III. Atomic spectra and the periodic system. IV. Band spectra and chemical binding in diatomic molecules. V. Band spectra and chemical binding in polyatomic molecules. VI. Optical and thermal dissociation. Each chapter ends with a bibliography and a list of references to the original literature. A special table of the electron configuration of the elements is appended. Any reader who would use this volume as a guide to a study of modern chemical physics and follow some of the literature cited, would gain a very complete picture of this fascinating subject.

George Glockler.

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