Anonyme. The Journal of physical chemistry. Published at Cornell university [puis Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1933 . Jan.-May.

1/ Les contenus accessibles sur le site Gallica sont pour la plupart des reproductions numériques d'oeuvres tombées dans le domaine public provenant des collections de la BnF.Leur réutilisation s'inscrit dans le cadre de la loi n°78-753 du 17 juillet 1978 :
*La réutilisation non commerciale de ces contenus est libre et gratuite dans le respect de la législation en vigueur et notamment du maintien de la mention de source.
*La réutilisation commerciale de ces contenus est payante et fait l'objet d'une licence. Est entendue par réutilisation commerciale la revente de contenus sous forme de produits élaborés ou de fourniture de service.

Cliquer ici pour accéder aux tarifs et à la licence

2/ Les contenus de Gallica sont la propriété de la BnF au sens de l'article L.2112-1 du code général de la propriété des personnes publiques.

3/ Quelques contenus sont soumis à un régime de réutilisation particulier. Il s'agit :

*des reproductions de documents protégés par un droit d'auteur appartenant à un tiers. Ces documents ne peuvent être réutilisés sauf dans le cadre de la copie privée sans l'autorisation préalable du titulaire des droits.
*des reproductions de documents conservés dans les bibliothèques ou autres institutions partenaires. Ceux-ci sont signalés par la mention Source Gallica.BnF.fr / Bibliothèque municipale de ... (ou autre partenaire). L'utilisateur est invité à s'informer auprès de ces bibliothèques de leurs conditions de réutilisation.

4/ Gallica constitue une base de données, dont la BnF est producteur, protégée au sens des articles L341-1 et suivants du code la propriété intellectuelle.

5/ Les présentes conditions d'utilisation des contenus de Gallica sont régies par la loi française. En cas de réutilisation prévue par un autre pays, il appartient à chaque utilisateur de vérifier la conformité de son projet avec le droit de ce pays.

6/ L'utilisateur s'engage à respecter les présentes conditions d'utilisation ainsi que la législation en vigueur, notamment en matière de propriété intellectuelle. En cas de non respect de ces dispositions, il est notamment passible d'une amende prévue par la loi du 17 juillet 1978.

7/ Pour obtenir un document de Gallica en haute définition, contacter reutilisation@bnf.fr.

Journal of physical chemistry

Tome 37

Volume 45

Washington 1933

The Journal of
PHYSICAL CHEMISTRY

(Founded by Wilder D. Bancroft)

Volume XXXVII

BALTIMORE
1933

CONTENTS

Number 1, January, 1933

Number 2, February, 1933

Communications to the Editor:

New Books:

Number 3, March, 1933

Communications to the Editor:

New Books:

Number 4, April, 1933

Communications to the Editor:

New Books:

Number 5, May, 1933

Communications to the Editor:

New Books:

Number 6, June, 1933

Number 7, October, 1933

New Books:

Number 8, November, 1933

New Books:

NUMBER 9, DECEMBER, 1933

New Books:

AN ISOTHERMAL CALORIMETER FOR SLOW REACTIONS[1]

E. D. COON AND FARRINGTON DANIELS

Laboratory of Physical Chemistry, University of Wisconsin, Madison, Wisconsin

Received October 15, 1932

This calorimeter has been designed for the study of phenomena involving the slow evolution of heat, particularly in the study of chemical kinetics and biological processes. It can be used at different temperatures. The heating effect is exactly counterbalanced by a cooling effect produced by evaporating carbon tetrachloride or other liquid in a regulated air stream. The amount of carbon tetrachloride evaporated is determined by adsorption in silica gel. The increase in weight is converted into calories by calibration with electrical heating. In its present form the calorimeter is limited to a precision of about one per cent, and it is not recommended for rapid reactions with plenty of material where standard calorimeters are now satisfactory.

Endothermic reactions can be measured accurately and easily by balancing with measured electrical heating. Exothermic reactions have been balanced by melting ice at 0°C. as in the Bunsen ice calorimeter, by vaporization of a liquid at its boiling point as in the ether calorimeter (1), by addition of cold water (2), cold mercury (3) or a salt which absorbs heat on solution (4). The Peltier effect existing between two dissimilar metals, when a current of electricity flows, has been used also (5, 6).

DESCRIPTION OF THE CALORIMETER

The calorimeter is shown in figure 1. It consists of two vacuum-walled vessels, I and N, mounted with various accessories on a frame, immersed in a large thermostat 20 cm. below the water level. The vessels are connected by a multiple junction thermel. The "reference" unit I, which stays at constant temperature, contains fine oil of low vapor pressure, an electric heater, and a stirrer. A second thermel (not shown) indicates equality of temperature between the oil and the water of the thermostat.

The "variable" unit N of 400 cc. capacity contains kerosene. The cover of nickel-plated iron sets into a mercury seal shown at F. A ring of sheet iron, held in place with rubber, contains the mercury and the whole seal is protected on the outside with large rubber tubing. Various ac-

---

[1] Further details of this investigation are contained in part of a Ph.D. thesis filed in the Library of the University of Wisconsin by E. D. Coon in January, 1932.

THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XXXVII, NO. 1

cessories, passing through small tubes in the cover, are attached with litharge-glycerine cement.

In the first models the whole calorimeter was filled with carbon tetrachloride and short sections of rubber tubing were exposed to the vapor, but it was found that the variable vessel was always a little colder than the thermostat even after standing twenty-four hours. This cooling effect, which persisted no matter whether the room was colder or warmer than the thermostat, was finally traced to solution of the carbon tetrachloride vapor in the rubber and a slow evaporation of the liquid to maintain full vapor pressure.

3321

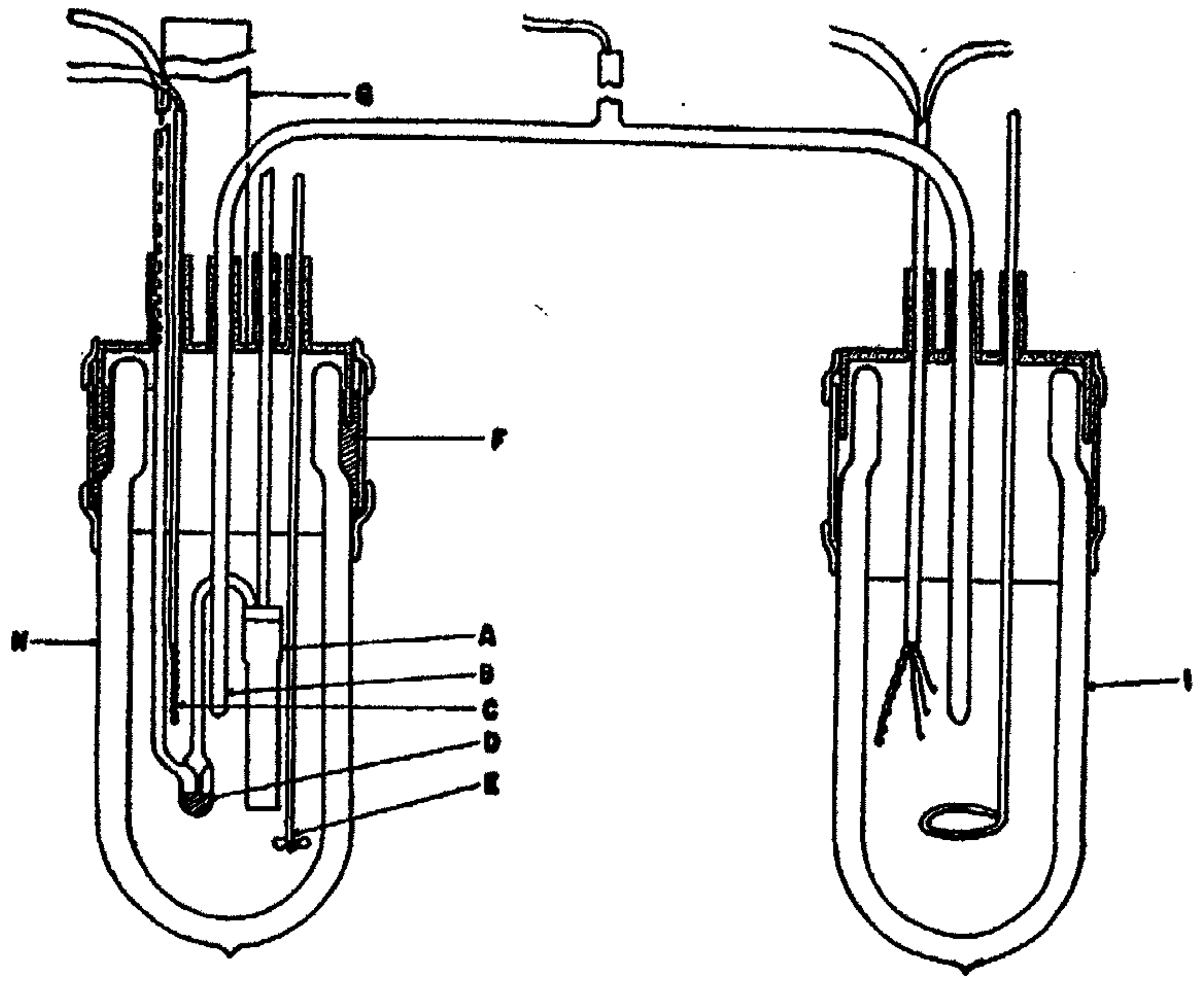


Fig. 1. Isothermal Calorimeter

The thermel B connects with the reference unit. The stirrer E of glass extends through a long bearing to the water level. The glass shaft is cemented to a brass rod which rotates in a bearing several centimeters above the cover. The heat generated in the bearing is prevented by the thermostat from reaching the calorimeter. The chimney G, for the admission of reacting materials, extends to the water level where it is provided with a stopper. The heating coil C of 50 cm. bare No. 28 constantan wire is wound on a glass tube and soldered to leads of No. 16 copper wire. The leads are set in paraffin in long snugly-fitting glass tubes passing through the thermostat water.

The cooling unit A is a cylinder of sheet copper containing carbon tetrachloride through which air is bubbled. Other inert liquids of different vapor pressures may be more suitable under other conditions. For high temperatures a higher boiling liquid is better. The mercury trap D is introduced to insure the same conditions at the beginning and at the end of a determination. A small glass tube (not shown) passes down through the exit tube and ends near the mercury level. By turning a stopcock, air is forced down through this tube and all the vapor beyond the mercury seal is swept out.

The air sent through the cooling unit must be dry and free from any substance which might be adsorbed by the silica gel. The rate of flow is regulated by four stopcocks drawn down to capillaries of different apertures. Connecting these in parallel, it is possible to send air through at any rate from ten to several hundred bubbles per minute. The air is dried by passing it through concentrated sulfuric acid, calcium chloride, phosphorus pentoxide, and silica gel. It is brought to the temperature of the calorimeter by passing through three glass tubes, 2 cm. in diameter and 80 cm. long, filled with copper turnings and immersed in the thermostat. In the last tube is an additional section of phosphorus pentoxide.

The amount of carbon tetrachloride evaporated is determined by adsorbing in two glass-stoppered U-tubes, each containing about 75 grams of silica gel. When the second tube increases in weight by more than about 1 mg. the first tube is rejuvenated by placing in an oil bath at 150° to 170°C. and drawing through dry air for two or three hours.

The thermostat of 750 liters capacity is kept constant within about 0.001° with the help of efficient stirring and a mercury regulator of the oscillating type. The contact wire dipping into the mercury in the capillary is forced up by a spring against the under side of a horizontal pulley wheel. The under side of the wheel is partly cut away so that the contact wire moves up and down for a distance of about 2 mm. during one revolution, thus making and breaking the circuit and insuring certain contact with the mercury.

The thermel, which indicates a difference in temperature between the "variable" and "reference" units, consists of two 11-junction elements. Each is used independently of the other and one acts as a check on the other. Constantan wire (No. 28) and copper wire (No. 24) were used. The resistances of the thermels were 39.92 and 40.29 ohms. When used with the galvanometer, having a sensitivity of 5 mm. per microvolt, a deflection of 1 mm. corresponded to 0.00025°C. The two thermels always agreed within 3 mm. A reversing switch was useful in correcting for possible stray potentials in the circuits. Other switches enabled the operator to use either one of the two thermels or to connect the galvanometer with the potentiometer for use with the heating coil. All connections and switches were well insulated and mounted on grounded copper shields.

PROCEDURE

The thermostat is first brought to the desired temperature (25°C., for example). The reference unit is brought to a temperature slightly lower and the whole calorimeter is set in the thermostat. The temperature of the "reference" is then brought to the temperature of the thermostat by means of the heating coil. The final temperature adjustment is effected simply by means of stirring. The galvanometer is then connected to one of the main thermels connecting the two units, and the temperature of the "variable" unit is brought to the same temperature, using either the heater or the cooler as necessary. These adjustments can be effected in a short time, but in order to insure complete equilibrium the system is left undisturbed for several hours,—preferably over night, when both thermels should read within 0.5 cm. of zero.

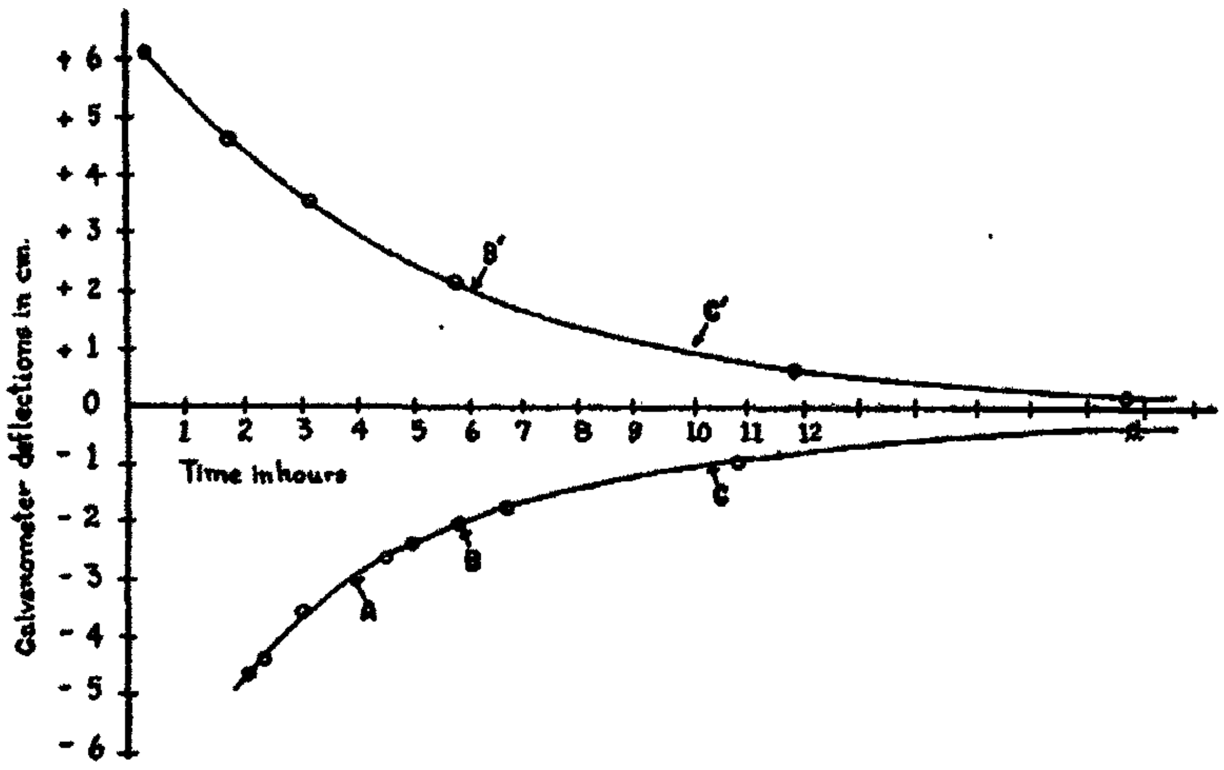


FIG. 2. RATE OF THERMAL LEAKAGE
Calories per hour. A = 0.25, B = 0.12, C = 0.06, B' = 0.12, C' = 0.07.

The next step is the establishment of a reproducible condition in the cooler. Air is bubbled through the carbon tetrachloride, and the vapor that passes through the mercury trap is washed out by a stream of air from the inner tube. The temperature is brought back with the heater until the galvanometer reads zero. The silica gel tubes are weighed separately and connected to the outlet of the cooling unit.

The reacting material is then introduced through the chimney, and during the course of the determination the temperature is maintained as nearly isothermal as possible. The galvanometer deflections of the thermel are kept within 3 or 4 cm. of the zero point and the times of the positive and negative deflections are kept about equal. With slow reactions evolving less than 3 or 4 calories per hour this control is not difficult, and with reactions involving more heat the control becomes relatively less important.

At the end of a determination the vapor in the exit tube of the cooler is again swept out and if necessary the original temperature is restored. The silica gel tubes are weighed and the heat of reaction determined by the amount of carbon tetrachloride adsorbed; 0.0206 gram is equivalent to 1 calorie as shown below.

It is easier—and also sufficiently accurate—to apply a small correction at the end of the experiment than to bring back the galvanometer exactly to zero. Experiments with the direct input of electrical heat showed that a deflection of 1 cm. corresponded to 0.357 calorie in the empty calorimeter and to 0.372 calorie when the calorimeter contained reacting material in a certain glass tube.

The errors introduced by thermal leakage when the calorimeter is not exactly balanced, are shown in figure 2. Tangents to these experimental curves give the rates of cooling or heating. A deflection of 1 cm. of the thermel-galvanometer indicates that the temperature of the variable unit differs from that of the reference unit and the thermostat by 0.0025°C., and that the transfer of heat then amounts to 0.06 calorie per hour.

CALCULATIONS

The input of electrical heat was determined by standard methods with a type K potentiometer.

The heat of stirring constitutes the least accurate part of the measurements but the correction is small—about 0.1 calorie per hour. In slow reactions it is necessary to maintain stirring only for a portion of the time, and in more violent reactions the total evolution of heat is large compared with the heat of stirring. After a rapid change in temperature it is necessary to stir for at least ten minutes to insure thermal equilibrium.

The heat of vaporization of carbon tetrachloride

It was not the object, in this investigation, to find the true heat of vaporization but rather to determine the heat of vaporization under the conditions of this calorimeter so that exothermic heats of reactions may be calculated from it. It is possible that a slight Joule-Thompson effect at the mercury trap and some loss of spray have prevented the determination of the true heat of vaporization. Nevertheless the value obtained here is not greatly in error and the method can be adapted easily for exact measurements of the heats of vaporization of liquids at various temperatures.

The carbon tetrachloride was purified by refluxing for 2 hours with potassium dichromate and sulfuric acid. It was fractionally distilled and the portion boiling between 75.18°C. and 75.20°C. at 734.2 mm. was used.

The rate of flow of air through the cooler was adjusted so that the heat absorbed in evaporating the carbon tetrachloride practically offset the electrical heating. The average value of the current through the heating coil was obtained by plotting the current against time and estimating the median height. The value obtained is at least one decimal place beyond significant figures. A small "end correction" was applied for failure to reach complete "isothermality" at the end of a determination.

Several experiments were carried out using a current of about 0.1 ampere for times ranging between fifteen and thirty minutes and evaporating 0.25 to 0.5 gram. It was found that at 25°C. the evaporation of 0.0206 ± 0.0002 gram of carbon tetrachloride is necessary to offset the evolution of 1.00 calorie (15° calorie) of heat. No calorimetric determination of the heat of vaporization of carbon tetrachloride at 25°C. is available in the literature as a check on this value. In fact most heats of vaporization have been determined only at the normal boiling point; a few at 0°C. A value of 0.0200 gram per calorie was obtained from the Clausius-Clapeyron equation, using the vapor pressure data from the International Critical Tables.

Heat of neutralization of hydrochloric acid

The accurately known heat of neutralization of hydrochloric acid by sodium hydroxide was chosen to test the calorimeter, even though such a fast reaction as this can be determined more accurately with other, simpler types of calorimeters. It was thought that a satisfactory check using only 2 cc. of 0.5 N hydrochloric acid would give confidence in measuring unknown heats of reaction.

Exactly 2.00 cc. of 0.4942 N hydrochloric acid was placed in the thin glass vessel shown in figure 3 and sealed off. A slight excess of 0.5 N carbonate-free sodium hydroxide was placed in the upper compartment and the whole vessel was brought to the temperature of the thermostat and then submerged in the calorimeter. When thermal equilibrium was established the tip of the inner tube was broken with a long rod and the upper solution allowed to flow down. Mixing was effected by gentle shaking. The reaction was so rapid that in attempting to keep the temperature constant, too much carbon tetrachloride would often be evaporated. In such cases it was necessary at times to use the heating coil. The results are summarized in table 1. The values in the last column are obtained by subtracting the sum of all the corrections from the calories absorbed by the vaporization of carbon tetrachloride.

Considering the small amount of material used the average value of 13.39 is in very good agreement with the best values in the literature obtained with large quantities. Recalculation of the data of Richards and Rowe (7) and of Richards and Hall (8) and a correction from 0.55 *N* give 13,909 calories for the heat of neutralization per mole in 0.50 *N* solutions at 20°C. Correcting to 25°C. this value becomes 13,642 calories per mole and 2.00 cc. of 0.4942 *N* hydrochloric acid then evolve 13.48 calories when neutralized with 0.50 *N* sodium hydroxide.

FIG. 3. MIXING VESSEL

TABLE 1

The heat of neutralization of 2 cc. of 0.4942 N hydrochloric acid

WEIGHT CCl_4	CALORIES EQUIVALENT CCl_4	HEATING COIL	TIME OF STIRRING	HEAT OF STIRRING	END CORRECTION	TOTAL CORRECTION	HEAT OF NEUTRALIZATION
gram		*calories*	*minutes*	*calories*	*calories*	*calories*	*calories*
0.4287	20.81	7.196	55	0.11	+0.145	7.45	13.36
0.3701	17.96	4.666	40	0.08	0.20	4.54	13.42
0.2772	13.44	none	40	0.08	0.10	0.18	13.26
0.2886	14.00	1.00	37	0.07	0.48	1.59	13.41
0.3256	15.80	2.67	55	0.11	0.48	2.30	13.50
						Average =	13.39

Heat of hydrolysis of methyl acetate

The reaction $CH_3COOCH_3 + H_2O + (N\ HCl) = CH_3COOH + CH_3OH + (N\ HCl)$ was chosen for study because it is a typical, slow reaction which can be readily followed by titrations. The reaction was catalyzed by normal hydrochloric acid. It is known that the reaction involves very little thermal change because the equilibrium is nearly independent of temperature. Subtracting the heats of combustion of the reactants from those of the products the reaction appears to be slightly exothermic, the exact heat evolved differing greatly with the various values accepted for the heats of combustion. A slight error in any of these large quantities makes a large relative error in their difference.

As carried out in the present investigation, the reaction proved to be endothermic. The cooling effect was counter-balanced with the heating coil and it was unnecessary to vaporize carbon tetrachloride in the cooler. Ninety cc. of *N* hydrochloric acid was placed in the thermostat and 10 cc. of methyl acetate was added. Ten cc. of the resulting solution was placed in the calorimeter and 2 cc. samples were withdrawn at intervals from the remaining solution for titration. The course of the reaction was thus followed simultaneously for a period of 3 hours and 42 seconds, by thermal analysis and by chemical analysis. The difference between the titrations at the beginning and end of this period showed that 0.00513 mole of methyl acetate had been hydrolyzed in the calorimeter during this time. To maintain the temperature constant it was necessary to add 5.61 calories from the heating coil. The heat of stirring was 0.405, so that the reaction absorbed a total of 6.015 calories, or 1170 calories per mole.

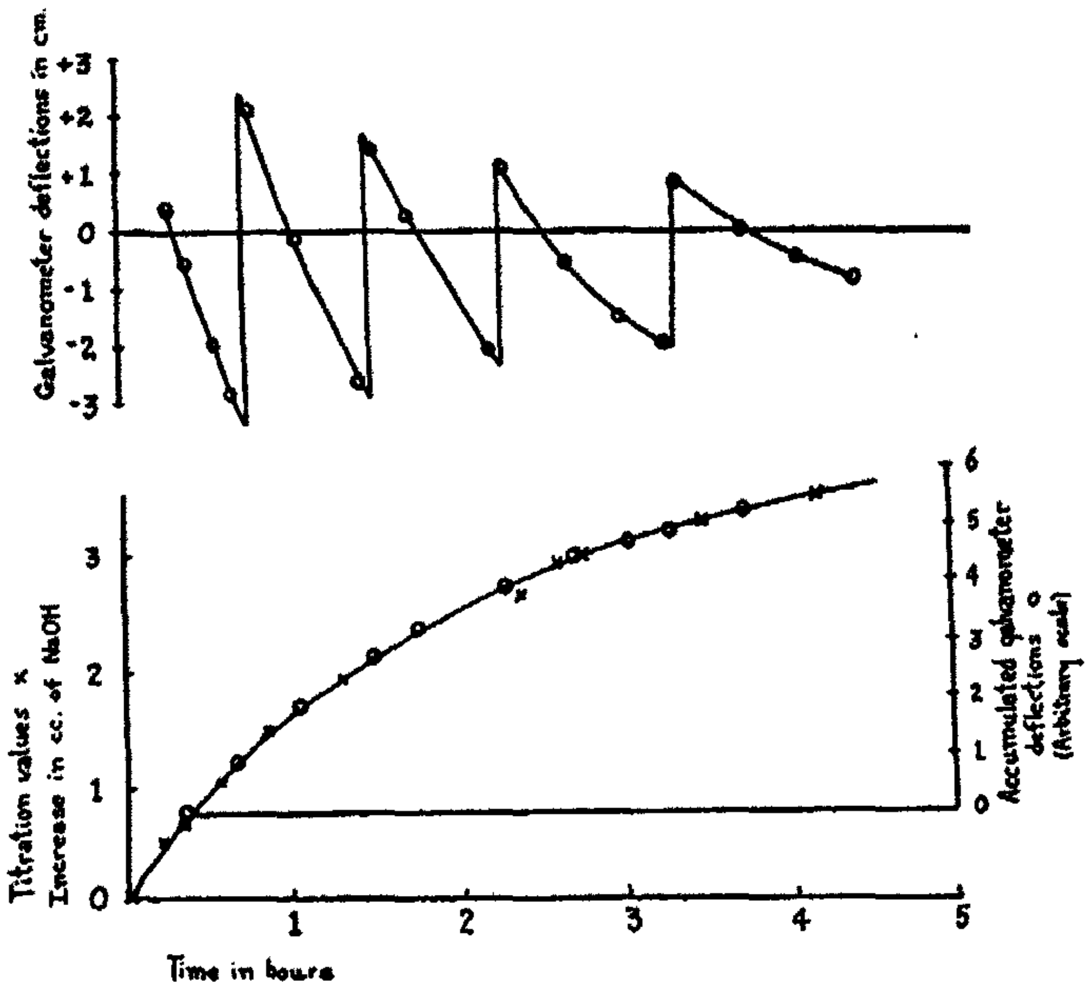


FIG. 4. HEAT ABSORBED IN THE HYDROLYSIS OF METHYL ACETATE
The vertical lines represent measured heat supplied by electric heating coil.
○ Titration data. × Calorimetric data

The course of the thermal reaction in a single determination is shown in the upper graph of figure 4, in which the four vertical lines represent the addition of heat—at approximately 0.1 ampere for intervals ranging from 1.5 to 2.5 minutes.

The true hydrolysis reaction is complicated by the presence of the hydrochloric acid, for as the reaction proceeds the reacting substances are removed from the solution and the products are added. Corrections for these heats of mixing were determined experimentally using the vessel shown in figure 3. Five-tenths of 1 cc. or 0.0065 mole of methyl acetate was added to 10 cc. of *N* hydrochloric acid, this quantity representing nearly the amount removed during the reaction in the calorimeter. The heat evolved was 11.45 calories, corresponding to 1763 calories per mole. Check determinations were 1800, 1793, and 1762 giving an average of 1779 calories.

Similarly, when 0.00705 mole of glacial acetic acid, purified by freezing, was added to 10 cc. of *N* hydrochloric acid solution, the heat evolved per mole was respectively 258, 232, 237, and 227, giving an average of 239 calories.

Adding 0.00748 mole of methyl alcohol to 10 cc. *N* hydrochloric acid, the heat of evolution was 1423, 1421, and 1422 calories per mole. The thermal change following the addition of a similar amount of water to *N* hydrochloric acid was negligible.

The summation of the several reactions is then as follows:

Removal of 1 mole methyl acetate from *N* HCl....	1779 calories absorbed
Removal of 1 mole water from *N* HCl.............	0 calories
Addition of 1 mole methyl alcohol to *N* HCl.......	1422 calories evolved
Addition of 1 mole acetic acid to *N* HCl...........	239 calories evolved
Total heats of mixing...............................	118 calories absorbed
Total reaction as measured.........................	1170 calories absorbed
Heat of reaction per mole, excluding thermal effects with *N* HCl....................................	1052 calories absorbed

One other direct determination of this reaction is reported in the literature (9), giving an absorption of 1070 calories per mole.

Heat of fermentation of yeast

The growth of yeast is an example of the type of reaction for which this calorimeter is uniquely suited. It is an exothermic reaction which proceeds too slowly for accurate measurement in an ordinary calorimeter. In each experiment three culture tubes of yeast and glucose having identical concentrations were prepared. Two were pasteurized at the time the third was placed in a tube in the calorimeter. At the end of the determination this culture was pasteurized also. All were titrated for glucose content and the difference gave the amount of glucose destroyed during the fermentation.[3]

The fermentation caused the temperature to rise slowly and every hour or so air was passed through the cooler, evaporating carbon tetrachloride and bringing the temperature slightly below the normal value. The course of determination I is shown in figure 5, where the vertical lines represent these periods of cooling.

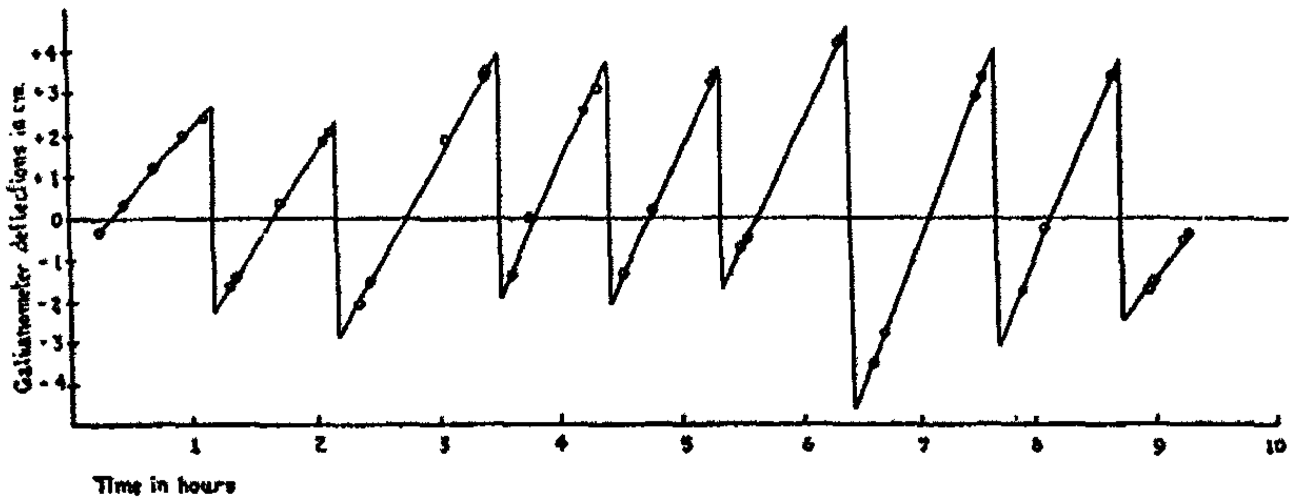


FIG. 5. HEAT EVOLVED IN THE FERMENTATION OF YEAST

The vertical lines represent the measured cooling effect produced by evaporating known quantities of carbon tetrachloride.

The heat of fermentation is calculated from the data of determinations I and II as follows:

	I	II	
Weight of carbon tetrachloride	0.4452	0.1777	gram
Heat compensated	21.60	8.64	calories
Time of stirring	9.1	5.5	hours
Heat of stirring	1.10	.66	calories
Heat of fermentation	20.50	7.98	calories
Correction for vaporization of water	0.59	.23	calories
Corrected heat of fermentation	21.09	8.21	calories
Weight of glucose at beginning	0.260	0.1575	gram
Glucose consumed	0.1617	0.0632	gram
Calories per gram of glucose consumed	130.4	129.9	

The average value of 130.1 calories per gram of glucose is in good agreement with the value 133.3 reported by Rubner (10) using a "microbiocalorimeter" and a Beckmann thermometer.

The correction necessitated by the carrying away of water vapor by the carbon dioxide liberated is calculated from the vapor pressure of water

---

[3] The authors are indebted to Dr. P. W. Wilson of the Department of Agricultural Bacteriology for the yeast cultures and their analyses.

(23.7), the volume of the gas, and the heat of vaporization (582 calories per gram).

The reaction of fermentation

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH$$

should evolve 147.9 calories per gram of glucose according to data on heats of combustion (11). The fact that the observed value differs from this value by 17.8 calories may be due in part to the heats of solution of glucose and ethyl alcohol in water and in part to the fact that other fermentation reactions are occurring also.

An unsuccessful attempt was made to measure the heat of bacterial growth, but the cultures of *Azotobacter* were not large enough to give a reliable value. Less than 0.2 calorie was evolved during a period of 6 hours.

Thermal studies of the decomposition of nitrogen pentoxide in liquid nitrogen tetroxide will be published later.

SUMMARY

1. An isothermal calorimeter is described, capable of measuring continuously for many hours reactions which evolve less than a calorie an hour.

2. Evolution of heat is compensated by evaporating carbon tetrachloride, or other liquid, absorbing the vapor in silica gel, and weighing. Absorption of heat is compensated by measured electrical heating.

3. Special precautions, including the elimination of rubber, are necessary in maintaining an organic liquid in a calorimeter at exactly the same temperature as its surroundings.

4. At 25°C., 48.5 calories was required to offset the vaporization of 1 gram of carbon tetrachloride.

5. Using only 2 cc. of solution, values for the heat of neutralization of 0.5 *N* hydrochloric acid in close agreement with accepted values have been obtained.

6. The hydrolysis of methyl acetate has been found to absorb 1052 calories per mole, after correcting for the heat of mixing with *N* hydrochloric acid.

7. The heat of fermentation of yeast at 25°C. has been found to be 130.1 calories per gram of glucose consumed.

REFERENCES

(1) Keyes and Beattie: J. Am. Chem. Soc. **46**, 1753 (1924).
(2) Waterman: Phys. Rev. **4**, 161 (1896).
(3) Hiroe: J. Faculty Sci. Imp. Univ. Tokyo, Sect. I, **6**, part 4.
(4) Wartenberg and Lerner: Z. physik. Chem. **122**, 113 (1926).
(5) Tian: Compt. rend. **178**, 705 (1924).

(6) Berenger-Calvert: J. chim. phys. **24**, 325 (1927).
(7) Richards and Rowe: J. Am. Chem. Soc. **44**, 699 (1922).
(8) Richards and Hall: J. Am. Chem. Soc. **51**, 735 (1929).
(9) Berenger-Calvert: J. chim. **24**, 325 (1927).
(10) Rubner: Arch. Hyg. **57**, 193 (1906).
(11) Wilson and Petersson: Chem. Rev. **8**, 455 (1931).

THE CRITICAL IGNITION OF EXPLOSIVE HYDROGEN MIXTURES

J. H. MAAS[1] AND CHARLES EWING[2]

University of Cincinnati, Cincinnati, Ohio

Received July 23, 1932

Thornton (1) observed that the least spark energy required to ignite an explosive mixture of a gas in air varies discontinuously as the composition of the gas is changed continuously. If this condition be represented graphically by plotting the least spark energy for explosion of mixtures with the proportion of explosive gas in air, the resulting ignition curve is composed of a series of distinct "steps." This phenomenon, which is called "stepped" or "critical" ignition, is shown to depend upon the presence of nitrogen in the gas mixtures considered here.

It was found that the ignition curve for hydrogen in air mixtures has two very distinct steps. On the other hand, smooth curves were found for mixtures of hydrogen and oxygen and also for mixtures of hydrogen, argon and oxygen wherein the argon was present in the same proportion as nitrogen in the air mixtures. The purpose of substituting argon for nitrogen was to determine if the action of nitrogen on ignition differed from that of an inert gas, and this seems to be the case.

EXPERIMENTAL

The explosions were carried out in an iron bomb of about 100 cc. capacity with a spark gap consisting of a steel needle cathode and a plane anode also of steel. This bomb was conveniently made of ordinary pipe fitting, the main piece a one and one-fourth inch cross. Two one-half inch holes in the cross on opposite sides of the spark gap were fitted with rubber stoppers to provide a safe outlet for the exploding gas, which blows the stoppers out. Steel phonograph needles were used for the cathode. These were replaced for each explosion.

The gas mixtures were made up in volumes of three liters by displacement of water from the gas container. The measurements were made on gases saturated with water vapor and at room temperature. The bomb is filled with gas by mercury displacement.

The electrical arrangement for discharging the spark in the gas consists

---

[1] Department of Physics, University of Cincinnati.

[2] Department of Chemistry, University of Cincinnati.

of charging condensers from a source of direct current with the electrodes wide apart. The direct current source is then disconnected and the condensers discharged by approaching the electrodes. Not more than three seconds need elapse between the time the direct current connection is broken and the time the electrodes are brought within sparking distance.

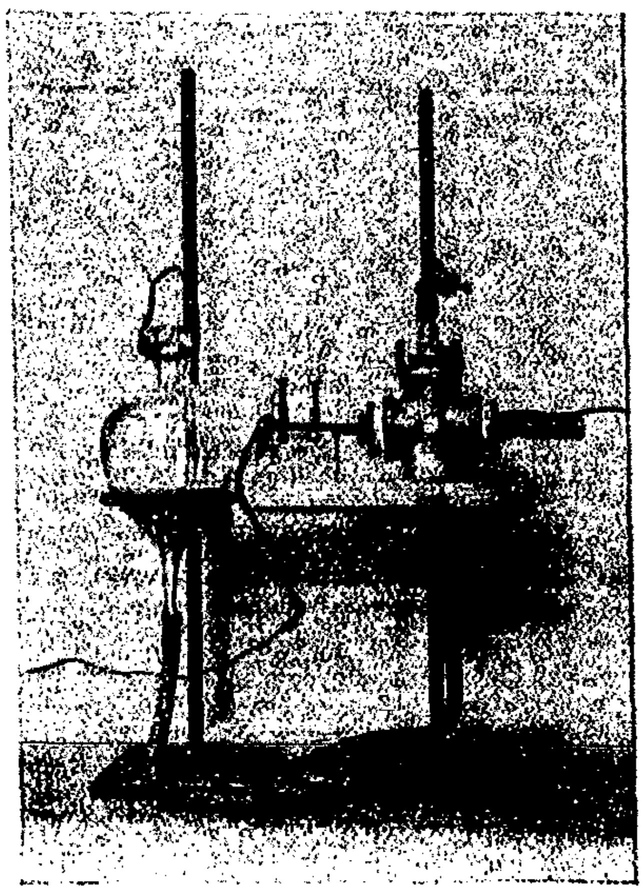


FIG. 1. EXPLOSION BOMB

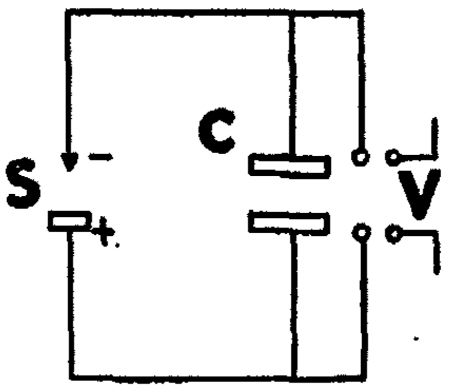


FIG. 2. WIRING DIAGRAM
S, spark gap; C, condenser; V, voltage of D. C. source

During this interval of time there is some leakage loss in the condensers, but it has been found that this loss is negligible up to about twenty seconds.

The energy "E" expressed in terms of the capacity and voltage of the condensers discharged in the spark is expressed as follows:

$$E = 1/2\ CV^2$$

The curves in figure 3 are for ignition at 160 volts, spark potential. Similar curves have been obtained for the ignition of the same hydrogen mixtures at 100 volts, but the least spark energy at this potential is higher than the least spark energy for ignition at 160 volts.

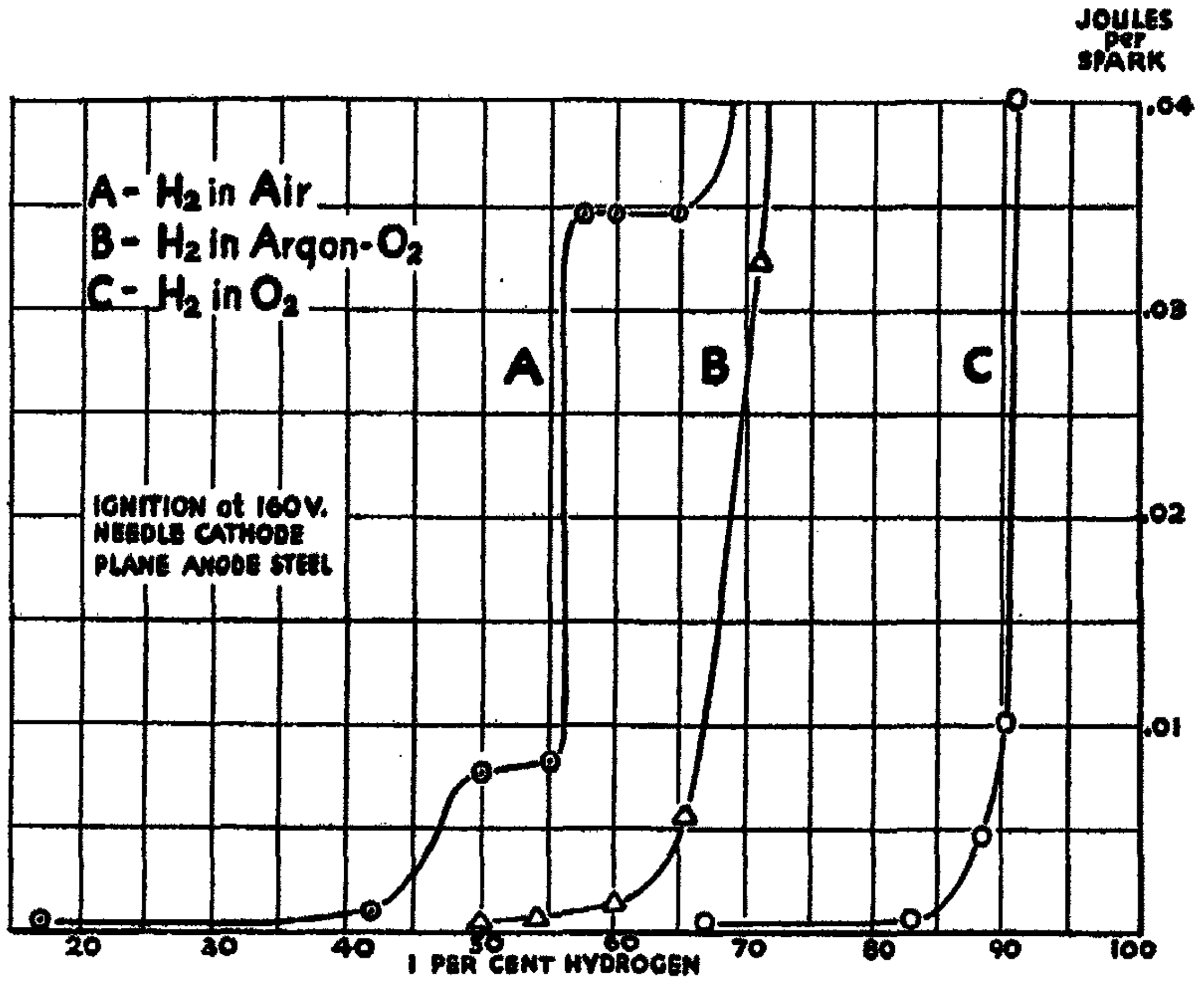


FIG. 3. IGNITION CURVES FOR IGNITION OF HYDROGEN MIXTURES

REFERENCE

(1) THORNTON: Proc. Roy. Soc. London 91, 17 (1914). The Ignition of Gases by Condenser Discharge Sparks.

APPLICATION OF BLAIR-LEIGHTON EQUATION TO X-RAYS

J. A. LESTER AND JULIAN M. BLAIR

Department of Physics, University of Colorado, Boulder, Colorado

Received July 25, 1932

Blair and Leighton (1) have presented an equation,

$$\frac{dx}{dt} = K_1x^{\frac{1}{2}}\,(b - x) - K_2x$$

for the time rate of growth of the latent photographic image, when a photographic emulsion was exposed to a blue light of constant intensity. In this equation, x is the developable density existing at any time t; b is the ideal maximum developable density (defined below); and K_1 and K_2 are reaction velocity constants of forward and reverse photographic reactions. In this paper an attempt will be made to show that this equation also holds for the rate of formation of the latent photographic image when produced by x-rays of constant intensity.

METHOD OF PROCEDURE

Ordinary x-ray plates were not used because of their relative opacity, but instead glass plates coated with regular lantern slide emulsion. For ease and greater accuracy in determining the density, this coating was made about one-third as thick as the ordinary lantern slide emulsion. The source of x-rays was a deep therapy machine. These x-rays were filtered through 1 mm. of aluminum to render them more homogeneous. The conditions during exposure were kept constant by keeping the current through the tube and the operating line potential constant. Under these conditions the intensity of the x-rays was found to be uniform and constant, by means of a dosimeter.

After coating, the plates were dried in an inclined position, making the emulsion slightly thicker on the lower end than the upper. To reduce the error which this would produce, the plates were cut into two longitudinal halves, one of which was turned end for end before exposure. Then exposures of increasing times were given to consecutive portions of the same plate. Several plates were necessary to obtain all the points shown on figure 1. The maximum exposure on one plate was repeated as the minimum exposure on the next. The plates were then developed in a ferrous oxalate developer described by Hurter and Driffield (2) for 20 minutes at 19°C. They were then fixed for 6 minutes in acid sodium thiosulfate solution, and washed and dried in the usual manner. The resultant densities were measured in the same manner as that described by Blair and Leighton (1). The densities of corresponding portions on each half plate receiving the same exposure were measured and averaged.

As the separate plates had emulsions of slightly different average thicknesses, the plotted densities would not form a continuous curve. In several cases there would be slight breaks between the series of data obtained from one plate and that obtained from the next one. The overlapping of times of exposure made it possible to express the densities of all the plates in terms of any one chosen as standard by the use of a small multiplying factor. This factor was the ratio between the average density of one portion of a plate and the average density of a corresponding portion of another, each having received the same exposure. The densities produced by exposures to x-rays are shown by the circles in figure 1.

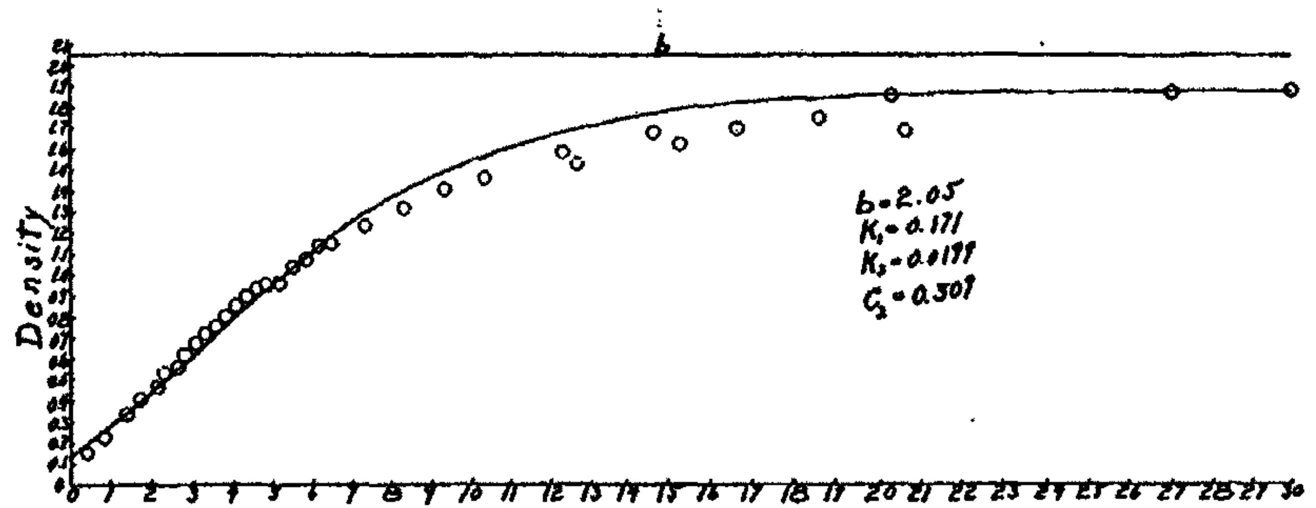


FIG. 1. THE DENSITIES PRODUCED BY EXPOSURE TO X-RAYS AND THE DENSITIES INDICATED BY THE BLAIR-LEIGHTON EQUATION

DETERMINATION OF b

The quantity, b, mentioned in the above equation is the ideal maximum developable density. It may be briefly defined as that density the plate would have if every grain of silver halide were developed. Blair and Leighton (1) have presented a chemical means of determining this quantity. It may also be determined in a much easier, but sufficiently accurate manner. Jones and Hall (3) have shown that increasing maximum developable densities are obtained by exposures to increasing intensities of light. They showed, using the terminology of Blair and Leighton, that when a plate was exposed to intense light, the maximum attainable density approached the ideal maximum developable density. On the basis of their work, one-half of a plate was exposed for the optimum time to the concentrated beam of a carbon arc projection lantern. The other half was exposed for 30 minutes to x-rays to produce the maximum attainable density from this source. The maximum attainable density, shown by the highest point on figure 1, was multiplied by the ratio of the developable density produced by the arc on one half of the plate, to that produced by the x-rays on the other half. This gave a close approximation to the ideal maximum developable density in terms of the plate chosen as standard. This quantity is shown by the straight line in figure 1.

INTEGRATION OF EQUATION

If, in the equation,

$$\frac{dx}{dt} = K_1 x^{\frac{1}{2}} (b - x) - K_2 x$$

we let $x^{\frac{1}{2}} = z$ and add and subtract the quantity $\frac{K_2^2}{4K_1^2}$ the equation may be put in the standard form of integration,

$$\frac{2dz}{K_1 \left[b + \frac{K_2^2}{4K_1^2} - \left(z + \frac{K_2}{2K_1} \right)^2 \right]} = dt$$

There are several integrals of this equation. In the paper by Blair and Leighton (1) it was integrated into a logarithmic form. It may, however, be integrated into the following form

$$\frac{2}{K_1 \sqrt{b + \frac{K_2^2}{4K_1^2}}} \tanh^{-1} \left(\frac{z + \frac{K_2}{2K_1}}{\sqrt{b + \frac{K_2^2}{4K_1^2}}} \right) = t + C_1$$

where C_1 is a constant of integration. Substituting $x^{\frac{1}{2}}$ for z and solving for x we obtain

$$x = \left[\sqrt{b + \frac{K_2^2}{4K_1^2}} \tanh \left(\frac{K_1}{2} \sqrt{b + \frac{K_2^2}{4K_1^2}}\, t + C_2 \right) - \frac{K_2}{2K_1} \right]^2 \tag{1}$$

where

$$C_2 = \frac{K_1 C_1}{2} \sqrt{b + \frac{K_2^2}{4K_1^2}}$$

EVALUATION OF CONSTANTS

From the data shown in figure 1 a ratio between K_1 and K_2 was determined where the slope is 0. Then K_1 and K_2 were evaluated by graphical means from the experimental curve by measuring the slope at some value of x. The constant C_2 was then found by taking the x and t coördinates of some point on the experimental curve. The curve in figure 1 shows the values of x for the times t given by equation 1.

SUMMARY

A different method of evaluating the ideal maximum developable density is described, and a different integral of the Blair-Leighton equation is presented. Evidence is presented that this equation also expresses the rate of formation of the latent photographic image by x-rays.

REFERENCES

(1) BLAIR AND LEIGHTON: J. Phys. Chem. **36**, 1649 (1932).
(2) HURTER AND DRIFFIELD: Phot. J. **38**, 76 (1898).
(3) JONES AND HALL: Proc. 7th Intern. Congr. Phot., p. 115 (1929).

SOLID POLYIODIDES OF CESIUM

H. W. FOOTE, W. M. BRADLEY, AND MICHAEL FLEISCHER

Department of Chemistry, Yale University, New Haven, Connecticut

Received November 21, 1932

It has recently been shown conclusively by Briggs, Greenawald, and Leonard (1) and by Briggs (2) that cesium iodide and iodine form two binary addition products having the formulas CsI_3 and CsI_4 and that the compound CsI_5 does not exist, at least above 25°C. Water solutions were used by these investigators in preparing the compounds at 25°C., but as the latter were anhydrous, they are undoubtedly the only stable binary compounds which can form at 25°C., independent of what solvent is used, or indeed of whether any solvent is used. On the other hand, Abegg and Hamburger (3) working on the system cesium iodide–iodine–benzene showed from solubility results that there was evidence of a higher polyiodide which they believed to be CsI_9. They made no attempt to determine whether a solvated ternary compound existed. Since it has recently been shown (4) that potassium iodide forms such a ternary compound with benzene we have investigated the system cesium iodide–iodine–benzene at 6°C. and at 25°C. and also the system containing toluene in place of benzene.

The cesium iodide used was an exceedingly pure sample which had been prepared by heating the higher polyiodide. The latter had been prepared by crystallization from water containing an excess of iodine. Benzene, toluene, and iodine were prepared by the methods described previously by Foote and Bradley (4). The apparatus and methods are also fully described in the same paper.

THE SYSTEM TOLUENE–CESIUM IODIDE–IODINE

In this system, qualitative tests showed that no solvated compounds were formed and that cesium iodide, like potassium iodide, is insoluble in the solvent. The investigation was therefore relatively simple. The original components were accurately weighed and by determining iodine in the solution after equilibrium had been reached, the composition of the solid residues, whether mixtures or pure compounds, could be calculated with probably greater accuracy than could be obtained by direct analysis. The results obtained are given in table 1.

The results show clearly at each temperature that there are three univariant points. At each, the solubility is constant and the residues consist of a variable mixture of two solids; the two pure compounds, which are in equilibrium with solutions of varying composition, exist between the univariant points. The average of the six results obtained for free iodine in CsI_4 is 59.35; and of the four results for CsI_3 is 49.73. The corresponding calculated percentages are 59.44 and 49.42. The results confirm those of Briggs and his coworkers (1) at 25°C., using water as the solvent, and show that the same compounds also exist at 6°C. No solvated ternary compound with toluene exists.

TABLE 1

The system toluene–cesium iodide–iodine

$T = 25°C.$			$T = 6°C.$		
Iodine in solution	Iodine in residue	Unsolvated solid residue contains	Iodine in solution	Iodine in residue	Unsolvated solid residue contains
weight per cent	*weight per cent*		*weight per cent*	*weight per cent*	
0.060	16.66	CsI and CsI_3	0.024	11.18	CsI and CsI_3
0.047	48.18	CsI and CsI_3	0.024	46.00	CsI and CsI_3
0.77	50.13	CsI_3	0.54	49.70	CsI_3
1.72	49.57	CsI_3	1.08	49.50	CsI_3
2.53	51.42	CsI_3 and CsI_4	1.53	52.30	CsI_3 and CsI_4
2.54	53.80	CsI_3 and CsI_4	1.53	56.25	CsI_3 and CsI_4
2.54	57.21	CsI_3 and CsI_4			
			4.35	59.76	CsI_4
3.09	59.25	CsI_4	6.74	59.79	CsI_4
9.90	58.53	CsI_4			
13.45	59.17	CsI_4			
14.66	59.58	CsI_4	10.39	64.06	CsI_4 and I_2
			10.43	89.77	CsI_4 and I_2
15.46	62.24	CsI_4 and I_2			
15.37	94.32	CsI_4 and I_2			

THE SYSTEM BENZENE–CESIUM IODIDE–IODINE

Qualitative tests showed that at the iodine end of the system the solids contained benzene, showing the existence of a ternary compound. The simple method of calculating the composition of the residue which was adopted with toluene therefore could not be used in this case and it was necessary to analyze the residues, at least when the pure solvated compound was present. The Schreinemaker methodof determining the composition of the solids by the analysis of the wet residues was entirely unsuitable in this case on account of the position and form of the solubility curve. We were therefore forced to determine the composition of the compound by

TABLE 2

The system benzene-cesium iodide-iodine

NO.	IODINE IN SOLUTION	SOLID RESIDUE			RESIDUE CONTAINS
		Iodine	Cesium iodide	Benzene	
		T = 25°C.			
	per cent	*per cent*	*per cent*	*per cent*	
[illegible]	0.049	10.00	90.00	none[*]	CsI and CsI_3
2	0.045	42.14	57.86	none[*]	CsI and CsI_3
3	0.77	49.38	50.62	none[*]	CsI_3
4	1.34	50.00	50.00	none[*]	CsI_3
5	2.35	53.15	46.85	none[*]	CsI_3 and CsI_4
6	2.34	56.68	43.32	none[*]	CsI_3 and CsI_4
7	3.89	59.40	40.60	none[*]	CsI_4
8	5.27	59.40	40.60	none[*]	CsI_4
9	7.76	58.6	33.3	8.1[†]	CsI_4 and T. C.[§]
10	7.74	66.2	14.7	9.1[†]	CsI_4 and T. C.[§]
11	8.88	75.54	15.96	8.50[‡]	T. C.[§]
12	12.19	73.23	16.22	10.55[‡]	T. C.[§]
13	14.09	79.9	12.5	7.6[†]	T. C.[§] and I_2
14	13.83	91.8	5.1	3.1[†]	T. C.[§] and I_2
		T = 6°C.			
15	0.022	12.07	87.93	none[*]	CsI and CsI_3
16	0.024	47.42	52.58	none[*]	CsI and CsI_3
17	0.55	49.25	50.75	none[*]	CsI_3
18	1.20	49.41	50.59	none[*]	CsI_3
19	1.31	53.98	46.02	none[*]	CsI_3 and CsI_4
20	1.30	56.85	43.15	none[*]	CsI_3 and CsI_4
21	2.00	59.37	40.63	none[*]	CsI_4
22	3.41	59.16	40.84	none[*]	CsI_4
23	3.80	59.8	39.9	0.3[†]	CsI_4 and T. C.[§]
24	3.80	67.3	27.1	5.6[†]	CsI_4 and T. C.[§]
25	3.81	71.31	20.15	8.54[†]	CsI_4 and T. C.[§]
26	4.55	74.22	16.74	9.04[‡]	T. C.[§]
27	6.25	75.23	15.23	9.54[‡]	T. C.[§]
28	6.60	76.33	15.64	8.03[‡]	T. C.[§]
29	8.59	81.2	11.7	7.1[†]	T. C. and I_2
30	8.58	92.3	4.8	2.9[†]	T. C. and I_2

[*] Composition of the solid calculated as in the toluene system. Residue unsolvated.

[†] Composition of the solid obtained graphically.

[‡] Composition of the solid determined by analysis (benzene by difference).

[§] Ternary compound.

analysis, after removing it from the solution and freeing it from the mother liquor by pressing rapidly between filter papers. The compound loses its benzene rapidly on standing. On the other hand, the color changes appreciably as it decomposes, so that it was not difficult to determine rather closely from the appearance when the mother liquor was removed. In analyzing the compound, free iodine was determined by titration with thiosulfate and cesium iodide by heating to remove free iodine and benzene. The latter was determined by difference. The composition of the residues at the univariant points could be determined graphically with sufficient accuracy when the composition of the solvated compound was known.

The results given in table 2 were obtained. The method used in determining the composition of the residues is indicated in each case.

The data in table 2 show in an entirely satisfactory manner the existence of the two compounds CsI_3 and CsI_4 at both 6°C. and 25°C. Besides these two compounds, however, there is a third solvated compound. It was present in pure condition, as shown by the solubility results, in Nos. 11 to 12 at 25°C. and in Nos. 26 to 28 at 6°C. The ratio $CsI:I:C_6H_6$ has been calculated for each of these residues, and the results are given in table 3.

TABLE 3

Showing the ratio $CsI:I:C_6H_6$ *for each of the five residues in which the pure ternary compound was present. The ratios are calculated from the analytical data in table 2*

NO.	RATIO		
	CsI :	I :	C_6H_6
11	1.0	9.64	1.77
12	1.0	9.24	2.16
26	1.0	9.07	1.79
27	1.0	10.10	2.08
28	1.0	9.99	1.71
Average =	1.0	9.52	1.90

In considering these ratios, it must be borne in mind that the material used in the analysis was very finely divided, and was of necessity contaminated with iodine from the solution, since the benzene in the latter was exceedingly volatile and deposited iodine as it evaporated. The ratio $CsI:C_6H_6$ appears to be definitely 1:2, and allowing for the fact that the analytical results should be high in iodine, the ratio CsI:I is nearly 1:9, so that the most probable formula, based on the above analyses, is $CsI_{10}\cdot 2C_6H_6$, in which the ratio CsI:I is less certain than the ratio $CsI:C_6H_6$.

It is evident, however, that the ratio CsI:I can be calculated just as in the unsolvated residues, provided the ratio of $CsI:C_6H_6$ in the residue is known. Judging from the results on the unsolvated residues, this method should give more reliable results than direct analyses. In table 4 we give the charges used, the calculated composition of the residue assuming the ratio $CsI:C_6H_6 = 1:2$, and the ratio CsI : I calculated from the composition of the residues.

The ratio I/CsI is nearly 9, and the formula is therefore $CsI_{10} \cdot 2C_6H_6$ or $2CsI \cdot 9I_2 \cdot 4C_6H_6$. The writers are not unaware that this formula is most unusual and *a priori* highly improbable. The composition as determined by analysis, and as calculated in table 4, however, seems to exclude any simpler ratio. The corresponding ternary compound of potassium has the formula $KI_9 \cdot 3C_6H_6$ and is therefore of different type, the only evident relationship being that the cesium compound may be derived from the potassium by the substitution of one atom of iodine for one molecule of benzene.

TABLE 4

Showing the weight of each component in the original mixtures; the calculated per cent of cesium iodide and of iodine in the residues, assuming the ratio $CsI:C_6H_6 = 1:2$; *and the molecular ratio* I:CsI *in the residues*

NO.	CESIUM IODIDE	IODINE	BENZENE	CALCULATED CsI IN RESIDUE	CALCULATED I_2 IN RESIDUE	RATIO $\frac{I}{CsI}$
	grams	*grams*	*grams*	*per cent*	*per cent*	
11	0.67	6.12	30.833	15.85	74.62	9.63
12	0.67	7.02	30.795	17.30	72.30	8.55
26	1.22	6.70	30.134	16.82	73.06	8.89
27	1.22	7.168	30.488	17.09	72.62	8.70
28	1.22	7.637	29.917	16.20	74.05	9.35

Average = 9.02

At any univariant point in the systems investigated two solids are present, and their dissociation pressure of iodine is equal to the partial pressure of iodine in the solution. The latter is closely proportional to the molar fraction of iodine in solution, as all the solutions are dilute. The dissociation pressure of any polyiodide compared with pure iodine (or the activity) is therefore given very closely by the expression $\frac{C}{C_0}$ in which C is the molar concentration of iodine in solution at a univariant point, and C_0 is the corresponding value for pure iodine. The latter is practically identical with that at the univariant point where iodine is one of the solid phases, as cesium iodide is insoluble.

In table 5, the necessary data and the values of the ratio $\frac{C}{C_0}$ are given at 25°C. and at 6°C. for both the benzene and the toluene solutions, so far as the data are comparable. The data for the point in the benzene system in which the solids consist of CsI_4 and the ternary compound have been omitted, as there is no comparable point for toluene.

The differences between comparable values of $\frac{C}{C_0}$ for the benzene and toluene systems is of the same order as the error in determining the composition of the solutions. Assuming the vapor pressures of iodine at 6°C. and 25°C. are 0.0546 mm. and 0.313 mm.,[1] and the values of $\frac{C}{C_0}$ in table 5, the dissociation pressures of CsI_4 at 6°C. and 25°C. are respectively 0.00775 mm. and 0.0479 mm. For CsI_3, the values are 0.000131 and 0.000970 mm.

TABLE 5

Values of the ratio C/C_0 at 25°C. and at 6°C.

SOLIDS PRESENT	WEIGHT PER CENT OF IODINE IN SOLUTION	MOLE PER CENT OF IODINE IN SOLUTION	$\frac{C}{C_0}$
Benzene. $T = 25°C.$			
I_2 and T. C.	13.96	4.75 (C_0)	
CsI_4 and CsI_3	2.35	0.73	0.155
CsI_3 and CsI	0.047	0.014	0.0030
Toluene. $T = 25°C.$			
I_2 and CsI_4	15.42	6.20 (C_0)	
CsI_4 and CsI_3	2.54	0.94	0.151
CsI_3 and CsI	0.054	0.020	0.0032
Benzene. $T = 6°C.$			
I_2 and T. C.	8.59	2.81 (C_0)	
CsI_4 and CsI_3	1.31	0.41	0.145
CsI_3 and CsI	0.023	0.0071	0.0025
Toluene. $T = 6°C.$			
I_2 and CsI_4	10.41	4.04 (C_0)	
CsI_4 and CsI_3	1.53	0.56	0.139
CsI_3 and CsI	0.024	0.0087	0.0022

From these values, the heats of dissociation of CsI_4 and CsI_3, calculated by van't Hoff's equation, are found to be respectively −15,800 and −17,500 calories. These values, as well as those for the dissociation pressures, are based on the solubility data. Since some of the solubilities are

---

[1] By interpolation from the data given in the International Critical Tables.

very low, the relative error in them causes a considerable error in these calculations. This error appears to be less than ±5 per cent.

SUMMARY

The systems cesium iodide–iodine–benzene and cesium iodide–iodine–toluene have been investigated at 6°C. and at 25°C. With toluene, no ternary compound exists, and the two binary compounds found were CsI_3 and CsI_4, confirming the results of Briggs and his coworkers at 25°C. With benzene, in addition to the two binary compounds, there is also a ternary compound.

The results on the dissociation pressures of the binary compounds show close agreement when calculated from the data on the benzene and on the toluene systems.

REFERENCES

(1) **Briggs, Greenawald, and Leonard**: J. Phys. Chem. **34**, 1951 (1930).
(2) **Briggs**: J. Phys. Chem. **34**, 2260 (1930).
(3) **Abegg and Hamburger**: Z. anorg. Chem. **50**, 403 (1906).
(4) **Foote and Bradley**: J. Phys. Chem. **36**, 673 (1932).

THE SOLID POLYIODIDE OF AMMONIUM

H. W. FOOTE AND W. M. BRADLEY

Department of Chemistry, Yale University, New Haven, Connecticut

Received November 21, 1932

It has been shown by Abegg and Hamburger (1), by investigating systems of the type alkali iodide-iodine-benzene, that a number of solid polyiodides exist, but the fact was overlooked that some of the compounds formed were in reality ternary compounds containing benzene. Such ternary compounds form with potassium iodide (2) and with cesium iodide (see preceding article). We give below the results obtained with ammonium iodide and iodine at two temperatures, using as solvents benzene and toluene. Unlike the potassium and cesium compounds, it has been found that ammonium forms only the binary triiodide.

The method of investigation has been described previously (3). Qualitative tests on the solid residues showed the absence of either benzene or toluene. It was therefore possible, starting with weighed amounts of each component and analyzing the solutions, to calculate the composition of the residues with entirely satisfactory accuracy. Ammonium iodide is practically insoluble in both the toluene and benzene solutions, so that it was only necessary to determine iodine. The results obtained are given in tables 1 and 2.

The data in these two tables show that ammonium triiodide is the only

TABLE 1

The system benzene–ammonium iodide-iodine

T = 25°C.			T = 6°C.		
Iodine in solution	Iodine in residue	Unsolvated solid residue contains	Iodine in solution	Iodine in residue	Unsolvated solid residue contains
weight per cent	*weight per cent*		*weight per cent*	*weight per cent*	
0.77	10.00	NH_4I and NH_4I_3	0.39	10.49	NH_4I and NH_4I_3
0.80	39.91	NH_4I and NH_4I_3	0.42	55.18	NH_4I and NH_4I_3
0.79	59.35	NH_4I and NH_4I_3			
5.60	64.17	NH_4I_3	3.45	63.90	NH_4I_3
10.34	64.33	NH_4I_3	5.77	63.96	NH_4I_3
13.94	94.96	NH_4I_3 and I_2	8.52	70.13	NH_4I_3 and I_2
			8.58	94.99	NH_4I_3 and I_2

polyiodide which forms, and that it is stable over a wide range of iodine concentrations.

TABLE 2

The system toluene–ammonium iodide–iodine

$T = 25°C.$			$T = 6°C.$		
Iodine in solution	Iodine in residue	Unsolvated solid residue contains	Iodine in solution	Iodine in residue	Unsolvated solid residue contains
weight per cent	*weight per cent*		*weight per cent*	*weight per cent*	
0.88	9.87	NH_4I and NH_4I_3	0.46	12.39	NH_4I and NH_4I_3
0.88	47.45	NH_4I and NH_4I_3	0.47	59.08	NH_4I and NH_4I_3
0.89	55.93	NH_4I and NH_4I_3			
5.84	63.95	NH_4I_3	2.92	63.88	NH_4I_3
10.85	63.93	NH_4I_3	5.36	63.95	NH_4I_3
15.75	68.14	NH_4I_3 and I_2	10.24	67.80	NH_4I_3 and I_2
15.75	86.09	NH_4I_3 and I_2	10.19	94.65	NH_4I_3 and I_2
15.91	94.88	NH_4I_3 and I_2			

The average of the eight results on available iodine in the residues consisting of the pure compound is 64.01 per cent. The calculated value for NH_4I_3 is 63.65 per cent of available iodine.

TABLE 3

The average percentage by weight of iodine in solution at each univariant point, the corresponding molecular percentages of iodine, C and C_0, and their ratio

SOLVENT	SOLIDS PRESENT	PER CENT OF IODINE IN SOLUTION	MOLECULAR PER CENT OF IODINE IN SOLUTION	$\frac{C}{C_0}$
	$T = 25°C.$			
Benzene	I_2 and NH_4I_3	13.94	4.75 (C_0)	0.0515
Benzene	NH_4I_3 and NH_4I	0.79	0.24 (C)	
Toluene	I_2 and NH_4I_3	15.80	6.37 (C_0)	0.0504
Toluene	NH_4I_3 and NH_4I	0.88	0.32 (C)	
	$T = 6°C.$			
Benzene	I_2 and NH_4I_3	8.55	2.80 (C_0)	0.0452
Benzene	NH_4I_3 and NH_4I	0.41	0.13 (C)	
Toluene	I_2 and NH_4I_3	10.22	3.97 (C_0)	0.0431
Toluene	NH_4I_3 and NH_4I	0.47	0.17 (C)	

Taking the average values of $\frac{C}{C_0}$ at each temperature, and the vapor pressure of iodine given in the preceding article, the calculated dissociation pressures of ammonium triiodide at 25°C. and at 6°C. are 0.0160 mm. and 0.00241 mm., respectively.

As pointed out in the preceding article on cesium polyiodides, the activity of the triiodide compared with pure iodine is given rather accurately by the ratio of molar concentrations of iodine at the two univariant points. In table 3, we give the average percentage by weight of iodine found in solution at the univariant points, the corresponding molecular percentages of iodine, and their ratio. The differences between the values of $\frac{C}{C_0}$ for the benzene and toluene solutions, at each temperature, are of the same order as the error in determining the iodine concentrations.

As ammonium triiodide can be prepared readily in very pure condition and is the only binary periodide of ammonium, it seems worth while to point out that it furnishes a very convenient way of maintaining a constant, low concentration of iodine vapor which can be varied at will by variation in temperature. Its behavior in this respect is similar to that of a hydrated salt in maintaining a constant humidity.

SUMMARY

Solubility results on mixtures of ammonium iodide and iodine in benzene and in toluene show that the compound NH_4I_3 is the only binary periodide which forms above 6°C. No solvated compound with benzene or toluene exists. The behavior of ammonium iodide is entirely unlike that of potassium iodide, which forms no binary periodide but does form a ternary solvated compound.

The results on the dissociation pressure of the triiodide at each temperature show close agreement when calculated from the data on the benzene and on the toluene systems.

REFERENCES

(1) Abegg and Hamburger: Z. anorg. Chem. **50**, 403 (1906).
(2) Grace, N. S.: J. Chem. Soc. **1931**, 594.
Foote, H. W., and Bradley, W. M.: J. Phys. Chem. **36**, 673 (1932).
(3) Foote, H. W., Bradley, W. M., and Fleischer, Michael: J. Phys. Chem. **37**, 21 (1933).

AN IMPROVED METHOD FOR THE DETERMINATION OF ISOTHERMALS BY THE RETENTIVITY TECHNIQUE

L. J. BURRAGE

King's College, London, England

Received October 18, 1932

INTRODUCTION

In a previous publication (1) a new method for the determination of sorption isothermals of vapors on charcoal was described; the present paper records a development of this method whereby the accuracy is greatly increased and the technique simplified. No experimental details are given, as these were described fully in the previous papers (1, 2).

This method consisted in the conversion of the approximate isothermals obtained under the retentivity test conditions into true isothermals. Briefly, this was achieved by carrying out a number of determinations employing columns of charcoal of different lengths and plotting the logarithm of the weight of vapor retained against the logarithm of the volume of charcoal for a constant volume of air passed, and then extrapolating the weight figures to 1 cc. to get rid of the "pressure-length effect." The tangents drawn to the retentivity curve obtained from these extrapolated data gave rise to the true isothermal.

At the time of publication it was realized that this method would not apply to an isothermal of the water type on or above that portion where the quantity of substance sorbed increases rapidly for a small increase of pressure, and an attempt was made to make it hold good under all conditions. As this technique seemed to allow of an extremely detailed examination being made of the structure of the isothermal, an experiment was carried out on a single column of charcoal of about 10 cc. volume, charged with water vapor, the flow of air being interrupted at very frequent intervals. By this means it was hoped to anchor the retentivity curve exactly over its entire range, and then by drawing an extremely large number of tangents, the detailed isothermal structure would be obtained.

The result of this experiment was characterized by one very striking fact; the retentivity curve was found to consist of a series of straight lines intersecting one another at definite points (e.g., figure 1, which represents the retentivity curve of a water isothermal on Charcoal K 2 at 15°C. Charcoal K2 was a peat charcoal activated with phosphoric acid; apparent density = 0.312). The resultant isothermal (figure 2, dotted lines) does not consist of a series of rounded loops as had been obtained heretofore; the breaks are all sharply rectangular. It was found that with isothermals on silica gel, as had been previously discovered in the case of charcoal, there are no breaks below 0.1 mm., the isothermal consisting of a smooth curve (3). This rectangular structure makes it possible for an improved method for the determination of adsorption isothermals to be put forward which will hold good under all conditions using but a single column of charcoal.

If one charges the charcoal column at a vapor pressure which is intermediate between two horizontal portions of the isothermal, then on desorption a linear section will result on the retentivity curve, and at a definite quantity value this line will be intersected by another. Now the straight lines correspond to constant pressures over the quantity ranges indicated and will give rise to two horizontal sections on the isothermal. Only the second of these corresponds to a true step, however, for the first is inherent in the experimental procedure, since it is caused by the formation of the gradient inside the column. Reference to a previous publication (1) will show clearly how this occurs. Owing to this gradient the average quantity of vapor in the column expressed as milligrams per gram is smaller than corresponds to the pressure over the end of the column. The error which this gradient introduces in the quantity value steadily diminishes until at a very small quantity figure it is zero, the average quantity in the column and the quantity corresponding to the pressure over the end of the column being identical.

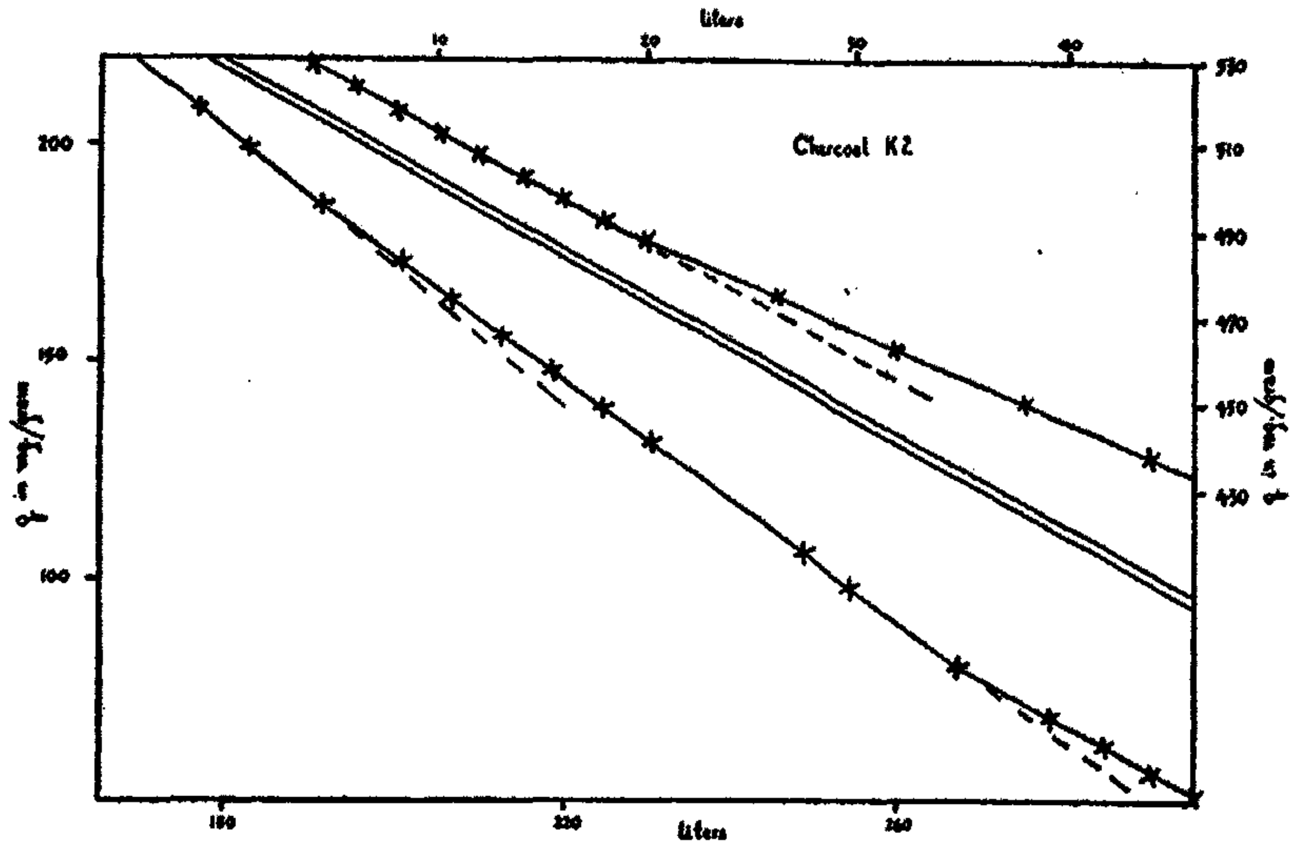


Fig. 1

The improved technique is essentially as follows:

(a) The pressure is calculated from the slope of the linear sections of the retentivity curve, the difference in the quantity values giving the amount of substance which has been carried away in a certain volume of air (the difference of the corresponding volume figures).

(b) The quantity values are calculated thus: The amount of substance held at zero pressure is subtracted from the quantity figures for all retentivity curve breaks. These are "corrected" quantity values. The ratio of the corrected saturation figure to the corrected quantity figure at the first retentivity break is calculated. The corrected quantity values for each break are then multiplied by this ratio and the amount held at zero pressure added, whereby the true quantity for each break is obtained, resulting in a true isothermal.

TABLE 1

(1)	(2)	(3)	(4)
542.8	519.2	—	—
488.0	464.4	519.2	542.8
390.3	366.7	410.1	433.7
284.5	260.9	291.8	315.4
186.1	162.5	181.7	205.3
80.4	56.8	63.5	87.1
35.7	12.1	13.5	37.1
29.0	5.4	6.0	29.6
26.3	2.7	3.0	26.6
23.6	0.0	0.0	23.6

A criticism may be advanced in the case where the initial charging pressure coincided with that at which a step occurred, in which case it would appear that the linear section on the retentivity curve due to the formation of the gradient and that due to the first step would be continuous, thus preventing a calculation of the true isothermal. It has been shown, however, by sorbing from an air stream charged to a definite pressure with vapor, that one must charge at a distinctly higher pressure value to pass along the horizontal portion of a step. This being so it is perfectly valid to use this new method, since the sorption point will not pass along the horizontal step but will remain on the vertical portion joining this step with the one below.

In table 1 the method of operation is shown in full. The vertical columns have the following significance: (1) quantity values at the retentivity curve breaks; (2) the corrected quantity figures; (3) the figures in the previous column multiplied by the ratio of the corrected saturation figure to the corrected quantity figure at the first retentivity break; (4) the latter column + the amount held at zero pressure, all figures being expressed as milligrams per gram. The quantity held at zero pressure is 23.6 mg. per gram.

The isothermal in figure 2 has been converted to a true isothermal (continuous lines) in this manner, the individual points being omitted. The figures for the pressure and quantity range of each step and the number of experimental points on that step are given in table 2.

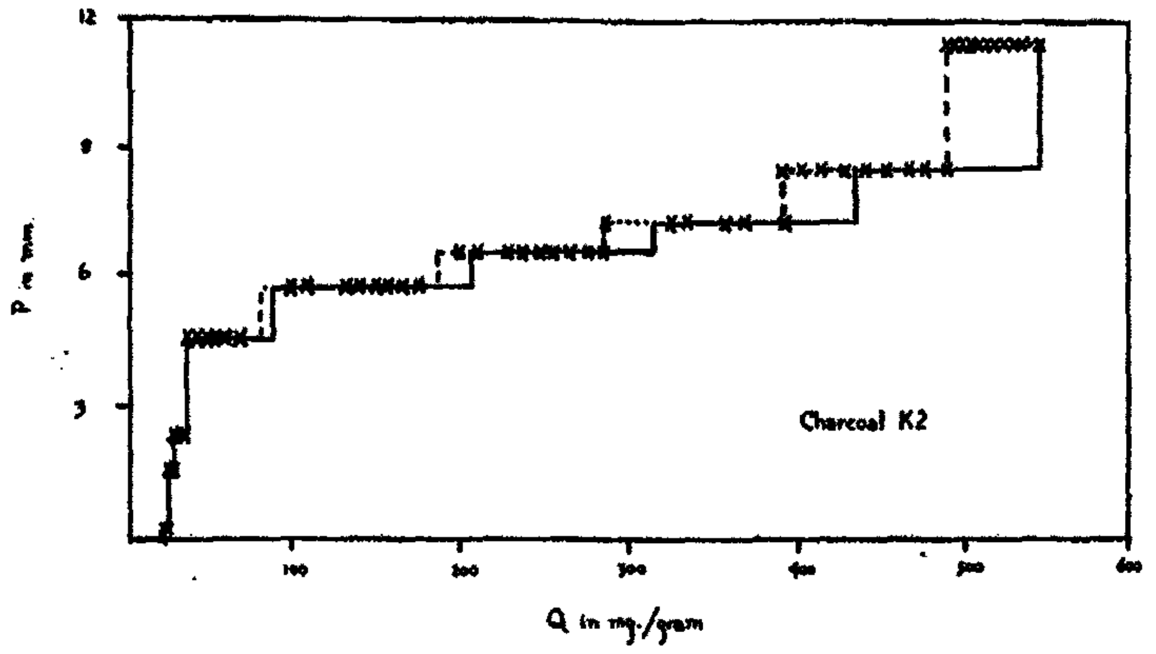


FIG. 2

TABLE 2

PRESSURE OF BREAK	QUANTITY RANGE OF STEP	DIFFERENCE	NUMBER OF EXPERIMENTAL POINTS
mm.	*mg./gram*	*mg./gram*	
11.53	—	—	10
8.60	542.8–433.7	109.1	8
7.35	433.7–315.4	118.3	6
6.61	315.4–205.3	110.1	9
5.80	205.3– 87.1	118.2	8
4.58	87.1– 37.1	50.0	6
2.35	37.1– 29.6	7.5	5
1.55	29.6– 26.6	3.0	4
0.25	26.6– 23.6	3.0	3

EXPERIMENTAL

Desorption experiments in an air stream charged with vapor at definite pressures

To verify the rectangular structure of adsorption isothermals and also to justify this new procedure, desorption experiments were carried out using an air stream charged to definite pressures with vapor, the points obtained being checked against the isothermals obtained by the improved retentivity method. Such experiments have been carried out with water and carbon tetrachloride on charcoal and on silica gel.

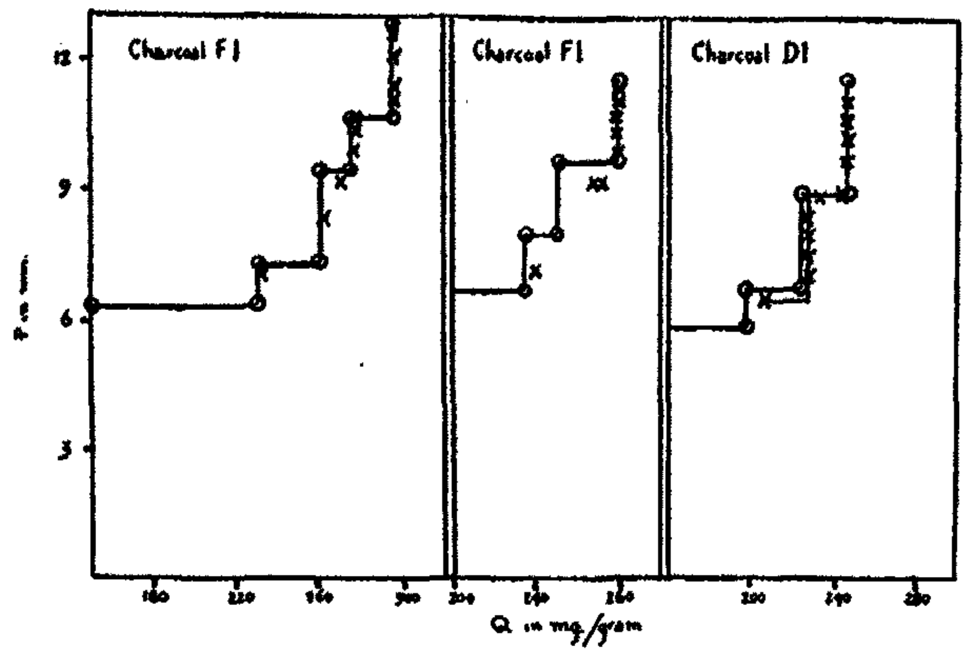


FIG. 3

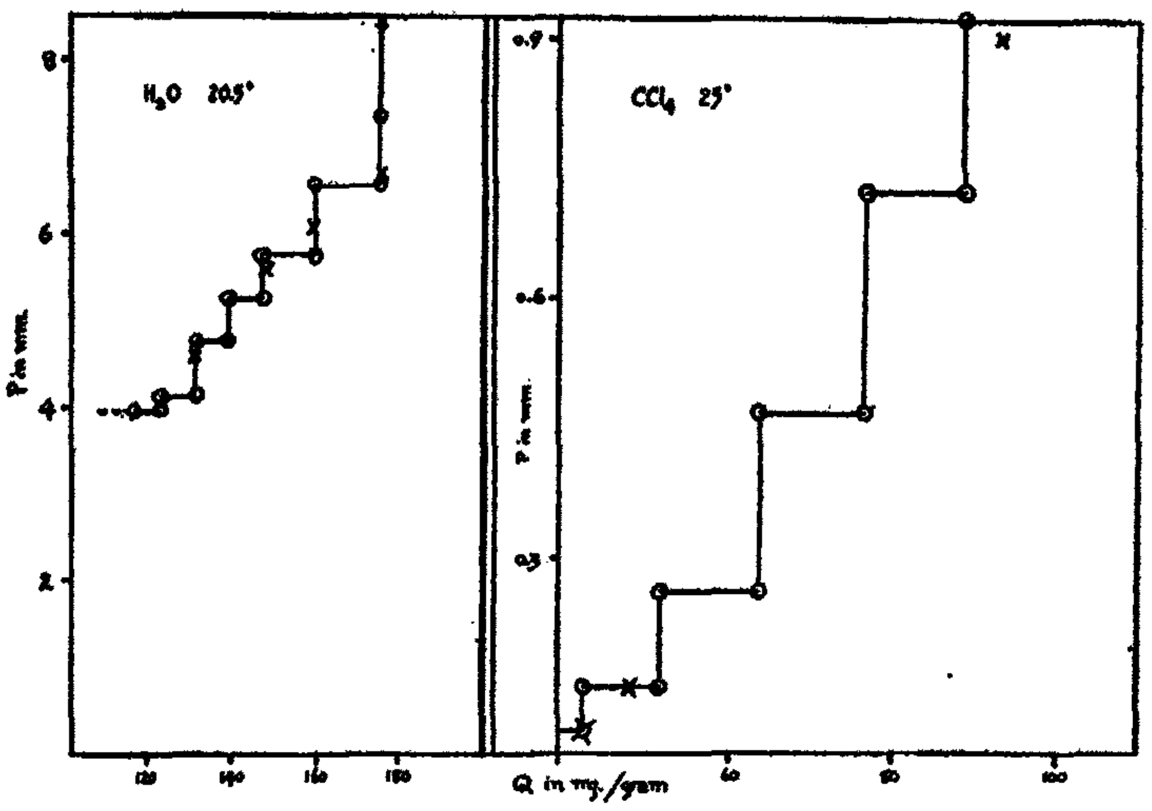


FIG. 4

The crosses represent such desorption points and the circles mark the ends of the steps (the individual points being omitted) in the isothermals derived by the modified retentivity technique. The results shown in figure 3, representing water isothermals on coconut charcoals at 15°C. (F1, steam activated; apparent density 0.534: D1, steam activated (4)) give definite evidence of this rectangular structure when dealing with the desorption points alone (crosses). In figure 4 are shown isothermals of carbon tetrachloride and water on silica gel. In every case there is close agreement between the desorption points and the isothermals derived by the improved technique. Figures are quoted in table 3 which show the variation in quantity values obtained by the two methods.

TABLE 3

ADSORBENT	ADSORBATE	TEMPERATURE	PRESSURE	QUANTITY	
				Desorption points	Improved retentivity method
			mm.	*mg./gram*	*mg./gram*
Charcoal D1	H_2O	25°C.	11.3	295.1	295.1
			11.0	295.1	295.1
			10.6	277.6	275.7
			10.3	276.8	275.7
			9.8	276.8	275.7
			9.1	270.0	260.3
			8.4	262.4	260.3
			8.1	262.4	260.3
			7.0	232.9	230.8
Silica gel	CCl_4	25°C.	8.4	175.8	182.0
			0.9	92.9	89.0
			0.15	48.3	48.3
			0.10	43.0	43.0
Silica gel	H_2O	20.5°C.	6.70	175.0	175.0
			6.10	159.5	159.8
			5.60	147.2	146.7
			4.60	130.3	130.4

DISCUSSION

It has been found (1) that the agreement is good between isothermals obtained by the static technique (air absent) and by the retentivity method, the chief difference being the speed of attainment of equilibrium. In the case of desorption isothermals, using the static technique, the vapor has to diffuse away and this is hindered markedly by the presence of foreign molecules (such as carbon dioxide) on the surface, whereas, in the presence of air, the vapor molecules are removed continuously by the moving stream, together with foreign molecules, the latter method, therefore, causing a quicker cleaning-up and thus a more rapid attainment of equilibrium.

In the case of water desorption isothermals, when desorbing to constant pressure, it is necessary to lower the vapor pressure below that at which a step occurs before the water comprising that step can be removed, hence the pressure at which a step occurs is lower than it would be if all disturbing factors were absent. In the present technique this cannot occur, as one is actually dealing with the quantity adsorbed in an infinitely small layer at the end of the charcoal column, and the pressure over this falls with sudden jumps from one step to another, hence there is no tendency for false equilibria to occur, the pressure drop being sufficiently large to allow all the water sorbed on that step to escape. This aspect will be treated more fully in a future publication on water hysteresis.

The results which have been obtained fully justify this improved technique which is considered to be distinctly in advance of other methods in accuracy and has the additional advantage of being rapid, while giving the exact form of the isothermal over its whole range.

SUMMARY

An improved technique for the determination of isothermals has been described.

The derived isothermals have been found to consist of a series of rectangular steps.

Comparison has been made with points obtained by desorbing to constant pressure.

The author desires to thank Prof. A. J. Allmand for the interest he has taken in this work.

REFERENCES

(1) Burrage: J. Phys. Chem. **34**, 2202 (1930).
(2) Allmand and Burrage: J. Soc. Chem. Ind. **47**, 372T (1928).
(3) Allmand, Burrage, and Chaplin: Trans. Faraday Soc. **28**, 218 (1932).
(4) Allmand and Burrage: Proc. Roy. Soc. London **130**, 610 (1931).

DISCONTINUITIES IN THE SORPTION PROCESS

L. J. BURRAGE
King's College, London, England

Received October 18, 1932

INTRODUCTION

In view of the discontinuous nature of desorption isothermals, it appeared to be of interest to establish the presence of these discontinuities in the sorption process. The new technique for the determination of isothermals (see preceding paper), of which brief mention has already been made (1), has shown that when disturbing factors are absent these isothermals consist of a series of rectangular steps. The presence of disturbing effects of various kinds all cause these steps to become curved, in some cases the actual number being increased by the addition of small breaks. The reasons for this will not be discussed here as this subject is dealt with in a further paper in course of preparation.

EXPERIMENTAL

A series of experiments was carried out to determine whether this step-like structure or any indication thereof could be obtained in the sorption process, despite the probability of drift causing disturbances owing to the cleaning-up effect.

Since in other experiments it has been found that the presence of carbon dioxide is a troublesome factor, which often partially vitiates the results, it was decided to carry out three experiments, using (1) a charcoal which had a high capacity for carbon dioxide, (2) one which was fair and (3) one which was poor in this respect, viz.:

(1) Charcoal A (see reference 2)
(2) Charcoal L 1 (Steam activated soft wood. Apparent density 0.445)
(3) Charcoal N 1 (Zinc chloride activated almond shell. Apparent density 0.416)

The procedure adopted was the reverse of the usual retentivity process (3). A column of dry charcoal 60 mm. in length was employed and air saturated with moisture at 11.5 mm. pressure was passed at 400 cc. per minute and 15°C. The air stream was interrupted at very small intervals of time and the adsorption curve constructed, portions of which are shown in figures 1a and 1b.

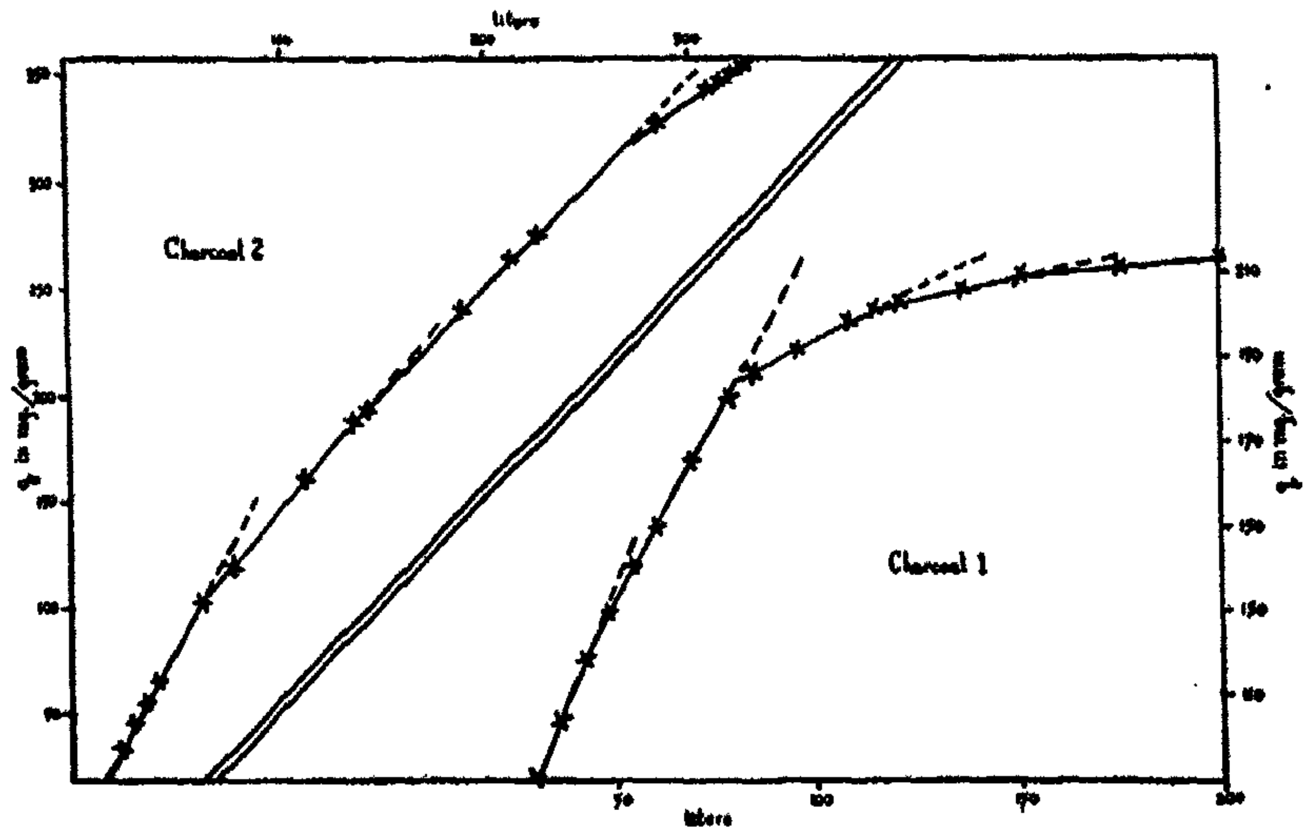


FIG. 1a

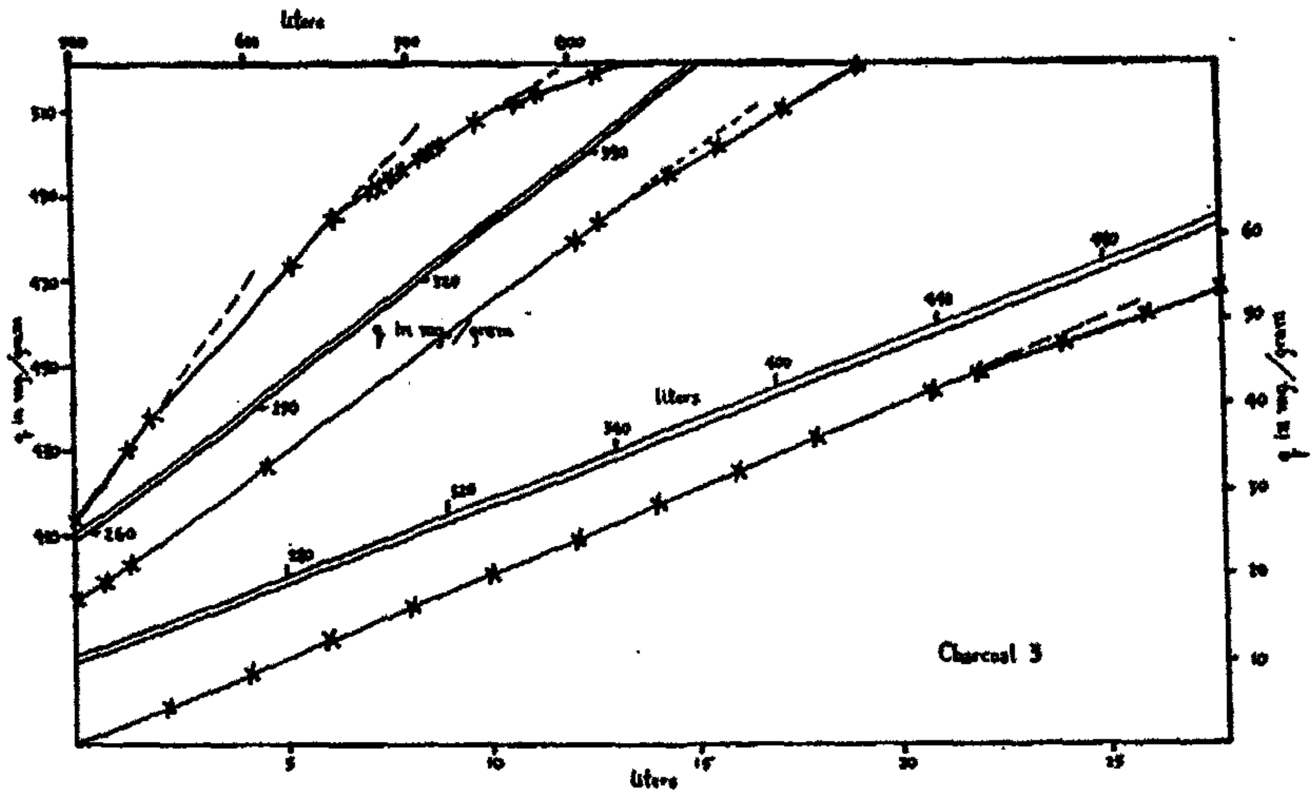


FIG. 1b

DISCUSSION

Figures 1a and 1b show quite conclusively that in spite of small fluctuations, the adsorption-time curves consist of a series of straight lines. These give rise to sorption isothermals shown in figure 2.

The pressure is calculated in the following manner: From the slopes of the linear portions of the retentivity curve, the weight of vapor adsorbed in a given time is obtained. Knowing the pressure, and therefore the quantity of vapor in the charging stream in the same period of time, the difference between this and the amount adsorbed represents the weight of vapor in the effluent gas, this giving the pressure of vapor over the end of the charcoal column.

These pressures are correct but the isothermals are approximate, since in each case the quantity is not a "true" value but an average one, for it represents the total water in the column expressed as milligrams per gram of charcoal and not that amount corresponding to the last layer of the charcoal column. This in no way vitiates the results, as the object of the present investigation was to demonstrate that sorption takes place in rectangular steps. This is shown by the pressure remaining constant over a given quantity range, irrespective of whether the quantity concerned is an average or true value. Figure 2 shows clearly that the sorption isothermal occurs in rectangular steps, the individual points being omitted except for those marking the beginning and end of these steps.

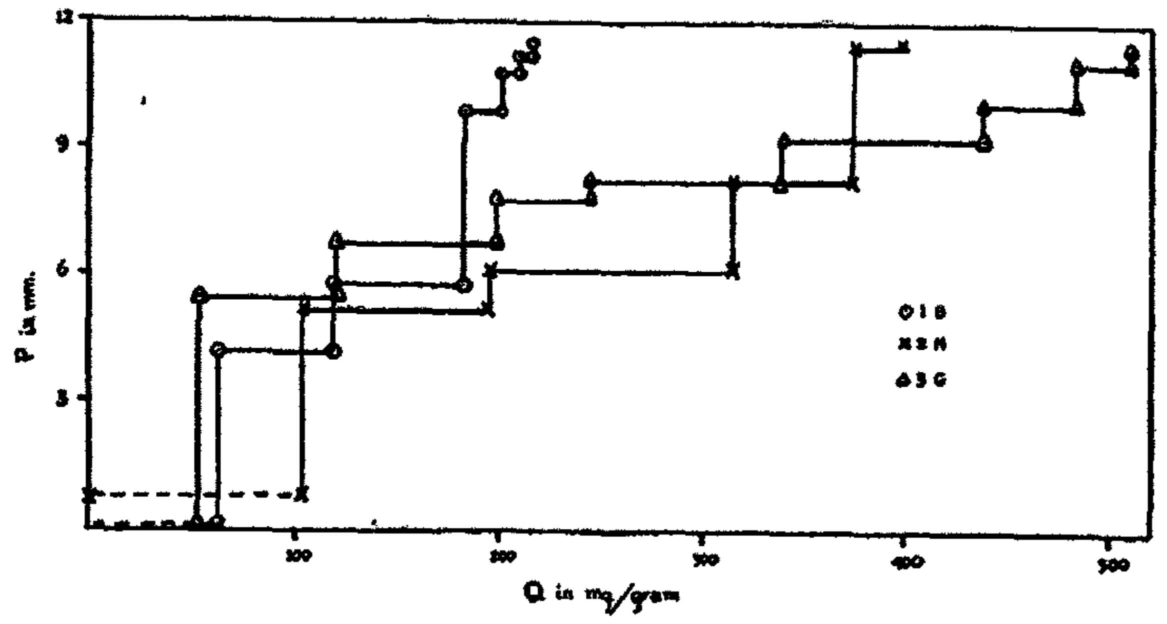


FIG. 2

Instead of ignoring the slight deviations from the straight lines in figures 1a and 1b, the average rate of adsorption between each two successive points was calculated and assumed to hold at the middle point of the time interval (figures 3a and 3b). If there were no disturbing factors the rate of adsorption along a step would be constant, the rate-time diagrams appearing in rectangular steps. Figures 3a and 3b, which greatly magnify the errors, show that (1) is the least rectangular, (2) more so, and (3) fairly well defined. These results fall in the inverse order of their capacity for carbon dioxide, as one might have expected. The carbon dioxide evolved during each run was noted qualitatively by passing the effluent gas through baryta water and noticing the change in depth of turbidity. In this connection it is of interest to note that the sudden increase in the rate of adsorption (figure 3b, point *) was definitely associated with a greatly increased evolution of carbon dioxide.

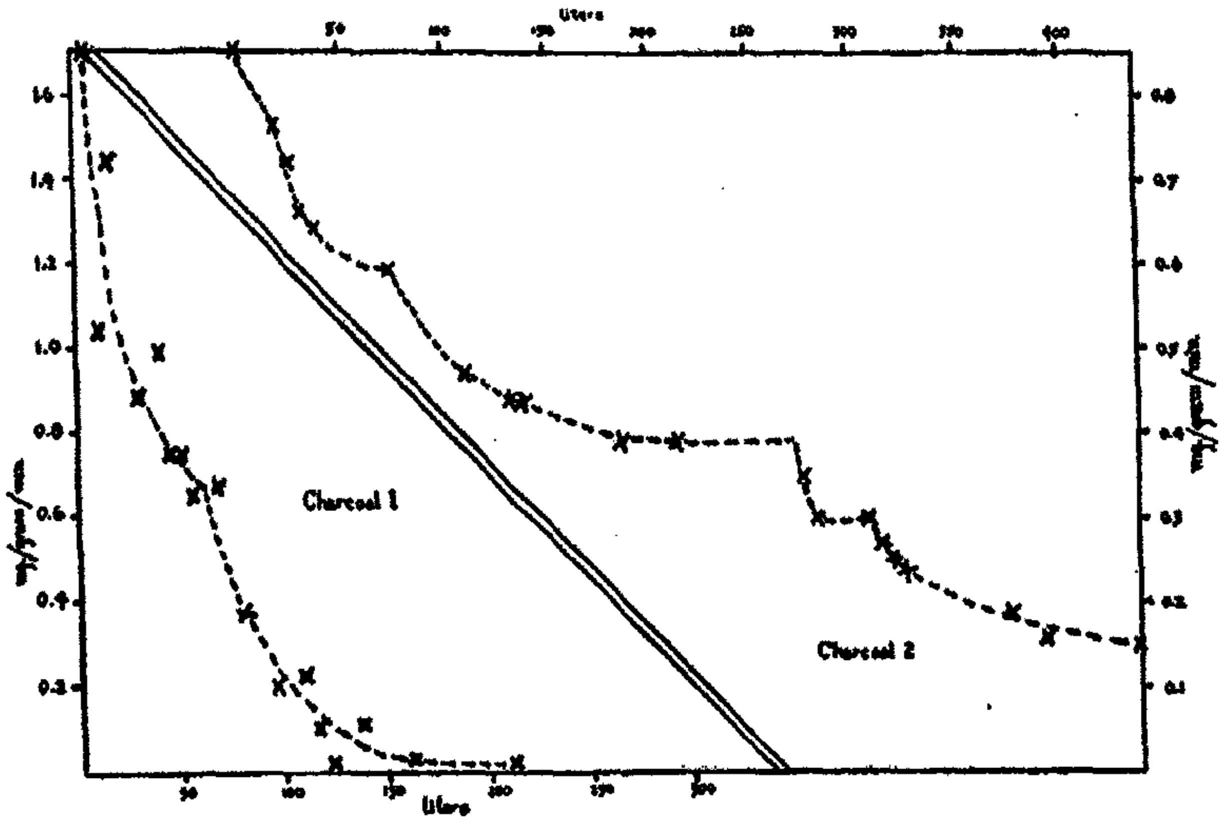


FIG. 3a

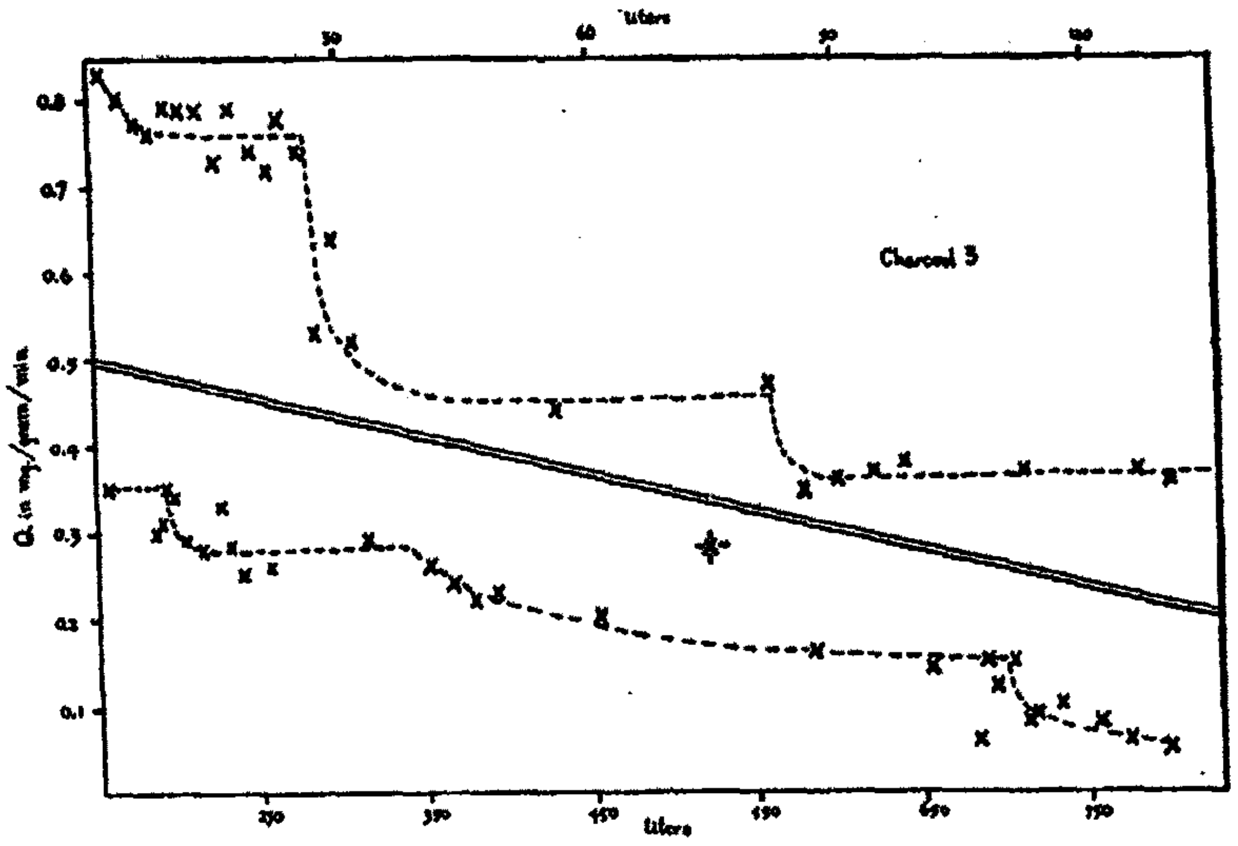


FIG. 3b

In figure 2, the pressure figures for the lowest step in each case can be neglected, as several smaller steps whose pressures are close together are represented here and one cannot accurately determine them. In general there is a tendency for the quantity per step to be small at low pressures, larger at intermediate and smaller again at higher pressures, similarly to that found in desorption isothermals.

To facilitate comparison with the pressures at which the steps occur in desorption isothermals to be submitted in a later publication the pressures at which the steps occur have been tabulated.

Charcoal 1	*Charcoal 2*	*Charcoal 3*
4.1 mm.	5.1 mm.	5.5 mm.
5.8 mm.	6.2 mm.	6.7 mm.
9.9 mm.	8.2 mm.	7.8 mm.
10.8 mm.	11.5 mm.	8.2 mm.
11.2 mm.		9.2 mm.
		10.1 mm.
		11.1 mm.

SUMMARY

Sorption isothermals have been shown to consist of a series of rectangular steps similar to desorption isothermals.

The effect of the carbon complex (C_xO_y) on the rate of adsorption has been noted.

The pressures at which steps have been found to occur have been tabulated for different charcoals.

REFERENCES

(1) Allmand, Burrage, and Chaplin: Trans. Faraday Soc. **28**, 218 (1932).
(2) Hand and Shiels: J. Phys. Chem. **32**, 441 (1928).
(3) Allmand and Burrage: J. Soc. Chem. Ind. **47**, 372 (1928).
Burrage: J. Phys. Chem. **34**, 2202 (1930).

A NOTE ON THE SORPTION OF WATER VAPOR BY GLASS

E. P. BARRETT[1] AND A. W. GAUGER[2]

Experiment Station of the School of Mineral Industries, The Pennsylvania State College, State College, Pennsylvania

Received October 8, 1932

A study of the condition of water in coals of various ranks which is now in progress in this laboratory requires a knowledge of the sorption of water vapor by the glass system used in the investigation, over a range of pressures from 10 to 1000 microns at temperatures varying from 25° to 30°C. The data available over this range are very meagre. Frank (1) has made a very precise measurement from 1 to 100 microns at 20°C. but the writers know of no published data, other than Frank's, which are reliable below 50 per cent relative humidity. Although the data were required simply to furnish a correction factor, it seemed unwise to extrapolate Frank's isotherm to 1000 microns, not only because of the effect of varying previous histories of Frank's glass and that of the authors, but also because the water vapor–glass isotherm must show a point of inflection somewhere between a relative humidity of 0.006, which is the upper limit of Frank's isotherm, and a relative humidity of 0.5, which is the lower limit attained by McHaffie and Lenher (2). Such a point of inflection must exist, since Frank's isotherm is *concave* toward the pressure axis while that of McHaffie and Lenher is convex. It was primarily to receive assurance that this point of inflection did not occur below 3.5 per cent relative humidity that the measurements herein described were made.

APPARATUS AND PROCEDURE

The apparatus is shown in figure 1. S_1, S_2, S_3, S_4 and S_5 are mercury seal stopcocks. T_1 contains the coal and was shut off at S_3 during these measurements. T_4 is used in the study of coal and is of no significance in these measurements. F is a 12-liter Pyrex flask and M a mercury manometer. This manometer was made from 17-mm. Pyrex tubing and, after careful cleaning, was sealed empty to the apparatus. It was then "torched out" under high vacuum for half an hour, and after cooling mercury was distilled into it through a side arm (not shown). It was read with a micrometer microscope and calibrated against the McLeod gauge, using

---

[1] Research assistant.

[2] Director, Mineral Industries Research.

dry air as the calibrating gas. It was self-consistent to one micron at pressures below 100 microns and its absolute accuracy was about one per cent at the highest pressure measured (ca. 1700 microns).

T_2 is a tube of distilled water kept at a constant temperature by the thermostat B. The volume between S_4 and S_5 including T_3 was measured before sealing to the apparatus. By closing S_4 and opening S_5, T_3 was saturated with water vapor at a pressure calculable from the temperature of the thermostat. Then by closing S_5 and opening S_4 a definite weight of water was introduced into the system.

Since the thermostat was operating only slightly below room temperature, the relative humidity in T_3 was fairly high, and it was necessary to add to the weight of water vapor in its free space the weight sorbed on the walls in order to calculate the weight of water vapor added to the system. This correction, which did not exceed 10 per cent of the total weight introduced, was obtained from McHaffie and Lenher's isotherm for high relative humidities.

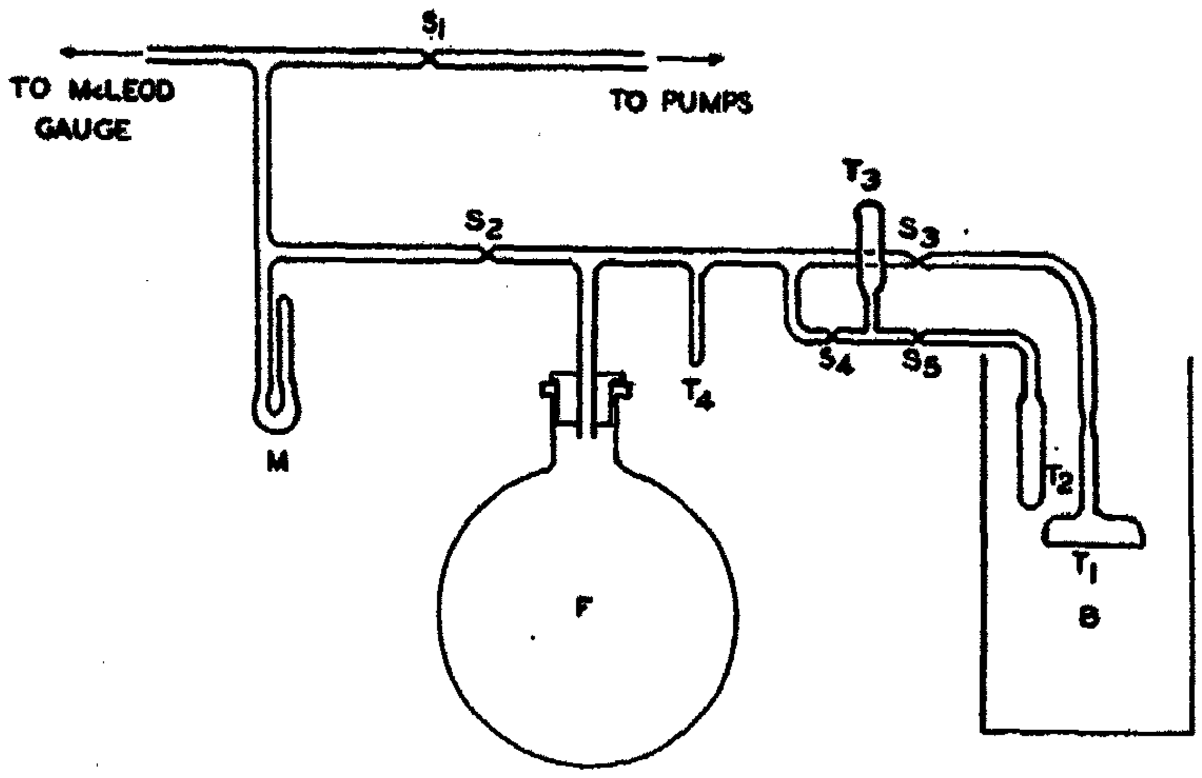


FIG. 1. APPARATUS FOR STUDYING AQUEOUS TENSION OF WATER IN COAL

As it was not convenient to thermostat the entire apparatus, consistent results were not easy to obtain, but by exercising some care to keep the laboratory temperature fairly constant, it was possible to test the rectilinear character of the relationship between the logarithms of relative humidity and the weight sorbed per unit area over the range in question.

Before starting a measurement, the system was pumped to a high vacuum (10^{-6} mm. or better) and pumping was continued for at least twelve hours. The glass was therefore "dry" in the ordinary sense, but it must be remembered that several days exposure to a vacuum of 10^{-6} mm. are necessary to remove the last traces of moisture at ordinary temperatures.

RESULTS

The data obtained are given in tables 1 and 2 and are shown graphically in figure 2. In the tables W, W_f, and W_g are, respectively, the weight of water vapor introduced, the weight in the free space (as calculated from the observed pressure), and the weight sorbed, all in grams × 10^3. W_g/A is the weight sorbed per unit area. P is the pressure in microns and *R. H.* is the relative humidity × 10^3.

TABLE 1

Isotherm at 302°K.

W	P	W_f	W_g	W_g/A	*R.H.*
0.58	41	0.476	0.104	2.9	1.4
1.16	86	1.00	0.16	4.5	2.9
1.74	133	1.54	0.20	5.5	4.5
2.32	182	2.11	0.21	5.9	6.1
2.90	731	2.68	0.22	6.2	7.8
3.48	277	3.21	0.27	7.5	9.3
4.06	375	3.77	0.29	8.2	11.0
4.64	374	4.34	0.30	8.5	12.6
5.22	423	4.91	0.32	8.9	14.2
8.70	717	8.32	0.38	10.7	24.1
11.60	960	11.15	0.45	12.7	32.3

TABLE 2

Isotherm at 298.5°K.

W	P	W_f	W_g	W_g/A	*R.H.*
0.542	37	0.436	0.109	3.1	1.5
1.08	78	0.92	0.16	4.5	3.2
1.65	123	1.45	0.20	5.6	5.1
2.17	164	1.94	0.23	6.5	6.8
2.71	207	2.44	0.27	7.6	8.6
3.26	250	2.95	0.31	8.7	10.4

Figure 2 is a logarithmic plot of the results and clearly shows the rectilinear character of the isotherm over the range in question. In figure 2 appears a line lying to the left of the experimental curve and with a slightly steeper slope. This is Frank's isotherm, shown as a solid line over the range of his observations and extrapolated as a broken line to cover the range of the authors' measurements.

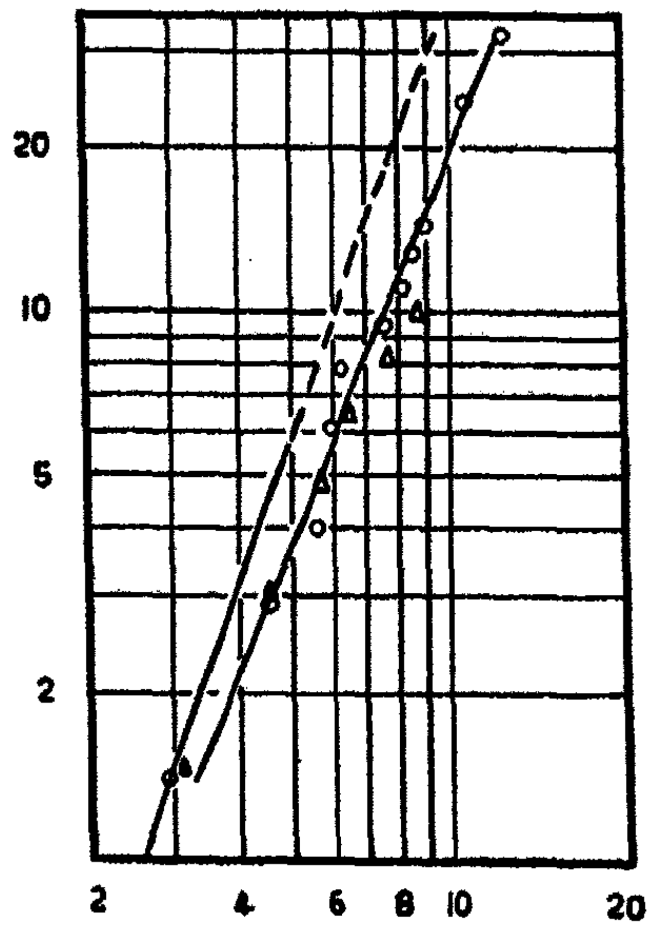


FIG. 2. SORPTION OF WATER VAPOR BY GLASS

The logarithms of the relative humidities × 10^3 are plotted as ordinates against the logarithms of weight sorbed in grams × 10^8 per sq. cm. as abscissae. Centers of circles are points obtained at 302°K. Vertices of triangles are points obtained at 298.5°K.

DISCUSSION

The results obtained are somewhat higher than Frank's. There are three factors which may account for the difference. First, a difference in the composition and history of the glass; second, a difference in the extent of drying before beginning a measurement; third, an error in McHaffie and Lenher's results used to correct the computation of the weight of water introduced.

It seems unlikely that the use of McHaffie and Lenher's data could introduce serious error, through being itself at fault, not only because it was used for making a fairly small correction, but also because of the good agreement between the two corrections made from quite different points on their isotherm. At 258.5°K. the correction is about 4 parts in 53 and at 302°K. it is about 2 parts in 56, and yet the writers' measurements at these two temperatures as corrected by McHaffiie and Lenher's data are in good agreement.

It is impossible to consider the second source of discrepancy, because Frank says simply that his adsorption chamber was "dried under vacuum." If Frank pumped his glass for considerably shorter periods of time than was used in these measurements, his results would, of course, be lower than those obtained in this laboratory.

It seems most probable that the chief source of difference lies in a different treatment of the glass. Frank allowed his glass to stand in contact with chromic acid for one week, during which time the acid was boiled several times. He thereafter cleaned the glass by soaking in distilled water and rinsing with conductivity water. The writers' sorption chamber was cleaned with boiling soap solution and rinsed with hot distilled water, and was then subjected to steam at atmospheric pressure for four hours. It was thereafter rinsed with hot distilled water several times before being attached to the system.

SUMMARY

A test of the rectilinear character of the logarithmic form of the sorption isotherm for the system water vapor–glass has been made over a range of relative humidities from 10^{-3} to 3×10^{-2}.

The results agree closely with the very precise measurements of Frank and indicate that his isotherm may be extrapolated to include pressures of the next higher order of magnitude.

The authors wish to express their thanks to the National Research Council for a Grant-in-Aid which made the study on the condition of water in coal possible.

REFERENCES

(1) Frank, H. S.: J. Phys. Chem. **33**, 970 (1929).
(2) McHaffie, I. R., and Lenher, S.: J. Chem. Soc. **127**, 1561 (1925).

THE EFFICIENCY OF CARBON DIOXIDE AS A RADIOCHEMICAL CATALYST

CHARLES ROSENBLUM[1]

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received July 29, 1932

The catalytic effect of carbon dioxide on the combination of carbon monoxide and oxygen in the presence of radon was found to be very small (1), only 14.5 per cent of the total ionization falling upon the sensitizing gas being utilized in promoting the reaction. That this low efficiency of carbon dioxide is characteristic of the gas is seen also from its effect on the radiochemical acetylene polymerization.

For the normal reaction in a sphere of 1.933 cm. diameter (2), the $-\frac{M_{C_2H_2}}{N_{C_2H_2}}$ ratio is 19.8, where $M_{C_2H_2}$ is the number of acetylene molecules disappearing from the gas phase, and $N_{C_2H_2}$ is the number of ion pairs produced in the gas by the alpha-particles from radon in equilibrium through RaC. The same M/N ratio was found for the greater part of the polymerization when sensitized by inert gases such as helium and neon (3), after correction was made for the ionization falling on the catalyst by assuming 100 per cent efficiency of the inert gas. That this assumption fails for the influence of carbon dioxide on this reaction is shown by the abnormally low initial $-M/N$ value of 16.4, which steadily decreases as the reaction proceeds. Table 1 taken from unpublished work of Lind and Bardwell[2] presents these data in detail.

Column I shows the decreasing $-M/N$ values calculated on the assumption of 100 per cent transfer of ionization on carbon dioxide to the reacting acetylene molecules.[3] However, more than 14.5 per cent of the carbon dioxide ionization is effective in speeding up the reaction, as is seen by inspecting columns II and III. Calculations in column II are based on the assumption of a 14.5 per cent catalytic efficiency[4] as was found in the carbon monoxide oxidation. Correcting for a fractional efficiency of 30 per cent, column III contains a satisfactory constant M/N

---

[1] Du Pont Fellow in Chemistry at the University of Minnesota, 1930–1931.

[2] These data are included with the kind permission of Professor S. C. Lind of the University of Minnesota.

[3] For details of this calculation see reference 3.

[4] For details of this calculation see reference 1.

ratio averaging 22.2, which is quite comparable with the value of 20 to be expected in a sphere of the size used. This small discrepancy of 10 per cent is readily accounted for when it is recalled that the measured reaction velocity, and therefore the *M/N* value, is approximately 10 per cent too high because of the disappearance of a small quantity of carbon dioxide from the gas phase.

That the efficiency of carbon dioxide in this reaction is greater than in the carbon monoxide oxidation may be due to the relative ionization potentials of 14.4 (4) and 11.6v (5) for carbon dioxide and acetylene respectively, a condition favorable to a flow of ionization from the catalyst to reactant (6). It appears that only a small part of the carbon dioxide ionization is available even in this reaction where conditions are favorable for a pronounced catalytic effect.

TABLE 1

The effect of carbon dioxide on the acetylene polymerization

$x\,C_2H_2(g) + CO_2(g) = (C_2H_2)_x + CO_2(g)$

$D = 1.930$ cm.; $E_0 = 0.0141$ curie radon

$e^{-\lambda t}$	$P_{C_2H_2}$	P_{CO_2}*	P_{H_2}	−*M/N* RATIO: I (assuming 100 per cent efficiency)	−*M/N* RATIO: II (assuming 14.5 per cent efficiency)	−*M/N* RATIO: III (assuming 30 per cent efficiency)
	mm. Hg	*mm.* Hg	*mm.* Hg			
1.0000	557.5	561.5	0.0			
0.9668	460.3	550.5	1.2	16.39	27.7	24.3
0.9578	436.1	547.8	1.5	10.38	29.3	25.2
0.9489	413.5	545.2	1.8	15.15	26.4	22.9
0.9208	349.9	538.0	2.7	13.82	26.6	22.4
0.8981	304.9	533.0	3.5	13.02	26.2	21.8
0.8384	200.3	521.3	5.2	12.82	28.7	23.0
0.8167	171.1	517.9	5.7	10.78	27.3	20.9
0.7866	133.0	513.6	6.3	10.78	29.6	22.1
0.7534	95.9	509.5	7.3	10.08	31.5	22.2
0.6720	25.4	501.5	8.4	8.6	34.9	21.5
0.5828	0.0	498.5	9.4	3.1	16.6	9.0
						Av. = 22.2

* About 35 mm. of the total of 63 mm. of carbon dioxide was recovered by heating the solid reaction product, indicating that the loss of carbon dioxide resulted from mechanical trapping of the gas.

Of greater interest is the behavior of carbon dioxide in the presence of a hydrogen–oxygen mixture. This two component system is similar to the $2CO{:}1O_2$ system. The stoichiometric relations are identical, both reaction products are radiochemically inert (7), and the relation between ionization potentials of components is the same for both systems. Accordingly, the catalytic efficiency of carbon dioxide in the water synthesis under the influence of radon should be very small and approximately that found in the carbon monoxide oxidation.

A possible objection to the execution of this experiment was the chance for reduction of carbon dioxide by hydrogen (8) which would mask any catalytic effect. However, oxidation was found to be as exclusive here as it was in other reactions (2). Measurements at liquid air temperatures showed no appreciable loss of carbon dioxide until the greater part of the reactants had been used up.

TABLE 2

The effect of carbon dioxide on the water synthesis

$2H_2(g) + 1O_2(g) + CO_2(g) = 2H_2O(l) + CO_2(g)$

$D = 2.006$ cm.; $E_0 = 0.105$ curie radon; $P_{CO_2} = 215.9$ mm.

$e^{-\lambda t}$	$P_{(2H_2 + 1O_2)}$	$\left(\frac{k\mu}{\lambda}\right)'_c$	$\left(\frac{k\mu}{\lambda}\right)'_{corr.}$
	mm. Hg		
1.0000	456.7		
0.9400	376.9	30.5	25.1
0.9139	347.5	29.7	23.6
0.8869	319.3	29.9	23.4
0.8511	286.1	29.3	22.4
0.8228	261.5	30.3	22.6
0.8198	(259.8)*		
0.7808	231.2	28.0	20.3
0.7284	195.1	30.9	21.5
0.6873	171.0	30.6	20.3
0.6847	(177.3)*		
0.6473	149.7	31.7	20.1
0.5949	125.2	32.6	19.4
0.4689	81.5	32.5	16.9
0.4006	64.5	32.7	14.3
0.3333	50.6	34.4	13.1
0.2315	35.7	32.7	10.3

[*] Pressures in parentheses were measured at liquid air temperatures.

The reaction mixture was prepared by adding carbon dioxide to a 2:1 mixture of hydrogen and oxygen obtained by electrolysis of a 10 per cent potassium hydroxide solution. This mixture was confined in a small spherical vessel containing a known quantity of radon, and the reaction was followed manometrically. Table 2 shows the course of the water synthesis in the presence of carbon dioxide. The column headed $\left(\frac{k\mu}{\lambda}\right)'_c$ was calculated from the usual expression for velocity constants in radiochemical reactions (9),

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{2.303\ \Delta\log P_{(2H_2+1O_2)}}{E_0\ \Delta e^{-\lambda t}}$$

ignoring the correction for ionization on carbon dioxide. In this equation $e^{-\lambda t}$ is the fraction of radon left after time t, E_0 is the initial quantity of radon in curies, λ is the decay constant of radon and $P_{(2H_2+1O_2)}$ is the partial pressure of the stoichiometric mixture at time t. The column headed $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ is the velocity constant of the catalyzed reaction correcting for the fractional efficiency of carbon dioxide according to the expression,

$$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} = \frac{2.303\ \Delta\log\left[P_{(2H_2+1O_2)} + x\,\frac{i_{CO_2}}{i_{(2H_2+1O_2)}}\,P_{CO_2}\right]}{E_0\ \Delta e^{-\lambda t}}$$

where $x = 0.145$, the specific ionizations i_{CO_2} and $i_{(2H_2+1O_2)}$ are 1.52 and 0.53, and the initial $P_{CO_2} = 215.9$ mm. The ionic equivalent of the carbon dioxide

$$\left[x\,\frac{i_{CO_2}}{i_{(2H_2+1O_2)}}\,P_{CO_2}\right]$$

is therefore 90.3 mm.

From the inverse square law (9), we should expect the velocity constant to equal 21.5 in a sphere of 2.006 cm. diameter. Evidently $\left(\frac{k\mu}{\lambda}\right)'_{c}$ is too high, indicating a decided catalytic effect of the carbon dioxide. Assuming the same efficiency of 14.5 per cent as found in the carbon monoxide oxidation, column $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ is obtained. Though not strictly constant, as shown by the decreasing $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ values, this correction is plainly of the proper order of magnitude. The decreasing velocity constants are in accord with the "depletion effect" which is characteristic of radiochemical reactions (3) sensitized by inert gases. This effect sets in when more than half of the total ionization falls on the catalyst. In the reaction considered in table 2, considerably more than half of the total initial ionization is falling on the carbon dioxide because of the great difference in specific ionization values of the reaction mixture and the catalyst. It is, therefore, not surprising that a decrease in the corrected velocity constant is obtained as the reaction proceeds.

This result is comparable with the effect of argon on the water synthesis. Here, too, a pronounced depletion effect is reported (3).

DISCUSSION

When Lind and Bardwell first discovered the pronounced catalytic effect of inert gases on radiochemical reactions, they assumed that the ionization falling on the foreign gas was completely effective in producing the reaction involved. Many of the cases studied justified this assumption. Thus, until the depletion effect sets in, helium, krypton, neon, and nitrogen are very efficient radiochemical catalysts.

Applying this assumption to catalysis by argon, xenon and carbon dioxide, the calculated values of velocity constants and M/N ratios are below those normally found for the reaction studied. The effect of carbon dioxide formed in the carbon monoxide oxidation was so small as to necessitate a study of its direct effect by the addition of a large initial quantity of the dioxide to a stoichiometric carbon monoxide–oxygen mixture. The results of this work showed carbon dioxide to have a definite effect on the reaction, but one which was small when compared with the efficient atmospheric gases mentioned. That this behavior of the dioxide is a characteristic property can readily be seen from its effect on the water synthesis and the acetylene polymerization. Thus in all three reactions where the effect of carbon dioxide has been investigated, it has been shown to be a very inefficient catalyst.

One must then attribute to every gaseous sensitizer a characteristic ability to accelerate radiochemical reactions, whether the effect results from direct clustering about the inert gas ions or from transfer of ions to reactants followed by clustering about reactants. Why certain gases, say helium and neon, should have a greater catalytic effect than others, such as carbon dioxide and argon, is not immediately evident; but the empirically determined fact remains that the efficiency of these gases varies.

From the point of view of a clustering mechanism, inefficiency of catalysts in these reactions may be interpreted as a tendency for neutral inert gas molecules to cluster about gaseous ions which would otherwise form clustering centers for reacting molecules. This crowding out effect has been suggested by Lind and Rosenblum to explain the course of the carbon monoxide oxidation.

It is, furthermore, reasonable to regard the depletion effect as resulting from a diminished efficiency of the inert gas, as an increasingly greater portion of the total ionization falls upon it. A simultaneous decrease in the concentration of reacting molecules creates a situation favorable towards a crowding out of reactants from clusters by inert gas molecules, accounting for the diminishing catalytic effect of even efficient inert gases as reactions approach completion.

SUMMARY

Carbon dioxide was shown to be an inefficient catalyst in radiochemical reactions. In the water synthesis, its efficiency is similar to that in the

carbon monoxide oxidation, namely 14.5 per cent. Even in the acetylene polymerization, a case conducive to a pronounced catalytic effect, only about 30 per cent of the carbon dioxide ionization is utilized in promoting reaction.

It is suggested that the inefficiency of a radiochemical catalyst is governed by the tendency of the inert gas to cluster about gaseous ions crowding out reactant molecules, and that the greater this tendency, the less efficient the catalyst. The depletion effect is considered as resulting from a lowered efficiency of the catalyst, as the quantity of reactant decreases and as a greater portion of the total ionization falls upon the catalyst.

REFERENCES

(1) LIND AND ROSENBLUM: Proc. Nat. Acad. Sci. **18**, 374 (1932).
(2) LIND, BARDWELL, AND PERRY: J. Am. Chem. Soc. **48**, 1556 (1926).
(3) LIND AND BARDWELL: J. Am. Chem. Soc. **48**, 1575 (1926).
(4) SMYTH AND STUECKELBERG: Phys. Rev. **36**, 472 (1930).
(5) TATE AND SMITH: Phys. Rev. **39**, 270 (1932).
(6) SMYTH, HARNWELL, HOGNESS, AND LUNN: Nature **119**, 85 (1927).
(7) DUANE AND SCHEUER: Le Radium **10**, 33 (1913).
LIND AND BARDWELL: J. Am. Chem. Soc. **47**, 2675 (1925).
(8) LIND AND BARDWELL: J. Am. Chem. Soc. **47**, 2675 (1925).
(9) LIND: J. Am. Chem. Soc. **41**, 531 (1919).

THE CHEMISTRY OF BERYLLIUM. V

ORGANIC COMPOUNDS OF BERYLLIUM[1]

HAROLD SIMMONS BOOTH AND DOROTHY GORDON PIERCE

Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio

Received August 3, 1932

INTRODUCTION

The organic compounds of beryllium have been very little studied. There have been many attempts to produce beryllium salts of organic acids, such as succinic, malonic, salicylic, and the fatty acids (1), but with the exception of beryllium trichloroacetate the products (2) have been mixtures of beryllium hydroxide with the respective acids, owing to the fact that they were prepared by neutralizing the acid with beryllium hydroxide or carbonate. Since solutions of beryllium salts (3) dissolve large amounts of beryllium hydroxide the products were contaminated by this excess. Some (4) have tried to overcome this difficulty by using an excess of the organic acid, but it is evident that this procedure must yield impure products except when the solubilities of the acid and salt differ enough to permit separation by recrystallization. Even this is often impossible because many beryllium salts hydrolyze as soon as the acid is removed. The trichloroacetate furnishes an example of this. This difficulty might be obviated by crystallization from organic solvents.

These mixtures were long thought to be true compounds because: (1) when washed with alcohol the products were finely granular although they showed no true crystals under the microscope; (2) the determination of their composition was based solely on the beryllium oxide content which we now know varies with temperature, concentration of acid, and amount of beryllium hydroxide or carbonate used; (3) the methods generally used for determining their molecular weights were inaccurate, because beryllium hydroxide dissolves in solutions of its normal salts, causing the freezing points to be abnormal (5).

A simple and satisfactory solution of the problem of their preparation in a pure state, at least in the case of the sulfonates, is described in this paper by a method which does not seem to have been used before. The beryllium salts were prepared by double decomposition of barium salts

---

[1] For former articles on beryllium, see This Journal 35, 2465, 2492, 3111 (1931); 36, 2641 (1932).

of the respective acids with beryllium sulfate. This method is not applicable to the preparation of easily hydrolyzed compounds, but the fact that the sulfonates are gummy when prepared by neutralization would seem to indicate that previous failure might not be due entirely to hydrolysis but partly to the excess of hydroxide dissolved by the beryllium salt solution. The extreme solubility of beryllium sulfonates made recrystallization from water impracticable and therefore mixtures of organic solvents were used.

To establish the definite chemical nature of the compounds (1) they were examined with the polarizing microscope; (2) the compounds were not analyzed in the usual way by ignition to oxide but after thorough drying were completely decomposed by fuming nitric acid in Carius tubes, and analyzed not only for the beryllium content, determined by the ignition of the precipitated hydroxide, but also for sulfate; (3) as a further proof a molecular weight determination was made by the boiling point rise method with acetone as solvent.

PREPARATION AND PURIFICATION OF MATERIALS

The ethyl acetoacetate, the ethyl benzoate, the benzene, chloroform, dichloromethane, carbon disulfide, sulfonic acid, and carbon tetrachloride used were pure chemicals as obtained. Acetophenone was redistilled. The acetone was dried over anhydrous sodium sulfate and redistilled. Toluene was stood over barium oxide for five hours, then distilled, and the fraction boiling at 108.5°C. was used.

Barium hydroxide

The crude barium oxide[3] was placed in a large evaporating dish and distilled water was added slowly, but rapidly enough to keep up a vigorous evolution of steam. When the addition of water caused no further reaction, the boiling hot mixture was poured quickly into another large evaporating dish full of distilled water to yield white crystals of barium hydroxide octahydrate. This mixture was brought to a boil, a few grams of barium peroxide were added to oxidize iron compounds, the mixture was boiled for 5 minutes and then allowed to cool, yielding colorless crystals of barium hydroxide octahydrate, iron free.

Beryllium sulfate tetrahydrate was made by evaporating pure beryllium nitrate tetrahydrate crystals, made from purified beryllium hydroxide, with concentrated sulfuric acid until no fumes were noticeable (6). The product was twice recrystallized.

Melting points were determined by the usual capillary method using a 360° thermometer calibrated at the highest point, at the transition point

---

[3] Kindly furnished by Mr. M. J. Rentschler, J. H. R. Products Company, Willoughby, Ohio.

of sodium sulfate decahydrate, at the steam point, and at the melting point of pure tin. For the determination of decomposition points the samples were heated in capillary tubes in a fused mixture of sodium and potassium nitrates. The molecular weights were determined by the boiling point method, using the electrically heated Beckman apparatus.

ANALYSES

All the compounds except beryllium dibenzoylmethane were decomposed by fuming nitric acid in Carius tubes and the beryllium was determined by precipitation with ammonium hydroxide as beryllium hydroxide and ignition to beryllium oxide. In the case of the sulfonates the filtrates from the beryllium hydroxide precipitate were used for the determination of the sulfates by precipitation as barium sulfate.

PART I

SULFONATES OF BERYLLIUM

As stated before, the sulfonates of beryllium cannot be made pure by neutralizing solutions of the sulfonic acids with beryllium hydroxide or beryllium carbonate, because solutions of beryllium salts dissolve beryllium hydroxide, the solutions remaining acid to litmus although they contain a large excess of beryllium hydroxide. Crystals sometimes separate from these solutions after several months, but they are gummy and coated with beryllium hydroxide. Too little attention to this has been the cause of serious error in the past (7). An exception to this is the recent work of Sidgwick and Lewis (4) who prepared beryllium benzenesulfonate and beryllium *p*-toluenesulfonate by evaporating a mixture of the hydroxide with a slight excess of the acid. The salt crystallized out on cooling a concentrated solution. They stated that both sulfonates separated with four molecules of water, but they did not obtain the anhydrous salts, because they decompose on heating. They based the composition simply on the weight of beryllium oxide obtained by ignition. They did not make a detailed study because the salts were not suitable for their purpose.

If the salts are made by neutralization, they may be separated from concentrated solutions containing beryllium hydroxide by precipitating the hydroxide with absolute alcohol, in which the beryllium salts are soluble, followed by filtering, and allowing the filtrate to evaporate. Even then, the crystals are gummy. If these crystals are allowed to stand for several months, the beryllium hydroxide becomes inactive and finally dehydrated, and will no longer dissolve in absolute alcohol, so that if the mixture is now dissolved in alcohol and filtered, good crystals may be obtained from the filtrate. This method is too slow and uncertain to be practicable.

In this laboratory a quick and easy way to prepare the pure salts was found to be by double decomposition of the barium salts with beryllium sulfate. The acid was neutralized with pure barium hydroxide, filtered, and evaporated to incipient crystallization. Most of the barium salts are beautifully crystalline and not very soluble. They were recrystallized from water when necessary. A solution of the pure salt was then mixed with one of beryllium sulfate, until further addition of either caused no precipitation. This point was determined by filtering a small portion of the mixture till clear, dividing into two portions, and testing one with a few drops of the solution of the barium salt and the other with the solution of beryllium sulfate. The mixtures were allowed to stand ten minutes. When exactly the right amount of beryllium sulfate had been added, the solution was digested to enlarge the barium sulfate particles, filtered, and evaporated nearly to dryness. If heated too strongly, or if evaporated to dryness, some of the salts hydrolyze or char, so the evaporation was completed in a vacuum desiccator. In some cases, crystals containing water of crystallization formed after the water had almost entirely evaporated. In other cases, only a crystalline mass remained. The products had to be dried in an over before they could be crystallized from organic solvents, because too much water prevents the formation of good crystals, and even if a precipitate does form, it partially redissolves. However, some water was evidently left in the salts, because the solvents used were free from water, and yet the products contained water of crystallization.[3] The salt was dissolved in as small a quantity of acetone as possible, and the toluene, carbon tetrachloride, or chloroform was added until considerable precipitate had been formed. The mixtures were then filtered as quickly as possible. Fine crystals separated at once. These were redissolved by heating the mixture. It was then allowed to cool slowly. Mixtures of toluene and acetone, carbon tetrachloride and acetone, or chloroform and acetone were found to be the best solvents from which to recrystallize them.

All these salts show polarization colors when examined under the microscope by polarized light. In dry acetone solution, the dried salts are not acid to litmus, but after a few moments exposure to the air, enough moisture is condensed on the surface of the solution to cause hydrolysis, and the litmus turns pink. All the sulfonates dissolve at once in liquid ammonia, and beryllium hydroxide is precipitated if the ammonia is not dry.

The analyses and the fact that the microscope showed only one kind of crystal in each case, indicate that the products are pure. The molecular

---

[3] The exact amount was not determined in all cases because we were interested in obtaining anhydrous salts, but the melting points showed that several hydrates exist for each salt.

weight determination shows that, when dry, they are not associated or combined with the solvent.

Beryllium p-toluenesulfonate

$[C_6H_4(CH_3)SO_3]_2Be$

Beryllium *p*-toluenesulfonate crystallizes from a mixture of acetone and chloroform in colorless, monoclinic needles containing water of crystallization. This may be driven off by drying in an oven, if the temperature is raised slowly enough. After being dried several hours at 190°C., the salt does not melt until it decomposes at 318.5°C. (cor.). The analysis also shows that all the water has been driven off.

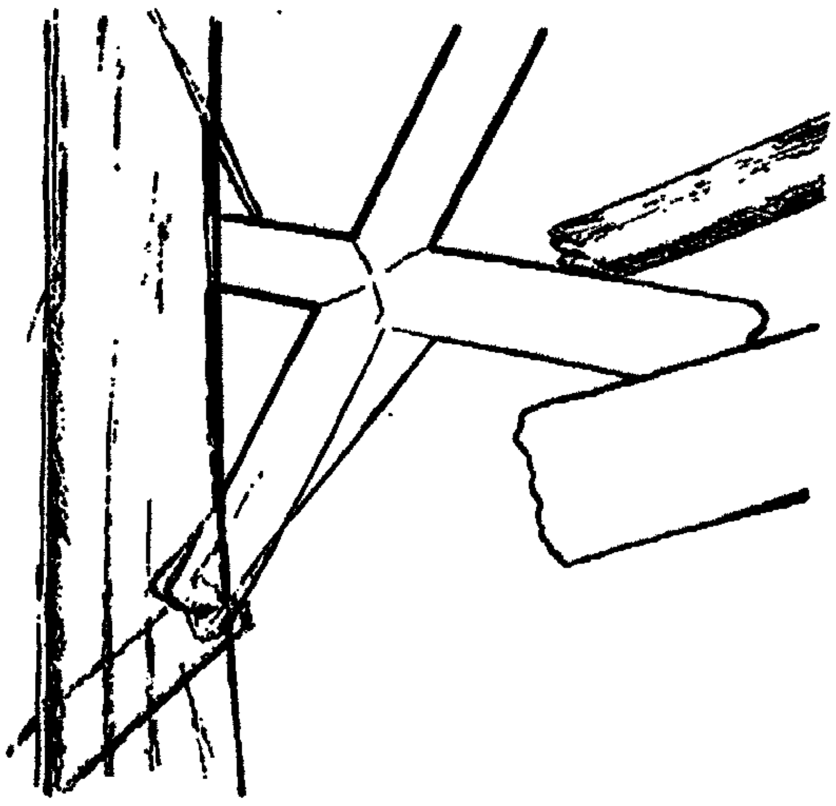


FIG. 1. BERYLLIUM *p*-TOLUENESULFONATE

Beryllium *p*-toluenesulfonate is very soluble in water, absolute alcohol, and acetone, and insoluble in ether, benzene, and dichloromethane. It is insoluble in cold glacial acetic acid, but very soluble in hot. It may be crystallized from water, but its extreme solubility makes this impracticable.

When crystallized from a mixture of acetone and chloroform, it melts in its water of crystallization at 133.8°C. (cor.), and again at 143.5–145.5°C. (cor.). It appears to lose water from 120°C. up, even if the capillary tubes are sealed. It decomposes at 318.5–319.5°C. (cor.).

Analysis. (1) 0.2078 gram sample gave 0.0154 gram BeO and 0.2760 gram $BaSO_4$. Calculated: BeO, 7.14; S, 18.25. Found: BeO, 7.41; S, 18.24. (2) 0.1902 gram sample gave 0.0142 gram BeO and 0.2558 gram $BaSO_4$. Calculated: BeO, 7.14; S, 18.25. Found: BeO, 7.47; S. 18.47.

Beryllium p-xylenesulfonate

$[C_6H_3(CH_3)_2SO_3]_2Be \cdot 5H_2O$

Beryllium *p*-xylenesulfonate, unlike the other sulfonates, crystallizes readily from water solution. It may be boiled to dryness without decomposition, although solutions are acid to litmus. Since it is not hydroscopic, like the other sulfonates, the water of crystallization was easily determined, by drying in an oven at 140°C. It was found to contain five molecules of water of crystallization.

Large, perfect crystals may be readily obtained on slowly cooling a hot water solution, if the concentration is correct. They are apparently monoclinic, having an extinction angle of 9° in one position, and showing parallel extinction in the other two. When thin, the crystals exhibit brilliant polarization colors.

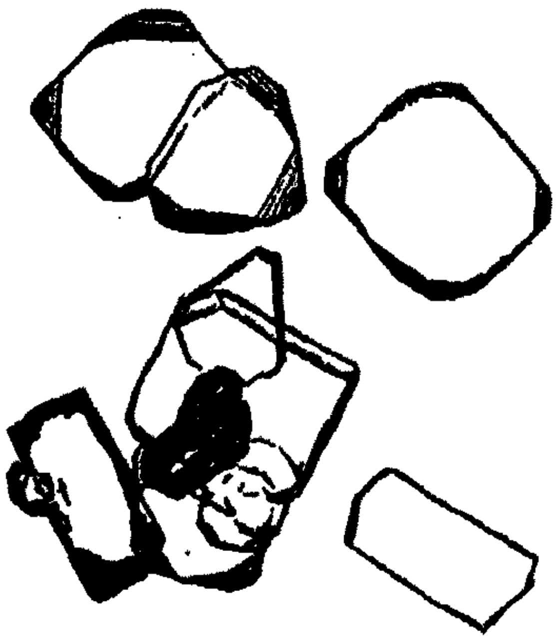


FIG. 2. BERYLLIUM *p*-XYLENESULFONATE

Beryllium *p*-xylenesulfonate is very soluble in water, absolute alcohol, hot glacial acetic acid, and acetone, and insoluble in ether, benzene, carbon tetrachloride, toluene, chloroform, dichloromethane, and carbon disulfide.

When crystallized from water, it melts in its water of crystallization at 143.2–144.2°C. (cor.), solidifies, and melts again at 177.8–178.8° (cor.). When dried at 190°C., it does not melt, but decomposes at 326.9–332.2° (cor.).

Analysis. 0.1428 gram sample gave 0.0096 gram BeO; 0.2474 gram sample gave 0.3042 gram $BaSO_4$; 0.2078 gram sample lost 0.0400 gram water. Calculated: BeO, 6.62; S, 16.90; H_2O, 19.20. Found: BeO, 6.72; S, 16.89; H_2O, 19.25.

Beryllium 2-chlorotoluene-5-sulfonate

$[C_6H_3(CH_3)(Cl)SO_3]_2Be$

Beryllium 2-chlorotoluene-5-sulfonate is the only one of the sulfonates which does not melt, and yet a few crystals were once obtained which did melt in their water of crystallization. A detailed study was not made, but it would appear that crystallization under different conditions might produce different hydrates. The crystals do not melt even if the melting point tube is sealed and suddenly immersed in the sulfuric acid bath every ten degrees, and yet they lose weight when heated in an oven at 190–200°C.

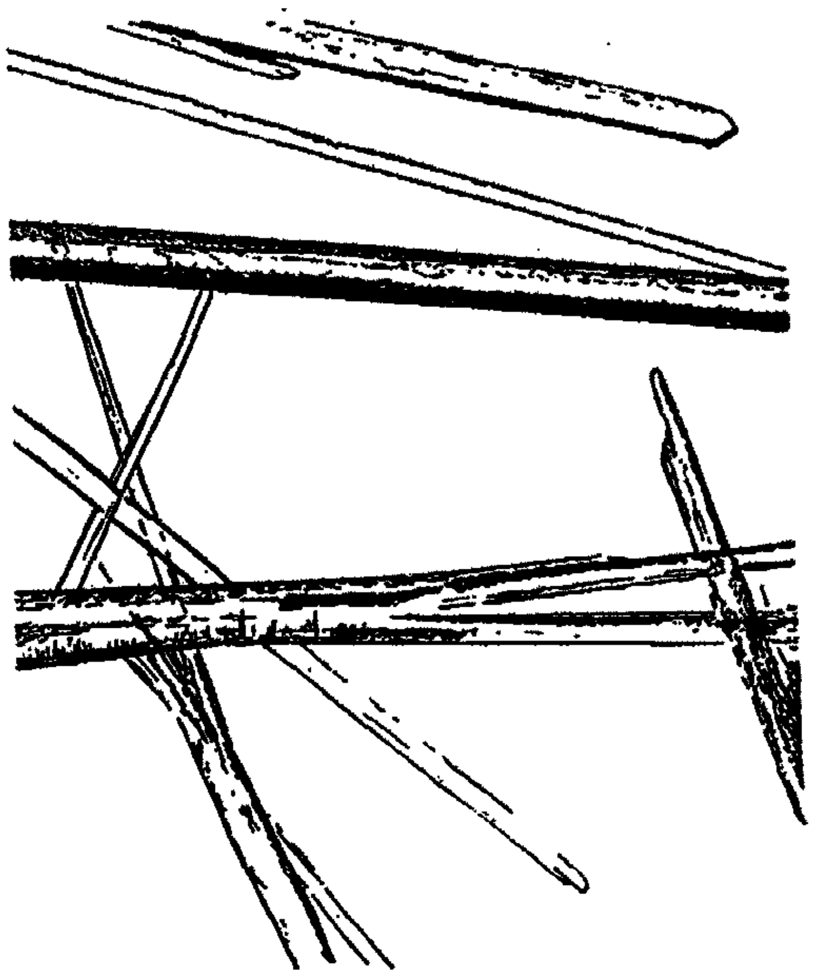


FIG. 3. BERYLLIUM 2-CHLOROTOLUENE-5-SULFONATE

The salt may be boiled to dryness without much hydrolysis. It crystallizes from a mixture of dry acetone and carbon tetrachloride in long, colorless needles which are apparently monoclinic, since they have an extinction angle of 4° in one position, and show parallel extinction in the other two.

Beryllium 2-chlorotoluene-5-sulfonate is very soluble in water, absolute alcohol, hot glacial acetic acid, and acetone, and insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, chloroform, and dichloromethane.

It decomposes at 384.7–399.7°C. (cor.).

Analysis. (1) 0.2964 gram gave 0.0178 gram BeO and 0.3378 gram $BaSO_4$. Calculated: BeO, 5.97; S, 15.26. Found: BeO, 6.01; S, 15.65.

(2) 0.2514 gram gave 0.0158 gram BeO and 0.2814 gram $BaSO_4$. Calculated: BeO, 5.97; S, 15.26. Found: BeO, 6.29; S, 15.37. Molecular weight: calculated, 420.24; found 440.3,418.0.

Beryllium benzenesulfonate

$(C_6H_5SO_3)_2Be$

The barium salt used in the preparation of beryllium benzenesulfonate was not made from the acid because it was not available. Instead, a mixture of benzene sulfochloride and water was boiled, barium hydroxide being added slowly, until, after boiling a few minutes, the solution no longer became acid. The solution was then filtered by suction, the barium benzenesulfonate immediately crystallizing out in colorless plates, apparently triclinic, showing brilliant polarization colors under the microscope.

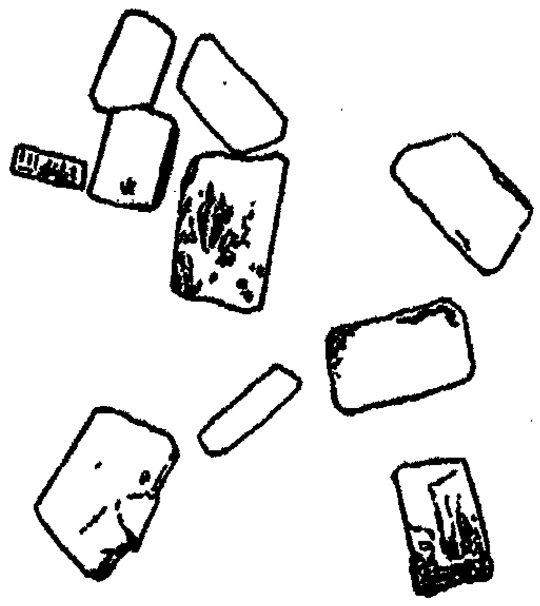


FIG. 4. BERYLLIUM BENZENESULFONATE

Beryllium benzenesulfonate was made by double decomposition in the usual way. If the solution is evaporated on a water-bath, a hard solid results, which contains water of crystallization. This cannot be entirely removed by drying in an oven because the salt decomposes. After drying at about 120°C., the salt was cooled in a desiccator, pulverized, and recrystallized from a mixture of acetone and chloroform. The product gave no test for chlorides, even though there was a large amount mixed with the crude salt.

Beryllium benzenesulfonate crystallizes from water in monoclinic plates having an extinction angle of 6° in one position and showing parallel extinction in the other two. These crystals appear to contain more water of crystallization than those recrystallized from a mixture of acetone and chloroform. The latter seem to be deliquescent.

Beryllium benzenesulfonate is very soluble in water, glacial acetic acid, alcohol, and acetone. It is insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, and dichloromethane. It seems to be very slightly soluble in hot chloroform.

When crystallized from a mixture of acetone and chloroform, the salt melts in its water of crystallization at 72.9–74.9°C. (cor.), and again at 94.4°C. (cor.), but if dried in the oven at 90–100°C., it melts only at 94.4°C. If it is carefully dried in the oven in a capillary tube, the temperature being slowly raised to 190°C., it does not melt. It begins to decompose at 358.7°C. (cor.).

For analysis, the samples were placed in small tubes and carefully dried to constant weight at 120–130°C. Some samples seemed to lose all their water at this temperature, but others decomposed, or else still contained water.

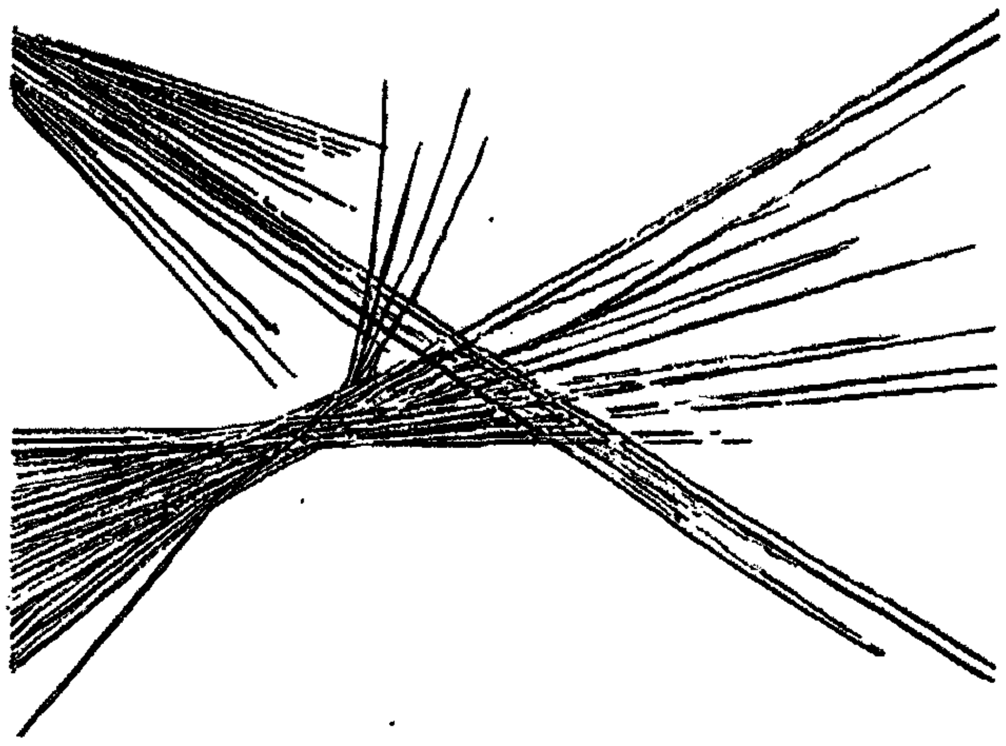


FIG. 5. BERYLLIUM 2-NITROTOLUENE-4-SULFONATE

Analysis. Calculated: BeO, 7.71. Found: BeO, 7.76.

Beryllium 2-nitrotoluene-4-sulfonate

$[C_6H_3(CH_3)(NO_2)SO_3]_2Be$

The barium salt used in the preparation of beryllium 2-nitrotoluene-4-sulfonate was also made by hydrolysis of the sulfochloride, instead of by neutralizing the free acid. It crystallizes from water solution in large yellow plates, which seem to be triclinic and show brilliant polarization colors.

The beryllium salt was made in the usual way, and recrystallized from a mixture of acetone and toluene. The salt crystallizes from this solution in monoclinic needles having an extinction angle of 6° in one position and showing parallel extinction in the other two. They exhibit polarization colors.

Beryllium 2-nitrotoluene-2-sulfonate is very soluble in water, absolute alcohol, acetone, and glacial acetic acid, and insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, chloroform, and dichloromethane. It appears to be slightly hygroscopic.

When crystallized from a mixture of acetone and toluene, it melts in its water of crystallization at 140.6 -141.6°C. (cor.), then solidifies, and melts again at 181.3–182.3°C. (cor.). If carefully dried in an oven at 160°C., it does not melt, but decomposition is noticeable at 273.6°C. (cor.).

Analysis. Calculated: BeO, 5.69; S, 14.53. Found: BeO, 6.05; S, 14.85.

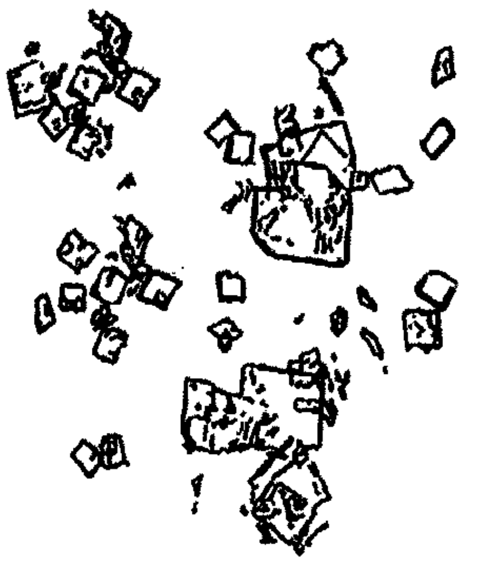


FIG. 6. BERYLLIUM *m*-NITROBENZENESULFONATE

Beryllium m-nitrobenzenesulfonate

$[C_6H_4(NO_2)SO_3]_2Be$

Beryllium *m*-nitrobenzenesulfonate was made in the usual way. The water solution cannot be evaporated to dryness over a flame without decomposition. After evaporation in a vacuum desiccator, it was carefully dried in an oven and recrystallized from a mixture of acetone and carbon tetrachloride. It is hygroscopic.

The crystal system of the salt when crystallized from a mixture of acetone and carbon tetrachloride was not determined, but the crystals forming on a slide as the solvent evaporated were monoclinic, having an extinction angle of 7° in one position and showing parallel extinction in the other two.

Beryllium *m*-nitrobenzenesulfonate is very soluble in water, absolute alcohol, acetone, and hot glacial acetic acid. It is insoluble in carbon disulfide, ether, benzene, carbon tetrachloride, toluene, chloroform, and dichloromethane.

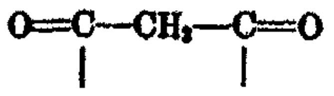
When crystallized from a mixture of acetone and carbon tetrachloride, it melts in its water of crystallization at 146.8°C. (cor). If dried at 180°C., it melts at 203.7–204.7°C. (cor.). It does uot solidify on further heating, but begins to decompose at 231.8°C. (cor.).

Analysis: Calculated: BeO, 6.07. Found: BeO, 5.95.

PART II

CHELATE BERYLLIUM COMPOUNDS

In striking contrast to the beryllium salts of organic acids, beryllium acetylacetonate is a well-defined chemical compound (8). It is the product formed by replacing one hydrogen atom of each of two molecules of acetylacetone by one atom of beryllium, and is one of a series of metallic salts of tautomeric enol-keto compounds, the so-called chelate compounds. The replaceable hydrogen atoms in the keto-form (9) are attached to a carbon atom which is between two carbonyl groups,

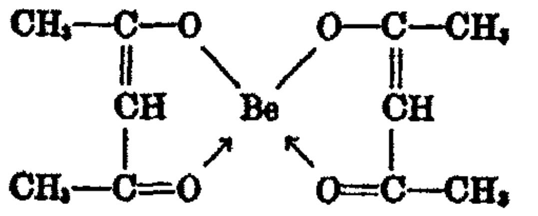


$$O{=}\underset{|}{C}{-}CH_2{-}\underset{|}{C}{=}O$$

The enol form, which forms salts, is

$$H{-}O{-}\underset{|}{C}{=}CH{-}\underset{|}{C}{=}O$$

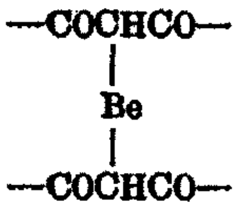
Or, as Sidgwick states, in beryllium acetylacetonate there are "rings with one definite coördinate link, in which the metallic (or hydrogen) atom is joined to the ring on one side by a normal link, and on the other by a coördinate link, .



Chelate rings of this type are very stable. Such compounds have very different properties from the ordinary salts of organic acids; for instance, they are soluble in most organic solvents and practically insoluble in water. The possibility of their being of use as solutes for the electrodeposition of beryllium and in other ways led to the second part of this work—the preparation of a few beryllium salts of such compounds.

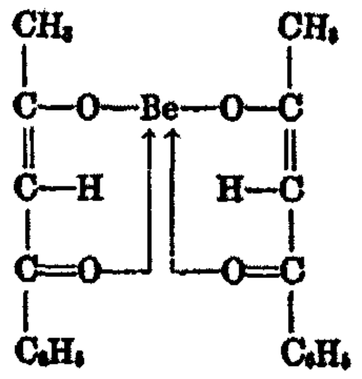
The copper salts of these compounds have been the most investigated. They are usually made by shaking an alcoholic solution of the ketone or ester or its sodium salt with copper acetate or sulfate, often with the addition of ammonia. If chlorides are used an addition product, consisting of the copper salt and the metallic chloride or hydrogen chloride, is formed. The copper salts, as well as those of most metals, are crystalline and insoluble in water and ether, but are easily recrystallized from hot alcohol, benzene, or chloroform. Although it is possible to make the beryllium salts in this way, it is not desirable, because the product is generally very impure, owing to the insolubility of beryllium hydroxide or carbonate in the ketone or ester used. Therefore a different procedure was followed in each case, according to the solubilities of the raw materials and products.

Two ketones, benzoylacetone, $C_6H_5COCH_2COCH_3$, and dibenzoylmethane, $C_6H_5COCH_2COC_6H_5$ and one ester, ethyl acetoacetate, $CH_3COCH_2COOC_2H_5$, were chosen as typical enol-keto compounds from which to make beryllium salts, in order to find out whether their properties resemble those of beryllium acetylacetonate. Each contains the grouping



$$\begin{array}{c}\text{—COCHCO—}\\ | \\ \text{Be}\\ | \\ \text{—COCHCO—}\end{array}$$

Beryllium benzoylacetonate



Enol form

We first tried to prepare beryllium benzoylacetonate by a method similar to that used by Combes (11). An alcoholic solution of benzoylacetone[4] was added to moist freshly precipitated beryllium hydroxide, to which a little absolute alcohol had been added. Since the benzoylacetone is very insoluble in water, it immediately precipitates, along with the beryllium benzoylacetonate. The latter may be separated from the excess beryllium hydroxide by extraction with chloroform, but, since this also dissolves the benzoylacetone, the product is very impure. However, the two may be separated by alcohol in which the salt is not very soluble, whereas the ketone is very soluble. The yield is very poor.

---

[4] The benzoylacetone was made according to Vanino, Präparative Chemie, Band 2, p. 537.

We found that the salt also may be made by allowing beryllium sulfate to stand in an alcohol solution of benzoylacetone, but this too is a poor method, yielding a mixture.

The best method we found was to add a weighed amount of beryllium nitrate dissolved in as little absolute alcohol as possible, drop by drop, to an equivalent weight of benzoylacetone also dissolved in as small a quantity of alcohol as possible, because the salt is soluble enough not to precipitate if the solutions are too dilute.[5] The crystals were washed with absolute alcohol to remove the mother liquor and any excess benzoylacetone, which is very soluble in alcohol. They were then stirred with water to remove any beryllium nitrate or nitric acid, again washed with alcohol, and then ether, and recrystallized from pure toluene or benzene. Large crystals may be obtained after a little practice. The temperature must be allowed to drop very slowly or else small crystals separate out even at 70°C. A small beaker containing the boiling toluene solution was placed in a boiling water-bath and the temperature of the latter was allowed to fall 20° every three hours. The solution was seeded at 75°C. At 55°C. the temperature was kept constant for two hours and then allowed to drop slowly to room temperature. Even then small crystals separated on filtering. The crystals were filtered immediately and washed with absolute alcohol and dry, fat-free ether. Large, perfect crystals may be obtained by allowing a benzene solution to evaporate, but on exposure to the air, these apparently lose benzene, becoming a white powder. Those crystallized

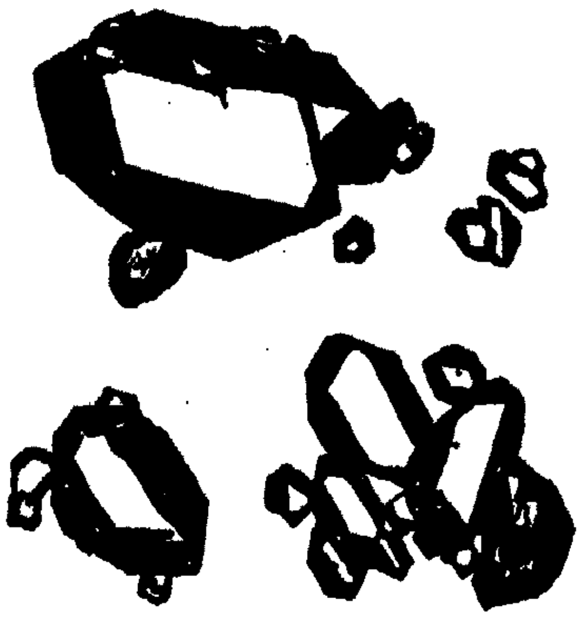


FIG. 7. BERYLLIUM BENZOYLACETONATE

---

[5] In the latter case, crystals will sometimes form on standing, but usually the salt decomposes, yielding a brown oil. The crystals formed on standing are yellow, but if immediately precipitated, the product is nearly white. Considerably more of the salt may be recovered from the filtrate by evaporation under reduced pressure at 50–60°C.

from toluene do not change. They have the same melting point as the white powder left after the benzene evaporates from the other crystals. This would seem to indicate that they contain no toluene.

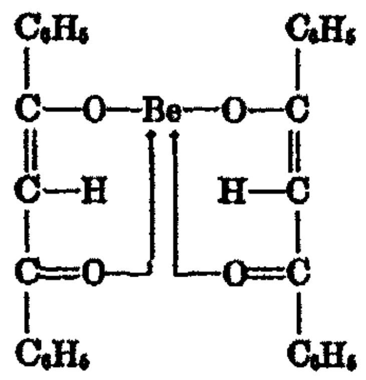
The crystals are highly refractive and show brilliant polarization colors. They show neither pleochroism nor absorption. They are monoclinic, having an extinction angle of 15° in one position and showing parallel extinction in the other two.

Beryllium benzoylacetonate is insoluble in water, almost insoluble in ether, fairly soluble in alcohol, benzene, carbon tetrachloride, toluene, and hot carbon disulfide, and very soluble in chloroform, acetone, and dichloromethane. It is insoluble in cold, but very soluble in hot glacial acetic acid. It is very slightly soluble in liquid ammonia. Ammonium hydroxide will not precipitate beryllium hydroxide, because the salt is insoluble in water, even if boiled seven hours, but if it is first boiled with nitric acid, and then made slightly alkaline with ammonium hydroxide, a heavy gelatinous precipitate results. It is very soluble in cold, concentrated sulfuric and nitric acids, and it dissolves in cold, concentrated hydrochloric acid on standing twenty-four hours. It is hydrolyzed by refluxing with dilute (1:4) nitric acid in half an hour, and dissolves in dilute hydrochloric and sulfuric acids after boiling four hours.

The crystals melt sharply at 210.2–211.2°C. (cor.), and begin to decompose noticeably at 224.8°C. (cor.). They may be sublimed if heated quickly, before they have time to melt.

Analysis. Calculated: BeO, 7.58. Found: BeO, 7.69, 7.65. Molecular weight: calculated, 331.24; found, 327.45, 343.6.

Beryllium dibenzoylmethane



Dibenzoylmethane was made by condensing ethyl benzoate with acetophenone by means of sodium and extracting the resulting sodium salt with a mixture of ice cold water and ligroin. The dibenzoylmethane was separated by adding acetic acid to the solution of the sodium salt, filtering, and recrystallizing from methyl alcohol. This method is exceedingly tedious, and gives a very small yield, because the sodium salt hydrolyzes easily, producing a brown oil (probably acetophenone or a derivative), which clogs the filter paper and cannot be separated from the product even by recrystallization. We found that a much quicker, easier way is to allow the ethyl benzoate, acetophenone, and sodium mixture to stand four or five days for the reaction to become complete, because a red-brown substance coats the sodium, making the reaction very slow. The resulting sodium salt was then washed with ether alone until it became nearly white, and dried in the air. The product was dissolved in water, and filtered quickly because it hydrolyzes easily. For the same reason it cannot be heated to get it into solution. The ketone was precipitated from this solution with acetic acid, at once. The crystals were collected on a filter, washed with water until a flame test showed only a trace of sodium, and allowed to dry in the air. The yield was fairly good, and the product almost white, although the melting point indicated that it was not pure.

The beryllium salt[6] was made by mixing equivalent amounts of the ketone and beryllium nitrate in absolute alcohol. The solutions must be made with as little alcohol as possible, because otherwise the crystallization is very slow, and the crystals impure. A warm solution of beryllium nitrate was added drop by drop to a warm solution of dibenzoylmethane. As soon as all the beryllium nitrate was added, and not before, needles of the beryllium salt began to separate[7] until the solution became almost solid. The crystals were filtered, washed with alcohol and ether and recrystallized from absolute alcohol. Since the salt is not very soluble, this is a slow process. It crystallizes in long, pale yellow needles, which are pure. The crystals are light and mat easily. They do not stick together, but adhere to everything else, so that it is practically impossible to make pellets of them for a molecular weight determination. They cannot be introduced into the tube by a paper funnel because they stick to the paper. If the salt is put into small glass tubes and then slid into a larger tube, it does not dissolve completely out of the tubes even if allowed to boil all day. Therefore a molecular weight determination was not made.

The needles show brilliant polarization colors and are apparently monoclinic, having an extinction angle of 5° in one position and showing parallel extinction in the other two. The ends are always jagged, as no pinacoid or prism faces form. (See figure 8, page 75.)

Beryllium dibenzoylmethane is insoluble in water, slightly soluble in

---

[6] It cannot be made by mixing the ketone with beryllium hydroxide because the ketone, being insoluble in water, precipitates immediately, along with what little of the salt is formed.

[7] If the materials are not in equivalent amounts, or if the dibenzoylmethane is not almost white, no crystals separate. If it stands long enough, or is distilled under reduced pressure, a brown paste results which cannot be easily purified. A very small amount may be recovered by leaching out the impurity with alcohol, in which beryllium dibenzoylmethane is not very soluble. If the dibenzoylmethane is pure, a good deal of the product may be recovered from the filtrate by evaporation under reduced pressure.

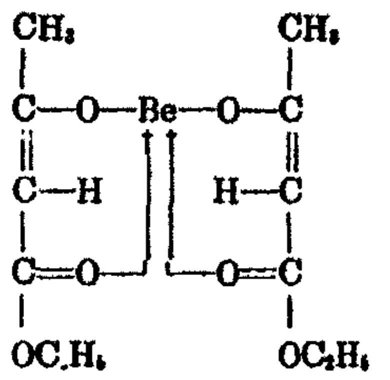
ether, fairly soluble in carbon tetrachloride, toluene, and hot alcohol, and very soluble in benzene, chloroform, acetone, carbon disulfide, and dichloromethane. It is insoluble in cold glacial acetic acid, but very soluble when heated. It is insoluble in liquid ammonia.

Beryllium hydroxide is not precipitated on addition of ammonium hydroxide to a mixture of the salt and water, owing to the insolubility of the salt, but after it is boiled a few minutes with nitric acid, ammonia causes a heavy gelatinous precipitate. It is neither dissolved nor hydrolyzed by water, even after seven hours boiling. It is very soluble in cold concentrated sulfuric acid and nitric acid. It does not dissolve in cold, concentrated hydrochloric acid, but dissolves when heated. It is insoluble in dilute sulfuric acid and hydrochloric acid, even when boiled seven hours. After two hours boiling, it dissolves in dilute nitric acid, with the separation of a white, powdery precipitate.

The crystals melt sharply at 214–215°C. (cor.), and do not decompose easily. A noticeable change in color occurred at 262° (cor.). The compound may be sublimed if heated quickly, before it melts.

Analysis. Calculated: BeO, 5.51. Found: BeO, 5.60.

Beryllium ethyl acetoacetate



Beryllium ethyl acetoacetate was prepared by stirring ethyl acetoacetate into moist beryllium hydroxide to which a little absolute alcohol had been added. As soon as the acetate was added, a salmon-pink oil began to separate. The reaction must be watched, because if allowed to stand too long, the mixture becomes a mass of crystals which cannot be separated from the excess beryllium hydroxide. The reaction may be complete in one hour or may take several days. The beryllium ethyl acetoacetate cannot be separated by extraction with ether, because some ethyl acetoacetate is dissolved also, contaminating the product. Therefore small portions of the oil were removed by a pipet about every five minutes and dropped into ice-cold distilled water. When a sample formed crystals immediately, the oil was quickly separated from the beryllium hydroxide by a pipet. The oil was separated by a suction filter from any beryllium oxide which might have been included and poured into about twenty times its own volume of ice-cold distilled water. The beaker was packed in ice and left until the oil had entirely solidified. If left in the water too long, the salt hydrolyzes. Since the crystals are light, they leave the oil and rise to the surface. As soon as this happened, the mass was separated from the liquid on a suction filter. The crystals were removed from the funnel and stirred with 400–600 cc. of distilled water at room temperature, and again filtered. The washing was repeated until the product was pure white. It must be done quickly in order to prevent hydrolysis. Dried in a vacuum desiccator, the salt becomes a pure white, fluffy, crystalline product which melts sharply at 60.6°C., giving a clear melt. It is too soluble in most organic solvents to be easily recrystallized. The product may be separated from any beryllium oxide by dissolving in fat-free ether and filtering. Since crystals do not form until the ether has evaporated, a photograph of the separate crystals is difficult to obtain. As the ether evaporates, crystals build up on the edges of the filter paper, and these were scraped off and photographed.

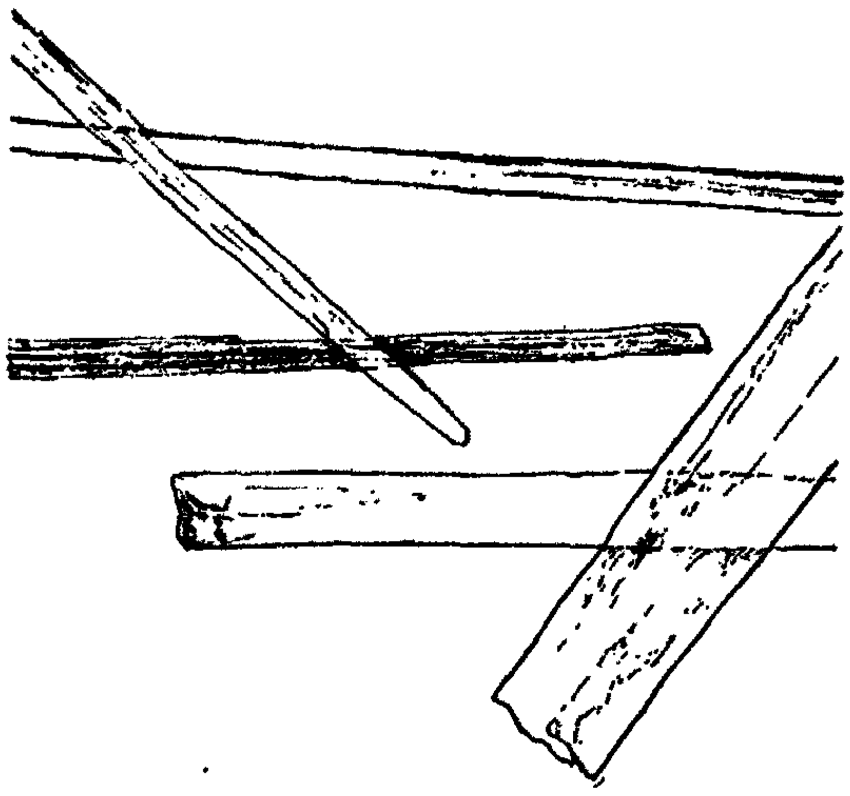


FIG. 8. BERYLLIUM DIBENZOYLMETHANE

Owing to the fact that the crystals could not be separated from the mother liquor, it was difficult to determine the crystal system to which they belong. They seem to be monoclinic, having an extinction angle of 7° in one position and showing parallel extinction in the other two.

Beryllium ethyl *acetoacetate is insoluble* in water and very soluble in alcohol, ether, benzene, carbon tetrachloride, dichloromethane, and glacial acetic acid. It is only slightly soluble in liquid ammonia contained in an open beaker. It begins to decompose into beryllium hydroxide and ethyl acetoacetate if allowed to stand in water a few moments, and hydrolysis is complete on boiling. It dissolves instantly in cold concentrated hydrochloric acid, in nitric acid, and in dilute sulfuric acid. In the latter case, an oil separates. Beryllium ethyl acetoacetate is very soluble in cold, concentrated sulfuric acid, in dilute hydrochloric acid, and in dilute nitric acid.

It melts sharply at 60.6–61.1°C. (cor.), giving a clear melt. If heated slowly, it begins to decompose at 228.5°C. (cor.), turning yellow.

Since the most carefully made salt still contained about 7 per cent of beryllium oxide, which was the only impurity provided the washing was thorough, this had to be removed before analysis. A pure product was obtained by dissolving the impure salt in dry, fat-free ether, filtering, and driving off the ether on a water-bath. The melted salt was then poured into a weighed glass tube, such as is used in Carius analyses, and cooled in a desiccator and analyzed.

FIG. 9. BERYLLIUM ETHYL ACETOACETATE

Analysis. Calculated: BeO, 9.39. Found: BeO, 9.52, 9.46. Molecular weight: calculated, 267.24; found, 266.8, 261.2.

After this work was finished, an article (13) appeared describing the preparation of beryllium ethyl acetoacetate by a slightly different method from that by which it was prepared in this laboratory. "Beryllium acetoacetic ester was prepared according to the method described by Konrad (Ann. **188**, 273) for the preparation of the aluminum compound. A berylate solution was prepared by adding strong potassium hydroxide to 10.1 grams of beryllium sulfate until the alkali was slightly in excess, and then adding 17 grams of freshly distilled acetoacetic ester. From the originally clear solution, there soon separated colorless leaflets, which could be recrystallized from petroleum ether, and which melted at 63°C. The yield was 3 grams, 20 per cent of the theoretical. The crystals may be *easily distilled in a vacuum at 166°C. under a pressure of 13 mm. They* are readily soluble in alcohol, benzene, etc."

SUMMARY OF PART II

Beryllium benzoylacetonate and beryllium dibenzoylmethane were found to be very similar to beryllium acetylacetonate. They are both crystalline, well-defined compounds, soluble in alcohol, acetone, chloroform, benzene, carbon tetrachloride, toluene, carbon disulfide, and dichloromethane, and insoluble in water. They melt sharply, but at much higher temperatures than the acetylacetonate, 210.2°C. and 214°C., respectively, and they do not sublime readily, although they may be sublimed if heated quickly, before they have time to melt; *beryllium acetylacetonate melts* at 108°C. and begins to sublime even before 100°C. They are soluble in concentrated acids, but are not hydrolyzed by water even after boiling seven hours.

Beryllium ethyl acetoacetate, however, although it dissolves in the same solvents, is much too soluble to be crystallized from any of them. It is very easily hydrolyzed to beryllium hydroxide and ethyl acetoacetate, even in cold water. Hydrolysis also takes place when toluene, benzene, or ether solutions are allowed to evaporate slowly and is probably due to water absorbed by solvent. Beryllium ethyl acetoacetate melts at a much lower temperature than the other two compounds, namely, 60.6°C. It may be sublimed if heated quickly under reduced pressure, but under atmospheric pressure it melts, and, if carefully heated, may be distilled at about 150°C., although some decomposition always takes place.

A comparison of the solubilities of the salts in ether is interesting. Beryllium ethyl acetoacetate is exceedingly soluble; beryllium acetylacetonate is soluble; beryllium dibenzoylmethane is slightly soluble; while beryllium benzoylacetonate is almost insoluble.

SUMMARY

The following compounds have been made and analyzed, and their properties studied: beryllium *p*-toluenesulfonate, beryllium *p*-xylenesulfonate, beryllium 2-chlorotoluene-5-sulfonate, beryllium benzenesulfonate, beryllium 2-nitrotoluenesulfonate, beryllium *m*-nitrobenzenesulfonate, beryllium benzoylacetonate, beryllium dibenzoylmethane, and beryllium ethyl acetoacetate.

REFERENCES

(1) PARSONS: The Chemistry and Literature of Beryllium, p. 71. The Chemical Publishing Co., Easton, Pa. (1909).

(2) PARSONS: J. Am. Chem. Soc. **31**, 1205 (1909).

(3) PARSONS: J. Phys. Chem. **11**, 659 (1907).

(4) SIDGWICK AND LEWIS: J. Chem. Soc. **129**, 1287 (1926).

(5) Reference 1, p. 17.
(6) Booth and Torrey: J. Phys. Chem. **35**, 2468 (1931).
(7) Reference 1, p. 69.
(8) Parsons: J. Am. Chem. Soc. **26**, 732 (1904).
(9) Sidgwick: The Electronic Theory of Valency, p. 240. Oxford University Press, London (1929).
(10) Morgan: J. Chem. Soc. **T105**, 189 (1914); **T117**, 1457 (1920) for a discussion of the structure of these compounds.
(11) Combes: Compt. rend. **119**, 1221 (1894).
(12) Vanino: Präparative Chemie, Zweite Auflage, Band 2, Organische Teil, p. 538.
(13) Weygand and Forkel: Ber. **59**, 2246-7 (1926).

THE ELECTRICAL CONDUCTIVITY OF MIXED SALT SOLUTIONS[1]

A. KAY SMITH[2] AND R. A. GORTNER

Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minnesota

Received July 25, 1932

An examination of the literature shows that few experimental studies have been made on the electrical conductivity of systematic mixtures of electrolytes. Two recent papers that do contribute directly to this subject are by Stern (1) and Ruby and Kawai (2). Stern examined the equivalent conductivity of systematic mixtures of the sodium and potassium halides from 0.1 M to 4 M at 25°C. He compared his experimental values with values calculated on the assumption that the conductivity of the mixture is additive. He did not find this rule to hold true. Ruby and Kawai studied the various combinations of sodium chloride, potassium chloride, and hydrochloric acid for the purpose of "discovering the nature of such solutions and to test the value of the methods of calculating the conductances of solutions of such mixtures of electrolytes." They did not find their experimental values to fit into any of the known methods for calculating such data. In addition to these two papers, H. C. Jones and C. M. Stine (3) worked with a variety of salt mixtures but their concentrations, with few exceptions, did not go below 0.5 N. Pascoe (4) worked with mixed salt solution in an attempt to correlate the conductivity of plant saps and of soils with their ionic concentrations. The present investigation was undertaken for the purpose of extending such conductivity data over a wider range of salts and into higher valence types in the hope of revealing the factor or factors that are responsible for their erratic behavior.

MATERIALS

The salts used in this investigation, namely, sodium chloride, sodium sulfate, magnesium chloride, magnesium sulfate, copper sulfate, zinc sulfate and potassium chloride, and the hydrochloric acid used were all of a C.P. grade and no further purification was attempted except for the magnesium sulfate, which was recrystallized once, and the hydrochloric

---

[1] Published as paper No. 1123, Journal Series, Minnesota Agricultural Experiment Station.

[2] Guest of the University of Minnesota.

acid, which was redistilled. The sodium chloride, potassium chloride, and sodium sulfate solutions were prepared by direct weighing of the dried salt; the hydrochloric acid was standardized according to the method of Hulett and Bonner (5); the other solutions were prepared by precipitating the sulfates as barium sulfate and the chlorides as silver chloride and weighing the respective precipitates. In general, the dilute solutions were prepared from the more concentrated ones. Double-distilled water was used in the preparation of the solutions that had a specific resistance of approximately 5×10^{-6} mhos and the solutions were preserved in Pyrex glass. The solutions were volume normal at 20°C. and burettes were used in proportioning them in the combinations desired. The combinations copper sulfate–sodium chloride, zinc sulfate–sodium chloride, sodium sulfate–sodium chloride, and magnesium sulfate–magnesium chloride were studied at 0.01 *N*, 0.1 *N*, 1 *N*, and 2 *N* concentrations; the other combinations did not cover as wide a range of concentration.

APPARATUS AND PROCEDURE

The usual Wheatstone bridge set-up was used in making the conductivity measurements, consisting of a Leeds and Northrup precision bridge with extension coil, a Leeds and Northrup precision resistance box, a type E Vreeland Oscillator at 1000 cycles, a telephone tuned to 1000 cycles, and three conductivity cells of the Washburn (6) type. The cell constants were 2.544, 17.11, and 115.0. Since most of the measurements were made during the warm part of the summer, a higher temperature than usual was used in this work, namely 30.17°C. ±0.02. The ratio of the bridge arms was determined and suitable corrections made in the calculations. The water correction was made in the solutions of 0.01 *N* concentration. All glassware was standardized and corrections were made, where necessary.

RESULTS

The results are given in table 1, which includes the names of the combinations studied, the proportion of each compound in the mixture, the experimental values and $\Delta\Lambda$, the difference between the experimental value and that calculated on the assumption that the conductance of the mixture is additive. $\Delta\Lambda$ is given a positive sign when the calculated value is greater than the observed value, and a negative sign when less than the observed value.

DISCUSSION

The data presented here do not show any decided regularity in their behavior. Such combinations as copper sulfate–sodium chloride, zinc sulfate–sodium chloride, sodium sulfate–sodium chloride, and potassium

TABLE 1

Conductivity data and $\Delta\Lambda$, the difference between the calculated and experimental values

$T = 30.17°C.$

CONCENTRATION OF SOLUTION								
NaCl	0.0100 N		0.1000 N		1.000 N		2.000 N	
$CuSO_4$	0.0100 N		0.1000 N		0.9295 N		1.859 N	
VOLUME OF SOLUTION Ratio NaCl : $CuSO_4$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$
100:0	131.2		119.0		95.50		83.30	
80:20	127.1	−4.0	110.1	−3.9	83.82	−0.71	71.20	0.87
60:40	121.0	−5.9	98.41	−5.0	71.55	−0.83	59.44	1.40
50:50	116.6	−5.6	91.50	−4.5	65.18	−0.65	53.86	1.36
40:60	111.8	−4.8	84.87	−4.3	59.00	−0.67	48.19	1.41
20:80	101.5	−2.6	70.47	−2.7	46.40	−0.46	37.53	0.84
0:100	90.87		55.01		33.55		27.14	

$T = 30.17°C.$

CONCENTRATION OF SOLUTION								
NaCl	0.0100 N		0.1000 N		1.000 N		2.000 N	
$ZnSO_4$	0.0100 N		0.1000 N		1.000 N		1.859 N	
VOLUME OF SOLUTION Ratio NaCl : $ZnSO_4$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$
100:0	130.9		118.9		95.52		83.32	
80:20	128.2	−4.5	110.5	−3.7	82.61	0.52	68.39	3.61
60:40	121.7	−5.5	99.32	−4.5	70.38	0.60	57.49	3.20
50:50	117.7	−5.1	93.70	−4.9	64.21	0.54	52.60	2.43
40:60	114.0	−5.1	87.80	−5.1	58.20	0.31	47.49	1.88
20:80	104.8	−3.3	73.52	−2.9	46.00	0.04	37.35	0.71
0:100	94.21		58.60		33.57		26.74	

$T = 30.17°C.$

CONCENTRATION OF SOLUTION								
NaCl	0.0100 N		0.1000 N		1.000 N		2.000 N	
Na_2SO_4	0.0100 N		0.1000 N		1.000 N		2.000 N	
VOLUME OF SOLUTION Ratio NaCl : Na_2SO_4	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$	Λ	$\Delta\Lambda$
100:0	131.0		118.9		95.52		82.09	
80:20	129.9	−0.1	115.5	−0.2	88.34	0.29	75.39	0.75
60:40	128.9	−0.3	111.9	−0.3	82.29	1.45	68.98	1.22
50:50	128.4	−0.3	109.9	−0.1	79.58	1.21	65.98	1.25
40:60	127.7	−0.2	107.8	0.2	76.69	1.15	62.97	1.28
20:80	126.4	−0.1	104.2	0.1	71.32	0.63	57.56	0.75
0:100	125.1		100.7		66.06		52.36	

TABLE 1—*Continued*

T = 30.17°C.

CONCENTRATION OF SOLUTION $MgCl_2$.................. Na_2SO_4..................	0.0093 N 0.0093 N		0.0927 N 0.0932 N		0.9270 N 0.9315 N		2.000 N 2.000 N	
VOLUME OF SOLUTION Ratio $MgCl_2$: Na_2SO_4	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ
100:0	127.4		110.9		80.85		64.38	
90:10			106.3	3.50	77.72	1.74		
80:20	121.8	5.0	103.3	5.41	75.39	2.67	59.78	2.2
70:30	120.1	6.4	101.1	6.51	71.94	4.73		
60:40	119.1	7.1	98.09	8.42	69.80	5.48	55.78	3.8
50:50	118.4	7.5	96.37	9.04	67.97	5.92	54.07	4.3
40:60	118.1	7.5	95.40	9.28	66.76	5.73	53.07	4.1
30:70	118.3	7.0	95.04	9.18	66.53	4.47		
20:80	120.4	4.6	96.57	5.55	66.00	3.71	52.02	2.7
10:90			98.16	2.87	66.43	1.88	52.16	1.4
0:100	124.4		99.93		66.92		52.36	

T = 30.17°C.

CONCENTRATION OF SOLUTION $MgCl_2$.................. $MgSO_4$..................	0.0100 N 0.0100 N		0.0927 N 0.0930 N		0.9270 N 0.9295 N	
VOLUME OF SOLUTION Ratio $MgCl_2$: $MgSO_4$	Λ	ΔΛ	Λ	ΔΛ	Λ	ΔΛ
100:0	128.9		111.9		80.57	
90:10			105.5	1.66	75.96	0.34
80:20	121.1	1.7			71.60	0.43
70:30			95.70	1.97	66.99	0.68
60:40	115.0	1.7	90.85	2.08	62.17	1.23
50:50	112.0	1.7	86.18	2.01	58.06	1.17
40:60	109.2	1.4	81.78	1.67	53.58	1.38
30:70					49.52	1.17
20:80	103.5	1.1	72.59	1.37	45.45	0.98
10:90			68.59	0.63	41.52	0.64
0:100	98.46		64.48		37.89	

TABLE 1—*Continued*

$T = 30.17$°C.

CONCENTRATION OF SOLUTION				
$MgCl_2$	0.0927 *N*		0.927 *N*	
NaCl	0.1000 *N*		1.000 *N*	
VOLUME OF SOLUTION Ratio $MgCl_2$: NaCl	Λ	ΔΛ	Λ	ΔΛ
100:0	109.8		80.46	
90:10			81.89	−0.01
80:20	111.7	−0.1	83.56	−0.26
70:30			84.90	−0.18
60:40	114.1	−0.7	86.65	−0.41
50:50	114.9	−0.5	87.74	−0.17
40:60	116.0	−0.7	89.17	−0.25
20:80	117.8	−0.7	92.11	−0.27
10:90			93.57	−0.31
0:100	118.9		94.68	

CONCENTRATION OF SOLUTION				
KCl	0.0100 *N*		0.5000 *N*	
HCl	0.0100 *N*		0.5000 *N*	
VOLUME OF SOLUTION Ratio KCl : HCl	Λ	ΔΛ	Λ	ΔΛ
100:0	156.2		128.2	
80:20	213.8	0.9	181.6	−0.2
60:40	272.1	1.0	234.5	0.0
50:50	301.5	0.9	261.5	−0.4
40:60	331.0	0.6	289.5	−1.8
20:80	390.0	0.0	341.7	−1.9
0:100	448.5		394.0	

$T = 0$°C.

CONCENTRATION OF SOLUTION		
NaCl	0.1000 *N*	
$CuSO_4$	0.1000 *N*	
VOLUME OF SOLUTION Ratio NaCl : $CuSO_4$	Λ	ΔΛ
100:0	58.28	
80:20	53.56	−1.47
60:40	47.43	−1.53
50:50	44.51	−1.71
40:60	41.30	−1.60
20:80	34.20	−0.69
0:100	27.32	

TABLE 1—*Concluded*

	$T = 30.17°C.$	
CONCENTRATION OF SOLUTION		
$CuSO_4$	0.0100 *N*	
$ZnSO_4$	0.0100 *N*	
VOLUME OF SOLUTION Ratio $CuSO_4 : ZnSO_4$	Λ	ΔΛ
100:0	90.55	
80:20	91.93	−0.66
60:40	92.62	−0.63
50:50	93.45	−1.09
40:60	93.66	−0.95
20:80	94.38	−0.94
0:100	94.16	

chloride–hydrochloric acid show positive, negative, and zero values for ΔΛ; other combinations, such as magnesium chloride–sodium sulfate and magnesium chloride–magnesium sulfate, show only positive deviations for the concentrations studied. The results, as a whole, suggest, however, that when a sufficiently wide range of concentrations has been studied for any combination, they will show all three variations from the straight line curve. Table 2 is a tabulation of these deviations expressed qualitatively; the table also includes data taken from Stern (1) and from Ruby and Kawai (2). Our data are not strictly comparable with those of Stern and of Ruby and Kawai since they used weight-normal solutions, whereas we used volume-normal; the general trend of all three researches, however, is the same.

No explanation is offered at the present time for the apparently erratic behavior of these conductivity measurements. Stern used the theory of complex ion formation to explain his data; this requires a positive value for ΔΛ and that this value should increase with increasing concentration. Our measurements do not reasonably substantiate this theory, since all the ΔΛ values found for the combination magnesium chloride–sodium chloride are negative and likewise for the combination potassium chloride–hydrochloric acid at concentrations above 0.5 *N*. Even the combinations magnesium chloride–sodium sulfate and magnesium sulfate–magnesium chloride, which gave positive values for ΔΛ for all values studied, do not support the complex theory since the values at 0.1 *N* concentration are larger than at either higher or lower concentrations. If complex ions do occur in these solutions and contribute to the erratic behavior of their conductivities, then it is evident that their effect is less than some other superimposed phenomena.

In considering the problem of complex ions it should be kept in mind also that the studies of MacInnes (7), Dewey (8) and others on the transport numbers of the sodium and potassium halides have failed to find complex ions in these solutions.

The inter-ionic attraction theory of Debye and Hückel (9) and its modification by Onsager (10) in its present state cannot be applied to these data since it has been developed for systems containing only two ionic species. While Bennewitz, Wagner, and Küchler (11) have extended Onsager's calculations to ternary ion mixtures it is still inapplicable, since their method requires that one of the three ionic species shall be limited to a small concentration in comparison to the other two ions.

TABLE 2

Showing the direction of the deviation of the experimental from the calculated values

NORMAL CONCENTRATION	0.01	0.1	0.5	1	2	4
Combination:						
$CuSO_4$–NaCl	–	–		–	+	
$ZnSO_4$–NaCl	–	–		+	+	
$CuSO_4$–$ZnSO_4$	–					
Na_2SO_4–NaCl	–	–		+	+	
$MgCl_2$–Na_2SO_4	+	+		+	+	
$MgCl_2$–$MgSO_4$	+	+		+		
$MgCl_2$–NaCl		–		–		
KCl-HCl	+		–			
KCl-HCl*			+	–	–	–
NaCl-HCl*			+	+	+	–
KCl-NaCl*			–	+	+	+
KCl-NaCl†		–	+	+	+	+
KBr-NaBr†		–	+	+	+	+
KI-NaI†		–	+	+	+	+

Sign is negative when observed value is greater than calculated; positive the converse.

* Taken from Ruby and Kawai.

† Taken from Stern.

The effect of solvation of the ions on their electrical conductivity is without a doubt a factor of considerable magnitude, but accurate information on solvation is too limited to be of much satisfaction. Attention should be called, however, to the similarity of our curves with those obtained by Jones and collaborators (3) wherein they measured the conductivity of salts in mixed solvents. Their data, which they obtained by varying the ratio of the solvent components and keeping constant the concentration of the salt, give curves that have essentially the same characteristics as those obtained by us. This permits the conclusion that the reaction between the solute and the solvent is of major importance in the interpretation of electrical conductivity data.

REFERENCES

(1) Stearn, A. E.: J. Am. Chem. Soc. **44**, 670 (1922).

(2) Ruby, C. E., and Kawai, J.: J. Am. Chem. Soc. **48**, 1119 (1926).

(3) Jones, H. C., and Stine, C. M.: Carnegie Inst. Wash., Pub. No. 180 (1913).

(4) Pascoe, T. A.: M. S. Thesis, University of Minnesota (1926). Cited by R. A. Gortner in Outlines of Biochemistry, pp. 269–270. John Wiley and Sons, New York (1929).

(5) Hulett, G. A., and Bonner, W. D.: J. Am. Chem. Soc. **31**, 390 (1909).

(6) Washburn, E. W.: J. Am. Chem. Soc. **38**, 2431 (1916).

(7) MacInnes, D. A.: J. Am. Chem. Soc. **47**, 1922 (1925).

(8) Dewey, Jane: J. Am. Chem. Soc. **47**, 1927 (1925).

(9) Debye and Hückel: Physik. Z. **24**, 185 (1923); **24**, 305 (1923); Trans. Faraday Soc. **23**, 333 (1927).

(10) Onsager: Physik. Z. **27**, 388 (1926); **28**, 277 (1927); Trans. Faraday Soc. **23**, 341 (1927).

(11) Bennewitz, Wagner, and Küchler: Physik. Z. **30**, 623 (1929).

THE SYSTEM ETHYL ALCOHOL–*n*-HEPTANE AT 30°C.

J. B. FERGUSON, M. FREED AND A. C. MORRIS

Department of Chemistry, University of Toronto, Toronto, Canada

Received November 18, 1932

In the published account of their work, Smyth and Engel (1) draw attention to the curious results obtained for certain systems of which, perhaps, ethyl alcohol–*n*-heptane is the most important. They offered no adequate explanation for their observation that for certain solutions the partial pressures of alcohol exceeded the vapor pressure of pure alcohol at the same temperature. Although they searched for evidence, they found none to support the suggestion that the system might not be a true binary system of the components considered.

If this system is a true binary system of alcohol and *n*-heptane the results should agree with the equation of Duhem-Margules within the limits set by the deviations from the laws of perfect gaseous solutions on the part of the vapor, and this agreement would be independent of the complexity of the liquid phase. When their results are tested by this method, not only do the partial pressures of both components for solutions rich in alcohol appear to be at variance with this equation, but those for solutions rich in heptane also cannot be reconciled with it. A wide range of liquid compositions are involved and it seems unlikely that the assumption made in selecting the components could be the primary cause of the discrepancy. On the other hand, one would hesitate before attributing it to experimental error were it not for the fact that such errors have not infrequently affected the results of other careful workers in this field. For these reasons we undertook the study of the system by a method in which such errors as occurred would differ from those likely to occur in the Sameshima (2) method used by Smyth and Engel.

MATERIALS

We requested the Ethyl Gasoline Corporation to send us a sample of *n*-heptane identical in character with that used by Smyth and Engel. The heptane obtained from them was re-distilled. Our crude alcohol was anhydrous ethyl alcohol (Squibbs). This was dried with sodium, distilled in a carefully dried apparatus, and promptly transferred to dry glass capsules which were sealed off and later inserted into our apparatus proper.

METHOD AND RESULTS

The apparatus was identical with and the procedure similar to that used for the study of the system methyl alcohol-*n*-hexane (3). The measurements were made at 30°C., since we feared that at higher temperatures and consequently at higher pressures the vapor would be very abnormal. We assumed that the deviation of the apparent formula weight $\left(F' = \frac{WRT}{PV}\right)$ from normal (100.13) was proportional to the partial pressure of the heptane and that this was the only complication in which the vapor was involved which merited consideration.

TABLE 1

The apparent formula weight of n-heptane

	TEMPERATURE	VAPOR COMPOSITION WEIGHT PER CENT OF HEPTANE	TOTAL PRESSURE	CALCULATED FORMULA WEIGHT
	°C.			
(1)	34.9	100	58.2	100.6
(2)	34.8	100	58.5	100.9
(3)	34.9	100	60.2	101.3
(4)	34.6	71.3	102.9	101.6

TABLE 2

Vapor pressure determinations at 30.0°C.

SUBSTANCE	VAPOR PRESSURE	OBSERVER AND REFERENCE
Ethyl alcohol	78.4	Freed and Morris
	78.2	Freed and Morris
	78.2	Smyth and Engel (1)
	78.06	Young (5)
	78.5	Regnault (6)
n-Heptane	58.4	Freed and Morris
	59.0	Freed and Morris
	58.2	Freed and Morris
	58.5	Freed and Morris
	58.2	Smyth and Engel (1)
	58.35	Young (5)
Water	32.0	Freed and Morris
	31.8	International Critical Tables (4)

Several experiments were carried out in order to determine a suitable value for the apparent formula weight of *n*-heptane vapor at 58.4 mm. and 35°C. The results of these are given in table 1. It may be noted that the highest value was obtained in the last experiment. This suggests a slight volume change on mixing the pure vapors and this point will be further investigated by us. However, at these low pressures an exact determination could not be made and we chose as a probable value 101.0.

Although our previous investigations indicate the method of study to be an adequate one, this is no check on the manner in which the present work was performed. To some extent, the vapor pressure measurements given in table 2 constitute such a check.

TABLE 3

The coexistent phases, the total and partial pressures at 30.00 ±.01°C.

NUMBER	FORMULA WEIGHT OF n-HEPTANE	WEIGHT PER CENT OF ALCOHOL		TOTAL PRESSURE	CALCULATIONS BASED UPON WEIGHT PER CENT RESULTS AND THE FORMULA WEIGHTS 46.05 AND 101.0			
		Liquid	Vapor		Mole per cent of alcohol		Partial pressures	
					Liquid	Vapor	Alcohol	n-Heptane
1		100.0	100.0	78.3	100.0	100.0	78.3	0.0
2	100.3	92.7	67.2	94.3	96.5	81.8	77.1	17.2
3	100.6	82.0	48.9	110.0	90.8	67.7	74.5	35.5
4	100.9	67.7	40.5	119.4	82.2	59.9	71.5	47.9
5	100.9	47.2	37.7	122.0	66.3	57.1	69.6	52.4
6	100.9	19.4	36.0	122.0	34.6	55.2	67.4	54.6
7	101.0	13.5	35.1	120.5	25.5	54.2	65.3	55.3
8	101.0	5.7	31.5	115.2	11.7	50.2	57.8	57.4
9	101.0	5.1	32.3	117.1	10.5	51.2	59.9	57.2
10	101.0	2.2	28.9	109.0	4.7	47.2	51.4	57.6
11	101.0	0.6	22.9	95.0	1.4	39.5	37.5	57.5
12	101.0		16.7	83.5		30.5	25.5	58.1
13	101.0	0.0	0.0	58.4	0.0	0.0	0.0	58.4

Our results for the two component system are given in table 3. The liquid composition for No. 11 is not given. It was too close to pure heptane for accurate determination nor can it be better obtained from the total pressure curve by interpolation. A probable value of 0.5 mole per cent alcohol might be tentatively assigned. No. 8 was our first experiment with systems of low alcoholic content and is in our belief a poor determination. It is included because we do not wish to present selected results.

The total and partial pressures (No. 8 omitted) are indicated in figure 1. For comparison, the results of Smyth and Engel were recalculated to a basis of 101.0 for heptane and are also included. This recalculation did not materially alter the nature of their results. When one considers the actual differences between the two total pressure curves, it would appear that the curves are in fair agreement except at the heptane end. Thus their maximum pressure is 119.9 mm. whereas ours is 122 mm. On the other hand, there are marked differences between our partial pressure curves. We found no evidence of points of inflection on these curves at their lower ends nor a maximum on the alcohol curve; in other words, no evidence of those peculiarities which were so markedly at variance with

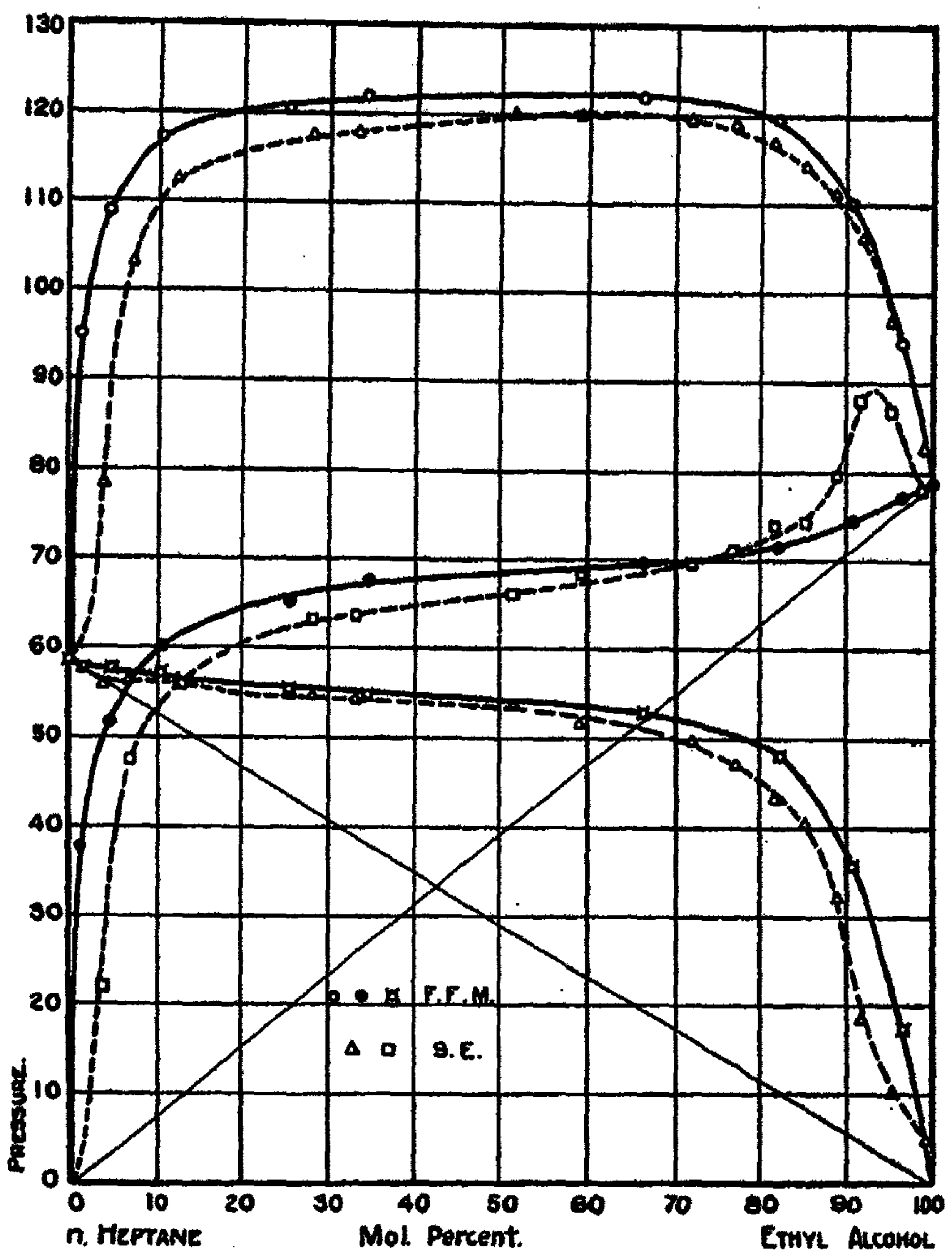


Fig. 1. Partial Pressures and Vapor Pressures

the equation of Duhem-Margules and which first excited our interest in this system.

SUMMARY

1. The compositions of the co-existent phases have been determined at 30.00°C. for the system ethyl alcohol-*n*-heptane.

2. The total pressures have been measured and the partial pressures calculated.

3. No evidence was obtained in support of the curious partial pressure curves which had previously been reported by others.

In conclusion, we wish to thank the Ethyl Gasoline Corporation for the sample of *n*-heptane furnished by them.

REFERENCES

(1) Smyth and Engel: J. Am. Chem. Soc. **51**, 2660 (1929).
(2) Sameshima: J. Am. Chem. Soc. **40**, 1482 (1918).
(3) Ferguson: J. Phys. Chem. **36**, 1123 (1932).
Beare, McVicar and Ferguson: J. Phys. Chem. **35**, 1068 (1931).
Ferguson and Funnell: J. Phys. Chem. **33**, 1 (1929).
(4) International Critical Tables, Vol. III, p. 212.
(5) Young: Proc. Roy. Dublin Soc. **12**, 374 (1910).
(6) Regnault: Mem. Roy. Acad. Sci. **26**, 339 (1862).

THE SOLUBILITY OF METALLIC LITHIUM IN LIQUID AMMONIA AT LOW TEMPERATURES[1]

WARREN C. JOHNSON AND M. M. PISKUR

George Herbert Jones Laboratory, University of Chicago, Chicago, Illinois

Received September 8, 1932

Seely (1) was the first to observe that liquid ammonia dissolves metallic lithium. Following this observation several investigations (2) have been reported relative to the physical properties of lithium solutions.

Although metallic lithium has been regarded as highly soluble in liquid ammonia, Ruff and Geisel (2a) are the only workers to carry out direct quantitative solubility measurements at different temperatures. They filtered the saturated solution through cotton and then analyzed the filtrate for lithium and ammonia. Measurements at 0°, −25°, −50° and −80°C. gave in each case a value of 3.93 gram-molecules of ammonia per gram-atom of lithium for the composition of the saturated solution. The solubility of metallic sodium in ammonia decreases with increasing temperature from −100° to 0°C., while that of metallic potassium increases with increasing temperature over the same temperature range (3). Although the changes in solubility with the temperature are relatively small in these two cases, it is difficult to understand the lack of change in the case of lithium. It appears that the method employed by Ruff and Geisel is not sufficiently accurate to detect small changes in the solubility.

Kraus and Johnson (2f) have measured the vapor pressure of solutions of lithium in liquid ammonia at −39.4°C. from the saturation point to a concentration of 60 gram-molecules of ammonia per gram-atom of lithium. A value of 3.61 NH_3/Li was found for the composition of the saturated solution. The pressure-composition curve offers a convenient means for the determination of the solubility of an alkali metal in this medium. When ammonia is added to the metal, the resulting solution shows a constant vapor pressure, that of the saturated solution, as long as any undissolved metal remains. The change in the vapor pressure in passing from the saturated solution to those less concentrated in metal is very abrupt. When this curve is extrapolated to intersect the horizontal line representing the vapor pressure of the saturated solution, there is obtained a point corresponding to the composition of this solution.

---

[1] From a thesis submitted by M. M. Piskur to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Master of Science.

In the present investigation the vapor pressure of solutions of lithium in liquid ammonia is determined at 0°, −32.7°, −33.2° and −63.5°C. in order to obtain the composition of the saturated solution as a function of the temperature. The results clearly show the solubility of metallic lithium to increase appreciably with increasing temperature.

APPARATUS AND MATERIALS

The method employed for the vapor pressure measurements was essentially the same as that previously described for lithium solutions (2f). Since most of the experiments were confined to concentrated solutions of the metal, only small amounts of hydrogen were found to be liberated due to a reaction between lithium and ammonia. The hydrogen was removed from the apparatus during the course of a series of measurements in order to obtain true equilibrium pressures.

The measurements were carried out at several different temperatures, 0°, −32.7°, −33.2° and −63.5°C. To maintain the temperature at 0°C., the vapor pressure tube was surrounded by a Pyrex Dewar flask containing finely-chipped ice in equilibrium with water. A thermometer calibrated by the Bureau of Standards was inserted in the bath and the temperature was noted to remain at 0°C. ± 0.05° for a period of several hours. A thin-walled glass tube was placed around the vapor pressure tube in order to keep the lithium separated from the ice-water mixture in case of accident. It was found more difficult to maintain constant temperature in the neighborhood of the normal boiling point of liquid ammonia. The ammonia in the Dewar tube was allowed to boil against a column of mercury of approximately 1 cm. which was exposed to the atmosphere. In addition, the height of the liquid ammonia in the Dewar tube was kept as constant as possible by frequent additions. However, owing to changes in the height of this column and changes in the atmospheric pressure, the variation of the temperature during the course of an experiment was ±0.1°. A temperature of −63.5°C. was obtained with a mixture of liquid nitrogen and chloroform. No difficulty was experienced in keeping this temperature constant to ±0.1°.

The metallic lithium used in the experiments was found to be free of iron and potassium and to contain a small amount of sodium. Liquid ammonia of commerce was siphoned into small steel tanks containing a few grams of metallic sodium as a dehydrating agent. The ammonia was distilled into a second steel container before being used for the experiments.

RESULTS

The results of two series of measurements at 0°C., one series at −32.7°C., one series at −33.2°C., and three series at −63.5°C. are given in table 1. The values obtained at 0°C. are plotted in figure 1, while those at the lower

TABLE 1

Vapor pressure of solutions of lithium in liquid ammonia at different concentrations and temperatures

CONCENTRATION NH_3/Li	PRESSURE	CONCENTRATION NH_3/Li	PRESSURE
Series 1. 0.2644 gram of lithium. T = 0°C.			
	mm.		*mm.*
3.623	34.1	4.323	938.0
3.647	34.9	4.350	876.0
3.667	57.0	4.658	1177.0
3.726	166.5	5.090	1542.0
3.810	252.0	5.590	1857.0
3.890	376.0	6.653	2288.0
3.990	509.0	7.701	2560.0
4.111	660.0		
Series 2. 0.1187 gram of lithium. T = 0°C.			
3.542	34.0	3.750	207.0
3.580	34.0	3.875	381.0
3.610	41.0	4.092	642.0
3.639	67.0	4.467	1048.0
3.680	115.5		
Series 3. 0.1968 gram of lithium. T = −32.7°C.			
3.739	3.3	4.363	260.5
3.741	3.4	4.521	310.0
3.764	8.0	4.715	360.8
3.802	26.0	4.938	409.5
3.858	56.0	5.175	449.2
3.921	94.5	5.446	490.4
3.987	119.0	5.723	525.7
4.056	146.5	5.950	550.0
4.142	178.8	6.288	580.0
4.242	218.4	6.495	597.5
Series 4. 0.1818 gram of lithium. T = −33.2°C.			
3.747	3.4	4.127	172.3
3.750	3.4	4.233	213.0
3.753	3.7	4.373	259.0
3.789	10.9	4.542	309.4
3.805	22.3	4.712	362.0
3.858	51.5	5.002	412.0
3.930	87.2	5.296	458.0
3.985	109.0	5.603	501.0
4.046	136.5	5.830	526.5

TABLE 1—*Concluded*

CONCENTRATION NH_3/Li	PRESSURE	CONCENTRATION NH_3/Li	PRESSURE
Series 5. 0.0762 gram of lithium. $T = -63.5°C.$			
	mm.		*mm.*
4.039	25.8	5.714	94.0
4.229	43.7	6.348	103.6
4.602	62.8	7.279	108.6
5.091	80.8		
Series 6. 0.0922 gram of lithium. $T = -63.5°C.$			
3.824	1.8	4.034	21.9
3.854	4.0	4.288	42.5
3.898	8.7		
Series 7. 0.1015 gram of lithium. $T = -63.5°C.$			
3.811	1.2	3.980	18.3
3.820	2.5	4.061	26.0
3.852	5.5	4.174	35.9
3.924	10.0	4.330	48.5

temperatures are shown in figure 2. Many of the values are not plotted, especially in the concentrated regions, owing to overlapping of points. The measurements at −32.7°C. and −33.2°C. are plotted together. Since most of these values appear at high lithium concentrations, where the change in the vapor pressure with the temperature is very small, the two series of measurements fall closely together. The concentrations are expressed in gram-molecules af ammonia per gram-atom of lithium, while the pressures are given in millimeters of mercury.

The composition of the saturated solution was determined at each temperature by an extrapolation of the curves shown in figures 1 and 2. Additional experiments were carried out with an excess of metallic lithium present in order to establish the vapor pressure of the saturated solution at these temperatures. The data are shown in table 2.

DISCUSSION OF RESULTS

Figures 1 and 2 show the vapor pressure of lithium solutions at different temperatures and over a relatively small range of concentration. These curves are identical in form with that obtained previously for lithium solutions at −39.4°C. (2f). There is no indication of a combination between lithium and ammonia; nor is there any evidence for the existence of a two-phase liquid system at the lowest temperature studied. Ruff and Zedner

(2b) point out the appearance of a two-phase liquid system for lithium solutions below −35°C. The above results indicate the non-existence of such a system within the range of concentrations employed, namely, between 3.81 and 7.28 gram-molecules of ammonia per gram-atom of lithium, since the vapor pressure curves do not show any irregularities.

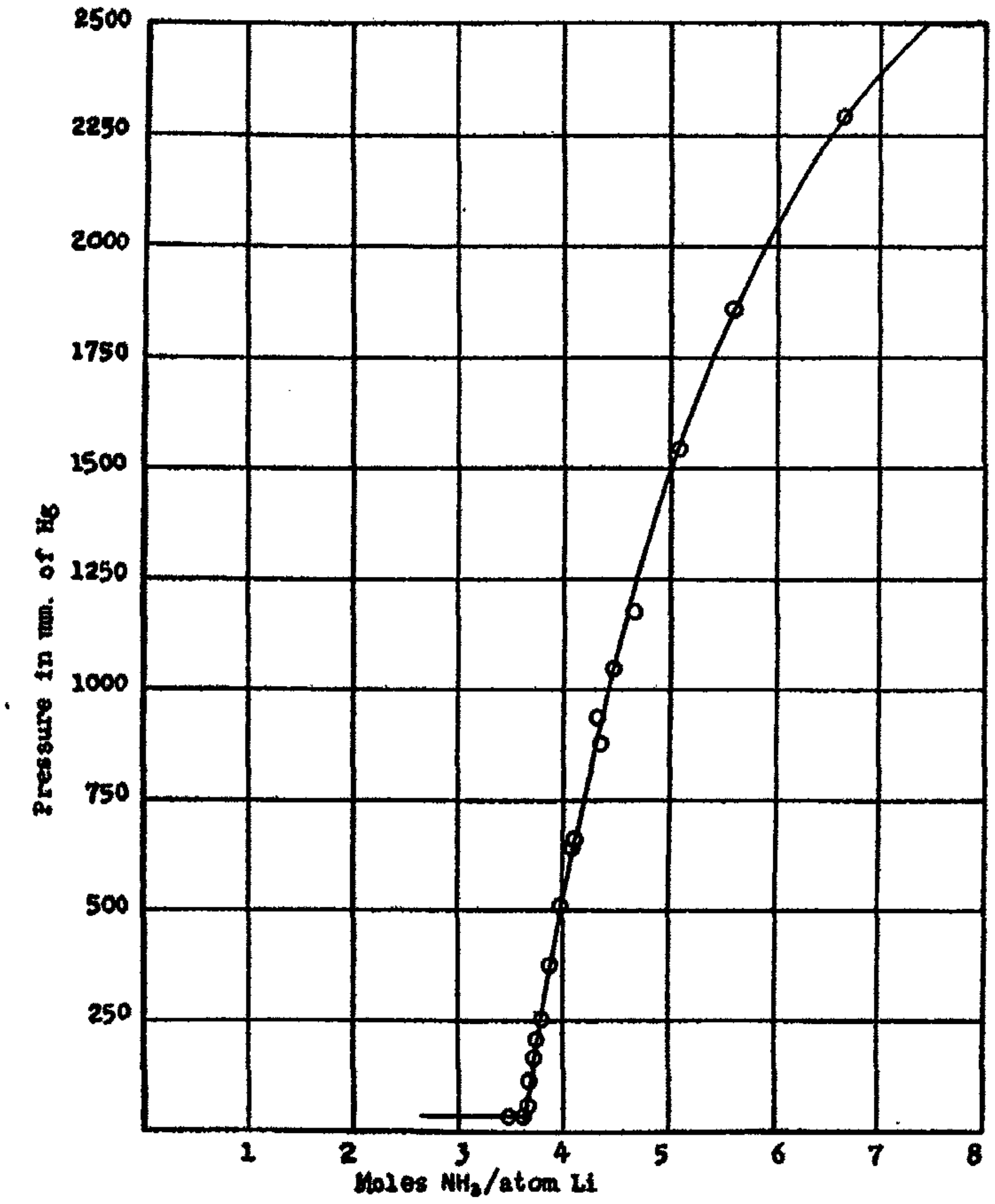


FIG. 1. THE VAPOR PRESSURE OF LITHIUM SOLUTIONS AT 0°C.

It is quite probable that a new liquid phase does appear at lower lithium concentrations as is the case with sodium solutions (4).

It is also evident that the solubility of metallic lithium in liquid ammonia increases appreciably with increasing temperature. This increase amounts to approximately 6 per cent from −63.5°C. to 0°C. The vapor pressure

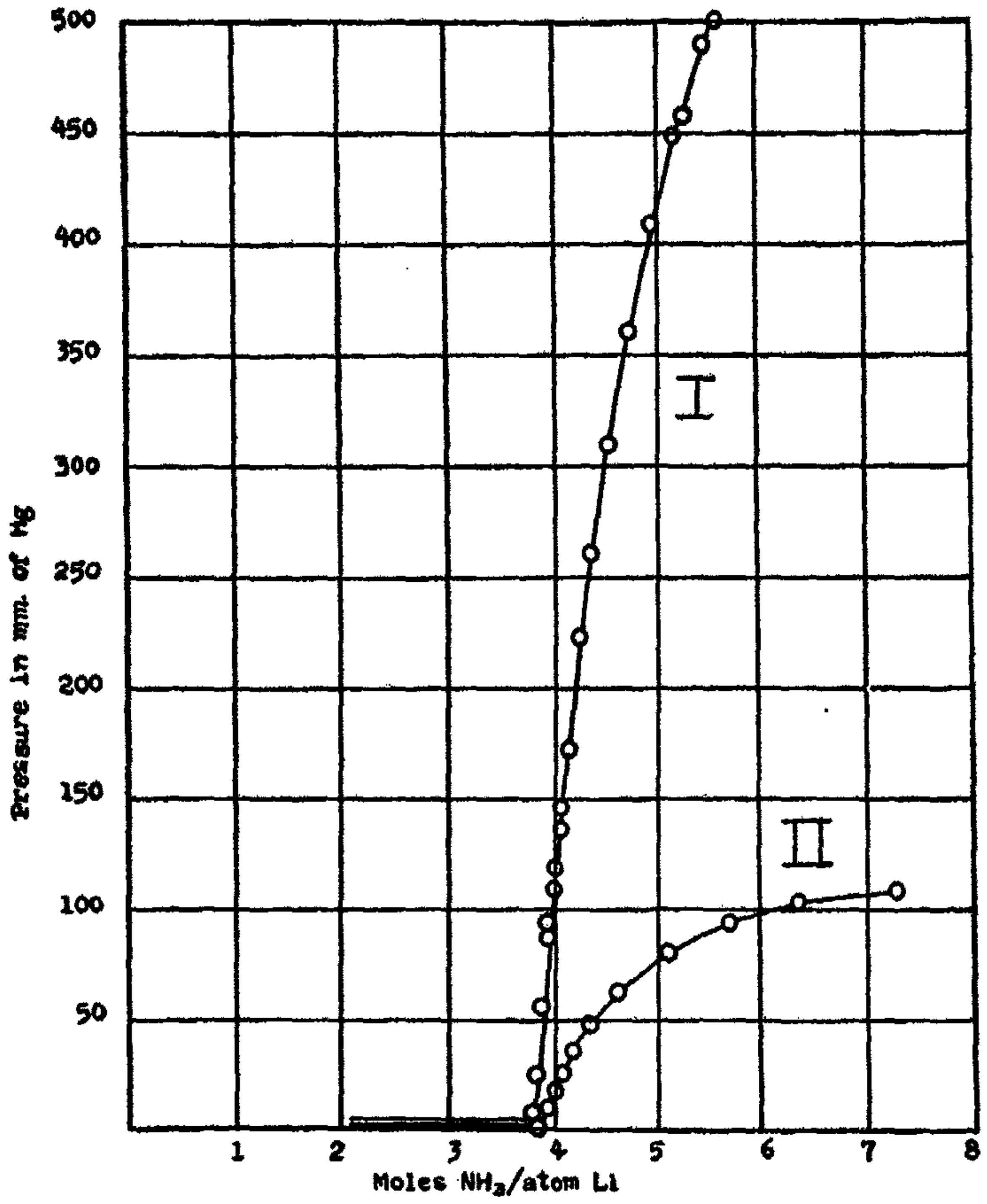


FIG. 2. THE VAPOR PRESSURE OF LITHIUM SOLUTIONS AT −33°C. (I), AND AT −63.5°C. (II)

TABLE 2

Vapor pressure and composition of saturated solutions

TEMPERATURE	VAPOR PRESSURE	MOLES NH_3/Li	GRAMS Li PER 100 GRAMS NH_3
°C.	*mm.*		
0°	34.0	3.60	11.319
−32.7°	3.4	3.74	10.895
−33.2°	3.4	3.75	10.866
−63.5°	1.1	3.81	10.698

of the saturated solution increases markedly throughout this same temperature range. The value obtained at 0°C., 34 mm., agrees well with that found by Kraus (2c), namely 33 mm. Kraus and Johnson (2f) found the composition of the saturated solution at −39.4°C. to be 3.61 gram-molecules of ammonia per gram-atom of lithium; our value at a slightly higher temperature is 3.74. This difference of approximately 3 per cent may be ascribed to the presence of foreign elements, particularly iron, sodium, and potassium, in the various samples of metallic lithium used in the two investigations. In the present work, samples of lithium were taken from the same source; each sample failed to show the presence of iron and potassium but appreciable quantities of sodium were found. However, the maximum amount of sodium that could be present with the lithium, according to the results of the analytical determinations, would not seriously change the composition of the saturated solutions in our experiments, certainly not more than 1 per cent. Experiments are now being undertaken to make direct solubility measurements of the alkali metals in liquid ammonia which promise to yield results of a higher accuracy than is allowed by the indirect vapor pressure method.

SUMMARY

The vapor pressure of solutions of lithium in liquid ammonia has been determined at high lithium concentrations and at several temperatures. An extrapolation method is used to obtain the composition of the saturated solution at each temperature. The results show the solubility of metallic lithium to increase appreciably from −63.5° to 0°C.

REFERENCES

(1) Seely: Chem. News **23**, 169 (1871).
(2) (a) Ruff and Geisel: Ber. **39**, 828 (1906).
  (b) Ruff and Zedner: Ber. **41**, 1948 (1908).
  (c) Kraus: J. Am. Chem. Soc. **30**, 653 (1908).
  (d) Kraus: J. Am. Chem. Soc. **43**, 749 (1921).
  (e) Benoit: Bull. soc. chim. **33**, 908 (1923).
  (f) Kraus and Johnson: J. Am. Chem. Soc. **47**, 725 (1925).
(3) Johnson and Meyer: Chem. Rev. **8**, 273 (1931) for data and references.
(4) Kraus and Lucasse: J. Am. Chem. Soc. **44**, 1949 (1922).

THE SYSTEM AMMONIA-WATER AT TEMPERATURES UP TO 150°C. AND AT PRESSURES UP TO TWENTY ATMOSPHERES

I. L. CLIFFORD AND E. HUNTER

Research Laboratory of I. C. I. (Alkali) Ltd., Winnington, Northwich, Cheshire, England

Received October 18, 1932

INTRODUCTION

The total vapor pressures of ammonia–water solutions at temperatures between 0°C. and 120°C. and at pressures up to 9 atmospheres have been measured by Mollier (1) who, however, determined no vapor compositions. Smits and Postma (2) examined the system in the region of the eutectic points and three-phase lines. They determined the pressures, temperatures, and compositions of certain solutions, including those existing in equilibrium with the various solid phases. Perman (3) has determined both total vapor pressures and vapor compositions between 0°C. and 60°C. at pressures below atmospheric.

Perman's method consists of passing a known volume of air through the ammonia solution, and determining the weights of ammonia and water the air takes up. The partial vapor pressures of ammonia and of water can then be calculated from these weights, and the total pressure of the air–ammonia–water vapor phase.

The work now reported was carried out in order to extend the knowledge of this system up to 150°C. and 20 atmospheres pressure. A dynamic method was used to determine vapor compositions between 60°C. and 100°C. and for pressures up to 1.5 atmospheres. The method was inconvenient for higher pressures.

The total vapor pressures in the system up to 9 atmospheres were already known (4).

For the higher range of temperatures and pressures it was found necessary to use a static method. Both total vapor pressures and vapor compositions were measured.

EXPERIMENTAL

1. From 60°C. to 100°C.; pressures up to 1.5 atmospheres

At temperatures as high as 60°C., Perman had difficulty in getting the air he passed through his saturators containing the ammonia solutions to take up its proper amount of ammonia and water. As saturators he used vessels of the wash-bottle type, and his difficulties were most probably due to the inefficiency of these when called upon to saturate air with the large quantities of ammonia and water provided by the high partial pressures at 60°C.

A very efficient saturator designed by Bichowsky and Storch (5) has been adapted for vapor pressure work by Pierce and Snow (6). Its design is shown in figure 1a.

The solution is held in the tube A. Air enters at B and breaks into bubbles at the jet C. These bubbles travel up the inclined tube D, becoming saturated with vapor from the solution. At the surface of the solution they break and the vapor travels back to the outlet at E. Behind and below the jet C, a vent F is blown in the tube D. Here solution is drawn in and carried up the tube D between the bubbles. This ensures thorough mixing of the solution. The neck G, provided for filling purposes, is closed by a rubber stopper which can be wired on. A sample of the solution can be withdrawn by way of the capillary tube H.

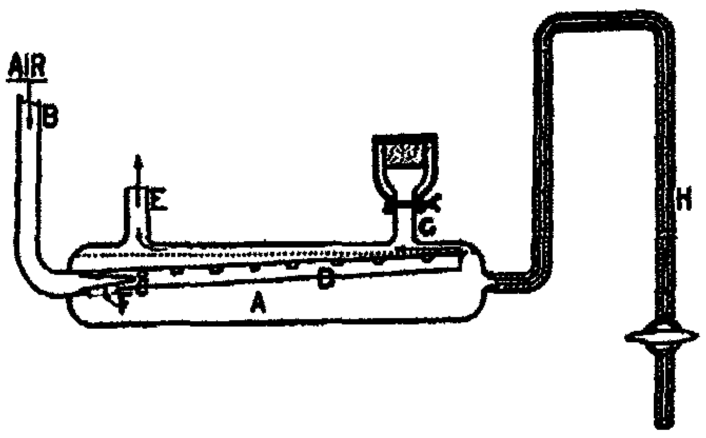


Fig. 1a

Four vessels of this pattern, each 10 in. x 1½ in., made of Pyrex glass, were joined together in series in the way shown in figure 1b. It was not considered necessary to provide the two inner vessels with sampling tubes. The inlet and outlet tubes A and B were vertical. The whole apparatus was mounted in a frame which could be held in a thermostat capable of regulation to ±0.01°C. The water level in the thermostat was maintained well above the stopper C. To prevent condensation from the gas on the walls of the tube B a heating coil D formed on a brass tube surrounding B was used. The tube was heated to 120–140°C.

The air supply was kept at a suitable pressure, indicated by the manometer E, by adjusting the screw clip F on a tube opening to the atmosphere. The clip G regulated the supply to the apparatus. Rubber pressure tubing was used, wired on at all connections.

The method of using the apparatus depended upon whether the solution in the saturators had a total vapor pressure below or above approximately 650 mm. at the working temperature. With the former type of solution it is possible to pass through a sufficient amount of air without taking the pressure above atmospheric; this method will be described first.

The saturators were filled to the correct level (the top of the inclined tubes) with an ammonia solution of known composition. After wiring on the stoppers the apparatus was placed in the thermostat and the heating coil was fitted over the outlet tube B. The pressure tubing from the air supply already described was wired on to the tube A with the clip G closed. A length of about 6 inches of Pyrex tubing (3-mm. bore) was sealed to the top of the tube B, and bent over at right angles, as shown at J in figure 2. The current to the heating coil and thermostat was then switched on, and the latter was brought to the working temperature and there regulated.

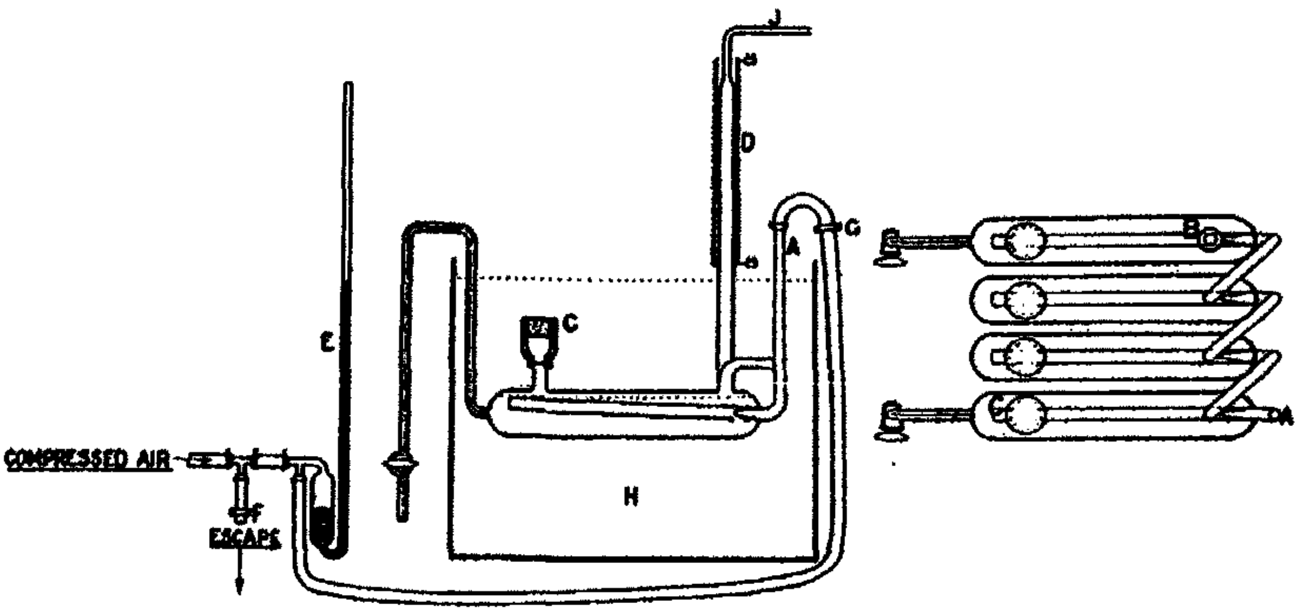


Fig. 1b

The absorption train consisted of two U-tubes, the first containing glass beads covered with 25 per cent sulfuric acid, the second, glass beads with concentrated sulfuric acid. A third tube filled with glass wool–phosphorus pentoxide absorbent was eventually discarded, for its weight never increased by more than one-fifth of a milligram during a run.

The absorption train, after preparation and weighing, was fitted to the tube J with pressure tubing.

The clip G was carefully adjusted to allow a slow, steady stream of bubbles to form and to pass through the apparatus and absorption system. During the run the tube J was gently warmed with a Bunsen flame to prevent condensation before the vapor reached the U-tubes. After a run, the clip G was closed and the absorption train was disconnected and weighed. The contents of the U-tubes were washed out, and the ammonia present was determined by distillation. The increase in weight of the U-tubes was normally between 0.5 and 1.0 gram.

Finally a sample of the solution in the saturators was removed for analysis. A change in composition of one part per hundred of the NH_3 percentage was sometimes observed in the first saturator, where the air was admitted; in the last saturator the composition of the solution was always within 0.2 part per hundred of the original NH_3 percentage. The composition of the solution in the last saturator was taken as that of the solution in equilibrium with the vapor collected.

For solutions of the second type, those with total pressures between 650 mm. and 1100 mm. at the working temperature, it was necessary to devise some way of keeping the pressure in the saturators and absorption train at least 100 mm. above the total vapor pressure of the solution, in order to provide sufficient air to take up the ammonia and water. The apparatus shown in figure 2 was used. The U-tube A was made of Pyrex tubing (3-mm. bore) widening to 11-mm. bore tubing at the U. To the base of the U, a third tube, B, was sealed and bent upwards. This was connected to the 50-cc. pipette bulb C, fitted to pressure tubing provided with the screw clip D. The apparatus was held in an oven, E, fitted with mica windows. The oven was heated to keep the vapor passing through the U above its dew point. The side arm F was connected to the absorption system, the far end of which was connected to the tube H, dipping into a column of mercury, and to the tap K. The U-tube A was filled with mercury to the level L.

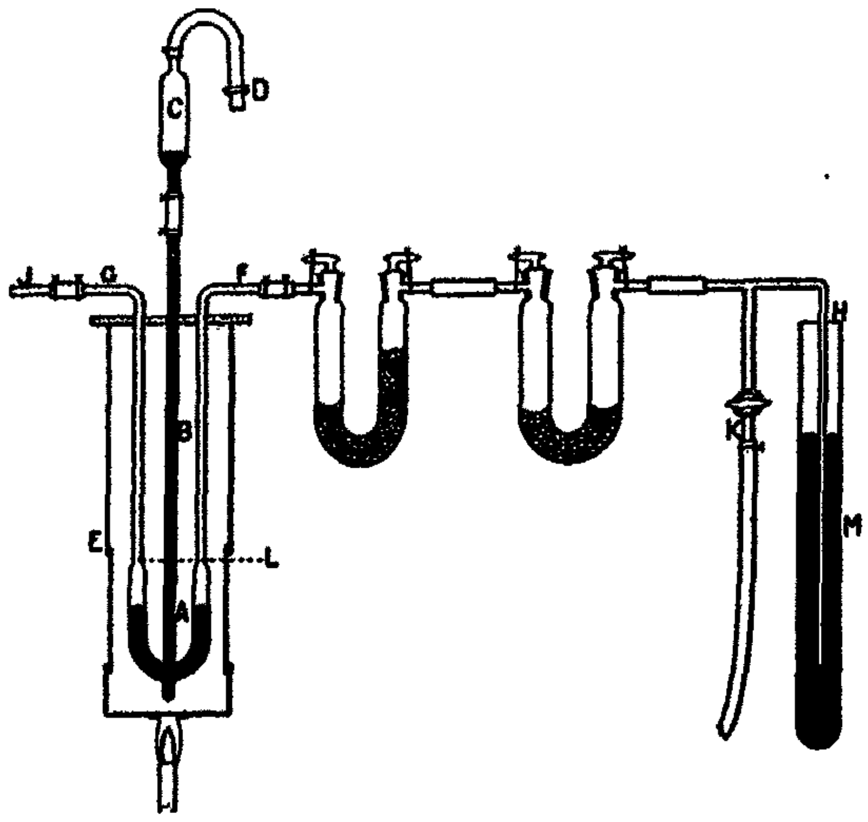


Fig. 2

In preparation for a run, the apparatus was assembled in the way shown in figure 3. The taps of the absorption tubes and all rubber connections were wired on, and the warming up of the oven E was begun. The saturators were prepared as before, but when the temperature of the thermostat had risen to a point where the total vapor pressure of the complex in the saturators had reached approximately 650 mm., the tube J (from the saturators) was connected to the limb G of the U-tube with pressure tubing which was wired on. Subsequently, as the temperature of the thermostat rose towards the working temperature, the pressure of air, ammonia vapor, and water vapor in the saturators rose steadily. This increase of pressure was balanced by applying a pressure of air through the tap K at intervals, and watching the level of mercury in the limbs of A. After the thermostat had reached the working temperature and had been regulated, the mercury in A was drawn up into the bulb C, until there was a free passage for the vapor from one limb of A to the other, and the clip D was closed. Air was then admitted to the saturators and the run proceeded. The air finally escaped through H, bubbling up the tube M. Again, it was necessary to keep the upper tubes J, G, and F gently warmed. The run was brought to an end by shutting off the air supply to the saturators and releasing the mercury in the bulb C, which closed the passage between G and F. The length of the limb F was usually sufficient to take

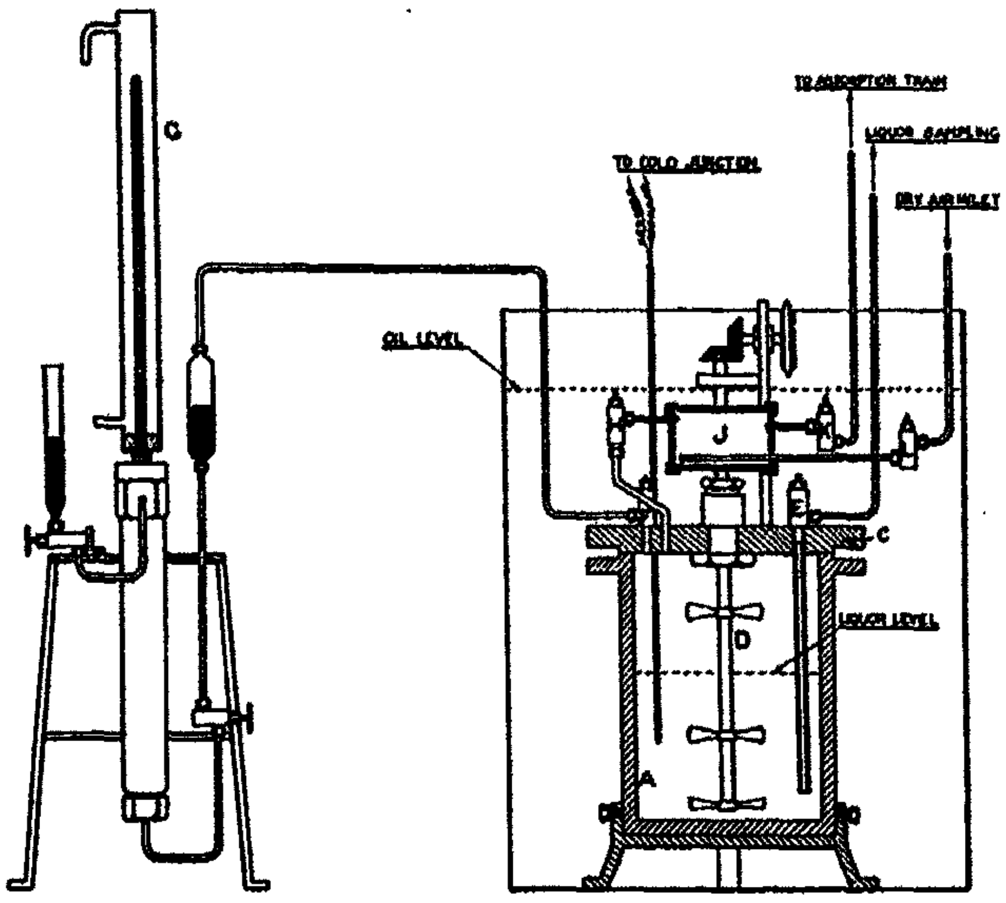


Fig. 3

the column of mercury which rose (owing to the pressure difference) when the absorption train was disconnected for weighing. At the highest pressures it was occasionally necessary to allow the thermostat to cool for some time before detaching the absorption tubes.

Results

The results which were obtained are given in table 1. The total vapor pressures were obtained by interpolation of the values given in the International Critical Tables, Vol. VIII, p. 362. The figures for the ammonia content of the vapors are probably accurate to 1.5 units for vapors of composition 30–70 per cent of ammonia. Beyond these limits these determinations are believed to be more accurate.

2. From 100°C. to 150°C.; pressures up to 20 atmospheres

The apparatus which was used had been designed for the determination of the equilibrium relations of pressure, temperature, and compositions of solutions and vapors in uncondensed systems, at temperatures above 100°C. and pressures below 20 atmospheres. A 4-liter bomb is used to hold the complex, the vapor volume being about two liters. There are arrangements for stirring, for measuring the temperature and pressure, and for withdrawing for analysis samples of solution and vapor.

The apparatus is shown diagrammatically in figure 3. The bomb A, of stainless iron, is closed by bolting down the cover, C, over a copper washer. In the centre of this cover is a pressure gland through which the stirrer D passes. The gland is packed with S. E. A. rings, and the stirrer rotates at 60 r.p.m. and has paddles in the liquor and vapor. Screwed on to the cover are two valves, E and F. Valve E has attached a tube which dips into the bomb to within an inch and a half of the bottom. The opening of F is flush with the lower side of the cover, and this valve connects the apparatus to the closed hydrogen manometer G, which is capable of measuring pressures up to 20 atmospheres. A connection from the cover of A to the valve H leads to a smaller bomb J (300 cc.) which is held on to the cover by a bracket. This smaller bomb is fitted with two valves K and L, K for withdrawing the vapor sample to an adsorption train, and L for the inlet of dry air to the farther end of J for sweeping out the contents. A copper–constantan thermocouple in a sheath is also fitted through the cover of A, a lens-ring joint being used. To avoid the use of compensating leads, the thermocouple wires run directly to a cold junction and potentiometer. The apparatus is held in position by fixing the bomb A in a tripod in the base of an oil thermostat, the oil level being above the top of the smaller bomb J.

The thermocouple was calibrated at 10°C. intervals up to 200°C., and can be read accurately to within 0.1°C. The closed manometer is filled with pure dry hydrogen, and the column of gas is water-jacketed. The volume of the capillary had been determined for each 2 cm. of its 70 cm. length. In order to calculate the pressure of the hydrogen from the height of mercury in the capillary, it was necessary to know the quantity of hydrogen enclosed in the capillary. This was found by calibration

TABLE 1

PRESSURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
$T = 60.0$°C.		
atmospheres	*per cent*	*per cent*
0.240	0.96	17.2
0.286	1.97	28.8
0.355	3.40	40.8 39.1
0.366	3.66	43.1
0.416	4.69	55.2 55.3
0.430	4.94	55.6
0.487	6.04	60.2
0.584	7.90	69.6
0.630	8.66	72.3
0.842	11.99	79.3 79.2
1.104	15.38	84.2
1.451	18.91	90.0
$T = 80.0$°C.		
0.546	0.96	14.3
0.634	1.97	28.2
0.761	3.40	38.1
0.786	3.66	41.1
1.030	6.04	53.1
1.224	7.90	63.1
1.705	11.9	73.6 73.4
$T = 90.0$°C.		
0.742	0.50	6.90
0.797	0.96	13.12
0.855	1.47	19.2
0.916	1.97	23.4
0.957	2.26	29.4
1.124	3.7	38.7
1.364	5.54	49.8
$T = 100.0$°C.		
1.064	0.50	6.14
1.205	1.47	18.0
1.433	2.98	31.6

against an open mercury column manometer at 2 atmospheres pressure. In addition, the higher pressure readings of the manometer (5 to 20 atmospheres) were checked against a calibrated Bourdon gauge. A cathetometer was used to read the position of the mercury in the capillary and to measure the difference in level of the mercury in the capillary and in the reservoir. The pressure due to this head of mercury must be added to the calculated hydrogen pressure to give the pressure applied to the manometer. By closing a valve which lies between the reservoir and the body of the manometer, the gas space above the mercury in the reservoir could be evacuated without removing hydrogen from the capillary.

To put a complex in the bomb the apparatus was evacuated while standing at room temperature and the valve H closed. Two liters of complex was then drawn into the bomb A through the liquor sampling tube, care being taken not to introduce air with the complex. The thermostat was heated to the working temperature and regulated, and the contents of the bomb were stirred at this steady temperature overnight. This was found to be a sufficient length of time to establish equilibrium. The manometer and thermocouple readings were taken. After evacuating the vapor sampling bomb J, the valve H was quickly opened and closed, isolating in J a sample of the vapor. The sample was drawn out by way of the valve K, through a sulfuric acid absorption train for analysis. When the pressure had been reduced to that of the service vacuum, air drawn through concentrated sulfuric acid was admitted through the valve L, and was swept through the bomb and train to remove the last traces of water and ammonia from J. Samples of solution were taken by opening the valve E and absorbing a few grams of the complex in a known weight of sulfuric acid in a system of traps which excluded the possibility of any loss of sample or acid.

Usually a given complex was examined at a whole series of temperatures between 100°C. and 150°C. New complexes were obtained either by emptying and re-filling the bomb, or by boiling off vapor from the previous complex. After some of the results had been obtained, it was found that the temperature of the complex in the bomb measured by the thermocouple, was always 3°C. below that of the outside bath, owing to heat losses through the connections from the bomb. This temperature difference was confirmed by experiments on the vapor pressure of water measured at a number of temperatures in this apparatus. In order to make use of these first results the work was continued at 97°C., 107°C., 117°C., 127°C., 137°C. and 147°C.

Results

The experimental results are given in table 2. The error in the compositions in most of these, is about one part per hundred of the ammonia

TABLE 2

Isotherms of the system, ammonia–water

PRESSURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	T = 97°C.	
atmospheres	*per cent*	*per cent*
0.899	0	0
2.4	9.3	63.3
3.8	16.0	78.3 76.0
6.76	25.5	89.76 89.58
7.04	25.9	89.6
	T = 107°C.	
1.277	0	0
3.27	10.0	61.0 60.0
5.12	16.0	75.3
8.55	25.0	86.4
	T = 117°C.	
1.780	0	0
3.35	6.5	—
4.35	9.5	61.5
5.8	14.7	73.2
10.63	—	83.1
	T = 127°C.	
2.435	0	0
4.37	6.43	45.3 43.7
5.62	9.5	59.0
7.31	—	68.5
12.44	—	79.1
13.6	25.0	82.5 82.8
	T = 137°C.	
3.274	0	0
5.7	6.5	42.0
9.06	—	66.2 65.9
14.90	—	78.5
—	25.0	80.2
	T = 147°C.	
4.332	0	0
7.3	6.5	40.2 40.6
9.3	9.5	50.2
11.84	13.6	62.4 62.0
16.3	19.5	75.0

percentage. In some cases, particularly at the highest temperatures, the error in the vapor compositions is two parts per hundred. The error in the total vapor pressure determinations is less than two per cent.

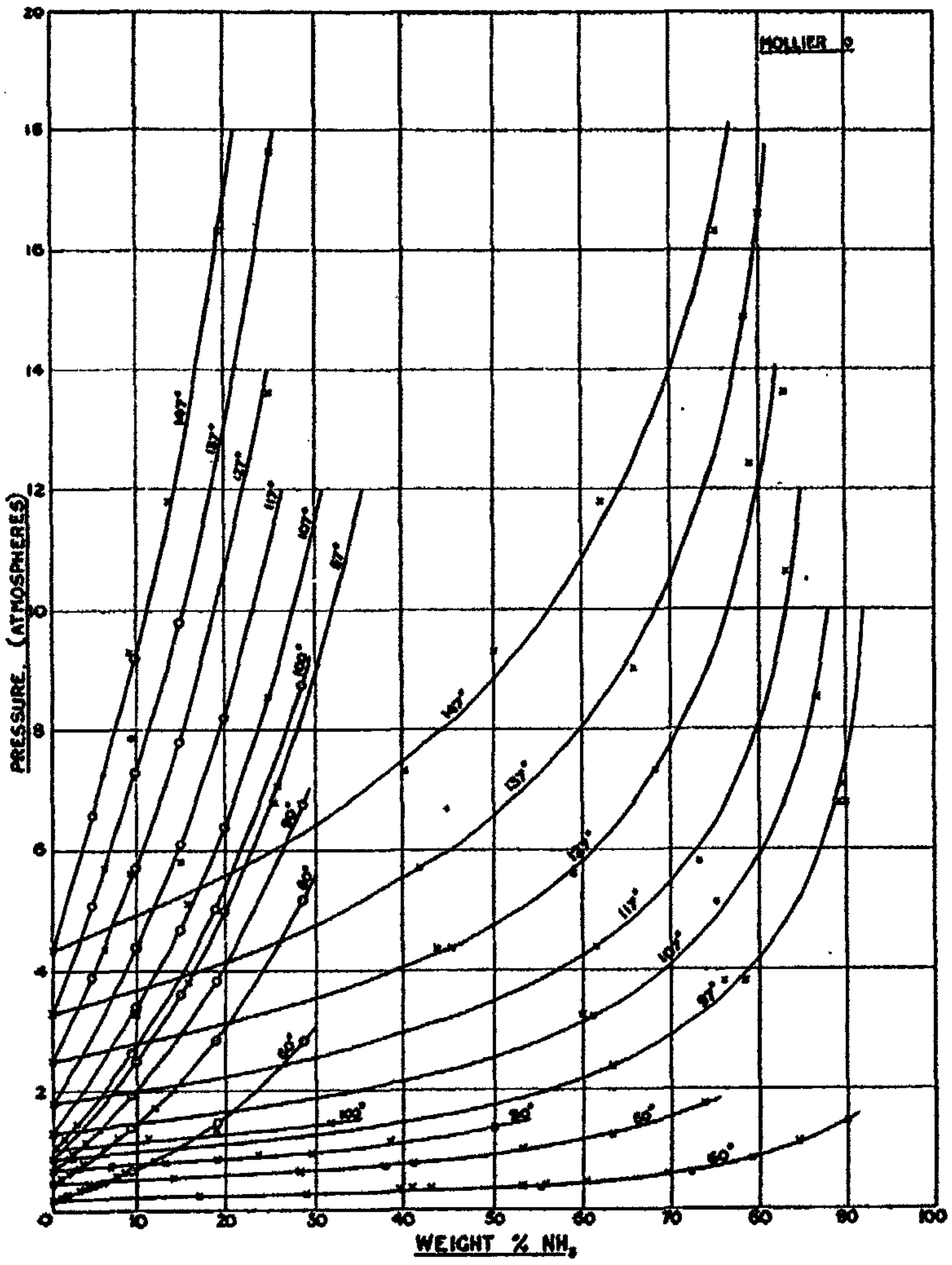


Fig. 4

THE ISOTHERMS AND ISOBARS IN THE SYSTEM

The experimental results are plotted as isotherms in figure 4. Data from tables of total vapor pressures given by Mollier (1) obtained by

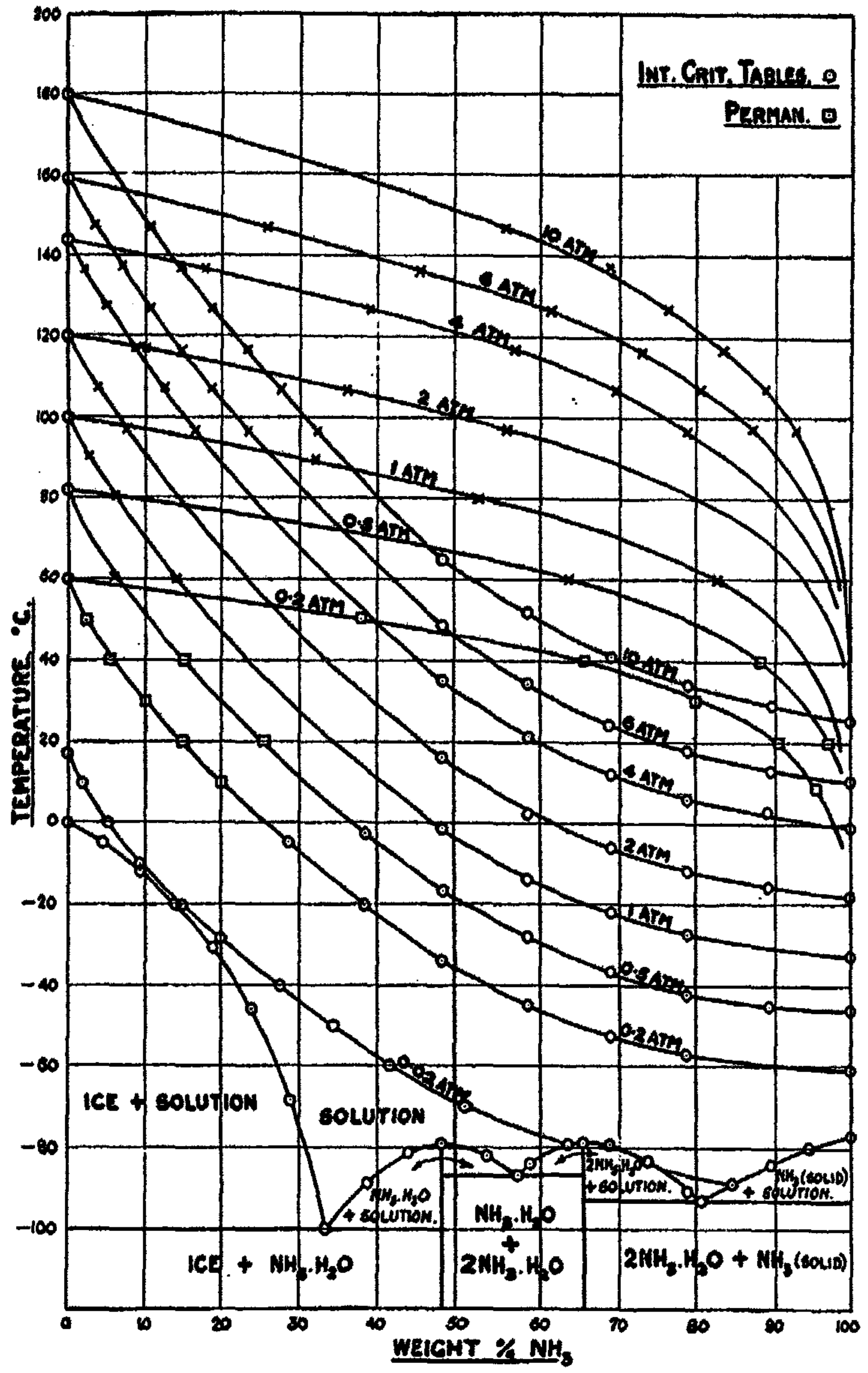

INT. CRIT. TABLES. ○
PERMAN. □
TEMPERATURE °C.
200
180
160
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
10 ATM
6 ATM
4 ATM
2 ATM
1 ATM
0·5 ATM
0·2 ATM
10 ATM
6 ATM
4 ATM
2 ATM
1 ATM
0·5 ATM
0·2 ATM
0·2 ATM
ICE + SOLUTION
SOLUTION
$NH_3.H_2O$ + SOLUTION.
$NH_3.H_2O$ + $2NH_3.H_2O$
$2NH_3.H_2O$ + SOLUTION.
NH_3 (SOLID) + SOLUTION.
ICE + $NH_3.H_2O$
$2NH_3.H_2O$ + NH_3 (SOLID)
0
10
20
30
40
50
60
70
80
90
100
WEIGHT % NH_3

FIG. 5

TABLE 3

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	Pressure = 10 atmospheres	
degrees C.	*per cent*	*per cent*
180.5	0	0
170	3.4	20.5
160	6.6	36.3
150	10.1	51.5
140	14.0	64.8
130	18.0	74.2
120	22.0	81.1
110	26.3	87.0
100	30.8	91.7
90	35.6	95.1
80	40.6	97.4
70	46.0	98.8
60	52.2	
50	60.0	
40	70.2	
30	87.0	
25.3	100	100
	Pressure = 8 atmospheres	
171	0	0
170	0.3	2.3
160	3.1	20.7
150	6.4	38.9
140	10.2	55.5
130	14.1	68.0
120	18.3	77.3
110	22.4	84.0
100	26.7	89.5
90	31.4	93.3
80	36.4	96.2
70	41.9	98.2
60	47.5	
50	54.1	
40	62.0	
30	73.5	
20	94.6	
18.5	100	100
	Pressure = 6 atmospheres	
159.3	0	0
150	2.6	19.5
140	5.9	40.0
130	9.6	57.1
120	13.5	69.9

TABLE 3—*Continued*

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	Pressure = 6 atmospheres—*Concluded*	
degrees C.	*per cent*	*per cent*
110	17.6	78.4
100	22.0	84.8
90	26.6	90.0
80	31.4	94.2
70	36.6	97.0
60	41.9	
50	47.5	
40	54.0	
30	62.0	
20	74.6	
9.7	100	100
	Pressure = 4 atmospheres	
144.1	0	0
140	1.0	9.8
130	4.2	33.0
120	7.7	52.2
110	11.5	66.3
100	15.5	76.0
90	19.8	83.6
80	24.4	90.0
70	29.2	94.8
60	34.2	97.3
50	39.7	
40	45.5	
30	52.2	
20	60.2	
10	71.5	
0	94.7	
−1.5	100	100
	Pressure = 2 atmospheres	
120.6	0	0
120	0.15	1.5
110	2.9	29.0
100	6.2	50.6
90	10.0	67.5
80	14.0	80.3
70	18.5	89.2
60	23.4	94.8
50	28.5	97.5
40	33.7	98.4
30	39.3	

TABLE 3—*Continued*

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
	Pressure = 2 atmospheres—*Concluded*	
degrees C.	*per cent*	*per cent*
20	45.6	
10	52.6	
0	61.4	
−10	75.0	
−18.5	100	100
	Pressure = 1 atmosphere	
100	0	0
90	2.9	31.8
80	6.1	52.6
70	10.0	70.0
60	14.4	82.5
50	19.0	90.2
40	24.0	94.5
30	29.1	97.0
20	34.6	98.5
10	40.6	99.2
0	47.3	
−10	55.3	
−20	65.4	
−30	86.0	
−33.2	100	100
	Pressure = 0.5 atmosphere	
81.7	0	0
80.0	0.3	4.5
60	6.2	63.6
40	15.0	87.5
20	26.0	97.5
0	37.2	
−10	43.1	
−20	51.2	
−30	60.0	
−40	75.3	
−46.3	100	100
	Pressure = 0.2 atmosphere	
60.4	0	0
50	2.7	38.0
40	5.5	65.5
30	10.0	80.0
20	15.0	90.5

TABLE 3—*Concluded*

TEMPERATURE	AMMONIA IN LIQUID	AMMONIA IN VAPOR
Pressure = 0.2 atmosphere—*Concluded*		
degrees C.	*per cent*	*per cent*
10	20.0	95.5
0	25.3	98.0
−10	31.8	99.0
−61.0	100	100
Pressure = 0.02 atmosphere		
17.7	0	—
10	1.7	—
0	5.0	—
−10	9.5	—
−20	15.0	—
−30	21.0	—
−40	27.5	—
−50	34.3	—
−60	41.5	—
−70	51.0	—
−79.8	62.8	—
−82.9	75.5	—

extrapolation of results determined up to 120°C. and 9 atmospheres, are also plotted on this graph and the agreement is good.

Points from these isotherms, and from those of Perman, together with total vapor pressure values given in International Critical Tables (4) have been used to construct the isobars from 0.02 to 10 atmospheres in figure 5.

The vapor branch of the 0.02 atmosphere isobar is unknown. A projection of the liquid and vapor and solid lines, determined by Smits and Postma, on the $t - x$ base is shown on this figure and defines the lower temperature limits of existence of the solution phase.

The course of the vapor branches of the isobars from 2 atmospheres to 10 atmospheres is somewhat uncertain in the temperature range 70° to 90°C., where no vapor compositions have been determined and where there is a rapid change of curvature, but from analogy with the isobars of lower pressures, it is believed that the curves given in figure 5 are substantially accurate to within 1 per cent of the ammonia concentration. There are no points above 147°C. except those for pure water, but there is little doubt of the positions of the isobars since the curvature is so small in this region.

Tables 3 and 4 have been constructed from figure 5. The values above 10 atmospheres in table 4 were obtained by interpolation of the straight

TABLE 4

AMMONIA IN LIQUOR	PRESSURE	AMMONIA IN VAPOR
T = 60°C.		
per cent	*atmospheres*	*per cent*
0	0.197	0
5	0.439	56.4
10	0.717	75.8
15	1.084	84.1
20	1.559	91.3
T = 80°C.		
0	0.467	0
5	0.90	47.8
10	1.48	69.9
15	2.19	81.2
20	3.05	87.0
25	4.14	90.8
30	5.55	93.3
T = 90°C.		
0	0.692	0
5	1.30	48.5
10	2.00	67.5
15	2.91	77.1
20	4.12	84.5
25	5.55	89.1
30	7.12	92.4
T = 100°C.		
0	1	0
5	1.82	45.6
10	2.75	64.5
15	3.88	75.3
20	5.31	82.8
25	7.18	87.9
30	9.48	91.3
T = 110°C.		
0	1.414	0
5	2.41	41.8
10	3.58	61.5
15	5.03	73.7
20	6.91	81.4
25	9.20	86.2
30	11.98	89.0

TABLE 4—*Concluded*

AMMONIA IN LIQUOR	PRESSURE	AMMONIA IN VAPOR
	T = 120°C.	
per cent	*atmospheres*	*per cent*
0	1.96	0
5	3.22	39.3
10	4.70	60.0
15	6.55	72.7
20	8.83	79.2
25	11.72	83.2
30	15.46	—
	T = 130°C.	
0	2.67	0
5	4.27	37.7
10	6.15	58.2
15	8.42	69.6
20	11.33	76.8
25	15.04	82.0
30	19.8	—
	T = 140°C.	
0	3.57	0
5	5.55	34.7
10	7.83	53.8
15	10.70	67.2
20	14.37	75.7
25	19.20	—
30	—	—
	T = 150°C.	
0	4.70	0
5	7.14	31.3
10	10.02	31.5
15	13.58	66.4
20	18.6	75.5
25	—	—
30	—	—

lines obtained when log P is plotted against the reciprocal of the absolute temperature.

SUMMARY

1. The compositions of the vapors in equilibrium with ammonia-water solutions have been determined at 60°C., 80°C., 90°C., and 100°C. for solutions with total vapor pressures up to 1.5 atmospheres.

2. The total vapor pressures and compositions of vapors in equilibrium with ammonia–water solutions have been determined within the limits 100–150°C. and 1 to 20 atmospheres.

3. The isotherms in the system have been constructed for temperature intervals between 60°C. and 150°C.

4. From the results of the work reported and those of Perman, Mollier, and Smits and Postma (3, 1, 2), the isobars for 10, 8, 6, 4, 2, 1, 0.5, 0.2 and 0.02 atmospheres have been obtained.

The authors wish to express their thanks to the Directors of Imperial Chemical Industries Ltd., for their permission to publish this work, which was carried out in the Research Laboratory of their subsidiary company, I. C. I. (Alkali) Ltd.

REFERENCES

(1) Mollier: Z. Ver. deut. Ing. **52**, 2, 1315 (1908).
(2) Smits and Postma: Proc. Acad. Sci. Amsterdam **17** (1), 182 (1914).
(3) Perman: J. Chem. Soc. **83**, 1168 (1903).
(4) International Critical Tables, Vol. III, pp. 362, 234.
(5) Bichowsky and Storch: J. Am. Chem. Soc. **37**, 2696 (1915).
(6) Pierce and Snow: J. Phys. Chem. **31**, 231 (1927).

THE ELECTRICAL CONDUCTIVITY OF COMMERCIAL DIELECTRICS AND ITS VARIATION WITH TEMPERATURE[1]

J. D. CLARK AND JOHN WARREN WILLIAMS

Laboratory of Colloid Chemistry, University of Wisconsin, Madison, Wisconsin

Received October 18, 1932

THEORY

It has long been known that the electrical resistance of a material to which the term "dielectric" is applied is a function of the temperature, decreasing as the temperature increases. Thus, in 1889 Curie (1) found that the specific volume resistance of quartz in the direction of the optical axis fell from 1.2 × 10^{14} ohm-cm. at 20°C. to 5.6 × 10^{7} ohm-cm. at 300°C., and Campbell (2) in 1913 reported that this quantity decreased from more than 2 × 10^{14} ohm-cm. at 15°C. to 2 × 10^{7} ohm-cm. at 800°C. for the same substance after fusion.

In 1906, Koenigsberger and Reichenheim (3), assuming that the conduction through dielectrics (oxides, sulfides, metals, and metalloids) is largely electronic in nature, developed an equation to express the change of resistance with temperature as follows:

$$R_t = R_0 \ (1 + at + bt^2) \ e^{-qt/273(273 + t)} \tag{1}$$

where R_t is the specific volume resistance at temperature t (in degrees Centigrade), R_0 is the specific volume resistance at zero degrees Centigrade, and q is a constant characteristic of the material. The quantities a and b, also constants, usually become negligible for dielectrics, so that the equation reduces to

$$R_t = R_0 \ e^{-qt/273(273 + t)} \tag{2}$$

This equation may also be expressed in logarithmic form

$$\log R = A + B/T \tag{3}$$

where R is the specific volume resistance, T is the absolute temperature, and A and B are constants. This form of equation, which may also be derived, as will be shown later, by assuming that the conduction process

---

[1] This article is adapted from the thesis of J. D. Clark, submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at the University of Wisconsin.

is an ionic one, was tested by Rasch and Hinrichsen (4) in 1908, by Pirani and Siemens (5) in 1909, by Dietrich (6) in 1910, and by Curtis (7) in 1914. In these investigations the behavior of both crystalline and amorphous dielectrics was studied.

In 1926 Saegusa (8) measured the resistance of quartz, calcite, ambroid, paper, and paraffin at temperatures ranging from 10°C. to 360°C., and developed another formula to express his results. The conductivity was assumed to be electronic in nature. The electrons are thermionic in origin according to this investigator. The formula developed was

$$\bar{\mu} = ATe^{-q/kT}\left(1 - BT^2e^{-q/kT} - CTe^{-q/kT}\right) \tag{4}$$

where $\bar{\mu}$ is the specific volume conductivity, T is the absolute temperature, k is the Boltzmann constant, q is the work of liberation of one electron, and A, B, and C are constants which are made up as follows:

$$A = l\bar{v}\epsilon^2\frac{A'}{4k},\quad B = 2\rho^2A',\quad C = 2\rho\epsilon^2\frac{A'}{k}$$

In these expressions l is the mean free path of an electron, $\bar{v}$ is the mean velocity of an electron, ρ is the effective radius of an atom of the dielectric, ϵ is the electronic charge, and A' is a constant specific for each material.

Joffe (9) has developed the following equation to express the conductivity of a pure crystal as a function of the temperature:

$$\log\bar{\mu} = -a/T + b \tag{5}$$

Here a and b are constants, $\bar{\mu}$ is the specific volume conductivity, and T is the absolute temperature. This equation, having the form of equation 3, was developed using the assumption that the conductivity is the result of an ionic process. It will be shown later that an equation of the same sort may be developed and applied with some success when the dielectric is not a pure crystal.

APPARATUS AND PROCEDURE

The usual method of measuring very high resistances involves the use of a ballistic galvanometer. The use of this instrument is disadvantageous from more than one point of view. The galvanometer must be calibrated and must be kept in calibration. A slight variation in the characteristics of any part of the apparatus, or a slight variation in the technique of operation, serves to introduce errors into any result. These disadvantages are inherent not only in a ballistic galvanometer, but also in a calibrated electrometer when it is substituted for the former, and in any type of instrument which depends upon a scale reading for the results. When it is possible to use it a null method is more desirable.

The Wheatstone bridge is the commonest of all zero reading instruments for this type of work. It is not usually adapted to the measurements of very high resistances, since the ratio of the two resistance arms of the bridge becomes very high near the limit of the range of operation, with a resultant loss in accuracy. However, it has so many advantages in ease of operation, in reliability and in stability with respect to slight variations in the indicating instrument that it was decided to modify it to an extent that would make it suitable for the measurement of very high resistances. In this modification a Compton electrometer was substituted for the usual galvanometer to increase the sensitivity of the arrangement. But the most important change from the usual bridge was the elimination of two variable resistances with the insertion of voltages in their places. A diagram of the apparatus as used is shown in figure 1. Thus by increasing the voltage on what would normally be the high resistance side of the

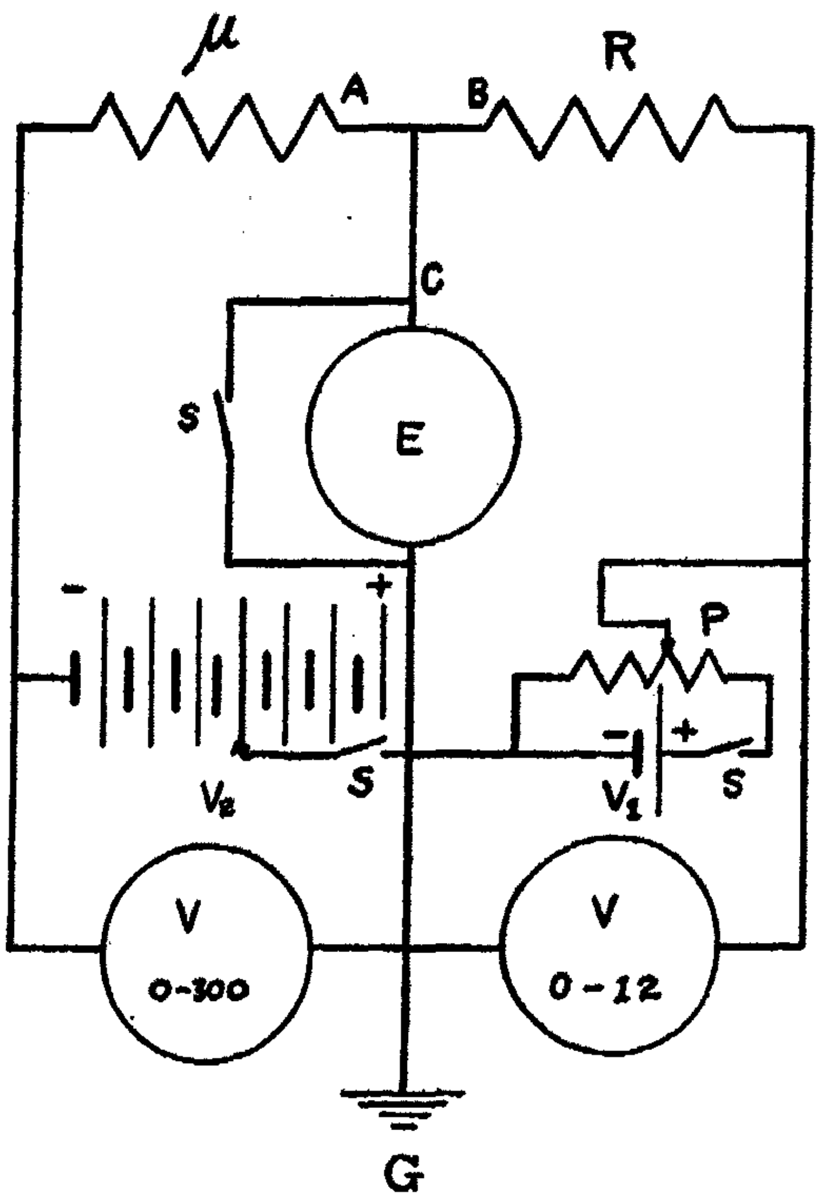


FIG. 1. DIAGRAM OF MEASURING CIRCUIT

μ, unknown resistance; R, standard resistance; P, potentiometer; V, voltmeter; E, electrometer; S, switch; G, ground.

bridge, it was possible to avoid the difficulties which arise when the resistance ratio becomes very high, since voltmeter readings can be made on each side with approximately the same precision. Their ratio, whether large or small, can now be obtained to a considerable degree of accuracy. Since it was necessary to vary these potentials, the voltage on the high resistance side of the bridge was arranged so that it could be controlled with a point switch. A potentiometer which made possible an accurate voltage adjustment was used on the low resistance side of the bridge.

The operation of the bridge may be described as follows: A standard resistance is inserted at R. Then, after the introduction of the unknown resistance, μ, the voltages are varied until there is no swing on the electrometer when the electrometer switch S is opened. The bridge is now balanced, and the resistances stand as follows:

$$\mu/R = V_2/V_1 \quad \text{or} \quad \mu = V_1/RV_2$$

The voltages V_1 and V_2 are those read from the voltmeters, and R is the standard known resistance. Good results may be obtained when the ratio of the voltages, and therefore of the resistances, becomes as high as 1000 to 1. At this ratio there is still sensitivity in the arrangement to permit of an accuracy which will be limited only by the precision with which the two voltages may be read. Calibration of high resistance standards is necessary for the work with dielectric materials. A low resistance standard is inserted at R, with a higher resistance at μ. The resistance of μ is then determined by bringing the bridge to a balance. It may then be used as the standard for the next step. This may be continued until a standard is obtained that has a high enough resistance for the range of measurements that are to be made.

The highest standard used had a resistance of 2440 megohms, which makes possible the measurement of a resistance of approximately 1.6×10^{13} ohms. It would be possible, of course, to go to higher resistances with a higher standard resistance, but at the higher resistances the static effects become appreciable and make measurements more difficult. In such cases the operator of the bridge must remain quiet while making a reading; otherwise the electrometer may swing back and forth, making an accurate balance impossible. The part of the wiring in the neighborhood of the points A, B, and C in figure 1 is that part which is the most sensitive to capacity effects. All metal parts were connected to a special outside ground whenever this was possible. It will also be appreciated that the operation of the bridge becomes difficult when the humidity is high.

The specific volume conductivities of ten substances, including six synthetics and four varieties of wood have been determined as a function of temperature. The synthetics include transparent Bakelite, ordinary black panel Bakelite, Du Pont Pyralin No. 1735, Glyptal resin, and two sorts of the resin known as "Beetleware" (No. 3 and No. 20), while the woods include birch, mahogany, red oak, and Sitka spruce. An attempt was made to measure the conductivity of hard rubber, but the conductivity was too low to be measured with the present apparatus at any temperature to which the rubber could safety be heated. All the synthetics were the usual commercial products, with the exception of the sample of Glyptal. The latter was prepared by us from glycerol and phthalic acid. After the cooking process had been completed the resin was cured in an oven kept at 120°C. for three days and at 150°C. for seven days. The conductivities of the woods were those of the woods in the dry state, as well as it could be attained. Before being used for the conductivity measurements the wood samples, cut as described in the next section, were kept at 105°C. in a dry kiln for several weeks, and during the measurements there was always a dish of anhydrous sulfuric acid in the constant temperature oven in which the samples whose conductivities were being measured were placed. The synthetics were kept in a sulfuric acid desiccator until they were taken out for measurement. The wood was apparently dry, since when the temperature of measurement was carried to 110°C. no break in the conductivity curve appeared.

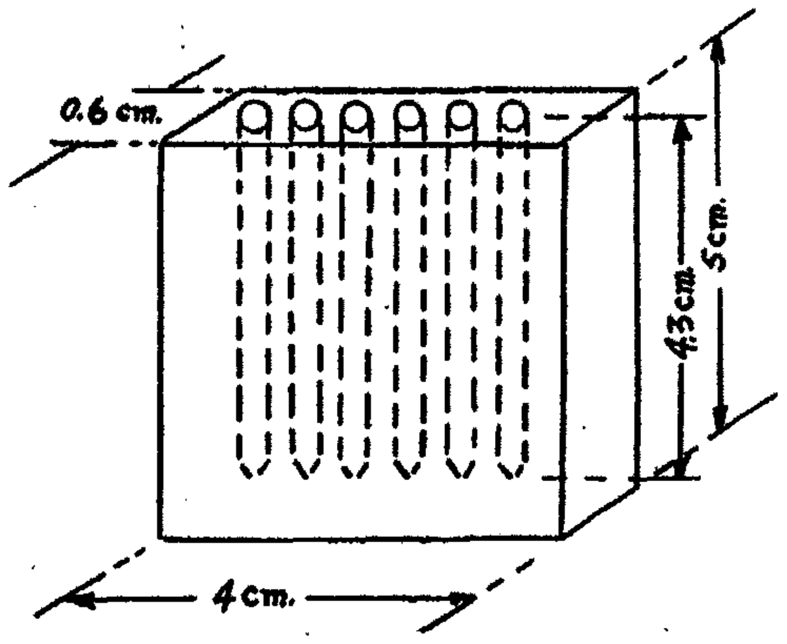


FIG. 2. CELL TYPE A

Electrodes formed by filling ⅛ inch holes, drilled with centers 0.5 cm. apart, with mercury. Alternate pools of mercury connected to form two electrodes.

Two types of conductivity cell were used. The cell of Type A is shown in figure 2. The woods, the panel Bakelite, and the Glyptal samples were cut to the shape of cells of this form. The wood samples were so cut that the conductivity was measured in a tangential direction relative to the direction of the grain. It would be very difficult to calculate the cell constant for such a cell with any degree of accuracy, so that it had to be obtained experimentally using a substance of known resistance. The apparent resistance was determined with the apparatus and the cell constant calculated. A sample of Bakelite AM-250, having a specific volume resistance of 8×10^9 ohms at 20–21°C., was the substance used as standard. All cells of Type A were made to have exactly the same dimensions. The conductivity of an unknown sample in this form was 168 times that of a centimeter cube. This constant probably should not be expressed to more than two significant figures, since the accuracy of the measurements of the conductivity of the Bakelite standard was given as 1 per cent, and since it is difficult to reproduce exactly the dimensions of the standard Bakelite cell in the other dielectrics.

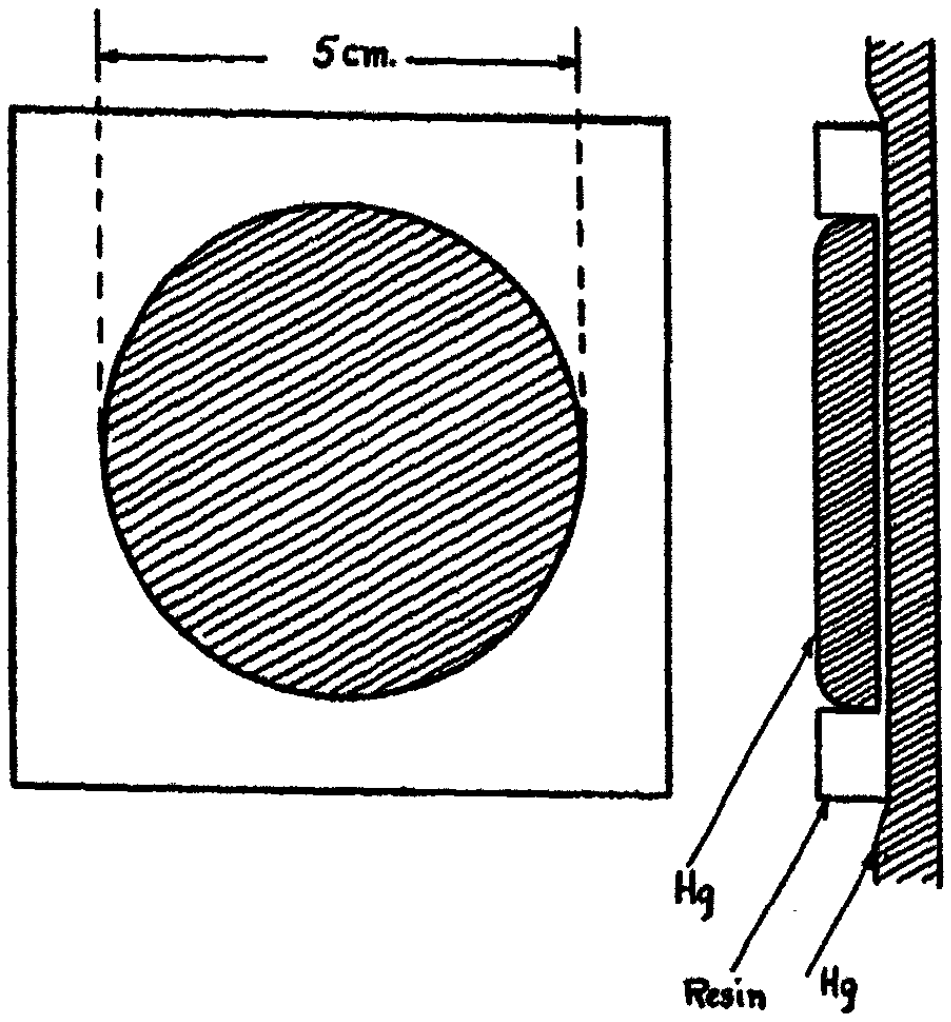


FIG. 3. CELL TYPE B
Uses mercury electrodes as indicated

The type B cell is shown in figure 3. The cell constant in this case was calculated from the diameter of the hole turned in the sample, and from the thickness of the bottom, as measured by a micrometer caliper. It was necessary to assume in this case that the part of the current which did not flow directly through the bottom from the inside mercury pool to the outer mercury was negligible. Measurements were made on the Pyralin, transparent Bakelite, and Beetleware samples using this type of cell.

An attempt was made in all cases to reduce the surface conductance to a minimum. The cells were so designed that this conductance would be as low as conveniently possible. It has already been mentioned that a dish of anhydrous sulfuric acid was always present when measurements were being made. Since the measurements were taken over a considerable range of temperature, and since there were no irregularities in the curves in passing from below 100°C. to higher temperatures, it is believed that the data given relate essentially to volume conductivity. In all cases the potential V_2 was applied to the sample for at least an hour before any measurements were taken, in order to reduce dielectric absorption effects to a small quantity.

During the course of the experimental work it was noted that the results could not be reproduced with any considerable degree of precision. The curves were only partially reversible, since either the composition or structure of the materials appeared to change irreversibly with increasing temperature. Experiments with different samples of one and the same substance did not give absolutely the same conductivity, though the differences were never great. Samples cut from the same section of a given material varied only slightly from one another, probably owing to unavoidable inaccuracies in the reproduction of the dimensions of the test cells.

EXPERIMENTAL RESULTS

As typical of the experimental results, conductivity data for one wood (birch) and one synthetic (Black panel Bakelite) are presented. The columns of the tables indicate, from left to right: the Centigrade temperature, the absolute temperature, values for the quantity $\mu = V_1/RV_2$ (R is the resistance of the standard used to obtain the balance), the numerical value of the conductivity represented by the quantity μ, the specific volume conductivity, its logarithm, and the reciprocal of the absolute temperature. These data are also presented as graphs (figures 4 and 5), in which the logarithm of the specific volume conductivity is plotted against the reciprocal of the absolute temperature. It is evident that the data are well represented by straight lines. This was true in the case of all substances investigated, with the possible exception of the sample of Glyptal resin, in which case the slope of the curve became somewhat less steep as the temperature was increased.

Because of the interest in a comparison of the relative ability of these substances to resist the passage of the electric current at ordinary temperatures, table 3 has been prepared. The specific volume conductivities at 20°C. have been obtained by extrapolation of experimental curves. In the cases of the Glyptal resin and of the woods this extrapolation is somewhat long (over a temperature interval of 50°C.), nevertheless the value as given is believed to represent the proper order of magnitude. There have also been included in this table values for E, a quantity which we shall call

TABLE 1

Birch wood. Conductivity in tangential direction

Cell Type A. Cell constant = 168.
Standard resistance B = 2440 megohms.

T	T	$\frac{V_1}{RV_2}$	μ	$\bar{\mu}$	LOG $\bar{\mu}$	1/T°K.
°C.	°A.					
68	341	$\frac{0.040}{249B}$	6.59×10^{-14}	3.91×10^{-16}	*16*.59	0.00293
74	347	$\frac{0.060}{249B}$	9.88×10^{-14}	5.86×10^{-16}	*16*.77	0.00288
80	353	$\frac{0.095}{249B}$	1.56×10^{-13}	9.28×10^{-16}	*16*.97	0.00283
84	357	$\frac{0.150}{249B}$	2.47×10^{-13}	1.47×10^{-15}	*15*.17	0.00280
87	360	$\frac{0.206}{249B}$	3.39×10^{-13}	2.01×10^{-15}	*15*:30	0.00278
91	364	$\frac{0.290}{249B}$	4.78×10^{-13}	2.83×10^{-15}	*15*.45	0.00275
110	383	$\frac{0.687}{124B}$	2.27×10^{-12}	1.35×10^{-14}	*14*.13	0.00261

TABLE 2

Black panel Bakelite

Cell Type A. Cell constant = 168.
Standard resistances D = 6.55 megohms, A = 43,300 ohms.

T	T	$\frac{V_1}{RV_2}$	μ	$\bar{\mu}$	LOG $\bar{\mu}$	1/T°K.
°C.	°A.					
21	294	$\frac{0.406}{262D}$	2.37×10^{-10}	1.41×10^{-12}	*12*.15	0.00340
26	299	$\frac{0.640}{262D}$	3.74×10^{-10}	2.22×10^{-12}	*12*.33	0.00335
32.5	305.5	$\frac{1.025}{152D}$	1.03×10^{-9}	6.09×10^{-12}	*12*.79	0.00328
35	308	$\frac{1.155}{109D}$	1.56×10^{-9}	9.26×10^{-12}	*12*.97	0.00325
38.5	311.5	$\frac{0.885}{44D}$	3.08×10^{-9}	1.83×10^{-11}	*11*.26	0.00321
46.5	319.5	$\frac{0.113}{262A}$	9.95×10^{-9}	5.91×10^{-11}	*11*.77	0.00313

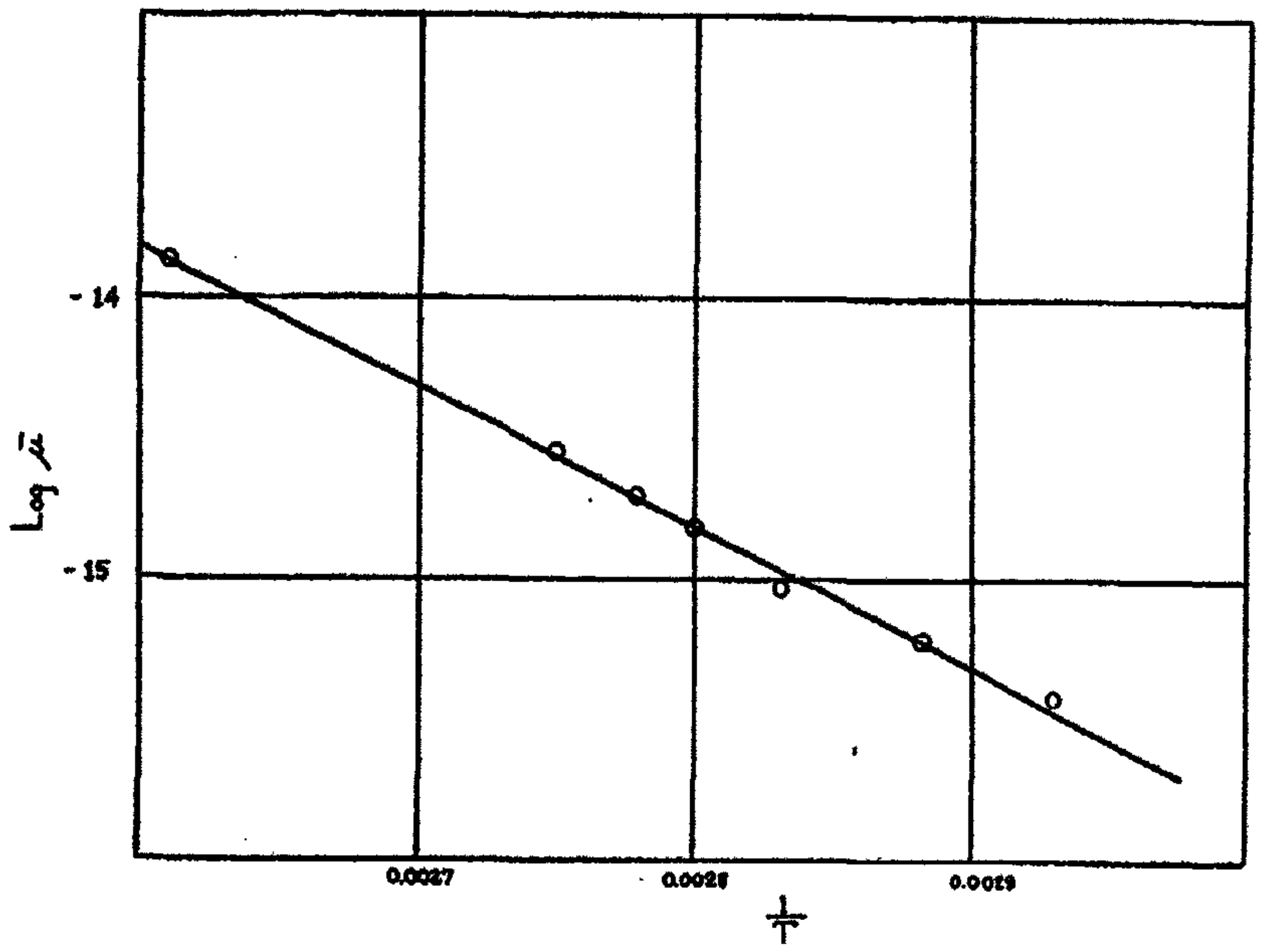


FIG. 4. BIRCH. CONDUCTIVITY IN TANGENTIAL DIRECTION

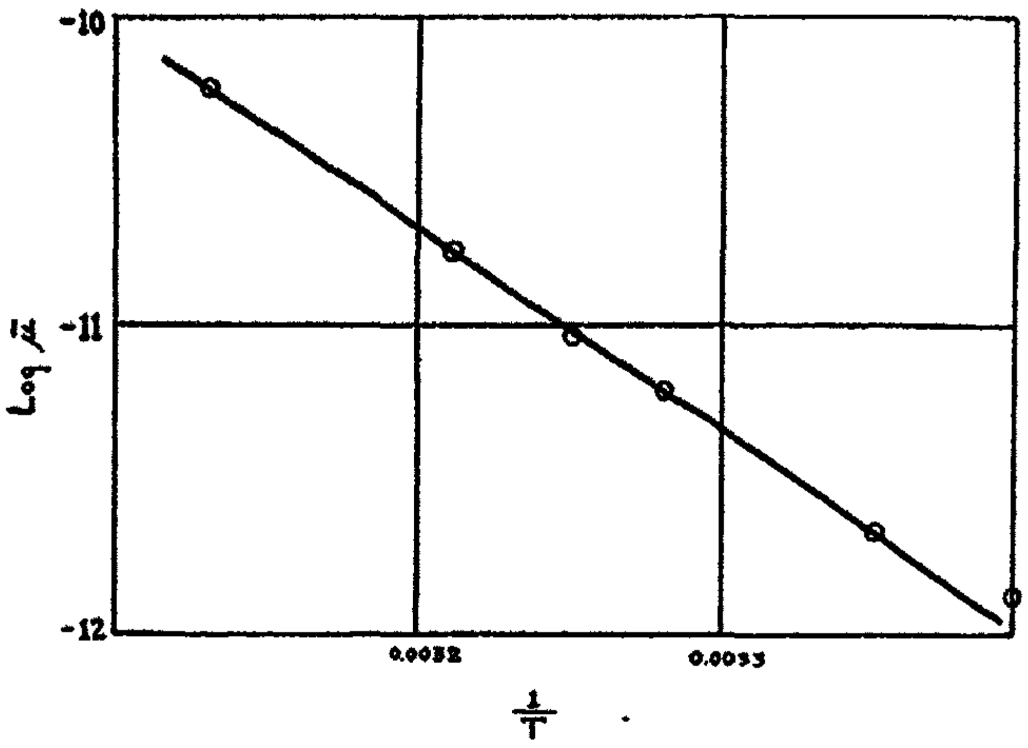


FIG. 5. BLACK PANEL BAKELITE

the energy of liberation of the carrier of the current. The significance of this quantity will be evident from the discussion to follow.

TABLE 3

Values of $\bar{\mu}$ and E for different materials

MATERIAL	$\bar{\mu}$ AT 20°C.	E
		calories
Transparent Bakelite	5.5×10^{-16}	37,500
Panel Bakelite	8.5×10^{-13}	29,700
Beetleware No. 3 (blue)	4.4×10^{-16}	42,500
Beetleware No. 20 (black)	6.0×10^{-13}	27,400
Pyralin	2.6×10^{-13}	29,300
Glyptal	ca. 1×10^{-23}	65,000
Birch	1.2×10^{-18}	22,900
Mahogany	3.7×10^{-19}	30,600
Red oak	3.2×10^{-19}	28,400
Sitka spruce	3.4×10^{-18}	32,000

DISCUSSION

It is believed that these conductivities and their variations with temperature could be explained as the result of an ionic process. The ions that carry the current appear to originate in the inevitable electrolyte impurities in the resins, and in the ionic impurities represented by the ash content of the wood. In the development of a mathematical relationship to express the conductivity as a function of temperature, the ions can be assumed to be distributed between two phases. There will be a certain number of ions adsorbed on the surface of the units of structure of the materials, and there will be another quantity in the free state between these units of structure, whose migration under the influence of the electric field causes a flow of current. This conductivity will be proportional to the number of free ions in any given substance, while the number of bound ions should not affect the simple conduction process. There will be an equilibrium at any given temperature between the free and the bound ions, thus

$$i_f/i_b = k \qquad (1)$$

In this equation i_f and i_b are quantities which measure the concentrations of free and bound ions respectively, and k is a constant. Since the bound ions are in a phase distinct from that of the free ions, their concentration may be considered constant. Thus we may write

$$i_f = K, \quad \text{and} \quad K \sim \bar{\mu}, \qquad (2)$$

where K is another constant, and $\bar{\mu}$ is the specific volume conductivity.

The general equation for the variation of an equilibrium constant with the temperature is

$$\frac{d \ln K}{dT} = \Delta H/RT^2 \qquad (3)$$

where ΔH is the heat of an activation, R is the gas constant, and T is the absolute temperature. Assuming ΔH to be constant over the temperature range involved, this expression may be integrated, with the result

$$\ln K = -\Delta H/RT + c \tag{4}$$

where c is a constant of integration. Assuming equation 2 to be correct it follows that

$$\ln \bar{\mu} = -E/RT + C \tag{5}$$

where E is the energy of liberation of a mole of ions and C is another constant. If the logarithm of the specific volume conductivity is plotted against the reciprocal of the absolute temperature and a straight line results, the quantity E may be assumed to be constant. When Briggsian logarithms are used E may be calculated directly from the slope of this line, according to the equation

$$-E = \text{slope} \times 2.303\,R, \quad \text{or} \quad -E = \text{slope} \times 4.576 \tag{6}$$

When the logarithms of the observed conductivities are plotted against the reciprocals of the absolute temperature a straight line with a negative slope results. This is taken to indicate that as the temperature is increased ions are liberated from the surface of the micells to the free condition in an endothermic process, causing thereby an increase in the conductivity as the temperature is increased.

At this point it is of interest to recall briefly the explanations given for the conductivity of a simple crystal as a function of temperature. Smekal (10) and his followers believe that in the case of crystalline dielectrics in which there are ionic conductors, the mechanism is essentially bound up with the deviation of the actual crystal structure from that of the ideal lattice. The ions which take part in conduction are assumed to be concentrated in positions in the crystal where these lattice imperfections are present and to move in adsorbed and free condition along the paths formed by these crystalline fissures. On the other hand Joffé (9), Phipps (11), and others believe that the conduction in such cases is due to a volume process in which either one or both of the ions is liberated from its normal lattice position by the absorption of energy in the form of heat. They believe the conductivity to be a property of the chemical substance rather than of the crystal and that it is independent of crystal imperfections. Thus, for sodium chloride Phipps, Lansing, and Cooke give for the quantity corresponding to our E the value 20,200 calories. It is defined as the heat of liberation of a gram ion in the crystal lattice, that is, the work necessary to produce a mole of ions (in this case, positive) in the interior of a crystal. As indicated in the introduction, there are certain types of crystal (sulfides, oxides) in which the conduction process may be electronic in nature.

Similar possibilities present themselves in the case of the materials in question and it will be equally difficult to decide between them. Amorphous dielectrics with electrolyte impurities may show increasing conductivity with temperature because ions are continually liberated from salts contained within them or because ions already present are removed from the inner surfaces to which they are adsorbed to the more mobile condition that we have described as free. It may be remarked that the presence of moisture is not necessary for the existence of an appreciable number of ions within a dielectric, since the electrolyte impurities present are already in the ionic form. It is true that dielectrics usually contain some water, the last traces of which are almost impossible of removal, so that dissolved salts will be ionized in solution but dissolved ions will tend to concentrate in the bulk of the water solution rather than at the interfaces, because salts as a class are capillary inactive. We have derived the mathematical relationship between conductivity and temperature assuming an equilibrium between the free and bound ions. However, we might also have derived an equation of the same form on the assumption that the amorphous dielectrics act, as far as the process of electrical conduction is concerned, in the same manner that Joffé and Phipps have explained the conductivity of a sodium chloride crystal. In this case we should have dealt with what might be termed a "dilute crystal," since relatively large volumes of inert materials would be present along with the electrolyte materials. An electronic process seems less probable in the case of amorphous materials, though it should not be excluded as a possibility without further information.

In view of the difficulties involved in a differentiation between the mechanisms which have been proposed to account for the conduction through a simple crystal, it is evident that one cannot hope to decide between the possibilities mentioned for the amorphous substances with the meager data now available. This assignment of a mechanism is rendered more difficult because the general form of the mathematical expression for the conductivity as a function of temperature will apparently be the same in the several cases. Nevertheless it is of interest that the conductivities of all the amorphous materials studied increase with the temperature according to a well-known physico-chemical law. It is hoped that further experiments with these substances containing known amounts of added electrolyte material will advance our knowledge of the conduction process taking place within them.

SUMMARY

There have been determined the specific volume conductivities of ten "amorphous" substances as a function of temperature. They include six synthetics and four varieties of wood. The resistances were determined by means of a modified Wheatstone bridge which has several advantages over the usual forms of apparatus for this type of work. The specific volume conductivity, $\bar{\mu}$, changes with absolute temperature, T, according to the law,

$$\bar{\mu} = k\,e^{-\frac{E}{RT}}$$

where E is an energy of liberation of the carrier of the current in calories, and k is a constant having the same dimensions as $\bar{\mu}$. Possible mechanisms of the conduction process are briefly discussed.

REFERENCES

(1) Curie: Ann. chim. phys. [6] **18**, 203 (1889).
(2) Campbell: Proc. Phys. Soc. London, **25**, 336 (1912-3).
(3) Koenigsberger and Reichenheim: Physik. Z. **7**, 570 (1906).
(4) Rasch and Hinrichsen: Z. Elektrochem. **14**, 41 (1908).
(5) Pirani and Siemens: Z. Elektrochem. **15**, 969 (1909).
(6) Dietrich: Physik. Z. **11**, 187 (1910).
(7) Curtis: Bur. Standards Bull. **11**, 359 (1915).
(8) Saegusa: Science Repts. Tôhoku Imp. Univ., First Ser., **15**, 795 (1926).
(9) Joffé: The Physics of Crystals. McGraw-Hill Book Company, New York (1928).
(10) Smekal: Z. Elektrochem. **34**, 472 (1928); Z. Physik. **56**, 579 (1929).
(11) Phipps, Lansing, and Cooke: J. Am. Chem. Soc. **48**, 112 (1926).

THE AUTOXIDATION OF STANNOUS CHLORIDE. II

A SURVEY OF CERTAIN FACTORS AFFECTING THIS REACTION[1]

ROBERT C. HARING AND JAMES H. WALTON

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received September 30, 1932

The autoxidation of stannous chloride has recently been investigated by Filson and Walton (1), who studied the effect of hydrochloric acid on the reaction velocity and showed a linear relation between the velocity and the hydrogen-ion concentration. This paper is a continuation of the above work and is a general survey of certain factors influencing the rate of reaction.

APPARATUS AND PROCEDURE

Twenty-five cc. of an acid solution of stannous chloride were placed in a 150-cc. Pyrex flask of the type used by Filson and Walton. The flask was placed in a thermostated shaking apparatus and connected to a water-jacketed burette containing oxygen gas at the temperature of the thermostat, 25°C. When the system had come to constant temperature, the shaking apparatus was started and readings were taken on the volume of oxygen absorbed. The speed of shaking was selected as about 1000, since Filson and Walton had shown that higher speeds have no effect on the reaction velocity.

REAGENTS AND SOLUTIONS

Several brands of stannous chloride were used and were found to give varying results. Baker's "purified" salt gave results which were only slightly changed by three recrystallizations under nitrogen from hydrochloric acid solution, consequently this preparation was used in the experimental work. Solutions made from stannous chloride which had been dehydrated by treatment with excess acetic anhydride and washed with anhydrous ether (2) gave results which agreed with those obtained from the recrystallized hydrated salt.

The solutions, made in 2-liter batches and stored under nitrogen, contained approximately 32 grams of stannous chloride per liter, and were

---

[1] This research was financed by a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman.

about 0.8 *N* in total hydrochloric acid (free acid plus that obtained by complete hydrolysis).

Table 1 gives the data for the solutions used in this work.

ORDER OF THE REACTION

By neglecting the first 80 to 120 minutes of the run, during which the absorption was not always reproducible, a value of *K* (*K* = milligrams of oxygen absorbed per minute) was obtained which corresponds to a zero order reaction, within an experimental error of 5 to 7 per cent in the course of a 4 to 5 hour run. This neglected period corresponds to about a 10 per cent absorption of the theoretical amount of oxygen required to oxidize the sample completely. Duplicate runs for solution No. 6 are given in table 2, this solution having an average value of *K* of 0.0572 mg. per minute. The 5 to 7 per cent drop in the value of *K* can be attributed to a decrease in the concentration of the free hydrochloric acid, since this substance is used up during the oxidation of the stannous chloride. Some hydrochloric acid will be available through hydrolysis of the stannic chloride, but since the complex equilibrium between Sn^{++}, Sn^{++++}, HCl, and complex chloro acids is not fully known it is impossible to define the system definitely.

TABLE 1

Composition of the stannous chloride solutions

SOLUTION NUMBER	SOURCE OF $SnCl_2$	$SnCl_2$	HCl (TOTAL)
		grams/liter	*Normality*
5	Baker's Purified	36.5	0.783
6	Baker's Purified	31.3	0.758
7	Baker's Purified	31.7	0.733
8	Mallinckrodt's C.P.	35.5	0.814
9	General Chemical Co. C.P. (dehydrated by acetic anhydride)	32.6	0.782
10	Mallinckrodt's C.P. (dehydrated by acetic anhydride)	32.7	0.811
11	Baker's Purified	33.6	0.840
12	General Chemical Co. C.P. (recrystallized three times)	33.1	0.815

EFFECT OF TEMPERATURE

Runs were made on solution No. 12 at different temperatures. It was impossible to calculate values of *K* for comparison, since the apparent order of the reaction varied with the temperature. This change can be attributed to several factors. First, the solubility of oxygen is higher at the low temperatures, allowing a higher saturation concentration of oxygen, and thus increasing the reaction rate. Then, too, the change of temperature affects the equilibrium between Sn^{++}, $SnCl_2$ and the chloro acid complexes. These factors mask the true temperature coefficient of the reaction, so that the results are of qualitative importance only. The results

TABLE 2

Data for duplicate runs at 25°C.

Solution No. 6

Stannous chloride, 31.3 grams per liter; hydrochloric acid (total) 0.758 *N*

TIME	RUN 165		RUN 168	
	Oxygen absorbed	*K*	Oxygen absorbed	*K*
minutes	*milligrams*	*mg./min.*	*milligrams*	*mg./min.*
10	0.60	0.0600	0.60	0.0600
20	1.17	0.0587	1.19	0.0593
30	1.77	0.0592	1.78	0.0594
40	2.35	0.0587	2.35	0.0587
50	2.87	0.0575	2.93	0.0587
60	3.48	0.0581	3.55	0.0591
70	4.01	0.0572	4.07	0.0581
80	4.56	0.0570	4.67	0.0583
90	5.10	0.0567	5.20	0.0578
100	5.67	0.0567	5.77	0.0577
110	6.19	0.0562	6.27	0.0570
120	7.29	0.0556	7.42	0.0570
140	7.86	0.0562	7.97	0.0570
150	8.37	0.0559	8.51	0.0567
160	8.96	0.0560	9.10	0.0568
170	9.48	0.0558	9.63	0.0568
180	10.06	0.0559	10.21	0.0567
190	10.70	0.0562	10.80	0.0568
200	11.19	0.0559	11.37	0.0568
210	11.75	0.0559	11.93	0.0568
220	12.31	0.0559	12.48	0.0567
230	12.89	0.0561	13.07	0.0568
250	13.91	0.0556	14.11	0.0566
270	15.00	0.0555	15.23	0.0565
		Av. = 0.0568		Av. = 0.0576

are expressed in terms of the time required to oxidize one-half of the stannous chloride, starting at the beginning of the run. From the curves in figure 1, the following "half-times" were interpolated:

At 45°C.	144 minutes
35°C.	228 minutes
25°C.	320 minutes
15°C.	384 minutes
0°C.	330 minutes

The solubility of oxygen between 15° and 0°C. shows a marked increase, and this is probably the cause of the decrease in the time of half absorption for the lower temperature.

EVIDENCE FOR A CHAIN REACTION

A number of tests were made to determine whether or not there is any evidence that the reaction under consideration belongs to the chain type of reaction similar to the oxidation of sodium sulfite studied by Alyea and Bäckström (3).

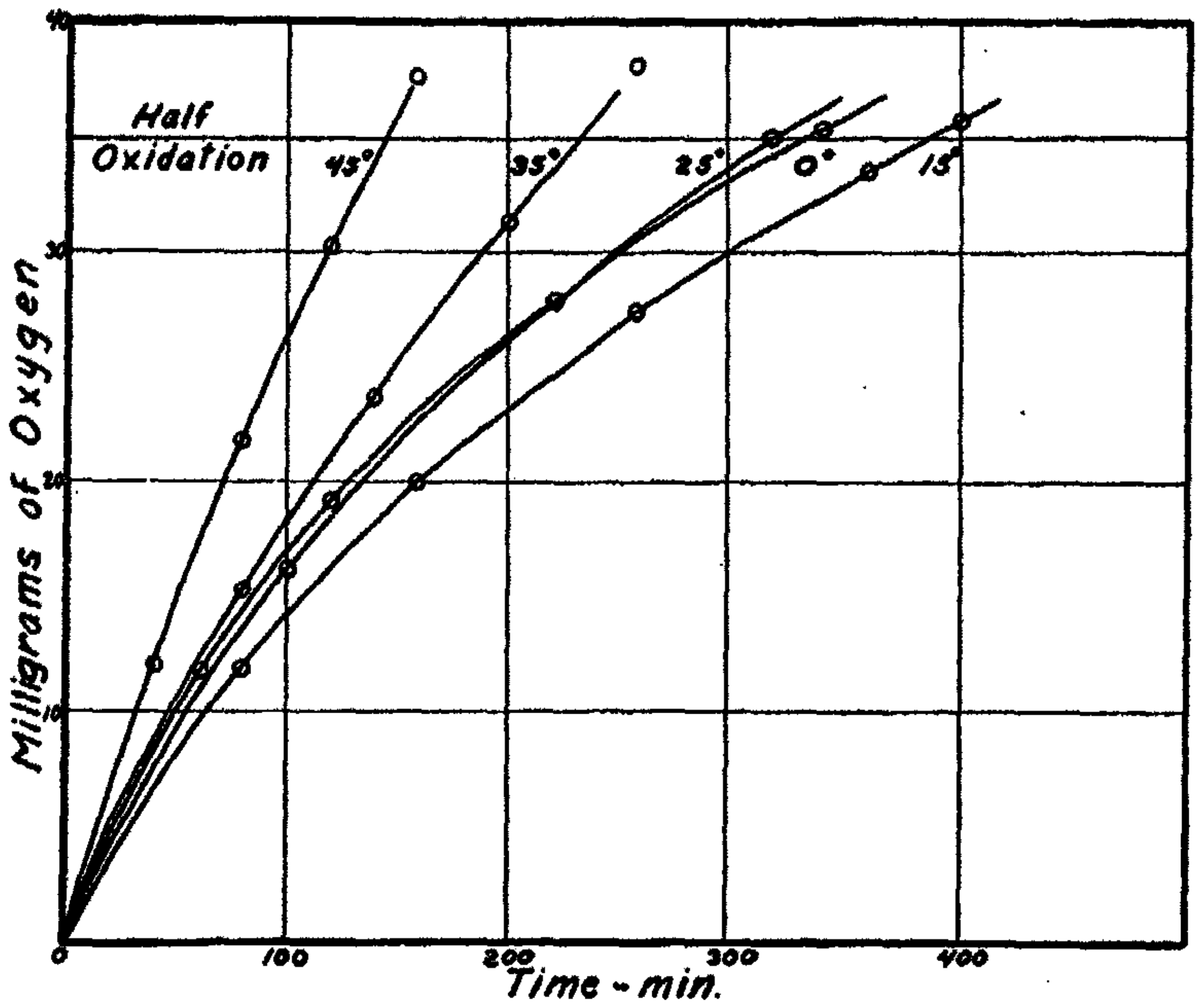


FIG. 1. THE EFFECT OF TEMPERATURE ON THE RATE OF OXYGEN CONSUMPTION BY STANNOUS CHLORIDE

This reaction meets the criterion of being exothermic, as was shown by Berthelot (4), whose work was done at 500°C. A confirmatory experiment in our laboratory, at room temperature, also indicated that the reaction is exothermic.

For the purpose of confirming the chain mechanism, tests were made on: (1) the influence of light; (2) the existence of an intermediate peroxide; (3) the effect of added substances, especially inhibitors; (4) the coupled oxidation of a second molecular species present in the system.

1. Effect of light

Visible light had no effect on the reaction rates. Two flasks were painted black, and the runs made in these showed no difference from those in unpainted flasks. In addition, some experiments were made in which a 250-watt tungsten light was placed adjacent to the reaction flask, and other experiments in which the direct beam of the strong green and yellow light from a high intensity capillary mercury vapor lamp was used. In both cases no acceleration of the reaction was noted. It was discovered, however, that ultra-violet light of wave length below 3070Å. was absorbed completely by the solution and that it speeded up the reaction very considerably. The details of these experiments will be discussed in a subsequent paper.

2. Detection of peroxide

A sample of the partially oxidized stannous chloride was found to give a peroxide test with titanium sulfate. This test could not be obtained after the solution had been allowed to stand for 2 or 3 hours, showing that the peroxide had been used up by reaction with more stannous chloride. No attempts were made to isolate the peroxide, because of the small amount present and its relative instability.

3. Catalytic effects of certain substances

One of the most important of the criteria of photochemical chain reactions, which can also be applied to thermal chain reactions, is the great effect of negative catalysts. The reaction of stannous chloride with molecular oxygen is very sensitive to the action of added substances, as shown both by our work and by that of Young (5). In attempting to duplicate Young's work on inhibition by alkaloids, it was found that cocaine, morphine, and brucine had little effect in 0.001 M solution. In 0.01 M solution a reduction to about 90 per cent of the normal rate was shown, and in a saturated solution, a reduction of 55–65 per cent of the normal values.

Because of the effect of the alkaloids it was of interest to investigate the action of other nitrogen compounds; accordingly a series of experiments was carried out in which many varieties of these compounds were used. The results are shown in table 3, in which the value of K is given, together with the percentage value of K in relation to the uncatalyzed value of K for the stock solution used in each experiment. It will be noticed that nitrogen compounds, in general, were inhibitors, but that the inhibiting power is affected by the position of the nitrogen and the nature of the other atoms bound to it. Amino compounds had little effect, some of them slightly inhibiting the reaction and some accelerating it slightly. Nitro compounds were the most effective of the inhibitors studied, and the mole-

TABLE 3

The effect of certain nitrogen compounds

Normal K values for the solutions: No. 5, K = 0.0626; No. 6, K = 0.0572; No. 7, K = 0.0583 mg. per minute

SOLUTION	CONCENTRATION	COMPOUND	K	PER CENT OF NORMAL
		Alkaloids		
	moles/liter		*mg./min.*	
5	0.001	Cocaine hydrochloride	0.0620	.....
5	0.001	Brucine	0.0574	91.7
5	0.1	Brucine	0.0345	55.1
5	0.01	Morphine hydrochloride	0.0565	90.3
5	0.1	Morphine hydrochloride	0.0407	65.0
5	0.01	Nicotine	0.0622	.....
6	0.01	Veronal	0.0552	96.5
		Nitro compounds		
6	0.01	*p*-Nitrotoluene	0.0112	19.6
6	0.001	Nitronaphthalene	0.0147	25.7
7	0.01	Nitromethane	0.0114	19.6
6	0.001	*o*-Nitrophenol	0.0106	18.6
7	0.01	*p*-Nitrophenol	0.0156	26.8
6	0.01	*m*-Nitroaniline	0.0012 to 0.0043[*]	About 5
6	0.001	*p*-Nitrobenzoic acid	0.0120	21.0
6	0.001	Nitrophenylhydrazine	0.0119	20.8
6	0.01	*m*-Dinitrobenzene	0.0029	5.1
6	0.001	*sym*-Trinitrobenzene	0.0081	14.2
6	0.01	Trinitrotoluene	0.0058	10.1
6	0.00001	Picric acid	0.0330 to 0.0444	About 60
6	0.0001	Picric acid	0.0170	29.7
6	0.0005	Picric acid	0.0154	26.9
6	0.001	Picric acid	0.0122 to 0.0179	About 25
6	0.01	Picric acid	0.0145	25.3
		Amino and imino compounds		
5	0.01	Glycine	0.0631	.....
5	0.01	*p*-Toluidine hydrochloride	0.0564	90.1
5	0.01	Phenylhydrazine hydrochloride	0.0382	61.0
6	0.01	Carbazole	0.0535	93.5
6	0.01	Hydroxylamine hydrochloride	0.0582	.....
6	0.01	Urea	0.0595	.....
7	0.002	Thiourea	0.0656	112.5
7	0.0045	Thiourea	0.1120	192.0
7	0.01	Thiourea	About 1.2	2060.0

---

[*] The two values of K in some experiments denote a rise in the value of K, due to the destruction of the inhibitor.

TABLE 3—*Concluded*

SOLUTION	CONCENTRATION	COMPOUND	K	PER CENT OF NORMAL
		Amino and imino compounds—Concluded		
	moles/liter		*mg./min.*	
7	0.01	Ammonium thiocyanate	0.0465	79.8
7	0.01	Sulfanilic acid	0.0584	.....
7	0.01	Acetanilide	0.0571	.....
7	0.01	Semicarbazide hydrochloride	0.0501	85.9
7	0.01	*p*-Aminophenol	0.1028	176.3
		Other nitrogen compounds		
6	0.001	Cellulose nitrate	0.0470	.....
7	0.01	Potassium nitrate	0.0564	96.7
7	0.01	Potassium cyanide	0.0517	88.7
7	0.01	Butyl cyanide	0.0536	91.9
7	0.01	Acetoxime	0.0567	97.3
7	0.01	Azobenzene	0.0208 *to* 0.0298	About 45
7	0.001	Aminoazobenzene	0.0587	.....
7	0.01	Aminoazobenzene	0.0642	110.0
7	0.01	Butyl nitrite	0.0576	.....
7	0.01	Azoxybenzene	0.0523	89.7
7	0.01	Guanidine nitrate	0.0421	72.2

cules with two or three nitro groups were more effective than those with one. In contrast with this, organic and inorganic nitrate salts showed little or no effect. The azo and hydrazine groups were fair inhibitors, while the cyanide, oxime, azoxy, amino, and nitrite groups had very slight inhibitory power, or none at all.

In general no attempt was made to discover whether or not the catalyst, either positive or negative, had been destroyed during the course of the reaction. In the case of picric acid the strong yellow color disappears during the course of the oxidation, and at the same time, a rise takes place in the rate of oxidation. Both of these facts indicate that the picric acid is destroyed during the reaction.

Thiourea is a marked exception to the other nitrogen compounds since it showed a strong acceleration of the oxidation in concentrations as low as 0.002 *M*. As the concentration was increased the amount of acceleration of the reaction increased, until at 0.01 *M* the initial rate was about 1750 per cent of the uncatalyzed value. However, at this concentration the rate of oxidation drops off rapidly, indicating that the thiourea is being destroyed. In studying the action of thiourea, two special runs were made, one using 0.01 *M* thiourea in 0.8 *N* hydrochloric acid, and the second similar, except for the addition of a small amount of stannous chloride

(0.007 *M*). In the first case, no absorption was noticed, indicating that under these conditions thiourea alone does not absorb oxygen. In the second run oxygen was absorbed until the stannous chloride was used up, when the absorption stopped. The accelerating action of thiourea is apparently due to the sulfur atom, since amino compounds have been shown to have little effect, and yet this action is very specific since some of the other sulfur compounds used had no effect (benzyl sulfide, sulfanilic acid, benzenesulfinic acid, and powdered sulfur). Some sulfhydryl compounds were used, such as cysteine, thiocresol, thiobarbituric acid, and thiosalicylic acid. These were all inhibitors, reducing the rate to 40–45 per cent of its normal value. Thioglycollic acid however had practically no effect on the rate. This is in agreement with Schöberl's work (6) in which he found a negative catalytic effect with cysteine and glutathione on the autoxidation of leuco methylene blue, but is opposite to the accelerating effect of sulfhydryl compounds in biological phenomena (7).

The oxygen compounds used had little effect. The aliphatic alcohols increased the absorption rate 5 to 10 per cent and phenol had no effect, but hydroquinone, pyrogallol, and mannite decreased the value of K to about 90 per cent, and quinhydrone to 67 per cent of its uncatalyzed value. Other oxygen compounds, of widely different types—acids, ketones, thymol, ethyl ether, benzoyl peroxide, and paraformaldehyde—showed no appreciable effect on the rate of absorption.

Tetraethyllead gave a value for K of 455 per cent of the uncatalyzed value. Ammonium thiocyanate was a good inhibitor; potassium cyanide, potassium nitrate, benzene, and anthracene decreased the value of K, 5 to 15 per cent. Certain other compounds had no effect; this group includes arsanilic acid, magnesium chloride, magnesium pyrophosphate, dibasic sodium phosphate, sodium arsenate, sodium pyrophosphate, and mineral oil. Silica gel, ground to 180 mesh, had no effect on the rate, showing that the reaction does not take place on the surface of the flask, but is a true solution reaction.

Catalysis by charcoal

The catalytic acceleration of many autoxidations by charcoal suggested its use in this study. Powdered willow charcoal accelerated the reaction but not in proportion to the weight used. For example, 0.12 mg. per cc. increased the rate to 167 per cent of its normal value; 0.6 mg. per cc. increased it to 228 per cent; and 1.2 mg. per cc. increased it to 253 per cent. This differs from the results of Lamb and Elder (8) who found for autoxidation of ferrous sulfate that the increase in oxidation rate was proportional to the amount of charcoal used.

As in other autoxidations in which charcoal has been used it was found that the "active centers" on the charcoal can be promoted or poisoned.

Promotion was shown by copper salts. The initial absorption rate for charcoal alone was 1.72 mg. per 10 minutes, for cupric chloride alone, 2.01 mg. per 10 minutes, while cupric chloride and charcoal together gave a value of 10.80 mg. per 10 minutes. These values are given in grams, since a value of K could not be calculated for the promoted catalyst.

The poisoning effect was shown by picric acid and by sodium arsenate. The latter compound had no effect on the reaction rate when used alone; charcoal alone increased the rate to 228 per cent of normal, but when the two were used together the rate was reduced to exactly the uncatalyzed value. This is similar to the results of Lamb and Elder (8), in which they found that phenylurea, amyl alcohol, and acetanilide when used alone showed no effect on the autoxidation of ferrous sulfate, but that they destroyed the accelerating influence of charcoal on the reaction. Picric acid showed a strong inhibition for the stannous chloride reaction, and when it was used in conjunction with charcoal, absorption rates were obtained which lay between the values for the two substances singly. According to the Taylor theory (9) these compounds are preferentially absorbed at the most active points and prevent the usual accelerating action of the charcoal.

4. Coupled oxidation

It was found that while an aqueous solution of allyl alcohol does not absorb oxygen, there is coupled oxidation of the allyl alcohol in the presence of stannous chloride. In order to determine the amount of excess absorption, the apparatus was arranged so that solid stannous chloride could be held above the solution in a glass capsule until the gas had come to constant temperature. The capsule was dropped into the acid solution with the first shake of the machine. In this way, it was possible to measure the total amount of oxygen absorbed by the system. By using pure oxygen as the atmosphere, the experiment was completed in a short time. Table 4 gives the results of this work, showing the effect of varying amounts of stannous chloride, allyl alcohol, and acid. The effects of temperature and of added substances are also given. The per cent excess absorption increased with increasing amounts of allyl alcohol, and decreased with increasing amounts of stannous chloride and hydrochloric acid. These effects may be explained by the assumption that the allyl alcohol is oxidized by the primary peroxide. With increased concentration of allyl alcohol more of the chains will involve alcohol molecules, and thus a larger amount will be oxidized.

Increased amounts of stannous chloride or hydrochloric acid cause an increase in the rate of consumption of oxygen, and at the same time cause a decrease in the amount of induced oxidation. Increased temperature, and homogeneous catalysts such as cupric chloride and thiourea, also have

TABLE 4

Induced oxidation of allyl alcohol

(a) Effect of varying amounts of stannous chloride

0.854 gram allyl alcohol in 25 cc. of 0.440 *N* HCl

$SnCl_2$	EXCESS O_2 ABSORBED
grams	*per cent*
0.127	45.1
0.381	34.8
0.635	28.1

(b) Effect of varying amounts of allyl alcohol

ALLYL ALCOHOL	EXCESS O_2 ABSORBED
(1) 0.381 gram $SnCl_2$ in 25 cc. of 0.440 *N* HCl	
grams	*per cent*
0.171	19.4
0.854	34.8
1.708	36.2
(2) 0.635 gram $SnCl_2$ in 25 cc. of 0.440 *N* HCl	
0.171	14.8
0.854	28.1
1.708	31.3

(c) Effect of temperature

0.381 gram $SnCl_2$ in 25 cc. of 0.440 *N* HCl

ALLYL ALCOHOL	EXCESS O_2 ABSORBED		
	15°C.	25°C.	35°C.
grams	*per cent*	*per cent*	*per cent*
0.085	16.8	....	....
0.171	20.1	19.4	16.4
0.854	37.2	34.8	27.6
1.708	40.1	36.2	36.3

(d) Effect of additional substances with allyl alcohol

0.381 gram $SnCl_2$ + 0.171 gram allyl alcohol in 25 cc. 0.440 *N* HCl

ADDED SUBSTANCE	EXCESS O_2 ABSORBED
	per cent
None	19.4
+0.1 gram thiourea	7.2
+0.1 gram charcoal	23.7
+0.1 gram $CuCl_2$	8.7

TABLE 4—*Concluded*

(e) Effect of acid

0.854 gram allyl alcohol; 0.381 gram $SnCl_2$

ACID	EXCESS O_2 ABSORBED
	per cent
None (25 cc. H_2O)	28.1
10 cc. 0.440 *N* + 15 cc. H_2O	44.4
25 cc. 0.440 *N*	34.8
25 cc. 4.0 *N*	7.7

TABLE 5

Induced oxidation in non-aqueous solvents

SOLVENT	SPEED OF REACTION	TOTAL GRAMS OF OXYGEN USED BY 0.320 GRAM OF ANHYDROUS STANNOUS CHLORIDE	EXCESS OXYGEN USED
			per cent
Ethyl alcohol	Rapid		About 50
Isopropyl alcohol	Rapid	0.04194	55.3
Amyl alcohol	Rapid	0.04450	64.3
n-Heptyl alcohol	Rapid	0.04777	76.9
Cyclohexanol	Rapid	0.04912	81.9
Benzyl alcohol	Slow		
Phenylethyl alcohol	Slow		
Cresol	Slow		
Acetic acid	Rapid	0.03585	32.3
Propionic acid	Rapid	0.04088	51.4
Ethyl acetate	Rapid	0.03169	17.4
Butyl butyrate	Rapid	0.03454	28.0
Acetone	Rapid		About 30
Acetophenone	Slow		
Aniline	Slow		
Pyridine	Slow		
Dibutyl ether	Slow		
Glycerine	Slow		
Benzene	Very slow		

the dual effect of speeding up the rate of consumption and of decreasing the amount of induced oxidation. Charcoal, on the other hand, while it is also a positive catalyst, increased the amount of induced oxidation. This may be explained by the higher concentrations of allyl alcohol produced at the surface of the charcoal by adsorption.

Several other substances were used in place of allyl alcohol in investigating the phenomenon of induced oxidation. It was found that there was no excess oxygen used when acetone, phosphorus acid, maleic acid, or *p*-aminophenol were used, but that butyraldehyde used 14.8 per cent excess.

Coupled oxidation was also found when stannous chloride was oxidized in non-aqueous solvents. The solvents used are shown in table 5 together with the total grams of oxygen used and the per cent excess over the theoretical amount necessary for oxidation of the stannous chloride. There seem to be two classes or types of solvents among those tried, one class in which the oxidation is fast and the second in which it is slow. In the former group the oxidation of the sample was complete in 3 to 10 minutes, in spite of the fact that no excess hydrochloric acid was present as in the case of oxidation in aqueous solution. In each solvent of this group an excess of oxygen was used. In the rest of the solvents the reaction was comparatively slow, so that it was not followed to completion. There is no relation between the phenomenon of molecular compound formation and this division into types, for substances which form molecular compounds with stannous chloride are found in both classes. Neither is there a relation between ease of oxidation and the separation into types, since compounds which are easy to oxidize and others which are hard to oxidize are found in both classes.

DISCUSSION

The results of the foregoing experiments are best explained by the well-known peroxide theory of autoxidation, in which it is held that oxidations of this type are attended by the intermediate formation of metastable or dative peroxides which are characterized by high energy content and great instability. Such peroxides are very active and account for many of the phenomena of autoxidation (10). Mention has been made of the fact that in the autoxidation of stannous chloride enough peroxide is formed to be detected qualitatively. Further evidence of the existence of a peroxide is afforded by the induced oxidation of many compounds, especially alcohols.

That this reaction is a chain reaction is supported by the great influence of added substances, particularly inhibitors, on the course of the oxidation, and also by the fact that the reaction is exothermic. There is also further support from photochemical data.

In the autoxidation of stannous chloride there is reason to believe that a complex chloro acid is the form in which the Sn^{++} is oxidized. Prytz (11) has shown that the complex ions $SnCl_3^-$ and $SnCl_4^{--}$ exist in aqueous solutions of comparatively low hydrochloric acid concentration. This conclusion is supported by the fact that an excess of hydrochloric acid has a great accelerating action on the autoxidation of stannous chloride. Complexes are also known between stannous chloride and potassium chloride or sodium chloride, and these substances act in a manner similar to that of hydrochloric acid in accelerating the autoxidation of stannous chloride, but to a less degree than does hydrochloric acid. In another paper further evidence will be given to show that in the photochemical autoxidation the substance which actually absorbs the light quanta and becomes activated is a complex ion of this type.

SUMMARY

1. Increased temperature increases the rate of autoxidation of stannous chloride, but the true temperature coefficient is masked by the change in the solubility of oxygen and changes in the complex equilibria existing in the solution.

2. Visible light has no effect on the reaction but ultra-violet light below 3070Å. is absorbed and accelerates the reaction.

3. A peroxide was detected in the fresh, partially oxidized sample of stannous chloride. This peroxide disappears by reaction with further stannous chloride.

4. Many organic substances, particularly nitro compounds, were found to be inhibitors of the reaction. Picric acid was the strongest inhibitor found, and this inhibitor was shown to be destroyed during the oxidation.

5. Thiourea was found to be a strong positive catalyst for the autoxidation.

6. Poisoning and promoter action were found for the catalysis of the reaction by powdered willow charcoal.

7. Coupled oxidation of a second molecular species was found in aqueous solution in the cases of allyl alcohol and butyraldehyde, and in many nonaqueous solvents such as alcohols, acids, esters, and ketones.

REFERENCES

(1) Filson, G. W., and Walton, J. H.: J. Phys. Chem. **36**, 740 (1932).
(2) Stephen, H.: J. Chem. Soc. **1930**, 2786.
(3) Alyea, H. N., and Bäckström, H. L. J.: J. Am. Chem. Soc. **51**, 90 (1929).
(4) Mellor, J. W.: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 7, p. 427. Longmans, Green and Company, London (1927).
(5) Young, S. W.: J. Am. Chem. Soc. **23**, 119 (1901).
(6) Schöberl, A.: Ber. **64**, 546 (1931).
(7) Milas, N. A.: Chem. Rev. **10**, 295 (1932), especially p. 312.
(8) Lamb, A. B., and Elder, L. W., Jr.: J. Am. Chem. Soc. **53**, 137 (1931).
(9) Taylor, H. S.: J. Franklin Inst. **194**, 1 (1922).
(10) Milas, N. A.: Chem. Rev. **10**, 295 (1932), for an excellent review of autoxidation.
(11) Prytz, M.: Z. anorg. Chem. **172**, 147 (1928).

NEW BOOKS

New Conceptions in Biochemistry. By N. R. Dhar. 23 x 16 cm.; pp. x + 168. Allahabad: The Indian Drug House.

In the preface the author says: "Since the days of Lavoisier, animal metabolism has been a fascinating subject of research for chemists and physiologists alike. Despite the attempts of numerous distinguished workers, the enigma of animal metabolism still remains unsolved. In this book an effort has been made to discuss the general physico-chemical principles underlying animal metabolism. The book deals with the chemical aspects of biochemistry which have any bearing on metabolism. It is therefore in no way to be a book of reference. No attempt has been made to describe systematically all diseased conditions occurring in cases of improper metabolism. The dominant idea in the book is that several diseases are due to a lack of a proper and balanced oxidation of the three classes of food materials, the carbohydrates, fats, and proteins."

The headings of the chapters are: an introduction to views on food principles and chemical aspects of metabolism; biological oxidations; carbohydrate metabolism; metabolism of fats; oxidation of mixtures of carbohydrates, fats, and proteins; actino-therapy; deficiency diseases, internal secretions, vitamins, and light; normal ossification, and the formation of crystalline deposits in diseases; gout, fever, and uses of alkali, phosphates, and iron preparations; acclimatization and physical interpretation of Rubner's law of surface—and the ageing of cells, catalysts, and body colloids—the problem of old age and death; coagulation of blood, serum, and milk.

"Oxidation is the central life process supporting the entire complicated machinery of the living being. The substances undergoing metabolism in the animal body, comprising proteins, carbohydrates, and fats, are entirely resistant to oxidation by molecular oxygen under ordinary conditions. Yet in the animal body they are oxidized with the greatest ease into their end-products," p. 14.

"It is evident that acetone bodies are not products of normal metabolism, but result from abnormal conditions. The author has suggested that under normal conditions, fats are mainly burned in the animal body directly to carbon dioxide and water, without the formation of intermediate products. An objection may be raised as to how a fatty acid containing 18 carbon atoms can be directly oxidized to carbon dioxide and water without the formation of intermediate products. Many physiologists are of the opinion that acetoacetic acid, with four carbon atoms in its molecule, undergoes complete oxidation to carbon dioxide and water. If a molecule with four carbon atoms can be directly oxidized, then the direct oxidation of more complex acids is not impossible," p. 41.

"In the absence of thyroid there is little oxidation of fat. When fat is being metabolized in the body, the oxidation of carbohydrate is retarded. From this it will be seen that in the cases of thyroid removal there will be rapid oxidation of glucose; added to this is the accelerating effect of insulin on glucose oxidation, if insulin is injected. Therefore, there will be a greater lowering of blood sugar in cases of thyroid removal than in cases where the thyroid is functioning normally. Hence the greater violence of symptoms following an overdose of insulin," p. 53.

"We have demonstrated that the oxidation of substances like sodium sulphite, ferrous hydroxide, etc., by air or oxygen is greatly retarded by the presence of sugars, sodium arsenite, etc., which in their turn, are oxidized in presence of sodium sulphite, ferrous hydroxide, etc. Similarly, we have proved that the oxidation of fats is retarded by carbohydrates and vice versa," p. 57.

"In the case of adrenal secretions, we assume that the oxidation of fat is also accelerated by the promoter action of the secretion, and consequently in this case also the main store of energy comes from the oxidation of fat, and so the glucose is not oxidized and glycosuria results.

"With pituitary the case is different; for we assume that in presence of this secretion it is mainly the oxidation of protein matter which is increased; and consequently the energy supply comes from this oxidation, leaving glucose and fats unoxidized. From this point of view it will be clear that the function of the pancreas secretion, which mainly accelerates the oxidation of glucose, need not be considered antagonistic to that of the thyroid, pituitary, or adrenals. We assume that the matter merely rests on the preferential oxidation of one variety of food material due to the presence of the promoter. In hyper-functioning of the pancreas the glucose will be readily oxidized, and will supply the energy. Hence, according to our point of view, the pancreas need not inhibit the action of the thyroid, or the adrenals; moreover, the adrenal or thyroid need not inhibit the action of the pancreas. We are strongly of the opinion that in normal health pancreas, thyroid, adrenal, and pituitary perform their proper function by promoting the oxidation of carbohydrates, fats, and proteins in the proper proportions. Consequently a combination of the respective hormones, especially thyroid and pituitary, should yield better results in many diseases than either singly," p. 58.

"Addison's disease is today regarded by most investigators as due to hypofunction of the adrenal glands. It develops gradually with general asthenia, lack of interest, and malaise; digestive disturbances are common, with vomiting or diarrhoea and constipation, which may be alternating in character. Addison's disease usually resists all methods of treatment. Organotherapy with adrenal substance offers great hope, and in the hands of numerous practitioners has proved far more effective than all other therapy," p. 86.

"Röhrig and Zuntz showed that a curarized warm-blooded animal at ordinary room temperature lost the power of maintaining its body temperature and that the intensity of metabolism decreased accordingly. Curare prevents the transmission of motor impulses to voluntary muscles. Krogh states that the curve of oxygen absorption as influenced by body temperature is the same in the anesthetized frog and fish as in the curarized dog," p. 123.

The author is attempting to show that many physiological disturbances are due to improper and unbalanced oxidation. The reviewer is attempting to show that many physiological disturbances are due to over-agglomeration or over-dispersion of proteins. Some day some intelligent person will show that these are two parts of the same point of view. Perhaps improper and unbalanced oxidation causes over-agglomeration or over-dispersion of proteins.

WILDER D. BANCROFT.

Physical Chemistry for Students of Biology and Medicine. By DAVID I. HITCHCOCK. 23 x 15 cm.; pp. xii + 182. Baltimore: Charles C. Thomas, 1932. Price: $2.75.

In the preface the author says: "The material presented in this book has been offered during the past five years to medical and graduate students in Yale University as a part of the course in physiology."

The chapters are entitled: gases; liquids and gases; solutions; solutions of electrolytes—the law of mass action; hydrogen ions, indicators and buffers; galvanic cells and electrometric pH determination; adsorption—the colloidal state; membrane equilibrium; equilibria in blood; reaction velocity and enzyme action; oxidation-reduction potentials—phase boundary of potentials; electrokinetic phenomena; transformation of energy.

The book is essentially orthodox. Distrubing facts are ignored conscientiously and effectively. No reference is made anywhere to the effect of solubility on partial pressures, as in the case of ether and water and consequently there is no reference to the absence of any solubility term in the so-called Raoult formula.

All proteins combine stoichiometrically with hydrogen chloride and albumin forms true solutions in water, p. 116.

Wilder D. Bancroft.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 59. Eisen. Teil A. Lieferung 4. 26 x 18 cm.; pp. 587-846. Berlin: Verlag Chemie, 1932. Price 41 Marks (Subscription Price 35.50 Marks).

This volume, written by Prof. Durrer of the Technische Hochschule, Charlottenburg, is a continuation of Lieferung A3, will be completed by Lieferung A4, and deals with the metallurgy of iron. It contains accounts of the puddling process, the Bessemer, Thomas and other Open-Hearth processes, electric furnace methods, and several minor processes. The references to the literature are very complete, including European and American publications, and there are numerous curves and illustrations of plant. The actual text is relatively meagre, most of the space being taken up by literature references, and numerical data, so that the volume is essentially intended for readers who have a good library available. It cannot replace the usual works on ferrous metallurgy, since the descriptions are far too sketchy to be of any particular value in themselves. It would seem that by branching off into chemical technology the editors of Gmelin have rather departed from the intention of the work, and if other parts of the subject are to be treated on the applied side in the same way as in the present volume, the result will be somewhat disappointing.

J. R. Partington.

Eisen- und Stahllegierungen Patentsammlung. Zugleich Anhang zur Metallurgie des Eisens in Gmelins Handbuch der anorganischen Chemie. By A. Grützner. 26 x 18 cm.; pp. 308. Berlin: Verlag Chemie, 1932. Price 32 Marks.

This volume, which is an appendix to the sections on iron and steel in Gmelin's Handbuch, consists entirely of references to patents, with brief statements of the contents, arranged in tabular form according to the chemical composition of the systems. The patents cover the period 1880 to 1932 and various countries, and there are 7000 references. There is no doubt that such a work will save an enormous amount of time and labour and the price must be considered reasonable. It should be in all technical libraries.

J. R. Partington.

The Sorption of Gases and Vapours by Solids. By J. W. McBain. 23 x 14 cm.; pp. xii + 577. London: Geo. Routledge and Sons, 1932. Price 25 shillings net.

The group of rather heterogeneous phenomena known as the sorption of gases and vapours by solids has been the subject of a great number of experimental and theoretical investigations, and has acquired an extensive and scattered literature. In view of the great general interest of the subject, a book merely giving a classified survey of the material and literature references would in itself be of appreciable utility, but when such a comprehensive treatment is accompanied, as it is in the present volume, by the critical and suggestive views of an expert, the book naturally becomes one of considerable interest and importance. In his book, McBain has provided not only workers in this field but also chemists and physicists in general with an account of the particular aspects of sorption indicated in the title which is likely to become the standard work of reference. The range of material dealt with is surprisingly large, and in his careful study of the literature, in the great majority of cases obviously in the original, the author has not only materially contributed to the attainment of a proper perspective but has also performed an exacting task for which he deserves the thanks of his readers. The literature references are very full, in a few cases the bibliography having been contributed by specialists, and the author index contains 1500 names. There is a short subject index and an index of substances, so that the use of the book for purposes of reference is easy. Numerous tables and curves are given in the text. In some cases the descriptions on the curves are in German, and some rather complicated diagrams of apparatus are not explained in the text.

The emphasis in the treatment is on the experimental side, although the theories are also discussed in a critical manner. For the detailed mathematical treatment of the theories the reader is referred to other works. The style is generally terse, sometimes even to the point of being in places rather difficult to understand, and the large amount of information given sometimes leads to a slight lack of coherence in the text, which makes the reading rather tedious. In compensation for this, the reader will find that the book covers a really amazing amount of ground and gives a well chosen selection of numerical data.

Among the contents are descriptions of the experimental methods; sorption by charcoal, zeolites, silica and other gels, glass, impermeable crystals, metals; the thickness of the adsorbed film; mobility in sorbed films; sorption by jellies; effect of sorption on the solid; heat of sorption; theories of sorption; contact catalysis; the electrical interpretation of sorption.

The author, as a result of his critical survey, concludes that Langmuir's theory of adsorption is the one which agrees best with all the available facts, although he admits that in some cases the same data have been used to support two conflicting theories. He claims (p. 459) that the condensed film theory has been disproved by some experiments by himself and Britton, but omits to mention that in the same issue of the journal in which these were published another set of experiments by Foote and Dixon were reported which, although not specifically designed to test that theory, were shown to be in agreement with it. The remarkable experiments of Hardy haunt the exposition of the monomolecular film theory in several places, and it is regrettable that the work of Bastow and Bowden came too late for inclusion.

The book is one which should find a welcome from many classes of readers and deserves the highest commendation. The great bulk of the literature might well have overwhelmed a less enthusiastic and energetic author, but McBain has not only mastered it but has been able to deal with it in a critical and suggestive manner which deserves great praise and adds materially to the value of the book.

J. R. PARTINGTON.

Wörterbuch der Kolloidchemie. By ALFRED KUHN. 19 x 13 cm.; pp. 179. Dresden: Theodor Steinkopff, 1932. Price RM. 8.

This book is not, as its title states, merely a dictionary of colloidal chemistry. The treatment lies between that adopted in a standard English dictionary and that in an encyclopedia, the more important topics being treated in greater detail; for example, the phenomenon of swelling is given over four pages, adsorption and its related phenomena in its general aspects, nine pages, while seventy-word paragraphs suffice for such subjects as the Hofmeister series, the smectic condition, and thixotropy. The name of the author of the term is given wherever possible, and sometimes the full reference, and at the end is a useful list of the important books on various aspects of colloid chemistry.

This book will satisfy a definite need at this time. There is such a vast output of literature on the subject, and the terms used have multiplied at such a rate, that it is often difficult even for a worker in this field to keep track of the many terms which research workers so delight in introducing. If colloid chemists have this difficulty, what must be the plight of those specializing in other branches—physicists, biologists, and technical scientists—when they encounter such terms as "eukolloid," "Pringheim's rule," "polyone" and "lyosorption?" A large number of these will, it is hoped, fall into disuse, and, indeed, one of the results of the publication of this dictionary should be a great simplification of colloid-chemical terminology.

It is difficult to find any serious omissions in this volume. It is inevitable that one wishes in one place for greater, and in another place for considerably less detail. Dr. Kuhn is to be congratulated sincerely on an achievement of very considerable value to colloid chemistry.

D. C. JONES.

Die Industrielle Herstellung von Wasserstoff. By DR. HEINRICH PINCASS. 22 x 15 cm.; pp. 82. Dresden & Leipzig: Verlag von Theodor Steinkopff, 1933. Price RM. 6.50; bound RM. 7.30.

The industrial preparation of cheap hydrogen is one of the outstanding problems of the heavy chemical industry. As the lightest gas its cost per ton remains high, although expressed per thousand cubic feet it appears remarkably low. A new industry of coal and oil hydrogenation awaits the advent of low priced hydrogen. Although there is an extensive literature on the subject, largely scattered in technical publications, there has been hitherto no book summarizing the present state of affairs. The present work is commendably short: it is primarily written for the chemist.

The alternative processes discussed are those starting from water gas, from coke-oven gas, from hydrocarbons, the iron contact process, sundry chemical processes, and the electrolytic, to which last the greatest space is allotted. A few pages are devoted to atomic hydrogen and to a list of patent numbers; at the end there is a critical summary and the usual author and subject indices.

This is not the place to discuss even the chief points of the various rival processes; the author, like other experts at the present time, leaves the reader to take his choice between water gas and coke-oven gas as the cheapest source of raw material according to the engineering conditions. The adoption of the hydrocarbon or electrolytic processes depends on the cost of these gases or of electric energy under specially favourable circumstances. Something below 1 shilling per 1,000 cubic feet of hydrogen appears to be the lowest price at which it can be produced even on the largest scale. This is a remarkable achievement in relation to the cost of a town's gas at a gas works.

E. F. ARMSTRONG.

STUDIES IN COPRECIPITATION.[1] III

THE WATER CONTENT OF CALCIUM OXALATE MONOHYDRATE

ERNEST B. SANDELL[2] AND I. M. KOLTHOFF

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received June 6, 1932

Calcium oxalate precipitated from aqueous solutions usually consists of the monohydrate. In addition to the one molecule of water of crystallization, the air-dried precipitate contains an excess of water, which may be present (a) in the form of a higher hydrate of calcium oxalate, (b) as occluded water in the interior of the crystal, (c) as adsorbed water at the external and internal surface of the monohydrate (hygroscopic water). In connection with a study of the coprecipitation of various ions with calcium oxalate, it was desirable to have some information on the conditions of formation of the higher hydrates, and their stability, if left in contact with the supernatant liquid. Calcium oxalate monohydrate has been recommended as a weighing form for calcium, the precipitate being weighed in the air-dry state or after heating at 100°C. to 105°C. From the analytical point of view, therefore, it is of great importance to obtain some definite information on the amount of water occluded by the precipitate, and on its hygroscopic character.

THE HIGHER HYDRATES OF CALCIUM OXALATE

The stable form of calcium oxalate is the monohydrate; it forms monoclinic crystals of widely varying appearance. According to G. Hammarsten (2) it is obtained in pure form either by precipitation from concentrated aqueous solutions of calcium salts and oxalate or from much more dilute solutions (0.001 to 0.002 *M*). Hammarsten states that the monohydrate is not hygroscopic in the real meaning of the word, but easily contains nearly 1 per cent of moisture, because of which it must be dried at 30–40°C. This statement is not exact; the pure monohydrate is definitely hygroscopic, as will be shown later in this paper. By precipitation from

---

[1] From a thesis submitted by Ernest B. Sandell (Du Pont Fellow in Chemistry) to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy (1932).

[2] Lack of space prevents the description of precipitations made in acid, alcoholic, etc. solutions. The conditions are merely indicated in table 1. For full details see the thesis of E. B. Sandell, University of Minnesota, 1932.

approximately 0.07 to 0.02 M aqueous solutions, a precipitate consisting of a mixture of the mono- and di-hydrate is obtained. At first view it may seem strange that the monohydrate alone is precipitated from more dilute solutions; this behavior, however, may be explained by assuming that at extreme dilutions the solutions are supersaturated only with respect to the monohydrate. According to Hammarsten it is hard to prepare the dihydrate, which crystallizes in the tetragonal system, in a pure form; it is much easier to isolate the trihydrate, which crystallizes in the rhombic system. Both higher hydrates have been prepared by precipitation from more or less dilute hydrochloric acid solutions. The di- and tri-hydrate are not stable when left in contact with the supernatant liquid and are transformed into the stable monohydrate. Excess of calcium ions inhibits the transformation, whereas oxalate ions favor it. Since in fairly strong acid medium most of the oxalate is present in the form of bioxalate ions and undissociated oxalic acid, it may be expected that free mineral acid will favor the stability of the higher hydrate.

In the following experiments, calcium oxalate was precipitated under conditions comparable with those obtaining in the study of coprecipitation phenomena. Precipitations were made either by (1) the ordinary method or (2) the method of Hahn (3). In the former case, if calcium was to be in excess during the precipitation, 20 cc. of 0.25 N ammonium oxalate were added from a buret to 24 cc. of 0.25 N calcium chloride (i.e., an excess of 20 per cent) mixed with sufficient water to give a final volume of 100 cc.; and, conversely, if oxalate was to be in excess, 20 cc. of calcium solution were added to 24 cc. of oxalate. The time of addition of precipitant was one minute. In the method of Hahn, 0.25 N calcium chloride and ammonium oxalate solutions were added simultaneously from separate burets to 50 cc. of water at such a rate that one solution was kept 1 cc. in excess of the other throughout the addition; the time of addition was 15 to 20 minutes.[2]

The precipitates were collected by filtration in sintered glass filtering crucibles, washed with alcohol, then with ether, dried by suction in laboratory air and weighed; they were then heated to 100–110°C. to remove water in excess over that of the monohydrate, cooled in a sulfuric acid desiccator, and again weighed; finally the weight was determined after constancy had been reached at room temperature and at the same humidity as before the heating. The difference between the first and third weighings gives the approximate amount of higher hydrate present in the original precipitate. The amount of water present as higher hydrate found in this way is only approximately correct, because it is assumed that the hygroscopic character of the precipitate is not changed by heating to 100–110°C., and that the occluded water is quantitatively taken up again after drying. The figures on the loss of non-hygroscopic water on drying at 100–110°C.,

TABLE 1

Loss of non-hygroscopic water of calcium oxalate precipitates heated at 100°C.

PRECIPITATE NUMBER	MANNER OF PRECIPITATION	LOSS OF NON-HYGROSCOPIC WATER AT 100°C. *per cent*
1a	Oxalate added to excess calcium solution at room temperature	13.7
1b	Oxalate added to excess calcium solution at room temperature	3.7
1c	Oxalate added to excess calcium solution at room temperature	11.4
2a	Precipitated as in 1a, but stood in solution 31 days	0.4
2b	Precipitated as in 1a, but stood in solution 12 days	0.1
2c	Precipitated as in 1a, but stood in solution 20 hours	0.15
3a	Calcium added to excess oxalate solution at room temperature	7.9
3b	Calcium added to excess oxalate solution at room temperature	7.8
4	Precipitated as in 3a, but stood 12 days	0.3
5a	Oxalate added to calcium in hot solution	0.25
5b	Oxalate added to calcium in hot solution	0.3
6a	Calcium added to oxalate in hot solution	0.35
6b	Calcium added to oxalate in hot solution	0.35
6c	As in 6a, except larger excess oxalate	1.0
6d	Precipitated as in 6a, but stood 17 days	0.2
7	Neutralization of cold acid solution containing excess calcium	3.0
8	Neutralization of cold acid solution containing excess oxalate	0.1
9	No. 7 repeated in hot solution	0.2
10	No. 8 repeated in hot solution	0.1
11	Precipitated in dilute HCl solution without neutralization	approx. 15.0
12a	Method of Hahn, cold, calcium in excess	approx. 1
12b	Method of Hahn, cold, calcium in excess	1.2
12c	Method of Hahn, cold, calcium in excess	0.5
12d	As in 12a, but stood 1 month	0.3
13a	Method of Hahn, cold, oxalate in excess	0.6
13b	Method of Hahn, cold, oxalate in excess	0.25
14	Method of Hahn, hot, calcium in excess	0.05
15	Method of Hahn, hot, oxalate in excess	0.1
16	Method of Hahn, cold acid solution, oxalate in excess	0.25
17	No. 16 repeated in hot solution	0.15
18	Method of Hahn, acetic acid solution, room temperature	approx. 6
19	Method of Hahn, alcoholic solution, room temperature	2.0

as reported in table 1, give the amount of water present as higher hydrate of calcium oxalate and part of the occluded water; if these figures are smaller than 0.5 per cent it may be safely assumed that no appreciable amount of higher hydrate was present in the original precipitates. It may be mentioned that the experiments described have not been carried out with the intention of finding the proper conditions of preparing the higher hydrates, but with the view to obtaining the approximate composition of the precipitates prepared under various conditions. Since the higher hydrates are more or less rapidly transformed into the monohydrate when left in contact with the mother liquor, it is difficult to get exactly reproducible results, as the time of filtration and washing differs in the various cases. Especially the precipitates formed at room temperature under ordinary conditions are very finely divided and require several hours to filter and wash.

Transformation of the pure dihydrate into the monohydrate results in a loss in weight of 10.98 per cent; of the trihydrate into the monohydrate of a loss of 19.78 per cent.

DISCUSSION OF RESULTS

1. Calcium oxalate precipitated at room temperature from approximately 0.1 N calcium solution contains more water than corresponds to the dihydrate. A lower water content is found if the oxalate is in excess during the precipitation; this may be explained by the fact that excess oxalate promotes the transformation of the higher hydrates into the monohydrate more than an excess of calcium does. In any case the transformation to the monohydrate is complete if the precipitate is allowed to stand in contact with the mother liquor at room temperature for a day or longer. This transformation takes place much more rapidly at higher temperatures.

2. If the precipitation is made at room temperature from extremely dilute solutions (Hahn's procedure (3)) very little higher hydrate is formed (experiments 12 and 13). Probably the conditions are such that the solution during the precipitation is supersaturated only with respect to the monohydrate. Addition of much acetic acid or alcohol favors the higher hydrate formation in Hahn's method of precipitation, for these substances materially decrease the solubilities of the various forms of calcium oxalate (experiments 18 and 19). Fairly slow precipitation of calcium oxalate from acid solutions at room temperature favors the separation of the monohydrate (solubility effect, experiments 7 and 8).

3. The monohydrate alone is formed under all conditions if the precipitations are carried out in hot solutions.

4. The dry higher hydrates are quickly transformed into the monohydrate on heating at temperatures of 100°C. and above. If kept at room temperature in an atmosphere of relative humidity between 25 and 60 per cent, they slowly lose water and finally are completely transformed into the monohydrate.

WATER OF HYGROSCOPICITY IN CALCIUM OXALATE MONOHYDRATE

Calcium oxalate was precipitated under most varied conditions, collected by filtration in a sintered glass crucible, washed free of electrolytes, and weighed after drying in the air or in a desiccator of constant humidity at room temperature (weight I). The air-dry precipitates were then heated at temperatures of 100–105°, 110°, 115°, 120°, and 125°C., respectively, until constant weight was obtained, then cooled in a sulfuric acid desiccator and weighed in a closed weighing bottle in order to prevent adsorption of water at room temperature (weight II). This precaution was necessary since most precipitates were so hygroscopic that they increased in weight on the balance, if weighed open to the air. The theoretical weight of the calcium oxalate monohydrate was found by one of the following methods.

1. Exactly known amounts of calcium in the form of calcium chloride solutions or of pure calcium carbonate were weighed out, and from this the weight of calcium oxalate was calculated (precipitates 2a, 2b, 8a, 8b, 9, 10, 11, 13, and 14 only).

2. In most cases the calcium content was determined in the precipitates, after they had been dried to constant weight, by converting the oxalate to calcium sulfate and weighing as such. By this procedure any coprecipitated ammonium oxalate or bioxalate was quantitatively removed, whereas all calcium present in the precipitate as calcium hydroxide or chloride was weighed as sulfate. In many cases the oxalate content of the dried precipitates was determined by dissolving a known part in warm dilute sulfuric acid and titrating with permanganate according to the standard procedure, using weight burets instead of ordinary burets, and correcting for the titration error by determining iodometrically the slight excess of permanganate which was required for the color change. These oxalate determinations were accurate to at least 0.1 per cent. As shown by the results in table 2, the ratio of calcium to oxalate is as a rule not exactly equal to 100:100. Sometimes there is a slight excess of oxalate, owing to coprecipitation of ammonium oxalate or bioxalate or oxalic acid; the precipitates obtained from neutral or ammoniacal solutions are usually deficient in oxalate because of coprecipitation of hydroxyl ions in the form of calcium hydroxide. These coprecipitations will be discussed more extensively in following papers. From the above it is evident that the difference between the "theoretical weight" of calcium oxalate and weight II does not give the exact amount of occluded water, even if the latter were entirely removed by drying at 100°C. to 110°C. Nevertheless, these deviations are reported in table 2, since these data are of greater analytical significance than those referring to the exact amount of occluded water.

The water of hygroscopicity was found by exposing the precipitates which had been dried to constant weight at 100–110°C. to air or to an atmosphere of constant humidity (the same as before the heating) until constant weight was obtained (weight III). The difference between weight I and weight II gives the hygroscopic water, which should be the same as that found from weights III and II, in case the adsorption of water is reversible and no higher hydrate is formed. It will be seen that

TABLE 2

Non-essential water of calcium oxalate monohydrate precipitates

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	CRYSTAL SIZE	RATIO Ca:C$_2$O$_4$	DEVIATION IN PER CENT FROM CALCULATED WEIGHT OF CaC$_2$O$_4$·H$_2$O				
				Air-dried	Dried at 100–105°C.	Dried at 110–115°C.	Dried at 115–120°C.	Rehydrated
		microns						
1a	0.200 *N* ammonium oxalate added to equivalent amount of 0.200 *N* calcium chloride at 100°C.	<1		+0.90	+0.35 (1)* +0.3 (18)	−0.1 (45)	−0.25 (3) −0.25 (15)	
1b	Same as 1a	<1			+0.45 (18)	+0.3 (18)	−1.4 (22) −1.55 (4) −3.4 (20)	
2a	Excess ammonium oxalate added to 200 cc. of dilute calcium solution at 100°C.			+0.85 *R. H.* = 57 per cent	+0.3 (5) +0.1 (15) +0.1 (15)	−0.15 (18)	−0.55 (22) −7.6 (20)	+0.7 *R. H.* = 57 per cent
2b	Same as 2a			+0.3	−0.2 (12) −0.3 (17)			
3a	20 cc. of calcium chloride added to 24 cc. of ammonium oxalate in 80 cc. of solution at room temperature	<0.5	100.0:100.55	+12.0 (1½) +11.6 (18)	+1.05 (4) +1.1 (18)			2.6 (3d)†
3b	Same as 3a	<0.5		+9.2 (18) +2.05 (3 weeks) *R. H.* = 29 per cent	+0.35 (22)			+1.3 (3d) *R. H.* = 29 per cent
4	3a repeated at 100°C.	1–2	100.0:99.61	+2.2 (2)	−0.20 (48)	−0.35 (1)		+1.79 (24) *R. H.* = 29 per cent

5	50 cc. of 0.25 *N* calcium chloride added to 50 cc. of 0.50 *N* ammonium oxalate in a volume of 350 cc. at 100°C.	1	100.0:100.0	+2.2 (3 days)	+0.45 (15)		+0.45 (66)	+1.4 (1 month) *R. H.* = 29 per cent
6	20 cc. of ammonium oxalate added to 24 cc. of calcium chloride in 80 cc. of solution at room temperature	<0.5	100.0:100.76	+16.1 (*R. H.* = 25 per cent +2.05 (3 weeks) *R. H.* = 29 per cent	+0.75 (22)			+1.4 (1 week) *R. H.* = 29 per cent
7	6 repeated at 100°C.	0.5-1	100.0:99.49	+2.15 *R. H.* = 40 per cent	+0.1 (18)			+1.5 (3 months) *R. H.* = 29 per cent
8a	Calcium precipitated from dilute solution very weakly ammoniacal with ammonium oxalate at 100°C.	Coarsely crystalline	100.00:99.00	+0.6 (23) +0.5 (25)	+0.6 (69)		+0.25 (20) −2.6 (45)	
8b	Same as 8a		100.00:99.69				−1.7 (20)	
9	As in 8a except temperature = 25°C.	<1					+0.25 (24)	
10	As in 8a except solution was strongly ammoniacal 20 cc. of 2.5 *N* ammonia in 200 cc.		100.00:98.34				−3.6 (5) −3.9 (2) −4.5 (3) −9.1 (15)	
11	Similar to 10; 10 cc. of 2 *N* ammonia in 200 cc. of solution		100.00:99.73	+2.0 +1.5 (66) *R. H.* = 0	+1.15 (2)		+1.05 (40)	
12	Oxalic acid added to calcium solution acidified with HCl; then neutralized at 100°C. with ammonia		100.00:100.09		+0.8 (1) +0.3 (17)		+0.35 (1) +0.2 (1) +0.3 (17)	

TABLE 2—*Continued*

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	CRYSTAL SIZE	RATIO Ca:C_2O_4	DEVIATION IN PER CENT FROM CALCULATED WEIGHT OF $CaC_2O_4 \cdot H_2O$				
				Air-dried	Dried at 100–105°C.	Dried at 110–115°C.	Dried at 115–120°C.	Rehydrated
13	Excess ammonium oxalate added to acid solution of calcium and neutralized at 100°C.	*microns* 5		+0.85 (20) +0.7 *R. H.* = 0	+0.7 (1)	+0.7 (2)		
14	50 cc. of 0.5 *N* ammonium oxalate added to 50 cc. of 0.25 *N* calcium solution in 300 cc. of hot water + 5 cc. of HCl. Neutralized with ammonia			+1.3 (1½) +0.85 (18) *R. H.* = 0	+0.7 (1) +0.65 (7)		+0.6 (18)	
15	Nearly the same as 14			+1.7 (2)	+0.7 (22) +0.7 (22)		+0.7 (66)	
16	Excess ammonium oxalate added to 50 cc. of calcium solution in volume of 250 cc. 10 cc. of 6 *N* acetic acid present. Temperature = 100°C.			+2.0 (½) +1.05 *R. H.* = 0	+1.05 (1) +1.05 (1)		+1.05 (2)	
17	20 cc. of ammonium oxalate added to 24 cc. of calcium chloride in 80 cc. of solution + 2 cc. of concd. HCl. Temperature = 100°C.			+1.1 (3 days)	+0.2 (20)			+0.95 (4) +1.2 (several weeks) *R. H.* = 57 per cent
18	Same as 17 except 20 cc. of calcium solution added to 24 cc. of diluted oxalate solution			+2.0	+0.9 (20)			+1.9 (4) 2.0 (4) *R. H.* = 60 per cent
19	Excess ammonium oxalate added to 200 cc. of hot dilute calcium solution containing 2 cc. of concd. HCl; then neutralized with dilute ammonia		100.00:100.34	+1.25 (2) +1.05 (2 weeks) *R. H.* = 0	+0.8 (2)	+0.35 (48)		+0.9 (3 weeks) *R. H.* = 29 per cent

20	Method of Hahn. Calcium in excess. Neutral solution. Room temperature	1-2	100.00:99.50	+2.7 (18) +2.6 (24)	+0.7 (2½)	0.5 (20)		+1.9 (44) *R. H.* = 29 per cent
21	Method of Hahn. Oxalate in excess. Room temperature	2-4	100.00:99.95	+3.3 (20) *R. H.* = 40-50 per cent	+1.05 (2½)	+0.85 (20)		+1.3 *R. H.* = 29 per cent
22	Method of Hahn. Calcium in excess. Hot solution	5-10	100.00:99.30	+0.4 (20) *R. H.* = 55 55 per cent	+0.15 (2)	−0.1 (20)		+0.25 (20) *R. H.* = 29 per cent
23	Method of Hahn. Oxalate in excess. Hot solution	ca.5	100.00:99.52	+0.5 (20)	0.0 (2½)	−0.15 (2)		+0.35 (20) *R. H.* = 29 per cent
24	Method of Hahn. Acid solution. Oxalate in excess. Room temperature	2-4	100.00:99.94	+2.3 (24) *R. H.* = 30-40 per cent	+1.05 (18)			+2.2 (100) *R. H.* = 29 per cent
25	Same as 24 except in hot solution.	4		+0.05 (48) *R. H.* = 40 per cent	−0.1 (1) −0.05 (48)			0.0 (100) *R. H.* = 29 per cent
26a	Precipitated in cold neutral solution, then digested at 100°C. for 24 hrs.	3	100.00:99.88	+0.1 (48)	−0.15 (72)			−0.10 (24) *R. H.* = 29 per cent
26b	Same as 26a	3	100.00:99.71	+0.20 (1) *R. H.* = 25 per cent	0.00 (2)			+0.2 (24) *R. H.* = 29 per cent
27a	Same as 26a except oxalate in excess	2-3	100.00:99.54	−0.5 (48)	−0.7 (3)			−0.6 (48) *R. H.* = 29 per cent
27b	Same as 27a	2-3	100.00:99.73	+0.11 (1) *R. H.* = 25 per cent	−0.26 (18)			+0.11 (48) *R. H.* = 29 per cent

TABLE 2—*Concluded*

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	CRYSTAL SIZE	RATIO Ca:C_2O_4	DEVIATION IN PER CENT FROM CALCULATED WEIGHT OF $CaC_2O_4 \cdot H_2O$				
				Air-dried	Dried at 100–105°C.	Dried at 110–115°C.	Dried at 115–120°C.	Rehydrated
		microns						
28	Same as 26 except precipitated in hot solution	1–2	100.00:99.58	−0.1 (48)	−0.35 (3)			−0.2 (24) *R. H.* = 29 per cent
29	Same as 27 except precipitated in hot solution	2	100.00:99.73	+0.2 *R. H.* = 30 per cent	−0.05 (3)			+0.1 (48) *R. H.* = 29 per cent
30	Precipitated in neutral solution. Calcium in excess. Then digested in presence of dilute HCl for 1 day	3–4	100.00:100.06	+0.05 (24)		−0.05 (48) −0.1 (20)		
31	Same as 30 except oxalate in excess	4	100.00:100.31	−0.2 (24)		−0.25 (48) −0.35 (20)		
32	Precipitation in acetic acid solution followed by digestion	2	100.00:100.2	+0.18 (½) *R. H.* = 30 per cent		−0.10 (1½)		
33	Precipitation in dilute acetic acid solution followed by digestion in ammoniacal solution	2	100.00:100.1	+0.38 (½) *R. H.* = 30 per cent		+0.05 (1½)		
34	Precipitation in acetate buffer, followed by digestion		100.00:100.3	+0.22 (½)	+0.02 (1)			
35	Precipitated as in 34 and digested in ammoniacal solution		100.00:99.8	+0.31 (½)	−0.06 (1)			
36	Precipitation in ammoniacal solution followed by digestion in acetate buffer		100.00:100.1	+0.26 (½)	+0.02 (1)			

---

* The figures in parentheses refer to the time of drying in hours.

† d = days.

within reasonable limits this water of adsorption can be reversibly removed and taken up. The rehydration takes place fairly rapidly; the weight of the dried precipitates was practically constant after twenty-four hours in most cases. By special experiments it was shown that the hygroscopic character is very strongly pronounced at low humidities; the hygroscopic water content did not materially change at relative water vapor tensions between 25 and 50 per cent.

EXPLANATION OF TABLE 2

In the third column the approximate average crystal size of the precipitate is given; in the fourth, the ratio calcium:oxalate as experimentally determined. The fifth column gives the difference in weight between the air-dried precipitate and the theoretical weight of calcium oxalate monohydrate (the relative humidity (= *R. H.*) of the air in all the experiments was within 25 to 60 per cent and is indicated in the table; *R. H.* = 29 per cent means that the drying was done over deliquescent calcium chloride crystals; *R.H.* = 57 per cent signifies that the drying was done over deliquescent sodium bromide dihydrate at 25°C.). The figures occurring in parenthesis after the percentage deviations refer to the time of drying in hours. The sixth, seventh, and eighth columns give the difference in weight between the dried precipitates and the theoretical. The last column in the table headed "Rehydrated" contains the deviations from the theoretical weights as obtained by exposing the precipitates dried at 100–130°C. to air at relative humidities of 25 to 60 per cent at room temperature and weighing when equilibrium was attained. Such treatment restores most, if not all, of the hygroscopic water lost by heating.

In table 3 the hygroscopic, or reversible, water of the various calcium oxalate precipitates has been given. The data presented in this table have been drawn from table 1 as well as from table 2 as indicated by the numbering of the precipitates. (I refers to table 1, II to table 2). The hygroscopic water was determined by obtaining the weight of the precipitate heated to 105°C., and then placing the precipitate over a saturated solution of calcium chloride hexahydrate or in some other atmosphere of humidity between 25 and 50 per cent, and reweighing after constant weight had been attained. The increase in weight is the amount of hygroscopic water in the precipitate.

In some cases the non-reversible water of the precipitate is also given. The amount of non-reversible water was obtained by weighing the precipitate kept over calcium chloride hexahydrate before and after drying at 105°C. (weight I − weight III). The weight of water not recovered after heating has been called the non-reversible water.

TABLE 3

Hygroscopic water of calcium oxalate monohydrate

PRECIPITATE NUMBER		MANNER OF PRECIPITATION	CRYSTAL SIZE	OXALATE CONTENT	HYGROSCOPIC WATER	NON-REVERSIBLE WATER
			microns	*per cent*	*per cent*	*per cent*
I*	1a	Oxalate added to calcium at R. T.†	<0.5		1.4	
I	1c	Oxalate added to calcium at R. T.	<0.5		0.9	
II‡	6b	Oxalate added to calcium at R. T.	<0.5	100.76	1.0	
I	1b	Oxalate added to calcium at R. T. Stood dry 3 weeks before heating	<0.5		0.5	
II	6a	Same as II b	<0.5		0.65	
I	2c	Oxalate added to calcium at R. T. Stood in solution 20 hours			0.65	<0.15
I	2b	Oxalate added to calcium at R. T. Stood in solution 12 days			0.5	0.1
I	2a	Oxalate added to calcium at R. T. Stood in solution 31 days			0.4	
I	3a	Calcium added to oxalate at R. T.	<0.5		1.7	
II	3a	Calcium added to oxalate at R. T.	<0.5		1.5	
I	3b	Calcium added to oxalate at R. T. Stood dry 3 weeks	<0.5		0.9	
II	3b	Calcium added to oxalate at R. T. Stood dry 3 weeks	<0.5		0.95	
I	4b	Calcium added to oxalate at R. T. Stood in solution 12 days, then dry 5 weeks			0.45	0.15
I	5a	Oxalate added to calcium at 100°C.			1.7	0.2
II	7	Oxalate added to calcium at 100°C.	0.5–1	99.49	1.45	0.6
I	5b	Oxalate added to calcium at 100°C. Stood dry 5 weeks	0.5–1		ca. 0.8	ca. 0.5
I	6a	Calcium added to oxalate at 100°C.			1.8	0.35
II	4	Calcium added to oxalate at 100°C.	1–2	99.61	2.0	<0.4
II	5	Calcium added to oxalate at 100°C. Stood dry 3 days	1	100.0	0.95	0.8
I	6b	Calcium added to oxalate at 100°C. Stood dry 5 weeks			0.7	0.15

I	6c	Similar to I 6a. Stood dry 3 days			0.7	1.0
I	6d	Calcium added to oxalate at 100°C. Stood in solution 17 days and then dry 20 days			0.5	0.2
I	7	Neutralization of acid solution containing excess calcium. R. T.	1-2		1.1	
I	8	Neutralization of acid solution containing excess oxalate. R. T.	1-2		1.05	0.1
I	9	Neutralization of acid solution containing excess calcium at 100°C.			0.7-0.9	0.0
I	10	Neutralization of acid solution containing excess oxalate at 100°C.			1.1	0.1
II	13	Neutralization of acid solution containing excess oxalate at 100°C. Stood dry for several weeks	5		0.15	0.0
II	14	Similar to I 10			0.5	
II	19	Similar to I 10. Stood over sulfuric acid 2 weeks before heating		100.34	0.0 (105°C.) 0.5(115°C.)	0.35
II	16	Oxalate added to calcium in dilute acetic acid solution at 100°C.			1.0	
II	17	Oxalate added to calcium in dilute HCl solution at 100°C.	Coarse		0.9	0.0
II	18	Calcium added to oxalate in dilute HCl solution at 100°C.	Coarse		1.1	0.0
I	12b	Hahn method. Calcium in excess. R. T.			1.4	
I	12c	Hahn method. Calcium in excess. R. T.			1.2	
II	20	Hahn method. Calcium in excess. R. T.	1-2	99.50	1.4 1.85 (125°C.)	
I	12d	Hahn method. Calcium in excess. R. T. Stood 1 month			0.6	<0.3
I	13a	Hahn method. Oxalate in excess. R. T.			1.6	
II	21	Hahn method. Oxalate in excess. R. T.	2-4	99.95	1.7	
I	13b	Hahn method. Oxalate in excess. R. T. Stood dry 1 month			0.45	<0.25
I	14	Hahn method. Calcium in excess at 100°C.			0.25	0.05

* I refers to table 1.

† R. T. = room temperature.

‡ II refers to table 2.

TABLE 3—*Concluded*

PRECIPITATE NUMBER	MANNER OF PRECIPITATION	CRYSTAL SIZE	OXALATE CONTENT	HYGROSCOPIC WATER	NON-REVERSIBLE WATER
		microns	*per cent*	*per cent*	*per cent*
II 22	Hahn method. Calcium in excess at 100°C.	5–10	99.30	0.2 0.45 (125°C.)	<0.2
I 15	Hahn method. Oxalate in excess at 100°C.			0.4	0.1
II 23	Hahn method. Oxalate in excess at 100°C.	5	99.52	0.35 0.7 (130°C.)	0.15
I 16	Hahn method. Acid solution. Oxalate in excess. R. T.			1.2	0.05
II 24	Hahn method. Acid solution. Oxalate in excess. R. T.	2–4	99.94	1.15	0.1
I 17	Hahn method. Acid solution. Oxalate in excess. 100°C.	4–5		0.1	0.1
II 25	Hahn method. Acid solution. Oxalate in excess. 100°C.	4		0.1 0.3 (130°C.)	0.05
I 19	Hahn method. Alcoholic solution	<0.5		2.8	
II 26a	Precipitated in neutral solution. Digested. Calcium in excess	3	99.88	0.05 0.45 (130°C.)	0.2
II 26b	Precipitated in neutral solution. Digested. Calcium in excess	3	99.71	0.2 0.1	0.0
II 27a	Precipitated in neutral solution. Digested. Oxalate in excess	2–3	99.54	0.35 (130°C.)	0.1
II 27b	Precipitated in neutral solution. Digested. Oxalate in excess	2–3	99.73	0.35 0.15	0.0
II 28	Precipitated in neutral solution at 100°C. Digested. Calcium in excess	1–2	99.58	0.45 (130°C.)	0.3
II 29	Precipitated in neutral solution at 100°C. Digested. Oxalate in excess	2	99.73	0.55	0.0
II 30	Precipitated in neutral solution at R. T. Calcium in excess. Digested with HCl	3–4	100.06	0.1 (120°C.)	
II 31	Precipitated in neutral solution at R. T. Oxalate in excess. Digested with HCl	4	100.31	0.1	
II 32	Precipitated in acetic acid at R. T. Digested	2	100.2	0.3	
II 33	Precipitated in acetic acid at R. T. Digested in ammoniacal solution	2	100.1	0.3	

DISCUSSION OF RESULTS

1. Calcium oxalate monohydrate, no matter how precipitated, always contains excess water after drying in the air (relative humidity 25 to 60 per cent) at room temperature. On heating to 100°C. and above, part or sometimes all of this is lost, but nearly all is regained if the dried precipitate is allowed to stand in the air. The water lost on heating, therefore, is mostly hygroscopic water. This water can be reversibly taken up and removed. This process, however, is not strictly reversible on account of internal structural changes taking place in the crystalline precipitates on aging (vide infra); but over a short period of time the reversibility of the adsorption of water seems fairly well established.

2. The presence of small amounts of impurities (coprecipitated foreign ions) in the calcium oxalate does not seem to affect the hygroscopicity of the precipitate. Precipitates formed from solutions in which oxalate has been in excess during the precipitation are usually slightly more hygroscopic than those formed in the presence of excess calcium ions. This also proves that the hygroscopicity of calcium oxalate is not primarily due to coprecipitated calcium hydroxide.

3. The monohydrate sometimes decomposes on continued drying at 115–125°C. by losing monohydrate water. The decomposition is generally slow and usually does not begin until the precipitate has been heated for some time. The loss of monohydrate water seems to be limited to precipitates formed in neutral or ammoniacal solutions, especially at 100°C., i.e., to those precipitates which have occluded calcium hydroxide or basic oxalate.

4. Precipitates formed from approximately 0.1 *N* solutions are fairly hygroscopic and contain in the air-dry state 1 to 1.8 per cent of adsorbed water. The hygroscopicity decreases with time of standing (especially at higher temperatures) before filtration, owing to recrystallization of small particles to larger ones and partly to internal perfecting of the crystals, by which process the internal surface is decreased. The distinct decrease of hygroscopicity after digestion in the mother liquor is clearly demonstrated by the results of experiments II 2ba to II 33; the phenomenon is of great analytical significance. Precipitates prepared under the worst analytical conditions, viz., at room temperature from fairly concentrated solutions, and which retain about 1.5 per cent water in the air-dry state if filtered immediately after the precipitation, contain only 0.1 to 0.3 per cent of water of hygroscopicity if digested at 90–100°C. for a day before filtration. *If the precipitation is made at room temperature from about 0.1 N solutions slightly acid* (acetic acid, or acetate buffer, pH 4–6) *and if the precipitate thus obtained is digested in the mother liquor for at least 20 hours at a temperature of approximately 90°C., then a product is obtained which in the air-dry state contains 0.1 to 0.3 per cent of adsorbed water and in*

which the ratio of calcium to oxalate is almost equal to the theoretical (100:100.1 to 100.2) (experiment II 32, 33). In a study of the coprecipitation of foreign ions with calcium oxalate (to be described in following papers), it was found that the purest precipitate is obtained under exactly the same conditions. *Precipitation of calcium oxalate from relatively concentrated solutions at room temperature followed by digestion, therefore seems to be the best procedure from the analytical point of view in spite of the fact that the precipitate is of relatively small size and as a rule cannot be filtered as rapidly as one obtained under ordinary analytical conditions.*

5. A distinct decrease in hygroscopicity is even noticed on the aging of air-dry crystals (experiments I 1b; II 4, 5; I 6b, c, d; I 10; II 13), enough water apparently being present in the interior of the crystals to allow internal structural changes to take place and thus cause a perfection of the crystalline precipitate, by which the porosity of the crystals appears to decrease. From the various examples given in the tables it is evident that a great deal of the adsorbed water is present at the walls of the capillaries in the interior of the crystals. As long as these canals remain in open communication with the exterior, the process of adsorption and desorption will be reversible. If during the process of inner perfection of the crystals the capillaries are all filled by the constituents of the precipitate itself, all the water in the interior of the crystals will be driven out. On the other hand, if dams or similar obstructions are formed in the capillaries, the hygroscopic character will decrease, but the water inside the dams will no longer be in communication with the exterior of the crystal and will remain in the inside as *occluded water;* the latter will be driven out only at high temperatures. From a preliminary study of the internal structural changes taking place in a fresh precipitate, to be described later, it was inferred that the process of "dam-formation" may be quite general, thus explaining why occluded water and coprecipitated foreign ions adsorbed during the growth of the crystals are only partly removed by digesting fairly coarse crystals after precipitation. A more thorough study of the behavior of occluded water under various conditions will be made in the future; calcium oxalate is not a suitable substance for such an investigation, since it already contains one molecule of water of crystallization and under certain conditions forms higher hydrates. The tremendous purification taking place during the digestion of calcium oxalate formed at room temperature from relatively concentrated solutions may be a more or less specific case, since a transformation of the higher hydrates and an entire recrystallization takes place on digestion.

6. Calcium oxalate formed at 100°C. more or less under analytical conditions, is strongly hygroscopic (1 to 1.5 per cent water adsorbed) if collected soon after the precipitation. On aging in contact with the mother liquor, or in the dry state, its hygroscopicity decreases three to four times,

but is higher than that obtained by digesting a precipitate formed in the cold. The phenomenon described under paragraph 5 explains this difference. That the original hygroscopicity is mainly due to the large internal surface is clearly demonstrated by the results of experiments in which the precipitation was made slowly at 100°C. from neutral or weakly acid solutions. The air-dry precipitate still contains about 1 per cent of water of hygroscopicity (I 7, 8, 9; II 16, 17, 18), although fairly coarse particles of calcium oxalate are formed. The same holds for a precipitate prepared at room temperature according to Hahn's procedure (precipitation from extremely dilute solutions). In spite of the fact that the crystal size is of the order of 1 to 4 microns the air-dry crystals still contain 1.5 to 1.8 per cent of water; on aging at room temperature, even in the dry state, the hygroscopic water content decreases three- to four-fold (experiments I 12d, 13a, 13b; II 20). Precipitates obtained according to Hahn's procedure in the presence of 30 to 40 per cent alcohol are strongly hygroscopic (I 19). On the other hand, if the precipitation is carried out at 100°C. according to Hahn, the crystals are only slightly hygroscopic (0.1 to 0.4 per cent of adsorbed water; experiments I 14, 15, 16, 17, 19; II 22, 23, 24, 25).

7. From the figures in table 2 under the heading "Deviation in per cent from calculated weight of calcium oxalate" it is evident that calcium oxalate even after drying at 110°C. is not an ideal weighing form for calcium. High results (indicated by +) must be attributed to occluded water and coprecipitated alkali oxalates or bioxalates, in cases where the ratio calcium : oxalate is smaller than 1.000. Low results may be obtained if there is a hydroxyl coprecipitation (calcium:oxalate larger than 1.000), although a compensation of errors takes place on account of the presence of occluded water.

From the analytical point of view it is gratifying to find that almost theoretical results (within 0.1 per cent) are obtained if calcium oxalate is precipitated at room temperature from not too dilute, weakly acid solutions and digested for twenty hours before filtration. Since such precipitates are virtually free from coprecipitated substances and not very hygroscopic, this procedure seems to be by far the best for the precipitation of calcium oxalate under analytical conditions. The analytical part of this study will be described elsewhere.

SUMMARY

1. Calcium oxalate precipitated at room temperature from approximately 0.1 *N* calcium solutions contains trihydrate. Oxalate promotes the transformation of the higher hydrates into the monohydrate more than calcium does. In any case this transformation is complete if the precipitate is allowed to stand in contact with the mother liquor at room

temperature for a day or longer, and takes place much more rapidly at higher temperatures. The dry higher hydrates are slowly transformed into the monohydrate at room temperature, if kept at a relative humidity of 25 to 60 per cent. At 100°C. the higher hydrates are quickly transformed into the monohydrate. The monohydrate alone is formed if the precipitations are made in hot solutions.

2. An extensive study has been made of the hygroscopic character of calcium oxalate prepared under various conditions. Calcium oxalate, no matter how precipitated, always contains excess water after drying in the air. The process of adsorption and desorption of water is fairly, but not strictly, reversible on account of internal structural changes taking place in a fresh precipitate on standing.

3. A great deal of the adsorbed water is present at the walls of internal capillaries in the crystals. On aging under the mother liquor, or more slowly in the air-dry state, a decrease in the amount of hygroscopic water is generally noticed. This may be explained by an internal perfection of the crystals on aging, which partly fills up the canals with constituents of the precipitate itself, and mainly by blocking up the canals. In the latter case part of the water remains in the occluded state and is only removed at high temperatures.

4. Calcium oxalate monohydrate, even after drying at 110°C., is not an ideal weighing form for calcium. The purest, and only slightly hygroscopic, calcium oxalate is obtained if the precipitation is made in relatively concentrated solutions, and the mixture is digested for about twenty hours at 90°C. before filtration. During this process a complete transformation of the higher hydrates and an entire recrystallization of the precipitate takes place.

5. Calcium oxalate monohydrate sometimes decomposes on prolonged drying at 115–125°C. with loss of water of hydration. This loss of water of crystallization seems to be limited to precipitates formed in neutral or ammoniacal solutions, especially at 100°C., i.e., to those precipitates which contain occluded calcium hydroxide or basic oxalate.

REFERENCES

(1) KOLTHOFF, I. M.: J. Phys. Chem. **36**, 860 (1931), for a general discussion of the phenomena of coprecipitation.

KOLTHOFF, I. M., AND PEARSON, E. A.: J. Phys. Chem. **36**, 549 (1932), for a discussion of the so-called coprecipitation of zinc with copper sulfide.

(2) HAMMARSTEN, GRETA: Compt. rend. trav. lab. Carlsberg **17**, No. 11 (1929), for the extensive study by Hammarsten, in which a literature review and the results of her own studies are given.

(3) HAHN, F. L., AND OTTO, R.: Z. anorg. allgem. Chem. **126**, 257 (1923).

THE CHEMISTRY OF BERYLLIUM. VI

REACTIONS OF SULFUR DIOXIDE WITH ORGANIC BERYLLIUM COMPOUNDS

HAROLD SIMMONS BOOTH AND VIRGIL D. SMILEY

Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio

Received October 31, 1938

PURPOSES OF THE INVESTIGATION

During studies of electrolysis of beryllium salts in non-aqueous solvents, Booth and Torrey (1) discovered that cold beryllium acetylacetonate rapidly absorbed sulfur dioxide to form a liquid. The sulfur dioxide could be boiled off by gentle warming and recondensed, dissolving the beryllium compound as frequently as desired without any apparent change in the beryllium acetylacetonate. A sample of the sulfur dioxide–beryllium acetylacetonate solution containing some crystals was sealed off in a test tube and has remained unchanged for the last eight years.

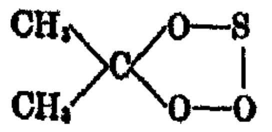
The remarkable absorbing power of this beryllium compound immediately suggested to the discoverers that, in the first place, the study of this reaction might yield information of interest, since it apparently represented a novel type of reaction, possibly a general one, with metallic compounds containing a C:O grouping. The second point is of course the possible application of this reaction to the development of an absorption type refrigerator.

HISTORICAL DISCUSSION

If, as Booth and Torrey thought, the reaction of sulfur dioxide on beryllium acetylacetonate was completely reversible, it would seem probable that the compound formed was of the so-called molecular compound type analogous to hydrates. In other words, the sulfur dioxide was absorbed as sulfur dioxide of crystallization. The question may be raised at once as to whether the absorption of sulfur dioxide is a function of the beryllium or of the organic part of the compound.

A search of the literature reveals no study of the action of sulfur dioxide on beryllium compounds, but certain reactions of sulfur dioxide on organic compounds have been studied.

H. O. Schulze (2) found that acetone absorbed a little less than two moles of sulfur dioxide per mole of acetone at 0°C. Boessneck (3) passed sulfur dioxide into acetone and found the gas to be absorbed with the evolution of considerable heat. He proposed the formula

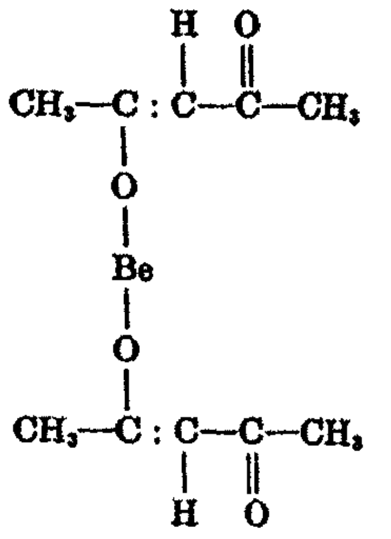


for this liquid compound. On heating it he found that it decomposed into its constituents. Apparently no one has studied this system precisely. Bellucci and Grassi (4) found that sulfur dioxide forms two compounds with camphor (a ketone of higher molecular weight), namely, (1) $SO_2C_{10}H_{16}O$, m.p. −45°C., and (2) $2SO_2.C_{10}H_{16}O$, m.p. −24°C. Very little else has been done with the reactions of sulfur dioxide and ketones.

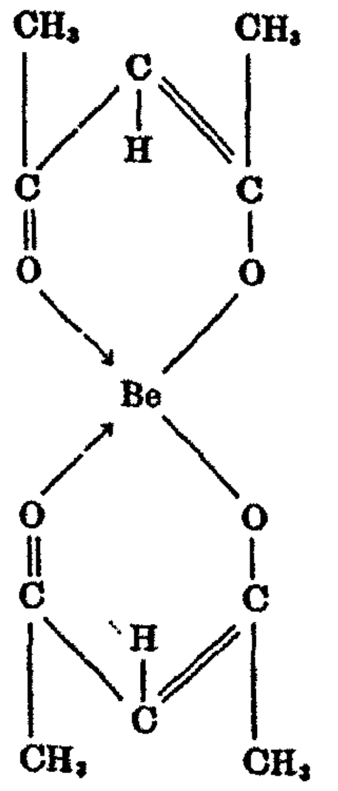
PLAN OF INVESTIGATION

It was thought that a study of the pressure-concentration relations in this system, at constant temperature, would best establish the nature of the reaction. This study would show: first, the solubility of the compound formed in liquid sulfur dioxide; second, the number of moles of sulfur dioxide reacting with one mole of the compound; third, the vapor pressure of the compound formed; fourth, the vapor pressure of the mixed salt and compound formed.

In order to determine whether it was a function of the beryllium or of other groups in the compound, other beryllium compounds were prepared and tested—such as beryllium basic acetate, beryllium ethyl acetoacetate, etc. Acetylacetone exists as an equilibrium mixture of the enol form and of the keto form, and the beryllium compound is probably



or



(Sidgwick)

There are two carbonyl groups still free through which the sulfur dioxide may react, or the sulfur dioxide may combine owing to the double bonds.

To see whether other similar enol-keto compounds were reactive with sulfur dioxide, beryllium ethyl acetoacetate and beryllium benzoylacetonate were tried. To check up on the importance of carbonyl groups in the reaction, such a compound as beryllium basic acetate, which contains both beryllium and carbonyl groups, was studied and also certain organic compounds such as benzophenone, urea, acetamide, etc., containing carbonyl groups but no beryllium.

The effect of replacing beryllium by sodium, magnesium, and aluminum, etc., was then tried, as well as a number of other salts of organic acids.

PREPARATION OF COMPOUNDS

The beryllium acetylacetonate, beryllium ethyl acetoacetate, beryllium basic acetate, beryllium benzoylacetonate and sodium acetylacetonate, were prepared in the course of study of the organic salts of beryllium (5). Compounds prepared in a similar manner were magnesium ethyl acetoacetate, magnesium acetylacetonate, and aluminum ethyl acetoacetate. Other compounds were from chemically pure material.

APPARATUS

The apparatus consists of three essential parts: the gas purification system (6), the constant temperature bath, and the baro-buret for measuring gas volumes and pressures (see figure 1). The entire apparatus was constructed of soda-lime glass fused together at all connections.

The constant temperature bath consisted of a gallon capacity Dewar flask, in which was mounted a thermostat (T), lamp for heating, stirrer (S), thermometer, and reaction tube (V). The lamp was controlled by means of a mercury–xylene expansion thermostat through a suitable relay and maintained a constant bath temperature within ±.001°C.

The baro-buret was used because it measures accurately and simultaneously pressure and volume in one instrument and thus cuts down the "dead space" from the buret to the reaction bulb to a minimum (7).

EXPERIMENTAL PROCEDURE

Preliminary tests

Before a system was studied a preliminary test was made in a sample bulb adjacent to the gas supply tank. Here the sample was placed in a suitable reaction bulb of about 5 cc. capacity and sulfur dioxide was condensed on it to see if the sample would dissolve. Slight solubility was checked by evaporating separately the supernatant sulfur dioxide. The preliminary tests showed that at the boiling point of sulfur dioxide, the following compounds were insoluble in sulfur dioxide and *apparently* did not react with it: barium acetate, copper acetate, lead acetate, sodium acetate, sodium formate, ammonium oxalate, ammonium tartrate, aluminum ethyl acetoacetate, magnesium ethyl acetoacetate, sodium acetylacetonate.

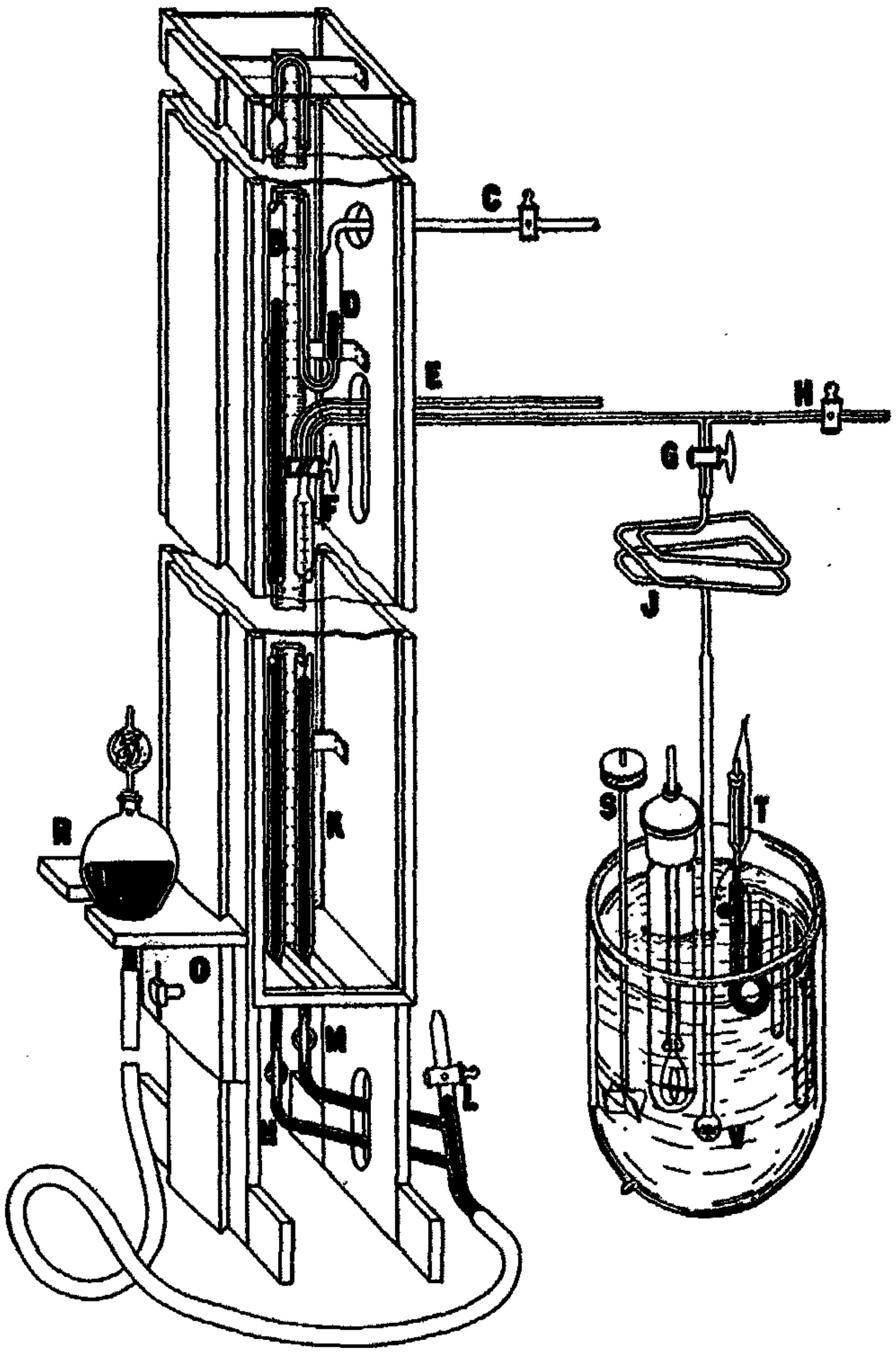


Fig. 1. Apparatus for Studying Absorption of Sulfur Dioxide by Organic Beryllium Compounds

The following substances seemed to show slight solubility or slight reaction with liquid sulfur dioxide at its boiling point: beryllium benzoylacetonate, magnesium acetylacetonate, benzophenone, urea. The urea seemed to swell in the liquid sulfur dioxide though it did not seem to dissolve.

The following were quite soluble in boiling liquid sulfur dioxide: beryllium acetylacetonate, beryllium basic acetate, beryllium ethyl acetoacetate, acetamide.

Course of a determination

Sulfur dioxide was purified by fractional distillation a sufficient number of times to eliminate all impurities, usually by from eight to twelve distillations. The chief impurities were sulfur trioxide and air. Finally, the remaining gas was solidified with liquid air and the system was evacuated to insure the removal of any residual gas other than sulfur dioxide, and the sulfur dioxide was then boiled into the storage reservoir.

The sample of the compound to be tested was then weighed into the reaction tube (V) (figure 1), which was then sealed into position.

The volume of the reaction bulb (V) connected to the baro-buret was next determined. The system was washed several times with dry, carbon dioxide-free air and the mercury reservoir (R) was lowered, bringing into the buret a sample of the dry carbon dioxide-free air. The stopcock (F) was then turned 180° connecting the baro-buret to the reaction bulb and a number of readings of volume at different pressures were made. From these readings the volume of the reaction tube (V) was calculated by means of the following formula:

$$V = \frac{P_1V_1 - P_2V_2}{P_2 - P_1}$$

The apparatus was evacuated and all but the reaction tube was flushed out with sulfur dioxide several times. A sample of pure sulfur dioxide was then drawn into the baro-buret (K) and its volume and pressure observed and calculated to standard conditions. Connection was then made with the reaction bulb (V) by turning the stopcock 180°, and the pressure was increased by raising the mercury reservoir (R), compelling absorption of the sulfur dioxide. This was continued at increasing pressures until the compound had turned to a liquid or until all the sulfur dioxide was absorbed that would be absorbed at the highest pressure attainable.

If more than one buret full of gas was required the stopcock (F) was turned 180° to draw in a fresh supply of gas from the gas reservoir, the volume and pressure being observed before and after the addition of the fresh quantity. The bath was maintained at 25°C. ± .001°C.

When the reaction had come to equilibrium the pressure, temperature, and volume were read and the total amount of the sulfur dioxide absorbed by the sample was calculated. The mercury reservoir was lowered sufficiently to diminish the pressure in the system about 2 cm.; after standing twenty-four hours to attain equilibrium, the pressure, volume, and temperatures were again observed.

The amount of gas still combined with the sample was calculated by subtracting the total volume passed from the buret from the volume of the gas present in the buret and reaction bulb. This gave the amount of gas freed at each equilibrium, and from this the amount still held was readily calculated.

TABLE 1

The system sulfur dioxide–beryllium acetylacetonate

PRESSURE	MOLES OF SO_2 PER MOLE OF BERYLLIUM ACETYLACETONATE
103.80	1.6600
85.75	1.3680
75.90	1.2090
69.35	1.0990
59.35	0.9620
53.75	0.8650
57.10	0.9110
67.70	0.1310 crystallized
70.40	0.1840
72.25	0.3660
72.65	0.4560
72.85	0.5120
73.05	0.5680
73.40	0.6500
73.65	0.7670
73.65	1.0270
74.40	1.1550
78.50	1.2490
56.40	0.9190
54.95	0.8940
53.55	0.8773
51.20	0.8355
50.45	0.8255
73.70	0.6015 crystallized
62.55	0.0980
53.40	0.0638
41.40	0.0568
16.30	0.0438
7.40	0.0378

This procedure was continued until the pressure reached zero. If the volume of the gas reached the capacity of the buret before the pressure reached zero, the stopcock (F) was turned 180°, exhausting most of the gas in the buret, and then the observations were continued as before.

RESULTS

The data obtained are given in tables 1, 2, and 3, and plotted in figure 2.

As the sulfur dioxide was forced into the reaction tube, there was a wetting of the compound on its surface; this became more pronounced as the pressure increased. Finally the entire compound assumed the liquid state, except in the case of beryllium ethyl acetoacetate, which changed first to a gel. As the pressure was reduced the compound remained in liquid state until the solution was considerably supersaturated when suddenly the liquid turned almost explosively to a white solid. This solid was the molecular compound with sulfur dioxide. The compounds could change to liquid under pressure, give up sulfur dioxide, and change to a solid state as many times as desired. In fact they seemed to take up sulfur dioxide more freely after the first pumping.

TABLE 2

The system sulfur dioxide–beryllium ethyl acetoacetate

PRESSURE	MOLES OF SO_2 PER MOLE OF BERYLLIUM ETHYL ACETOACETATE
132.15	1.7820
99.80	1.8000
97.15	1.8300
94.40	1.8580
89.05	1.5570
83.00	1.7260
79.22	1.6020
70.80	1.5470
67.80	1.4290
64.83	1.4630
60.50	1.2990
59.00	0.5676
52.65	0.3590
44.90	0.3100

TABLE 3

The system sulfur dioxide–phenyl benzoate

PRESSURE	MOLES OF SO_2 PER MOLE OF PHENYL BENZOATE
112.85	0.0689
93.40	0.0397

Beryllium acetylacetonate combined with one mole of sulfur dioxide and this compound then dissolved in the sulfur dioxide gas forming a liquid. The portion of the curve (see figure 2) from pressures of 75 cm. to 104 cm. is merely the vapor pressure curve for increasing dilution of this compound dissolved in sulfur dioxide. On cooling, supersaturation is shown in the curve of beryllium acetylacetonate as a dotted line. The beryllium acetylacetonate solution could be supersaturated to the point where approximately only one-half mole of sulfur dioxide per mole of beryllium acetylacetonate was left in the cell. The vapor pressure of the compound $Be(CH_3COCHCOCH_3)_2 \cdot SO_2$ varies between 72 and 76 cm. and averages 73 cm. On carrying the pressure to zero, all the sulfur dioxide was removed and the beryllium acetylacetonate was found to be unchanged.

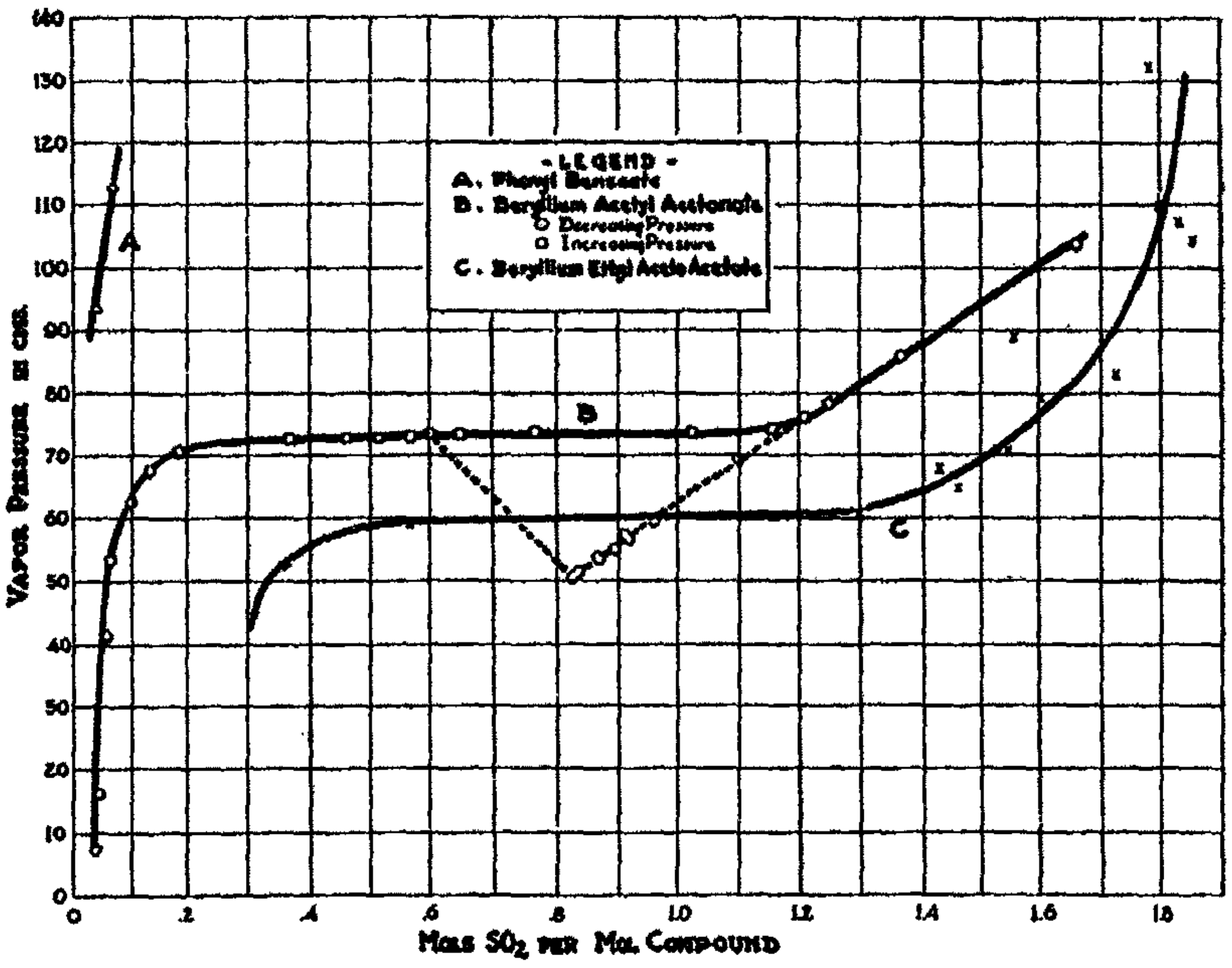


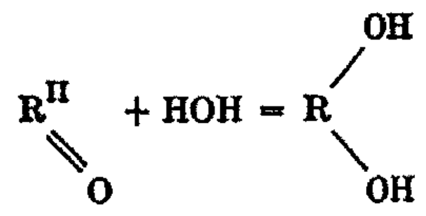
FIG. 2. ABSORPTION OF SULFUR DIOXIDE BY ORGANIC BERYLLIUM COMPOUNDS

In the case of beryllium ethyl acetoacetate quite a different condition was found. Instead of combining and forming a true solution, apparently a colloidal solution was formed, since on pumping off the sulfur dioxide during the determination, the liquid first became viscous and then set to a gel. This gel remained quite stable at pressures from 132 cm. down to 60 cm. Finally after pumping off sulfur dioxide at a pressure of 59 cm., the gel suddenly decrepitated leaving a fine powder. The gel formation hindered the free loss of sulfur dioxide and so gave a rather irregular set of points on the upper slope of the curve, although the points are uniformly placed on the horizontal part. The authors restudied this system three times over a period of eight months, without being able to improve the irregularity of these points. This is probably a hysteresis phenomenon (8, 9) due to variation of the capillary pore size as the sulfur dioxide of the gel leaves the solid $Be(CH_3COCHCO \cdot OC_2H_5)_2 \cdot SO_2$ structure. This is also suggested by the sudden collapse of the gel on further removal of the sulfur dioxide. The phenomenon may be further complicated by solubility of the compound in the sulfur dioxide. However, the curve shows a general shape similar to the other and the gel reverted to the solid state, showing an approximate composition of 1.0 mole of sulfur dioxide per mole of compound. The vapor pressure of this compound, $Be(CH_3COCHCO \cdot OC_2H_5)_2 \cdot SO_2$, averages 80 cm.

The phenyl benzoate absorbed so little sulfur dioxide that the curve showed plainly that it was merely an adsorption curve; since its further study would contribute nothing it was discontinued.

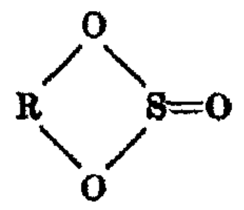
CONCLUSION

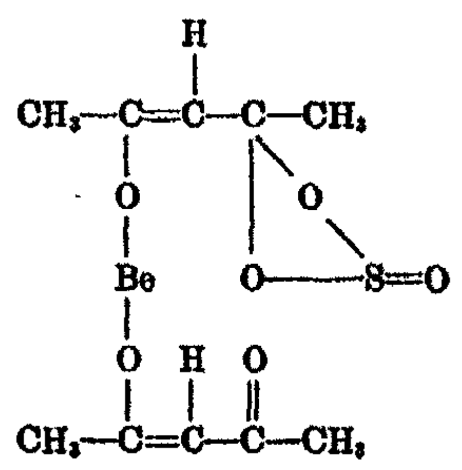
It has been established that sulfur dioxide forms addition compounds with beryllium acetylacetonate and beryllium ethyl acetoacetate. In attempting to explain the addition of sulfur dioxide to these compounds several possibilities may be considered. Any rearrangement that is involved must be an easily reversible one; this seems to preclude the possibility of oxidation or reduction. These compounds are apparently of the so-called molecular compound type analogous to the hydrates. Both beryllium acetylacetonate and ethyl acetoacetate formed additive compounds containing one mole of sulfur dioxide to one of the compound. That the addition of sulfur dioxide is not a function of the beryllium alone is suggested by the fact that both Schulze and Boessneck (2, 3) showed that acetone formed an additive compound with sulfur dioxide. However, the organic compounds formed in which sodium and aluminum replace the beryllium apparently do not react with sulfur dioxide—at least below two atmospheres pressure, though the magnesium acetylacetonate shows slight solubility or reaction. These latter compounds are probably more polar than the corresponding beryllium compounds, while the beryllium atom does not change the essentially non-polar character of the original organic compound. The reaction may be analogous to hydration where one of the bonds of the oxygen is opened, permitting the addition of (OH) and (H) thus:



$$R^{II}{=}O + HOH = R(OH)_2$$

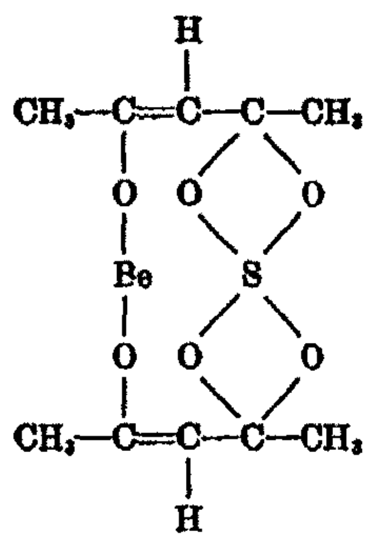
which by analogy in the case of sulfur dioxide would be:





On this basis, however, one wonders why another sulfur dioxide molecule is not taken up by the other =CO group.

An arrangement such as the following in which both =CO groups are involved is unorthodox, since it produces a twelve-membered ring of which other examples are practically unknown; furthermore the sulfur dioxide compound should be more stable if this were its structure:



The fact that only beryllium chelate compounds, beryllium acetylacetonate, beryllium ethyl acetoacetate, and beryllium basic acetate react with sulfur dioxide readily would suggest that the reaction took place via the atom of beryllium were it not for the fact that magnesium acetylacetonate also reacts to a certain extent, and that acetone itself reacts readily.

It will be remembered that liquid sulfur dioxide is an excellent solvent for non-polar compounds in general, particularly esters and fats, in which of course there is a =CO group. It may be that the character of the beryllium in these chelate compounds is sufficiently negative so that they behave towards sulfur dioxide exactly like such non-polar compounds as the fats, which contain no metals. In a former paper (10) it was reported that the hydrolysis of beryllium basic acetate was very slow and difficult, indicating extremely slight ionization to yield Be^{++} ions and that the beryllium was acting in a rôle not unlike that of carbon itself.

The evidence seems to point to the formation here of molecular compounds as a function of the carbonyl group of compounds in which the metal present does not diminish the non-polar character of the organic compound. It would be interesting to test boron chelate compounds with sulfur dioxide if they could be prepared. They should react in a similar fashion, though this would be complicated by the known characteristic of boron compounds to form molecular compounds.

SUMMARY

1. The systems sulfur dioxide-beryllium acetylacetonate and sulfur dioxide–beryllium ethyl acetoacetate have been studied at 25°C. It is found that these beryllium compounds combine in the ratio of one mole of compound to one mole of sulfur dioxide.

2. The vapor pressure of the compound $Be(CH_3COCHCOCH_3)_2 \cdot SO_2$ averages 73 cm. and that of the compound $Be(CH_3COCHCO \cdot OC_2H_5)_2 \cdot SO_2$ averages 60 cm.

3. The nature of these compounds and their possible structure is discussed.

4. The baro-buret is found to be a valuable tool in studying gas-solid equilibria.

REFERENCES

(1) Booth, H. S., and Torrey, G. G.: J. Phys. Chem. **35**, 2476 (1931).
(2) Schulze, H. O.: J. prakt. Chem. [2] **24**, 168 (1881).
(3) Boessneck: Ber. **21**, 1906 (1888).
(4) Bellucci and Grassi: Atti accad. Lincei **22**, II, 675–80 (1913).
(5) Booth, H. S., and Pierce, D. G.: J. Phys. Chem. **37**, 59–78 (1933).
(6) For description of operation see J. Chem. Education **7**, 1249 (1930).
(7) Booth, H. S.: Ind. Eng. Chem., Anal. Ed. **2**, 182–6 (1930).
Booth and Jones: Ibid. **2**, 237 (1930).
Booth and Willson: Ibid. **4**, 427 (1932).
(8) Van Bemmeln: Die Absorption, pp. 196, 214, 232 (1910).
(9) Van Bemmeln and Anderson: Z. physik. Chem. **88**, 191 (1914).
(10) Booth, H. S., and Torrey, G. G.: J. Phys. Chem. **35**, 2468 (1931).

SOME ERRORS INHERENT IN THE USUAL DETERMINATION OF THE BINARY FREEZING POINT DIAGRAM

EVALD L. SKAU[1] AND BLAIR SAXTON

Department of Chemistry, Yale University, New Haven, Connecticut

Received September 19, 1932

It has long been known that there are marked abnormalities in the freezing points of many binary mixtures near the eutectic composition, but it has never been shown definitely whether they are inherent in the system or whether they are merely apparent abnormalities due to experimental error. If, however, one were to study by the usual approximate method a nearly ideal system for which the accurate data are available, a comparison of the corresponding freezing point-composition diagrams should disclose some interesting facts, since all the differences would be due to experimental error.

Most of the temperature-composition diagrams in the literature have been constructed by the use of the Beckmann method, which consists essentially in cooling the melt below the freezing point, inoculating with the proper kind of crystal, stirring, and noting the maximum temperature to which the thermometer rises. The freezing points so obtained are usually low, owing mainly to two causes: (1) the change in the composition of the liquid due to the solid frozen out, and (2) the thermometer lag.[2] The errors thus involved increase as the eutectic is approached. In many cases the eutectic point itself is not experimentally determined but is obtained by extrapolation of the two branches of the curve.

This investigation had for its purpose the study of the nature and the possible magnitudes of the effects due to such inaccuracies on the freezing point-composition diagram, the calculated heats of solution, and on the conclusions drawn as to the ideality of the system. The system β-chlorocrotonic acid–β-chloroisocrotonic acid, for which the accurate freezing point

---

[1] Du Pont Fellow at Yale University, 1924–1925. Present address Trinity College, Hartford, Connecticut.

[2] This error may undoubtedly be quite considerable and the fact that in the system here studied it was eliminated, partially counterbalances the fact that our other error was deliberately enhanced. Another cause of low freezing point results is the use of too little undercooling. Since this has been repeatedly discussed (see, for example, Ostwald-Luther, Hand- und Hilfsbuch zur Ausführung physikochemischer Messungen, Leipzig, 1925) and has been eliminated in this work, it will not be considered here.

and heat content data have recently been published (1), affords an excellent opportunity for a study of this kind. The results obtained show that the eutectic composition as well as the eutectic temperature is affected by the usual inaccuracies of the data. Other causes of error near the eutectic point are pointed out by means of cooling curves.

EXPERIMENTAL

The freezing point method used was one which exaggerated the error due to the separation of the solid, but which practically eliminated the error due to the lag in the thermometer registration.

Apparatus

The apparatus used was the inner part of the cooling curve apparatus previously described (1). It consisted essentially of a small thin-walled glass tube, 6 mm. in diameter, containing the sample (0.7 to 1.0 gram) into which a thermoelement, protected by a thin-walled capillary glass sheath, was inserted through a stopper. This stopper was provided with another small opening through which the undercooled melt could be inoculated by introducing the proper crystals on the end of a glass thread. The thermoelement used was the same as that used in the accurate construction of the diagram for this system.

Procedure

The freezing point determinations for this system were made as follows. A known weight of the component A was placed in the freezing point tube and a small amount of component B was then weighed in by difference without removing the thermoelement. After the mixture was made homogeneous by melting completely and stirring, the freezing point was found by allowing the system to cool in the air (without any shield), seeding at the proper time, stirring, and noting the maximum to which the temperature rose. This was repeated with various degrees of undercooling and the highest maximum obtained was taken as the freezing point for that composition. A little more of substance B was then weighed into the tube and a new determination made. The error in composition is thus cumulative but is estimated to have been at all times less than 0.3 per cent.

Materials

The synthesis and purification of the two acids has been described (1).

The experimental results

The data obtained by the present method are given in table 1. N is the mole fraction in the liquid of the form crystallizing at the freezing point, t°C., T°K; t' is the true freezing point obtained by interpolation of the experimentally correct[3] data for the system. These data are plotted in figures 1 and 2.

The following facts should be noted:

From the temperature-composition diagram, figure 1, it is obvious that the values obtained by the rough method are all lower than those accurately determined. Further, it is apparent that the deviations become increasingly greater as the eutectic is approached and that the eutectic point is shifted by these inaccuracies not only along the temperature axis but also along the composition axis, the extrapolated temperature being about 38.9°C. instead of 41.5°C., and the per cent of β-chlorocrotonic acid being about 33.2 instead of 30.8.

TABLE 1

Experimental freezing point data for the system β-chlorocrotonic acid–β-chloroisocrotonic acid

N	$1 + \log N$	t	$\frac{1000}{T}$	t'	$t' - t$
β-chlorocrotonic acid branch					
1.000	1.0000	93.6	2.727	93.6	0.0
0.475	0.6767	55.5	3.043	59.1	3.6
0.434	0.6375	52.4	3.072	55.4	3.0
0.389	0.5900	47.0	3.124	50.9	3.9
0.350	0.5440	41.1	3.183	46.8	5.7
β-chloroisocrotonic acid branch					
1.0000	1.0000	60.5	2.998	60.5	0.0
0.9555	0.9802	57.8	3.022	57.9	0.1
0.9271	0.9671	56.0	3.038	56.3	0.3
0.9077	0.9579	54.8	3.049	55.2	0.4
0.889	0.9489	53.9	3.058	54.2	0.3
0.840	0.9243	50.7	3.088	51.3	0.6
0.810	0.9085	48.5	3.109	49.5	1.0
0.788	0.8965	46.9	3.125	48.1	1.2
0.750	0.8751	44.1	3.153	45.7	1.6
0.725	0.8603	42.3	3.171	44.1	1.8
0.706	0.8488	41.3	3.181	42.8	1.5

Eutectic point by extrapolation = 38.9°C.

From the plot of $(1 + \log N)$ against $\frac{1000}{T}$, figure 2, it is seen that a straight line may be drawn through the inaccurate data in such a way that

---

[3] With a maximum error of 0.25°C. near the eutectic point.

the greatest deviation corresponds to only about 0.5°C. The heats of solution calculated from the slopes of these lines by means of the ideal freezing point-solubility equation are 4970 and 3940, as compared with the values 5220 and 4120 calories per mole calculated from the accurate lines for the β-chlorocrotonic and the β-chloroisocrotonic acid respectively. It is further apparent that the points near the eutectic show a tendency to fall off gradually, especially on the β-chlorocrotonic acid branch where the eutectic composition is considerably removed from the pure substance. If curved lines be drawn through the points and the heats of solution calculated from their initial slopes, the error would obviously be lessened.

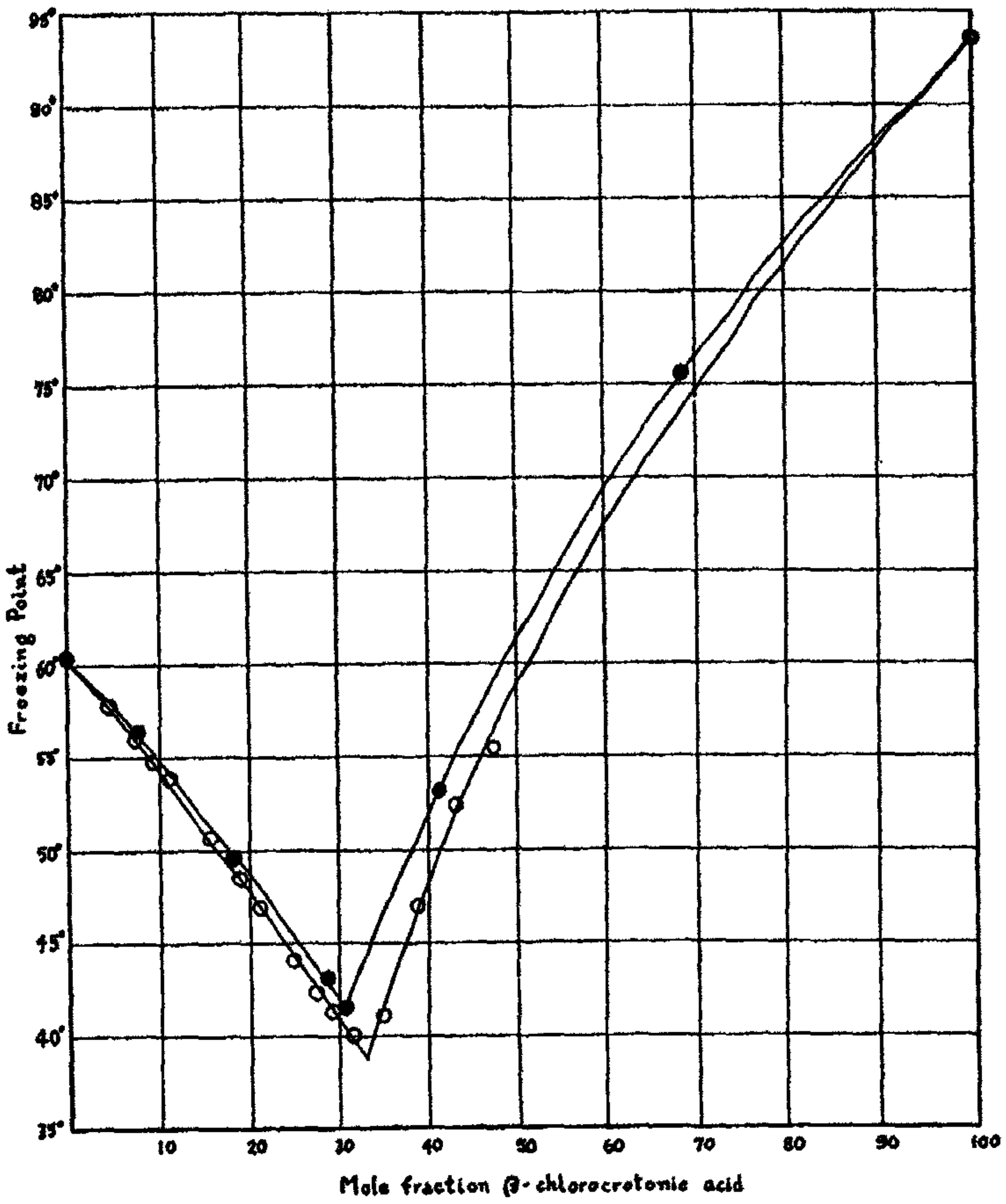


FIG. 1. FREEZING POINT-COMPOSITION DIAGRAM OF THE SYSTEM, β-CHLOROCROTONIC ACID–β-CHLOROISOCROTONIC ACID

Dots represent accurate freezing points; circles represent rough freezing points

DISCUSSION

There are several possible reasons for the increased deviations near the eutectic point which should be pointed out since, to the best of our knowledge, this situation has never been carefully analyzed.

(1) It can be shown that for purely mathematical reasons the error in the mole fraction caused by the freezing of a given fraction of a component of a binary solution increases with the mole fraction of the added component until the two mole fractions are about equal. Let n_A and n_B be the number of moles of A and B respectively in a binary solution and let a be the number of moles and $x = a/n_A$, the fraction of A crystal-

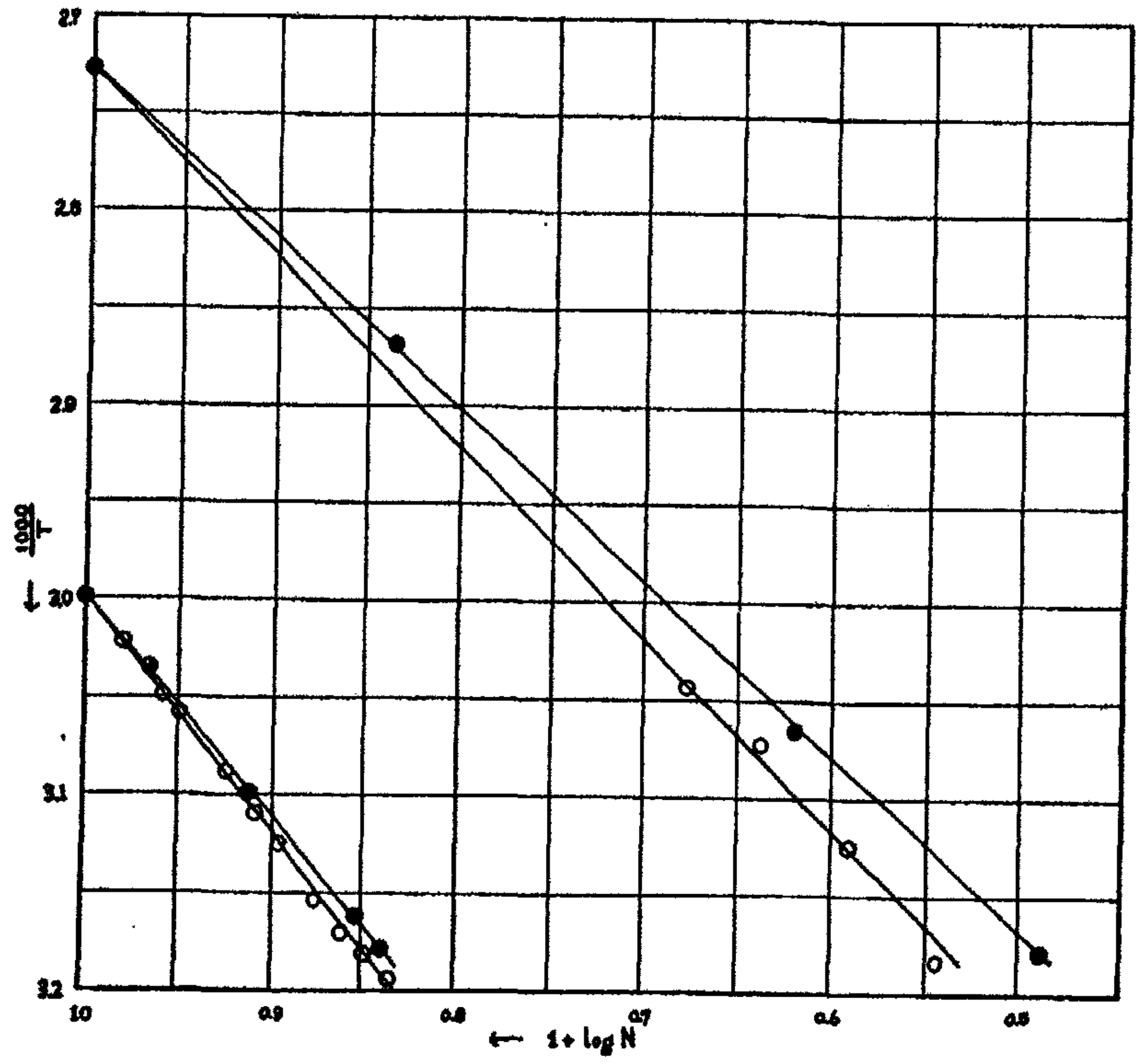


FIG. 2. Log $N - \frac{1000}{T}$ PLOT FOR THE SYSTEM, β-CHLOROCROTONIC ACID–β-CHLOROISOCROTONIC ACID

Dots represent values calculated from accurate freezing points; circles represent values calculated from rough freezing points. Upper curves are for β-chlorocrotonic acid; lower curves are for β-chloroisocrotonic acid.

lized from this solution in a freezing point determination. Let N_A and N_B be the mole fractions of A and B, respectively, in solution before crystallization and N'_A and N'_B be the corresponding quantities after a moles of A have been crystallized. Then

$$\Delta N_A = N'_A - N_A = \frac{-aN_B}{n_A + n_B - a} = \frac{-xN_AN_B}{1 - xN_A} \doteq -xN_AN_B \qquad (1)$$

Differentiating, we obtain

$$\left[\frac{\partial(-\Delta N_A)}{\partial N_B}\right]_x = \frac{x(N_A - N_B - xN_A^2)}{(1 - xN_A)^2} \doteq x(N_A - N_B) \qquad (2)$$

From the approximate derivative the change in composition reaches a maximum when $N_A = N_B$. From the accurate derivative the maximum is reached when $N_A = \frac{1 - \sqrt{1 - x}}{x}$. Thus when $x = 0.01$ the maximum occurs at $N_B = 0.4987$.[4]

(2) The general shape of the freezing point-composition diagram adds another source of error. Suppose the error mentioned in (1) be made uniform and small by keeping ΔN_A constant throughout the range of concentration, that is, by decreasing the value of x as we approach the eutectic so as to satisfy equation 1. The error would still usually increase owing to the fact that the change in freezing point for a given change in composition also commonly increases as the eutectic point is approached. This is obvious from the fact that the freezing point-composition lines are ordinarily curved downward. For the ideal solution at constant pressure this follows from the well-known equation,

$$s = \frac{dT}{dN_A} = \frac{RT}{N_A\,\Delta S_A} = \frac{RT^2}{N_A\,\Delta H_A} \qquad (3)$$

where, at temperature T, N_A is the mole fraction in solution, ΔS_A is the molal entropy of fusion, ΔH_A the molal heat of fusion of the component crystallizing, and s is the slope of the freezing point-solubility curve. Differentiating we obtain,

$$\frac{ds}{dT} = \frac{1}{N_A\Delta S_A}\left[2R - \Delta S_A - \frac{R\Delta Cp_A}{\Delta S_A}\right] = \frac{T}{N_A\Delta H_A}\left[2R - \frac{\Delta H_A}{T} - \frac{RT\Delta Cp_A}{\Delta H_A}\right] \qquad (4)$$

where ΔCp_A is the molal increase in heat capacity of pure A on fusion. Hence whenever $2R < \frac{\Delta H_A}{T} + \frac{RT\Delta Cp_A}{\Delta H_A}$, s increases with fall in tempera-

---

[4] It is thus obviously true that for a certain definite *amount* of component A crystallizing from a solution, the error in composition so caused increases as the eutectic point is approached.

ture. This is the usual case. If ΔH_A is independent of T then the slope must increase as T decreases whenever[5]

$$2R < \frac{\Delta H_A}{T}$$

It also follows that the slope changes with temperature in the converse manner whenever ΔS_A is less than $2R$, 3.97 calories or 16.63 joules per degree per mole, and will remain constant if $\Delta S_A = 2R$ entropy units per mole. Thus the solubility in an ideal binary system may start with a positive value of s, pass through an inflection point and approach the eutectic point with a negative value of s. This may even happen when ΔH_A is independent of T and ΔCp_A is zero, for although ΔS_A is then independent of T alone it is a function of N_A which decreases with temperature and consequently ΔS_A actually increases as T decreases. This follows from the relation, valid at constant pressure,

$$d\Delta S = \frac{\Delta Cp}{T}\,dT - R d \ln N$$

It also follows directly from the definitional relation between ΔS_A, ΔH_A and T. Values of the increase in s with falling temperature calculated by means of equation 4 agree satisfactorily with those determined by us for the system composed of the two β-chlorocrotonic acids.

For most of the substances for which apparently reliable direct calorimetric data are given, and especially for organic compounds, the molal entropies of fusion at the freezing points exceed $2R$. The comparatively few exceptions which we have noticed are hydrogen bromide (one crystalline form), hydrogen chloride, hydrogen iodide, pyrosulfuric acid, nitric acid, silver bromide, strontium chloride, sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, carbon tetrachloride, methane, methanol, cyclohexane, cyclohexanol, and 1,4-dihydronaphthalene. The elements comprise the largest list of exceptions. Indeed, all the elements for which we have data have entropies of fusion at their melting points which are less than $2R$ per formula weight, except chlorine, bromine, bismuth, gallium, and antimony.

There are a few substantially ideal[6] binary systems in which one compo-

---

[5] This relation for the special case where ΔH_A is constant has been developed in a somewhat different manner by van Laar (Proc. Acad. Sci. Amsterdam **5**, II, 424 (1903)).

[6] The criterion of ideality used is that

$$\Delta H_A = -2.303\, R \frac{d \log N_A}{d\,(1/T)}$$

where ΔH is the calorimetrically measured molal heat of fusion of component A, the solvent. Strictly, this heat of fusion should be taken at temperature T, but in many cases it can only be evaluated at the melting point.

nent is one of the substances listed above. These systems bear out, at least qualitatively, the relations demanded by equation 4. For example, from the heat data of Latimer (2), the slope of the T—N curve for carbon tetrachloride should decrease with falling temperature until the transition temperature is reached and then increase. Judging from the data of Biltz and Meinecke (3), this is exactly what happens when chlorine is the solute. The same condition should exist for cyclohexane (4) and is actually realized in the binary system with methyl cyclohexane (5).

The combined effect of the above two sources of error upon the observed freezing point of an ideal binary solution can be calculated from equation 3 integrated assuming ΔH_A to be independent of T. Then, in general,

$$T = \frac{T_A \Delta H_A}{\Delta H_A - RT_A \ln N_A} \tag{5}$$

and

$$-\Delta T = T - T' = \frac{RT_A^2 \Delta H_A}{(\Delta H_A - RT_A \ln N_A)(\Delta H_A - RT_A \ln N'_A)} \ln \frac{N_A}{N'_A} \tag{6}$$

in which T_A is the freezing point of pure A; T is the true, T' the observed freezing point of the solution; $-\Delta T$ is the lowering of the freezing point of the solution caused by the crystallization of some of component A; the other terms have the same significance as before. Since N'_A would be nearly equal to N_A in any properly conducted experiment,

$$\ln \frac{N_A}{N'_A} \doteq \frac{N_A}{N'_A} - 1$$

hence,

$$-\Delta T \doteq \frac{RT_A^2 \Delta H_A}{(\Delta H_A - RT_A \ln N_A)^2} \frac{x}{1-x} N_B \tag{7}$$

Thus for an ideal solution of a given composition the error in freezing point due to crystallization is directly proportional to x provided this is small compared to unity.

Upon differentiating equation 7 we obtain,

$$\left[\frac{\partial(-\Delta T)}{\partial N_B}\right]_x = \frac{R^2 T_A^3 \Delta H_A}{(\Delta H_A - RT_A \ln N_A)^3} \frac{x}{1-x} \left[\frac{\Delta H_A}{RT_A} - \ln N_A - \frac{2N_B}{N_A}\right] \tag{8}$$

Whether the error in T increases, remains constant, or decreases with N_B is then determined by whether

$$\frac{\Delta H_A}{RT_A} - \ln N_A \gtrless \frac{2N_B}{N_A}$$

Thus the entropy of fusion at the freezing point and the mole fraction are the determining factors. The entropy of fusion of many organic compounds is about 13 calories per degree per mole (6). A substance with this entropy of fusion will show an increase in $(-\Delta T)$ with N_B until the latter reaches 0.8; while if its entropy of fusion is as low as 2.6 it will show an increase in $(-\Delta T)$ up to $N_B = 0.5$. Hence, if the eutectic composition is not too near that of either pure component (B in this case) it is fair to assume that as component B is continuously added to a fixed amount of A and the amount of A crystallized is kept constant the error in the freezing point will usually continuously increase until the eutectic is reached. This would also be the case for varying amounts of A if the fraction removed each time were kept constant. For example, in the case of β-chlorocrotonic acid, whose entropy of fusion is 13.5 calories per degree per mole at its freezing point, if one per cent be crystallized during a freezing point determination the error in T would be 0.05°C. when its mole fraction is 0.9. This error would increase continuously and become 0.27°C. when its mole fraction is 0.308. This is the composition of the eutectic with β-chloroisocrotonic acid.

In order to maintain a constant error in T along a single branch of the curve, x should be decreased as N_B increases in accordance with equation 7. Again using β-chlorocrotonic acid as an example, we find that for a value of $(-\Delta T) = 0.1$°C. we may crystallize 1.9 per cent of the acid when $N_B = 0.1$, but only 0.37 per cent at the eutectic with its isomer when $N_B = 0.692$. Thus x must be decreased fivefold. Since the molal heat capacities of these two isomers in the liquid state are nearly equal (1), it follows that x is practically proportional to the amount of undercooling; hence the latter should be decreased about fivefold in going from $N_B = 0.1$ to the eutectic.

(3) A third error is introduced by the fact that a actually *increases* as the eutectic is approached, owing to the decrease in the rate of crystallization with the decrease in temperature and the attendant increase in viscosity. That slow crystallization in general causes a larger amount of solid to separate before the maximum is reached can perhaps be shown best by a comparison of cooling curves. In figure 3 the line ABC′D′ represents a typical time-temperature curve for a slow crystallization and the line ABCD, a curve for a more rapid one. GH represents the course taken by the temperature of the shield or surroundings. The shaded area in each case, horizontally and diagonally respectively, is proportional to the amount of solid separated at the maximum temperature (7). It is obvious that the area A′BC′F′E′ is greater than the area ABCFE. It was actually found on reëxamining the cooling curves obtained in the earlier study of this system (1) that those for the nearly pure substances were of the rapid type whereas those for compositions near the eutectic were of the slow type.

All of the errors so far considered have been due to failure to correct for the change in composition when the solid separates and they are involved in the case of all solutions, being usually greatest at the eutectic and decreasing as the pure substance is approached. Another source of very considerable error, which may or may not be quite general to all systems, is illustrated by a number of cooling curves obtained for compositions near the eutectic. In these curves the first maximum after inoculating was actually below the true eutectic temperature and after the usual fall in temperature there followed another rise, this time to a higher maximum corresponding to the eutectic temperature. In one case the primary freezing point, after roughly correcting for the amount of solid separated, was 0.5°C. below the eutectic temperature which in this case is actually about 0.5°C. low. This curve, for the composition 31.2 per cent β-chlorocrotonic acid, is reproduced schematically in figure 4 and the cause of the behavior can be explained by a consideration of figure 5 in which the effect is shown much exaggerated.

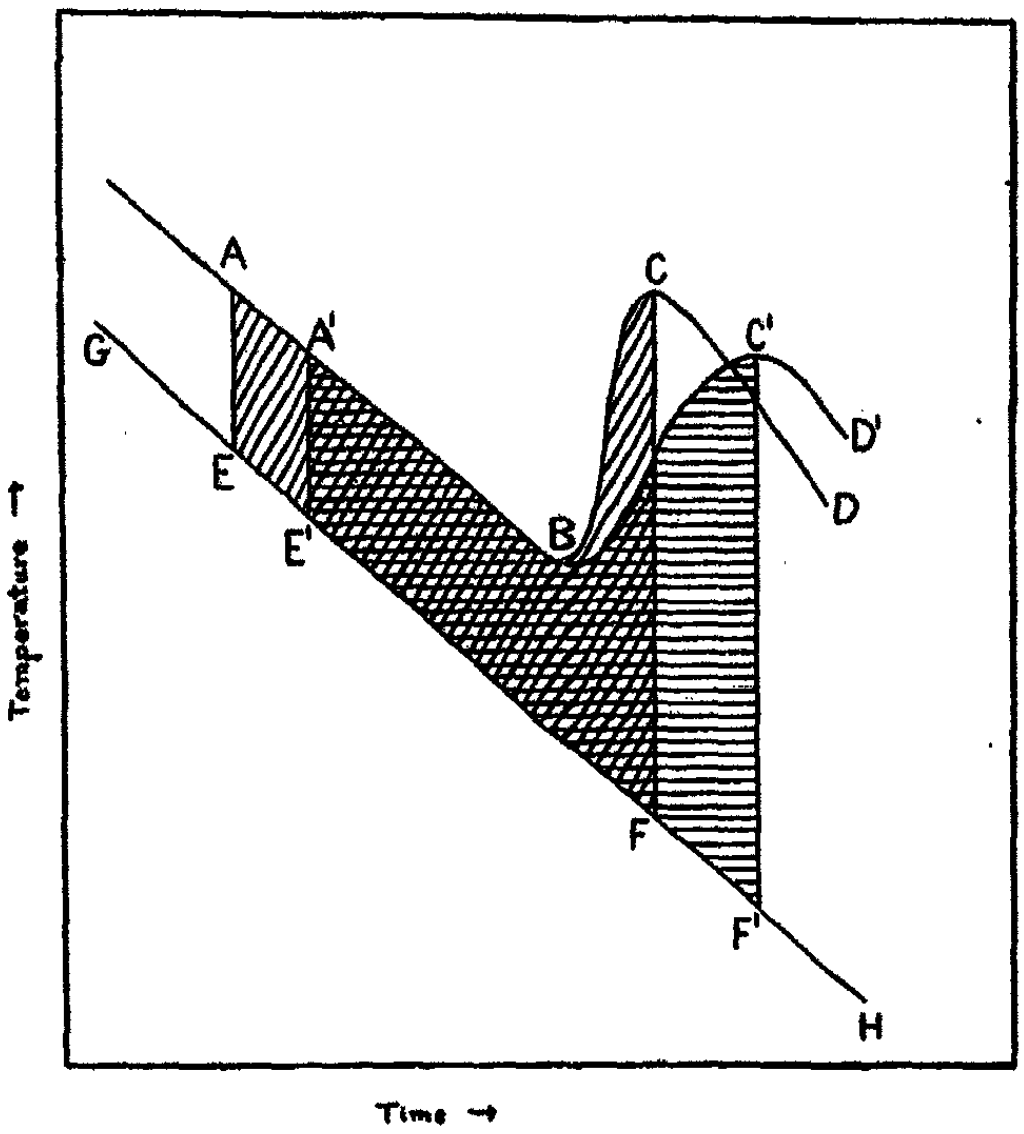


FIG. 3. TYPICAL COOLING CURVES FOR RAPIDLY AND SLOWLY CRYSTALLIZING BINARY MIXTURES

Let us consider that AEB (figure 5) is the correct freezing point-composition diagram for a system as obtained by an accurate method. Owing to the tendency to undercool, a melt of the composition X fails to crystallize, when inoculated with both kinds of crystals, until the temperature is *below* F. The component A then crystallizes giving a primary freezing point corresponding to F (when corrected for the pure A which has separated) and after the maximum is reached, A continues to separate changing the composition of the liquid as it cools, along the line FG until B begins to crystallize.[7] The composition and temperature then change to the eutectic point.[8]

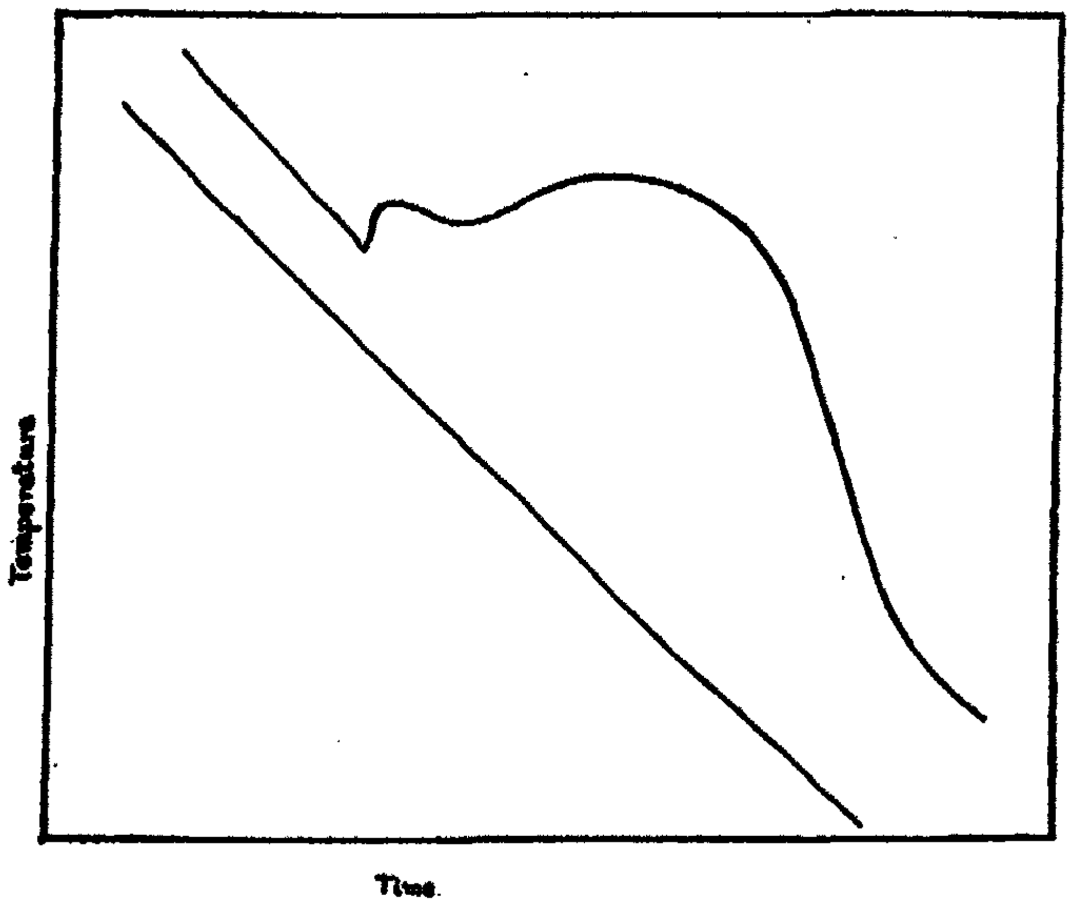


FIG. 4. TYPICAL COOLING CURVE SHOWING PRIMARY FREEZING POINT BELOW THE EUTECTIC TEMPERATURE

For the true eutectic composition the first maximum should on this basis fall below the eutectic flat, but the freezing point obtained by the proper correction for the solid separated should be the true eutectic temperature.

---

[7] It will be noted that below the eutectic the increase in the degree of undercooling with respect to B is the resultant of two superimposed effects: (a) the lowering of the temperature of the liquid, and (b) the increase of the true freezing point of the liquid due to the continual change toward a composition richer in B.

[8] The true eutectic temperature may never be reached, however, owing to a low rate of crystallization of B, or owing to the fact that the amount of liquid left is so small that its heat of crystallization is insufficient to raise the temperature of the whole sample through the required range. Thus, as mentioned above, the second maximum in figure 4, though higher than the first, is still about 0.5°C. below the true eutectic temperature.

In fact, one would expect that compositions even a little richer in A would show this same characteristic. Cooling curves of this type were actually realized; for example, the sample containing 30.0 per cent of β-chlorocrotonic acid upon inoculation at 38.5°C. came to a maximum of 41.5°C., and then dropped to 39.9°C., and finally rose again to 41.5°C., the eutectic temperature.[9] For compositions richer than the eutectic in component B, the degree of undercooling necessary in order to reach curve AG increases

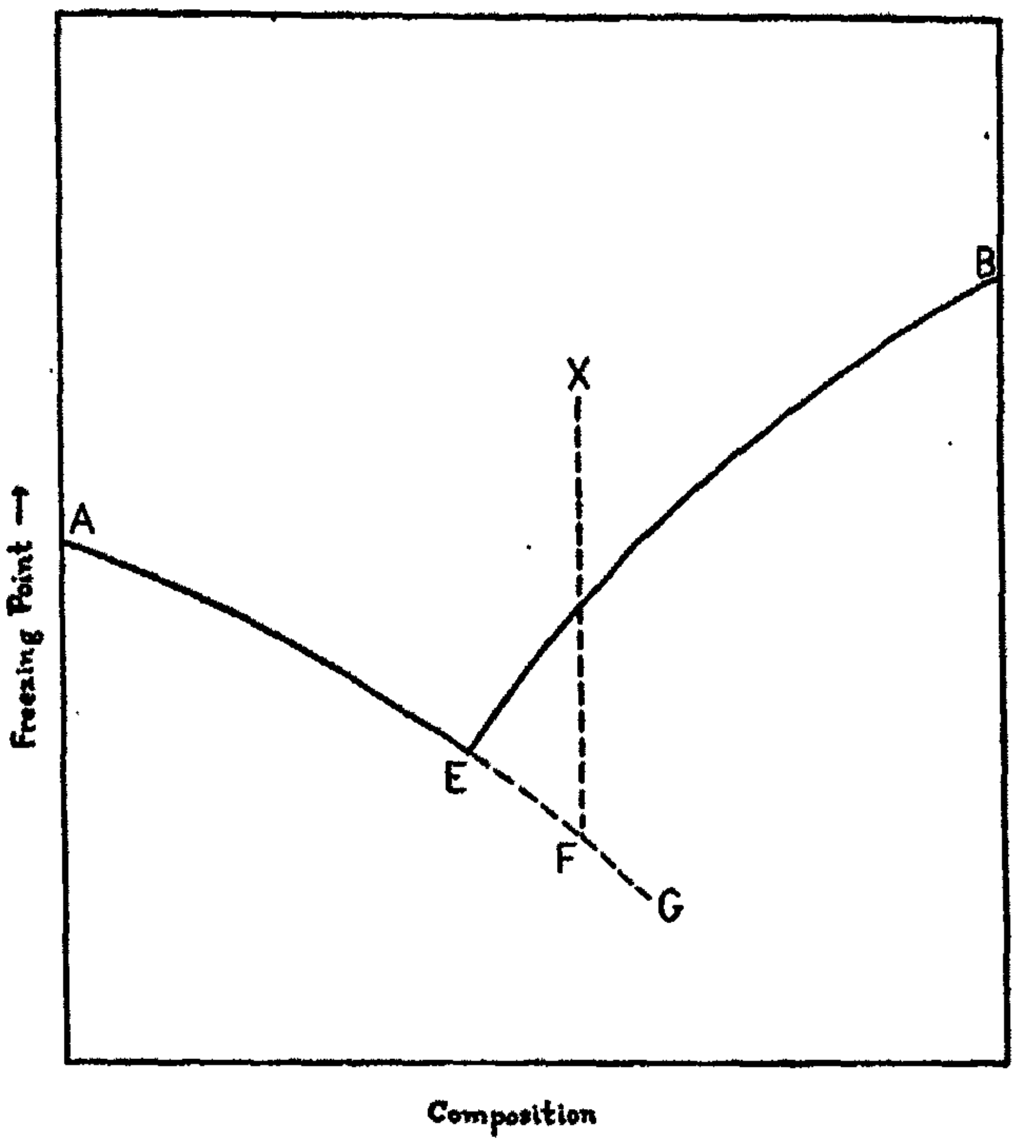


FIG. 5. SCHEMATIC BINARY FREEZING POINT DIAGRAM WITH ONE BRANCH EXTENDED BELOW THE EUTECTIC

and eventually attains such a value that B is the first to crystallize upon inoculation. The resulting effect on the temperature-composition diagram

---

[9] It is no novel observation that a system can be undercooled below its eutectic point. Indeed, it is claimed that this can usually be done intentionally whenever one, or both, of the components is capable of being undercooled when pure. To the best of our knowledge, however, no cooling curve like our figure 4, with two maxima, the second higher than the first, has been reported. Such a curve affords the first experimental proof of the validity of the explanation usually given for the cause of such abnormal freezing points.

would be the extension of the A branch beyond the true eutectic and the distortion of the other branch to meet it.

It is probable that in many systems the cooling of the liquid below the eutectic temperature can occur only to a very limited extent. In such cases the effect on the diagram would be such as to indicate compound formation; that is, a horizontal line would extend between the two branches of the diagram at or just below the eutectic temperature. A case of this kind has actually been pointed out by Bell and McEwen (8), who upon reconstructing the diagram for the binary system of *m*-nitrotoluene with *p*-nitrotoluene found it to be a system of the simple eutectic type instead of one showing compound formation as had been reported previously by Gibson, Duckham, and Fairbairn (9).

CONCLUSIONS

When it is considered that the usual method employed for freezing point determinations involves merely the determination of the height of the first maximum after inoculation and that there is no correction for the solid separated, it becomes obvious that the construction of the freezing point diagrams of many of the binary systems in the literature may be considerably in error. This is particularly in evidence near the eutectic point and may lower the apparent eutectic temperature; in fact, as shown by the discussion of figure 4, this danger exists even if correction is made for the separation of the solid. A shift in the eutectic composition is also to be expected where the temperature deviation on the two branches of the curve is not the same at the true eutectic composition. It should be noted, however, that whereas all the errors discussed in this paper conspire to make the apparent eutectic temperature too low, they may conceivably have opposing effects on the shift of the eutectic composition. Such would have been the case, for example, if the branch BE instead of AE in figure 5 were the one that could be extended. If the extension of neither of these branches were realizable, the diagram obtained might conceivably lead one to believe that there was compound formation. This is obvious from inspection of figure 1.

Erroneous data would, in general, be expected to give a $\log N - \frac{1}{T}$ plot with a curvature which is too great, and the heat of solution calculated from its slope would be too low and would vary more over the temperature range in question than the true heat of solution.

Little can be said in a general way in regard to the possible magnitude of the errors in a system whose rough diagram alone is known except that they are dependent upon the degree of undercooling used and upon the rate of crystallization of the particular substances (i.e., upon the amount of solid separated out), upon the lag in the thermometer registration, and upon the possibility of following either curve below the true eutectic temperature.

SUMMARY

The freezing point-composition diagram for the system β-chlorocrotonic acid–β-chloroisocrotonic acid has been constructed by a rough method in which no correction was made for the amount of solid crystallizing and this diagram as well as the $\log N - \frac{1}{T}$ plot for these data have been compared with those obtained from the accurate data. It has been shown that the errors involved cause a shift of the observed eutectic not only along the temperature axis, but also along the composition axis. In some cases false indications of compound formation may be given.

Cooling curves have been described which are a direct proof that it is possible to follow a branch of the temperature-composition diagram to temperatures below the eutectic.

The relation between the entropy of fusion and the shape of a branch of the $T - N$ diagram of an ideal binary system has been discussed.

An analysis of the causes of increased errors near the eutectic point is made and it has been pointed out that it is dangerous to draw definite conclusions from the abnormalities or distortions in the freezing point diagrams unless the method of obtaining the data eliminates the sources of error mentioned.

REFERENCES

(1) Skau and Saxton: J. Am. Chem. Soc. **50**, 2693 (1928).
(2) Latimer: J. Am. Chem. Soc. **44**, 90 (1922).
(3) Biltz and Meinecke: Z. anorg. allgem. Chem. **131**, 1 (1923).
(4) On the basis of the data of Parks, Huffman, and Thomas: J. Am. Chem. Soc. **52**, 1032 (1930).
(5) Timmermans: Bull. soc. chim. Belg. **37**, 409 (1928).
(6) Mortimer: J. Am. Chem. Soc. **44**, 1429 (1922).
(7) Andrews, Kohman, and Johnston: J. Phys. Chem. **29**, 914 (1925).
(8) Bell and McEwen: Ind. Eng. Chem. **14**, 536 (1922).
(9) Gibson, Duckham, and Fairbairn: J. Chem. Soc. **121**, 270 (1922).

THE FREEZING POINT-SOLUBILITY RELATIONS OF GEOMETRICAL ISOMERS. II

THE DYNAMIC ISOMERISM OF THE ANISALDOXIMES

EVALD L. SKAU[1] AND BLAIR SAXTON

Department of Chemistry, Yale University, New Haven, Connecticut

Received September 23, 1932

In a series of articles published about 1900 (1) it was pointed out that certain geometric isomers exhibit the phenomenon known as "dynamic isomerism", i.e., the *cis* and the *trans* modifications tend to transform one into the other until an equilibrium mixture is reached. In those investigations the binary freezing point diagrams for a few such systems were studied and the equilibrium compositions were then estimated by freezing point measurements. If these compositions could be determined with a sufficient degree of accuracy, it should be possible to calculate the heat of transformation of the one modification to the other.

There are many difficulties involved in this method, however, for in many cases the rate of transformation is rapid enough at the melting point so that the composition of the mixture changes very appreciably during the freezing point determination.[2]

Inasmuch as all previous work on such systems was done by the capillary melting point method or at best by the Beckmann apparatus, it seemed of interest to find out what controlled cooling curves and heating curves would show and to test out the applicability of an apparatus previously described (2) to a system of this type. The system, *cis*-β-chlorocrotonic acid–*trans*-β-chlorocrotonic acid, which was reported in the first (2) of this series of papers, showed no signs of "dynamic isomerism" at moderate temperatures. The supposed "unstable equilibrium" of the system, crotonic acid–isocrotonic acid, on the other hand, proved on investigation

---

[1] Du Pont Fellow, Yale University, 1924–1925. Part of this paper was written during the tenure of a Guggenheim Fellowship at the Bayerische Akademie der Wissenschaften, Munich, Germany. Present address Trinity College, Hartford, Connecticut.

[2] In fact, in some cases the freezing point and the melting point are different. When the rate of transformation is extremely rapid, the solid obtained upon freezing a liquid mixture of any composition will be one of the modifications in pure form. For a detailed discussion of these interesting possibilities see ROOZEBOOM: Die heterogenen Gleichgewichte, II, Part 3, Vieweg, Braunschweig (1918).

to be a much more complicated equilibrium phenomenon, probably involving polymerization (3).

Carveth (4) studied the system, *cis*-anisaldoxime–*trans*-anisaldoxime, and finally came to the conclusion that it was impossible to construct the temperature-composition diagram even roughly. He found that the freezing points could not be determined either for the pure forms or for mixtures by means of a Beckmann freezing point apparatus, owing to the rapid transformation toward a definite equilibrium composition. The freezing point obtained by this method was always in the neighborhood of 54.2°C., which he interpreted as the "natural freezing point" of the system, i.e., the freezing point of the equilibrium mixture. He determined the melting points of the pure substances by the capillary tube method as 62.8°C. and 132°C., respectively, and showed that the less stable, *cis* form would liquefy if kept at 89.5°C. for twelve hours. He concluded that the eutectic was about 0.2° below the "natural freezing point", since that was the lowest temperature he was able to reach by changing the composition and since he was unable to detect a second break in the rough cooling curves which he ran. He attempted to get the melting temperatures of various mixtures of the two forms by means of the capillary tube method, but failed to get even approximately reproducible results. He stated, "It has been found absolutely impossible to obtain with any accuracy the composition of the triple point."

The benzaldoxime system, which was studied by Cameron (5), seemed to exhibit the same phenomena, but in this case it was found possible to construct a rough freezing point-solubility diagram. Since the results of Patterson and MacMillan (6) on the rates of transformation in ethyl tartrate solution show that *cis*-anisaldoxime and *cis*-benzaldoxime are equally stable[3] it seemed that it should be possible to construct the diagram for the anisaldoxime system.

We have found that the cooling curve method is not entirely applicable to the case, but we were finally able to construct the binary freezing point diagram, to follow the transformation involved, and to determine the composition at the "natural freezing point" with a fair degree of accuracy by means of controlled heating curves.

SYNTHESIS AND PURIFICATION OF COMPOUNDS

The *trans*-anisaldoxime was synthesized by Schmidt and Söll's method (7) from anisaldehyde and hydroxylamine hydrochloride in alcohol solution containing a large excess of barium carbonate in suspension.

---

[3] Brady and Dunn (J. Chem. Soc. **123**, 1783 (1923)) state that *cis*-anisaldoxime is more stable at atmospheric conditions than *cis*-benzaldoxime.

The yield of crude oxime was 95 per cent. This product was recrystallized repeatedly from methyl alcohol and carbon tetrachloride.

The *cis*-anisaldoxime was prepared from the *trans* modification by Dunstan and Thole's method (8) as modified by Brady and Dunn (9). These authors mention the difficulty of drying the *cis*-oxime. In this particular case we found that the drying of the solid could be omitted if the sample, after being sucked dry on the Buchner funnel, was extracted with boiling benzene, the water layer being reëxtracted. The purification was effected by repeated recrystallization from benzene. The final product melted quite sharply in a capillary tube at about 127°C., the temperature being raised at the rate of about 2° per minute as the melting point was approached.

The apparatus used for running cooling and heating curves has been described elsewhere (2).

EXPERIMENTAL RESULTS AND DISCUSSION

Limitations of cooling-curve method

It was found that, in accordance with the conclusions of Carveth, it was impossible to get the freezing point of either pure modification by means of cooling curves, since there was always a partial transformation to the other form as soon as the melting took place. However, we did find it possible to follow the transformation of the *trans* form to the equilibrium mixture for the system by means of a series of successive cooling curves on a sample of *trans*-anisaldoxime. The first curve was a very rapid one carried out by the method described in another paper (10), that is, by cooling the melt to a temperature just below the freezing point and then inoculating and stirring, the surroundings being at the temperature of the room. The other curves were obtained by the usual method, except that the crystallization took place extremely slowly and the mixture had to be stirred vigorously to cause the rise in temperature to the maximum, whereas ordinarily the maximum is reached without any further stirring after the inoculating crystals have once been stirred into the melt.

The first cooling curve gave a maximum temperature of 60.7°C. (not a "flat"), the second curve, 60.0°C. The sample was then heated to 92°C. and allowed to cool in the course of ten minutes, and the maximum came at 57.5°C. The next curve gave 57.4°C. and the last 57.4°C. A number of cooling curves were run on this sample and the area-maximum plot[4] was made, but the results were not self-consistent, many maxima being decidedly low. From all these results it was estimated that the true primary freezing point of the equilibrium mixture was above 57°C.

---

[4] To correct for the solid separated out at the maxima, see Andrews, Kohman, and Johnston: J. Phys. Chem. 29, 914 (1925).

The heating curve method

Since it was found impossible to obtain satisfactory cooling curves, owing to the rapid rate of transformation, heating curves were used and they proved to be much better adapted.[5]

The same apparatus was used as for cooling curves, but the copper shield was heated at a constant measured rate, the adjustment being made by means of a variable resistance shunted across the heating coil. This served as the only source of heat for the melt, whose temperature was then followed in the usual way. The breaks were in most cases quite sharp and the results in general very consistent. By means of such heating curves it was found possible to obtain the melting point of the pure untransformed *trans*-anisaldoxime and to follow the transformation toward an equilibrium mixture whose freezing point was determined. Since it was also possible to construct the temperature-composition diagram of the binary system using this same method, the composition of the equilibrium mixture was disclosed by its freezing point.

TABLE 1

Successive curves on the same sample of trans-anisaldoxime

CURVE NUMBER	TYPE OF CURVE	RATE OF HEATING (OR COOLING)	POINT *a*	POINT *b*	POINT *c*
			degrees C.	*degrees C.*	*degrees C.*
I	Heating	Medium	—	—	72.5
II	Heating	Medium	56.5	59.9	75.5
III	Heating	Medium	56.5	59.0	72.6
IV	Heating	Medium	56.8	58.6	70.9
V	Heating	Medium	56.4	58.4	76.3
VI	Cooling	Very slow	—	—	—
VII	Heating	Very rapid	56.0	60.0	82.9
VIII	Heating	Very slow	56.2	59.7	67.0
IX	Heating	Medium	56.0	58.7	74.0
X	Cooling	Very slow	—	—	—
XI	Heating	Medium	56.2	59.6	—

Following the transformation by heating curves

A number of *successive* heating curves were run on the same sample of pure *trans*-anisaldoxime. On plotting the data for the first and second runs, two curves of the types shown in figure 1, A and B respectively, were obtained. The straight lines show the change of the temperature of the shield with time and the curved lines below show the corresponding tem-

---

[5] The heating curve method is not suggested as a general method for determining accurate freezing points of binary mixtures. It is much less satisfactory when the primary freezing point is far removed from the eutectic temperature.

peratures of the sample. The breaks in these curves and in the rest of the curves, all of which had the same general shape as figure 1, B, have been tabulated in table 1. In figure 1, A, a "flat" was obtained (constant within one microvolt, 0.02°) lasting for eight minutes at the temperature 62.6°C., which is, therefore, the melting point of pure *trans*-anisaldoxime. The second curve, of the type shown in figure 1, B, is decidedly different. There is a partial flat, presumably at the eutectic temperature (point *a*), at the end of which there is a sharp change in direction, and later there is a second break (point *b*) after which the temperature rises rapidly to the temperature of the shield. Point *b* corresponds to the temperature where the last crystal disappears or to the primary freezing point of the mixture. These points were determined by plotting the time-deviation curves, the deviation being the difference between the temperature of the shield and that of the melt at any given time. The breaks are thus much more marked. Point *c* is the highest temperature to which the sample was raised before cooling and running the next curve.

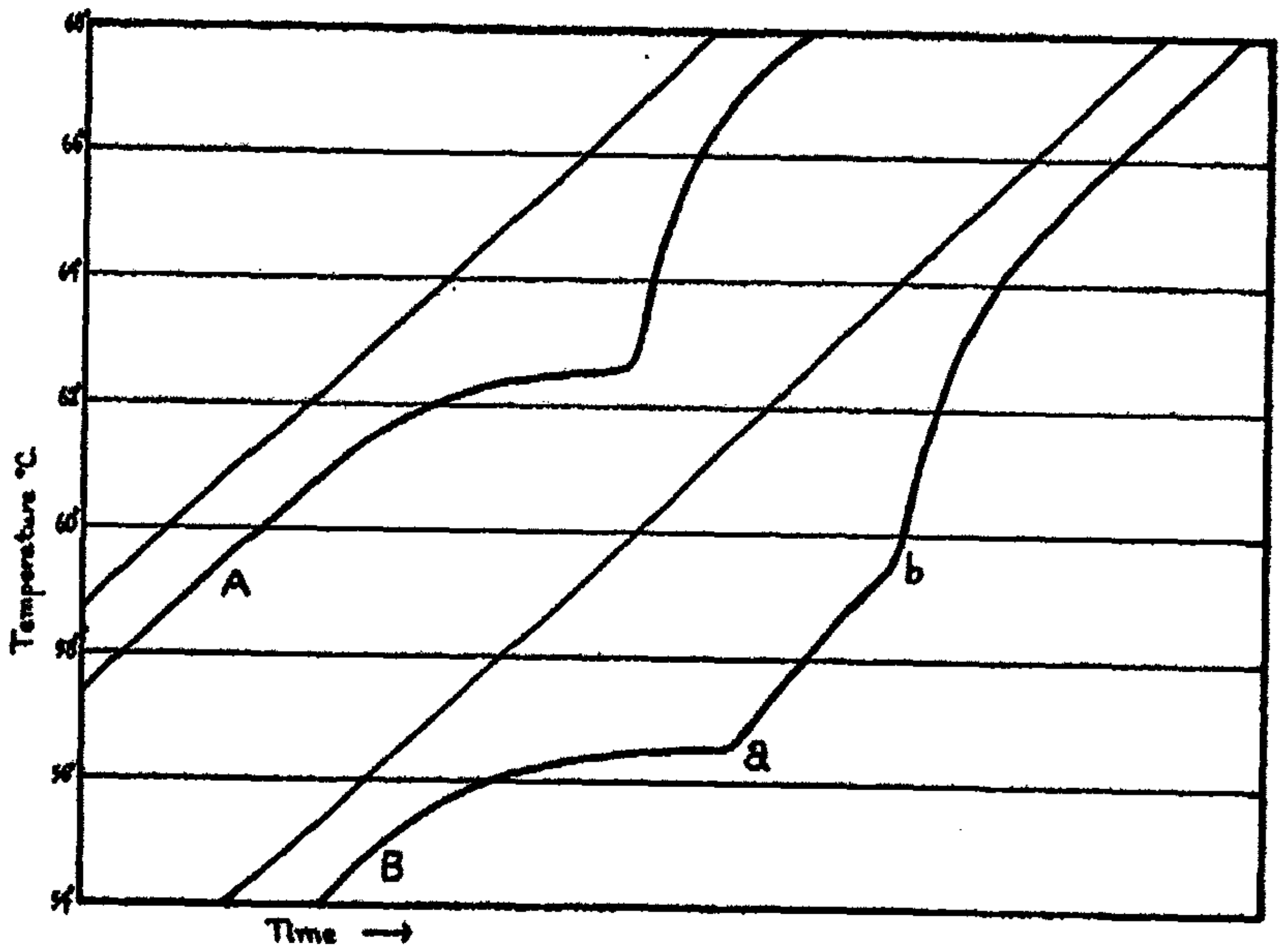


FIG. 1. TYPICAL SUCCESSIVE HEATING CURVES OF A SAMPLE OF PURE *trans*-ANISALDOXIME

A number of interesting facts are brought out by this series of curves. In the first place, it shows that the heating curve method is vastly superior to the Beckmann freezing point method. This follows from Carveth's statement (4) that after heating the pure *trans*-anisaldoxime to 64°, 100°, or 125°C. for thirty minutes, the primary freezing points could not be distinguished from the "natural freezing point", namely, 54.2°C. In spite of the fact that in the course of runs I, II, and III the temperature was kept well above 64°C. for about fifty minutes in each case, the resulting mixtures were very definitely distinguishable from the equilibrium mixture. The fact that the eutectic temperature *a*, was a little lower in the later curves indicates that this heating had caused a slight oxidation or decomposition of the oxime.

A study of the table also shows that the natural freezing point is probably on that side of the eutectic nearer the pure *trans* form.

The rise in point *b* after curve VI is perhaps also worthy of notice. This seems to be explained best by assuming that it was due to the slow cooling of the melt in curve VI; that is, that as the solid *trans* form separated at the "natural freezing point", and the liquid thus became richer in the *cis* form, transformation took place toward the reestablishment of the equilibrium composition in the liquid, so that the resulting solidified melt contained less of the *cis* form. This is verified by the fall in *b* for the next two curves and a rise again after another cooling curve, X.

TABLE 2

Freezing points for the binary system, cis-anisaldoxime-trans-anisaldoxime

Cis	T_1	T_2	T_3	T_E
per cent	*degrees C.*	*degrees C.*	*degrees C.*	*degrees C.*
0	62.6			
4.23	60.8	60.6		56.4, 56.6
7.62	59.5			56.3
10.61	58.6	58.5		56.6, 56.6
14.79	57.8			56.8
19.48	56.7	56.6	56.8	56.7, 56.2, 56.4
22.76	(64)			56.6
33.63	(80)			56.6
100.00	127*			

* Melting point by capillary tube method.

Construction of the temperature-composition diagram

The various compositions were made by intimately mixing the pulverized crystals of the two forms in the right proportions on a small piece of plate glass and then transferring to the freezing point tube. The thermoelement was then inserted in the well-packed sample and the whole was put into the freezing point apparatus without first melting. The heating curve obtained in each case was of the type shown by figure 1, B.

In all cases the melt was immediately chilled as soon as the point *b* had been passed and a second heating curve was run on the solidified material.

Thus, the least possible time was allowed for transformation to take place, and the second curve usually checked the first one to within 0.3°C. when the temperature of melting was not much above 60°C. On the *cis*-side of the curve, however, the transformation seemed to be much more rapid

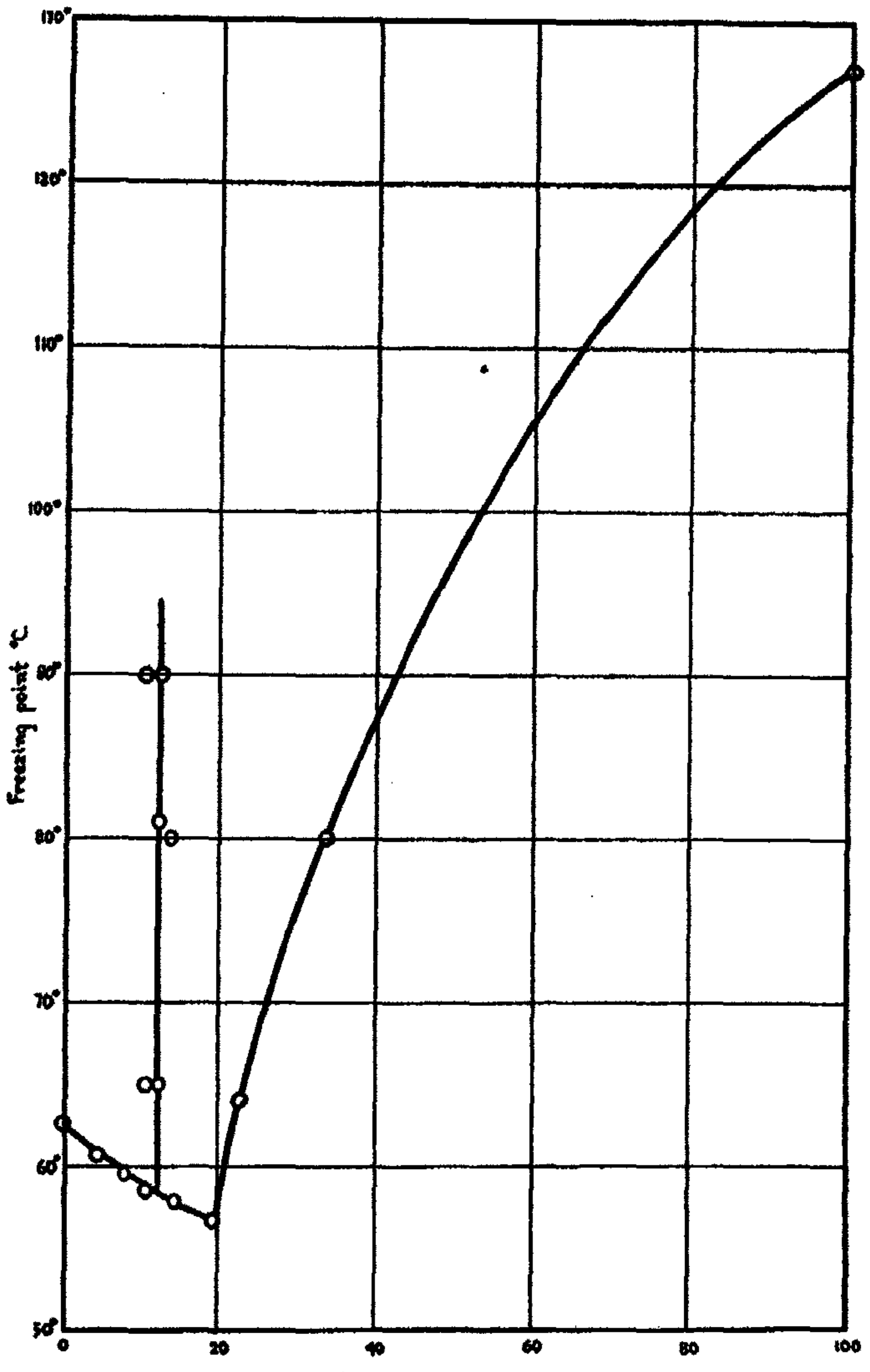


FIG. 2. FREEZING POINT-COMPOSITION DIAGRAM FOR THE SYSTEM, *cis*-ANISALDOXIME–*trans*-ANISALDOXIME

and the freezing points for this branch are, therefore, probably as much as 2°C. too low. The second curves in these cases failed to check the first ones; for example, the curves for the 22.76 per cent mixture gave the freezing points 64° and 58.9°C., respectively, and the 33.63 per cent sample gave the freezing points 80°C. for the first and 58.3°C. for the second curve.

The data obtained from these curves are given in table 2 and are plotted in figure 2. The values obtained for point *b* in successive curves on the same sample are designated by T_1, T_2, and T_3, and the corresponding values obtained for the eutectic temperature, T_E, are given in their respective order. It was impossible to get the melting point of the pure *cis* form by any but the capillary-tube method (see below) and thus this value may be in error by 3° or 4°C. since the value obtained depends to a considerable extent on the rate of heating. The eutectic temperature, obtained by averaging all the values for T_E, is 56.5°C. The eutectic composition, gotten by extrapolation of the two arms of the binary freezing point curve, is about 19.5 per cent *cis*- and 80.5 per cent *trans*-anisaldoxime.

The formation of another compound above 100°C.

The successive heating curves obtained for a sample of the pure *cis* form prove that the transformation is not so simple as the one suggested by Carveth, that is, to an equilibrium mixture of the *cis* and *trans* modifications, but that some other substance or substances are formed. In the first curve the shield was started at 121.6°C. and raised about 0.5°C. per minute. The unmelted sample of *cis*-anisaldoxime, which was at room temperature when inserted, rose very rapidly to 106.6°C., then dropped to 100.1°C. (indicating a considerable absorption of heat), and then rose without any further breaks to 132°C. The sample was then chilled to room temperature and a second curve run on it. This showed a eutectic flat at 39.5°C., about 17°C. below that found for the binary eutectic above, and then a rise toward the temperature of the shield, the last crystals disappearing at about 49.5°C. In another case in which the first heating was carried up to 140°C., the second and third heating curves gave eutectic flats at 39.2°C. and 39.0°C., respectively. In both of these cases the final sample was decidedly yellow in color. On the other hand, the mixture of anisaldoximes containing 33.63 per cent of the *cis* form (see table 2) gave the normal eutectic break, at 56.6°C., even though it had been subjected during a previous curve to a temperature of over 80°C. The facts seem to indicate that at about 100°C. or over, another compound is formed.

It was actually found possible to isolate this compound in crystalline form from mixtures obtained by heating the pure *trans* form to corresponding temperatures. (1) A small amount of the pure *trans* form was heated in a sealed evacuated tube at 125°C. It first became yellow, then red, and when finally removed from the oven, after forty-eight hours, it was deep reddish brown in color and long needle-like crystals separated at a high temperature. The primary freezing point of the mixture was about 129°C. It was found that a slightly yellow crystalline compound could be precipitated from the alcohol solution of the mixture by adding the right amount of water. Without further purification this compound melted in a capillary tube at 168–172°C. to a brown liquid. (2) Another sample heated at 110°C. for a number of months did not discolor to as great an extent. In this case there were some well formed yellow crystals at the top of the tube, evidently deposited by sublimation, which gave a melting point of 160–166°C. without purification. The formation of the compound is accompanied by the evolution of ammonia,[6] judging from the development of considerable pressure in the tube and from the distinctive odor and the action on litmus paper of the gas evolved.[7] At higher temperatures there seems to be a distinct odor of tertiary amines.

The composition of equilibrium mixtures at various temperatures

The formation of the compound in the neighborhood of 100°C. and above makes it impossible to follow the binary equilibrium mixture above that temperature. Unfortunately this narrows the possible range of study of the change of equilibrium composition with the temperature to a 30° range between the "natural freezing point" and about 90°C.

A number of samples of *trans*-anisaldoxime and of mixtures with the *cis* modification were heated at various temperatures in sealed tubes. Their freezing points were then determined by means of heating curves and their compositions estimated by comparison with the binary freezing point diagram. The values obtained are tabulated in table 3 and have been included in figure 2.

The results show that, owing to the short temperature range permitted, a more sensitive method than the one at hand will have to be used to determine with sufficient accuracy the slope of the equilibrium curve.

---

[6] It was noticed that when pure *trans*-anisaldoxime was left for some time in a desiccator over sulfuric acid, the exposed surface of the sample became slightly yellow. As this was not investigated further, we are unable to say whether it was due to the formation of the yellow compound isolated.

These observations are quite similar to those of West (J. Am. Chem. Soc. 47, 2780 (1925)) on the aldoxime of 4,6-dicarbethoxyl-5-formyl-3-methyl-2-cyclohexenone. He found that water and ammonia were evolved when the aldoxime was heated for twenty to thirty minutes at 100°C. under a pressure of 20-30 mm. He also observed that "when dried in a vacuum desiccator for eighteen hours over sulfuric acid the compound lost weight (water and ammonia (?)) and passed into a substance that began to turn brown at 126°C. and melted at 140°C. with decomposition."

Hurd (The Pyrolysis of Carbon Compounds, p. 660 ff., The Chemical Catalog Co., New York (1929)) cites several cases in which ammonia is evolved on heating ketoximes.

[7] This reaction is now being studied further.

The values for the individual samples show very good agreement among themselves and the freezing points of the equilibrium mixtures obtained by heating the pure *trans* form fall within 0.15°C. of their mean value, 58.4°C. For some reason, however, the mixtures obtained by approaching equilibrium from the other side do not show the same good agreement.

It should be noted that in approaching the equilibrium from the *trans* side of the diagram the freezing point drops to the value for the equilibrium mixture, whereas in approaching it from the *cis* side, the freezing point drops to the eutectic point and then rises to its final value. Thus in the case of the 33.63 per cent *cis* mixture at 80°C., where the duration of heating was only one and one-half hours, the final freezing point was low and this may have been due to the fact that the transformation was incomplete. It seems probable, however, that true equilibrium was reached in all the other cases, for sufficient time was allowed and the results showed good agreement, except that the mixtures approached from the *cis* side gave values about 0.5°C. higher than expected—most likely owing to the fact that for some unknown reason the breaks in the heating curves were actually much less distinct and that therefore the freezing point could not be determined with the same degree of accuracy. It seems logical therefore to give more weight to the values for the equilibrium mixtures which were obtained by heating the pure *trans* form.

TABLE 3

Change of "equilibrium" composition with temperature

COMPOSITION OF ORIGINAL. PER CENT OF *cis* COMPOUND	HEATING		POINT *a*	POINT *b*
	Temperature	Duration		
	degrees C.	*hours*		
0	90	12.5	56.1	58.2
			56.2	58.3
26.22	90	73	56.5	58.9
0	81	47	56.5	58.5
			56.7	58.4
33.63	80	1.5	56.6	(57.9)*
0	65	50	56.4	58.3−
			56.5	58.3+
22.76	65	69	55.9	58.9

* Probably not yet at equilibrium.

On this basis, the data of table 3 show that the freezing point of mixtures which have been brought to equilibrium at temperatures between 65°C. and 90°C. is 58.4°C. ± 0.2°, corresponding to a composition of 12.3 per cent of the *cis* and 87.7 per cent of the *trans* form. This value is in accord with the data of table 1.

SUMMARY

The "dynamic isomerism" in the *cis*-anisaldoxime–*trans*-anisaldoxime system has been investigated. The binary freezing point-composition diagram of this pair of geometric isomers was constructed and was then used as a basis for a method of analysis of unknown mixtures.

Owing to the rapid rate of transformation in the liquid state toward the equilibrium composition, it was found necessary to substitute a controlled heating curve method for the usual cooling curve method, although it was found possible to follow the transformation roughly by means of the latter.

When either form is heated to about 100°C. or above, a reaction takes place involving the formation of a compound which has been isolated. The study of the change of the simple binary equilibrium with temperature is thus limited to a narrow range between about 60°C. and 90°C.

The "natural freezing point" of the simple binary system was found to be 58.4°C. ± 0.2°C., corresponding to a composition of 12.3 per cent of the *cis* form. This equilibrium composition did not change perceptibly with the temperature up to 90°C.

REFERENCES

(1) DUHEM: Z. physik. Chem. **22**, 545; **23**, 193, 497 (1897).
BANCROFT AND COWORKERS: J. Phys. Chem. **2**, 143, 159, 245, 364, 376, 409 (1898); **3**, 144, 437 (1899).
(2) SKAU AND SAXTON: J. Am. Chem. Soc. **50**, 2693 (1928).
(3) SKAU AND SAXTON: J. Am. Chem. Soc. **52**, 335 (1930).
(4) CARVETH: J. Phys. Chem. **3**, 437 (1899).
(5) CAMERON: J. Phys. Chem. **2**, 409 (1898).
(6) PATTERSON AND MACMILLAN: Proc. Phil. Soc. Glasgow (1911); Brit. Chem. Abstracts **100**, i, 648 (1911).
(7) SCHMIDT AND SÖLL: Ber. **40**, 4257 (1907).
(8) DUNSTAN AND THOLE: Proc. Chem. Soc. **27**, 233 (1911).
(9) BRADY AND DUNN: J. Chem. Soc. **123**, 1783 (1923).
(10) SKAU AND SAXTON: J. Phys. Chem. **37**, 183 (1933).

STUDIES IN AUTO-OXIDATION. III

THE INITIAL ACT IN AUTO-OXIDATION[1]

H. N. STEPHENS

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

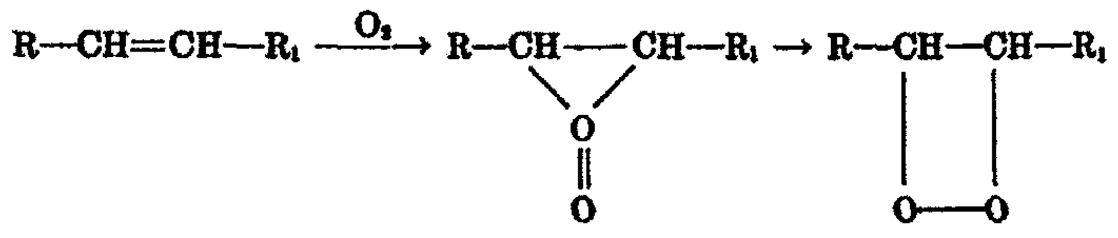
Received October 18, 1932

Although peroxide formation is quite generally accepted as the initial step in auto-oxidation, much debate has centered around the question as to whether the isolable peroxide is actually the primary addition product or whether there is first formed a more active and unstable substance, which rearranges into the isolable compound.

This question was first raised by Engler and Weissberg (1), following the observation that benzaldehyde, dissolved in benzene together with indigo, and exposed to oxygen, decolorized the indigo much more rapidly than the same concentration of benzoylhydroperoxide, in the same solvent, exposed to an atmosphere of carbon dioxide. This observation seemed to indicate that, during the process of auto-oxidation, there was formed a more active intermediate than the isolable benzoylhydroperoxide.

At the time when this observation was made, it was, of course, impossible to draw the necessary distinction except on the basis of two distinct compounds. In view of our present knowledge of activated molecules, however, it seems unnecessary to assume any difference, other than one of energy content, between the freshly formed peroxide and the known compound. At the moment of formation the energy-rich molecules would be expected to be much more efficient in the destruction of the indigo than would the normal molecules of the same substance.

A conclusion similar to that of Engler and Weissberg was reached later by Staudinger in connection with his work on the ketenes and, in particular, on the basis of some work of Erdman (2) upon which Staudinger (3) commented. According to the latter, the addition of oxygen to the ethenoid linkage yields, as a primary product, a highly active, unsymmetrical peroxide, or *moloxide* (I), which may later rearrange into the more stable, symmetrical compound (II).



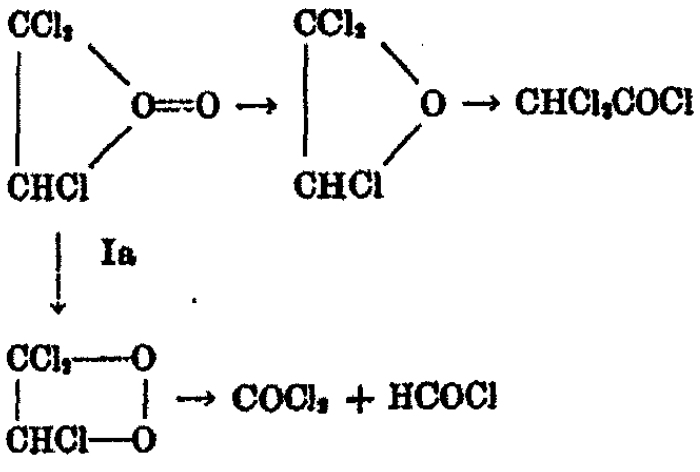
$$R{-}CH{=}CH{-}R_1 \xrightarrow{O_2} R{-}\underset{\substack{\diagdown\;\diagup\\ O\\ \|\\ O}}{CH{-}CH}{-}R_1 \rightarrow R{-}\underset{\substack{|\quad\;\;|\\ O{-}O}}{CH{-}CH}{-}R_1$$

I II

---

[1] Presented at the 15th annual Canadian Chemical Convention at Hamilton, Ontario, June 1 to 3, 1932.

In support of this viewpoint, it is pointed out that the products obtained by Erdman from trichloroethylene can be most simply accounted for by assuming that the "moloxide" (Ia) is, in part, reduced to the oxide and, in part, isomerizes to the normal peroxide (IIa).



IIa

This argument, however, appears unconvincing to the present writer, as the oxide would be a normal product of the interaction of peroxide with the original substance (4).

Quite recently, Jorissen and Van der Beek (5) have revived the question of the nature of the initial peroxide as a result of an observation on the oxidation of benzaldehyde in the dark, presumably at room temperature. Under these conditions a strong peroxide test was obtained, although it had been shown previously (6) that in direct sunlight no peroxide survived. The authors state that their peroxide could not have been benzoylhydroperoxide, otherwise it would have reacted with the benzaldehyde. Finally, the conclusion is drawn that the substance is probably the primary addition product of oxygen and the aldehyde, which may later revert to the isolable benzoylhydroperoxide.

The interpretation given by these authors to their experimental evidence seems to the present writer to be inconsistent with one of their own observations, namely, that exposure to direct sunlight of a mixture partially oxidized in the dark resulted in the destruction of the peroxide in a few minutes. The fact that the peroxide survived in the dark need only be ascribed to the difference in its rate of reaction with benzaldehyde in the dark and in direct sunlight, as Bäckström (7) has already shown that the reaction between benzoylhydroperoxide and benzaldehyde is sensitive to light in the near ultra-violet. There seems every indication, therefore, that the peroxide obtained by the dark reaction is benzoylhydroperoxide. Again, the assumption that the primary product is a substance of weaker oxidizing ability (lower energy content) than benzoylhydroperoxide is one which can hardly be justified thermodynamically, as the primary product should be richer in energy than the substance into which it rearranges.

The most recent attempt to revive the conception of a structural difference between the primary peroxide and the isolable product is found in the recent papers of Milas (8), whose theory is based on his interpretation of recent work in band spectroscopy by Mulliken (9), Birge (10), and others. This evidence indicates clearly that diatomic molecules of the type of CO, CO^+, BO, BeF, CN, etc., possess electrons in excess of eight which behave essentially as the valence electrons of *atoms*. The explanation advanced by Mulliken and by Birge (11) is that the two nuclei, together with their *K* electrons, are enclosed in a common shell of eight, with the remaining electrons in an outer shell. Such outer electrons might properly be designated as "molecular valence electrons."

To outline briefly some of the main assumptions underlying Milas' theory, the following might be mentioned:

(1) Auto-oxidation is assumed to be possible "only when the auto-oxidants possess unshared or 'exposed' electrons." These unshared electrons are referred to as "molecular valence electrons," the inference being that they are, in all cases, essentially similar to the valence electrons of diatomic molecules of the type mentioned above (12).

(2) These unshared electrons are assumed to have their spins unpaired and to be more loosely bound to the molecule than shared pairs (reference 12, p. 299).

(3) The first change assumed to take place in any auto-oxidation is a change in energy level of these "molecular valence electrons." That is, electronic activation is assumed to be a necessary preliminary to all auto-oxidations (reference 12, p. 299).

(4) A pair of such electrons already raised to some higher energy level is then assumed to be donated to the oxygen molecule, with the formation of a "dative" peroxide.

(5) The "dative" peroxide rearranges into the more stable peroxide or undergoes other reactions.

For the sake of brevity and convenience may we examine these assumptions in order.

(1) The present writer knows of no evidence from band spectroscopy or from any other source that would indicate that all unshared electrons may be properly regarded as "molecular valence electrons." To take one typical example as an illustration, that of aldehydes, the carbonyl group might be considered as a pseudo-atom, having its valence electrons shared with hydrogen and organic radical, respectively. However, there seems no reason for assuming, with Milas, that unshared oxygen electrons in such molecules are capable of behaving as valence electrons.

(2) The assumption that the spins of such unshared electrons are not paired would seem to require some justification in order to carry weight against the current opinion that they are paired. Likewise, there seems

some need of substantiation for the assumption that these electrons are more loosely bound to the molecule than others.

(3) Most, if not all, auto-oxidations are thermal reactions. It is true that light is apparently universally effective in accelerating these reactions, but they are not exclusively photochemical. It seems entirely improbable, then, that electronic activation is a necessary preliminary to auto-oxidation, for electronic excitation levels lying below the visible part of the spectrum are very rare. In any event, excitation of oxygen electrons in ethers and aldehydes (reference 12, pp. 352–5) seems quite impossible in view of the fact that the lowest excitation level of oxygen is of the order of 8 volts.[3] In spite of this fact, however, Milas assumes an excitation of oxygen electrons in the water molecule by supersonic vibrations (reference 12, p. 317). For the frequency in question, 750,000 cycles, the corresponding energy of activation would be 3×10^{-9} volts, or approximately 7×10^{-5} calories per mole!

(4) The donation of a pair of "molecular valence electrons" to the oxygen molecule is represented through the use of the following electronic structure for oxygen

$$\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:$$

As oxygen is known to have zero electric moment (13), this cannot represent the normal oxygen molecule. If it represents an electronically activated state there seems no possible way of accounting for the energy of activation in thermal reactions. It should be pointed out further in this connection, that the electronic structures used for some of the donor molecules are subject to similar criticisms. For example, the structure for ethylenic compounds

$$\mathrm{R}:\ddot{\mathrm{C}}:\underset{\cdot\cdot}{\ddot{\mathrm{C}}}:\mathrm{R}_1$$

cannot be considered as representing the normal molecules, as the electric moment of ethylene is known to be zero (14). If it represents an electronically activated state there seems to be no place for such a structure in the representation of auto-oxidations which are thermal reactions.

(5) In the foregoing pages it has been shown that there exists no acceptable evidence in favor of the existence of two structurally different forms of the peroxide; therefore the conception of the "dative peroxide," "moloxide," or any other hypothetical intermediate seems to serve no useful purpose.

---

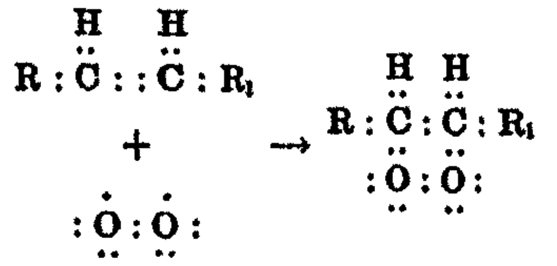
[3] This, I *think* quite justifiably, leaves out of the question the metastable level at 1.65 volts, which apparently has a very low probability of formation by direct absorption of light.

THE MODE OF ACTIVATION IN AUTO-OXIDATIONS

In view of the fact, already mentioned, that auto-oxidations in general are thermal reactions, it seems necessary to exclude any such energetic activation as that postulated by Milas. Vibrational activation appears to be quite sufficient to account for experimental facts. It cannot be denied, of course, that when such reactions are hastened by photochemical means electronic activation must occur. However, as there is no evidence indicating that the use of light changes the primary step in the reaction, it seems safe to assume that the accelerating effect of light is due to the increase in vibrational energy following the absorption of a quantum of light. It will, therefore, be assumed in this paper that all auto-oxidations involve the primary addition of oxygen to a linkage which has been activated by vibration, whether the necessary vibrational level has been attained purely by thermal means or by absorption of light.

Ethenoid compounds

In the case of compounds containing the ethenoid linkage it is quite easy to understand, on the basis of conventional structures, the vibrational weakening of one of the bonds between the two carbon atoms and the pairing of the two odd oxygen electrons at this point. The preferred structure for the oxygen molecule is that of G. N. Lewis (15), since it is the only one which is in agreement both with the paramagnetism and the absence of electric moment. Using electronic structures the addition of oxygen would be represented in the following manner.

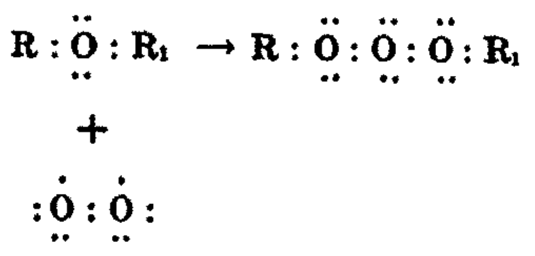


$$\begin{array}{c} \mathrm{R:\overset{H}{\ddot{C}}::\overset{H}{\ddot{C}}:R_1} \\ + \\ \mathrm{:\dot{O}:\dot{O}:} \end{array} \longrightarrow \begin{array}{c} \mathrm{R:\overset{H}{\ddot{C}}:\overset{H}{\ddot{C}}:R_1} \\ \mathrm{:\ddot{O}:\ddot{O}:} \end{array}$$

The addition of oxygen to the $C\equiv C$ bond may be considered in a similar manner.

Ethers

It is well known that ethers, on pyrolysis, usually undergo rupture adjacent to the ether oxygen. It is evident then, that the C—O linkage is the weak point in the molecule. Addition of oxygen to ethers would, therefore, be represented as follows:

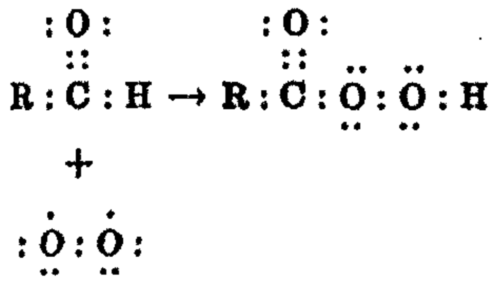


$$\begin{array}{c} \mathrm{R:\ddot{O}:R_1} \\ + \\ \mathrm{:\dot{O}:\dot{O}:} \end{array} \longrightarrow \mathrm{R:\ddot{O}:\ddot{O}:\ddot{O}:R_1}$$

In this case the original linkage consists of only one electron pair instead of two, as in the case of ethenoid compounds. Hence the addition of oxygen at this point effects a complete separation of the atoms sharing that pair.

Aldehydes

In the case of aldehydes, the facility with which dehydrogenation takes place justifies the assumption that the weakest linkage in simple aldehyde molecules must be the C—H bond. Therefore, the addition of oxygen would be expected to take place at this point through pairing of the odd oxygen electrons with carbon and hydrogen respectively.

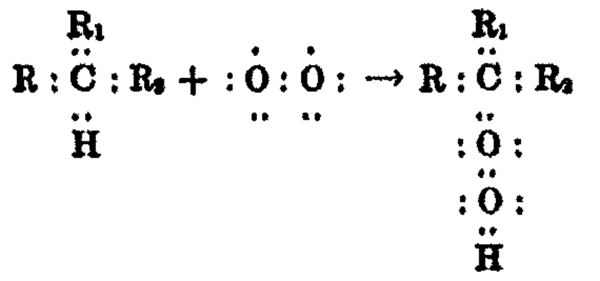


$$\mathrm{R:\overset{:O:}{\overset{::}{C}}:H} + \mathrm{:\underset{\cdot\cdot}{\dot{O}}:\underset{\cdot\cdot}{\dot{O}}:} \rightarrow \mathrm{R:\overset{:O:}{\overset{::}{C}}:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}:H}$$

Saturated hydrocarbons

The fact that saturated hydrocarbons are auto-oxidized offers an instance of the complete failure of the general theory of Milas, as these compounds possess no "molecular valence electrons." In his most recent publication Milas recognizes this fact and proposes a special mechanism to fit this particular case (reference 12, page 346). This mechanism is essentially the one which follows from the viewpoint developed in the present paper.

In the case of the paraffins, it is evident from the work of Pope, Dykstra, and Edgar (16) that oxidation tends to take place on the terminal carbon atom of the longest open chain. On the other hand, the oxidation of the alkyl benzenes has been shown by the writer to take place at the carbon atom alpha to the ring (17). The apparent discrepancy in these results, is, of course, due to the well-known fact that hydrogen attached to the alpha carbon atom in the alkyl benzenes is abnormally reactive. In each of the above cases, as well as in other recent investigations (18), the oxidations have been thermal reactions, which fact necessarily precludes electronic activation. According to the theory developed in this paper the oxygen molecule would be expected to attach itself at the bond most susceptible to vibrational activation. At the time of writing, the evidence seems to indicate that the C—C bond has a lower energy of dissociation than the C—H bond; therefore the former would be expected to be preferentially attacked. However, recent work (19) indicates that the difference in the above dissociation energies is very small; therefore, it seems quite possible that the weakest C—H bond in a given hydrocarbon molecule might have a lower energy of dissociation or activation than the weakest C—C bond. In any event, it is quite obvious that C—H bonds are usually attacked in preference to C—C bonds. The initial act in the auto-oxidation of saturated hydrocarbons would then be represented by the following scheme:



$$\begin{array}{c} R_1 \\ \cdot\cdot \\ R:C:R_2 \\ \cdot\cdot \\ H \end{array} + :\dot{\underset{\cdot\cdot}{O}}:\dot{\underset{\cdot\cdot}{O}}: \rightarrow \begin{array}{c} R_1 \\ \cdot\cdot \\ R:C:R_2 \\ \cdot\cdot \\ :O: \\ \cdot\cdot \\ :O: \\ \cdot\cdot \\ H \end{array}$$

where R_1 and R_2 might represent hydrogen and / or hydrocarbon radical, depending on whether the hydrocarbon was a paraffin (16), an alkyl benzene (17), or an alkyl cyclane (18b, 18c).

Miscellaneous compounds

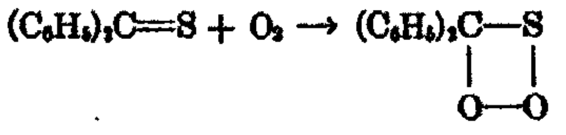
The foregoing illustrations deal with only a limited group of compounds, but it seems to the writer unnecessary to multiply examples by discussing in detail other types. However, brief mention might be made of two additional examples, which are of some interest. One of these compounds, thiobenzophenone, has been the subject of recent controversy as to the point in the molecule at which oxygen adds (20; and 10, p. 328).

Thiobenzophenone is an unstable substance which decomposes at 160–170°C. in the following manner:

$$2(C_6H_5)_2C{=}S \rightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 2S$$

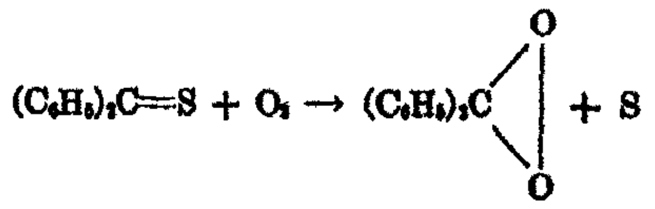
The oxidation products obtained by Staudinger and Freudenberger were benzophenone, sulfur and small amounts of sulfur dioxide; the fact that the latter appeared only in small amounts led them to the belief that the oxygen added to the carbon atom. Milas, in dissenting from this viewpoint, represented the initial act as the addition of oxygen to the sulfur atom, implying, as in other cases, an electronic activation.

It seems evident, from the ease with which thiobenzophenone is decomposed thermally, that the assumption of electronic activation of this substance is unnecessary to account for its auto-oxidation. From the point of view developed in the present paper the oxygen would be expected to add at the linkage of least thermal stability, which is obviously the C=S linkage,



$$(C_6H_5)_2C{=}S + O_2 \rightarrow \begin{array}{rcl} (C_6H_5)_2C & - & S \\ | & & | \\ O & - & O \end{array}$$

However, in this case, the complete rupture of the double bond in the C=S group takes place so easily that it seems probable that the oxygen molecule obtains both the necessary electrons from the carbon atom, forming an alkylidene peroxide and liberating sulfur.



$$(C_6H_5)_2C{=}S + O_2 \rightarrow (C_6H_5)_2C\langle\begin{matrix}O\\|\\O\end{matrix} + S$$

The appearance of only traces of sulfur dioxide would indicate such a small amount of side reaction that we need not concern ourselves with its nature.

The second compound of interest belongs to a general class mentioned by Milas (21) as typical examples of compounds possessing "molecular valence electrons." Triethylphosphine possesses an unshared pair of phosphorus electrons and Milas assumes, with other previous workers, that the addition of oxygen takes place at that point. However, the experimental evidence on the subject seems entirely at variance with this viewpoint (22). Leaving aside the reactions that take place in the presence of water, it has been found that the main isolable product of the oxidation of the dry substance is the compound,

$$(C_2H_5)_2PO.OC_2H_5$$

Now, the simplest explanation of the origin of this compound is on the basis of initial formation of the peroxide

$$(C_2H_5)_2P.O.O.C_2H_5$$

which might rearrange in a very obvious manner to give the above diethyl phosphinic ester. Therefore, it seems reasonable to conclude again that the oxygen attaches itself at a vibrationally activated bond, in this case the carbon-phosphorus bond.

A comparison of the mechanism of auto-oxidation reactions suggested in the present paper with those presented by Milas reveals the fact that the initial stage of the present writer corresponds with the second stage of Milas in all cases except the last two mentioned. The formation of the intermediate peroxide in auto-oxidations is thus considered as a single act rather than as consisting of two stages. As has already been implied, this does not mean that no distinction is recognized between the freshly formed peroxide molecules and the normal molecules of isolable product. A difference in energy content admittedly does exist, but there appears to be no reason for associating this with a structural difference which can be represented by any present system of notation.

REFERENCES

(1) Engler and Weissberg: Kritische Studien über die Vorgänge der Autoxydation, p. 90. Braunschweig, 1904.
(2) Erdman: J. prakt. Chem. **85**, 78 (1913).
(3) Staudinger: J. prakt. Chem. **85**, 330 (1913).
(4) Lenher: J. Am. Chem. Soc. **53**, 3737 (1931).
(5) Jorissen and Van der Beek: Rec. trav. chim. **49**, 138 (1930).
(6) Jorissen and Van der Beek: Rec. trav. chim. **45**, 245 (1926).
Van der Beek: Rec. trav. chim. **47**, 286 (1928).
(7) Bäckström: Medd. Vetensk. Acad. Nobelinst. [6] **16**, 15 (1927).
(8) Milas: J. Phys. Chem. **33**, 1204 (1929); Chem. Rev. **10**, 295 (1932).
(9) Mulliken: Proc. Nat. Acad. Sci. **12**, 144 (1926).
(10) Birge: Nature **117**, 300 (1926).
(11) See also Langmuir: J. Am. Chem. Soc. **41**, 868 (1919); Grimm: Z. Elektrochem. **31**, 474 (1925); Glockler: Proc. Nat. Acad. Sci. **12**, 522 (1926).
(12) Milas: Chem. Rev. **10**, 298–9 (1932).
(13) Smyth: Dielectric Constant and Molecular Structure, p. 85. Chemical Catalog Co., New York (1931).
(14) Smyth and Zahn: J. Am. Chem. Soc. **47**, 2501 (1925).
(15) Lewis, G. N.: Chem. Rev. **1**, 243 (1924).
(16) Pope, Dykstra, and Edgar: J. Am. Chem. Soc. **51**, 2203 (1929).
(17) Stephens: J. Am. Chem. Soc. **48**, 1824, 2930 (1926); **50**, 186, 2523 (1928).
(18) (a) Brunner and Rideal: J. Chem. Soc. **1928**, 2324.
(b) Chavanne: Bull. soc. chim. Belg. **36**, 206 (1927).
(c) Chavanne and Bode: J. Am. Chem. Soc. **52**, 1609 (1930).
(d) Mondain-Monval and Quanquin: Compt. rend. **191**, 299 (1930); Ann. chim. [1] **15**, 309 (1931).
(19) Mecke: Nature **125**, 526 (1931).
(20) Staudinger and Freudenberger: Ber. **61**, 1836 (1928).
(21) Milas: J. Phys. Chem. **33**, 1211 (1929).
(22) Engler and Weissberg: Ber. **31**, 3055 (1898).

THE pH OF GELATIN SOLUTIONS

J. GILBERT MALONE AND MARY G. MALONE

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

Received August 5, 1932

The authors are led by the recent paper of Hartman and Fleischer (1) to make the following comments.

The pH of a solution is theoretically rather poorly defined, since the idea of concentration has lost its early significance. The usual accepted methods of determination and comparison are useful and satisfactory in many cases, but as is well-known they are subject to influences which more or less invalidate the results obtained. Thus, the hydrogen electrode is usually considered the most fundamentally sound, with the colorimetric methods subject to errors due to influences such as salt, alcohol, and proteins. It is therefore surprising to come upon an article where the colorimetric methods are given preference over the electrometric methods. In such a case substantial proof would appear to be necessary before the conclusions can be accepted.

Hartman and Fleischer have determined the pH of gelatin solutions by several methods. These included the use of two sets of colorimetric buffers and indicators, the use of the hydrogen and quinhydrone electrodes, and the use of the glass electrode, although in this latter case the pH values were not determined, as sufficient data was lacking.

With the colorimetric methods the values agreed, but with the electrometric methods, especially in the case of the hydrogen electrode, variation with time was enormous. With the quinhydrone electrode the values obtained at different times agreed well, but did not agree with the values obtained colorimetrically. The results obtained with the glass electrode varied with time, but not to the same degree as shown by the hydrogen electrode.

The authors have had occasion to determine the pH of gelatin solutions over a rather wide range in connection with a study of the dielectric constant and dispersion in gelatin solutions. They have used the glass electrode as a means of making these determinations and have no reason to doubt the accuracy of the records obtained. A vacuum tube voltmeter using the FP 54 tube and following the general lines of Hill's apparatus (2), was constructed through the coöperation of Prof. H. H. Willard. The apparatus was shielded by means of metal boxes and the grid circuit was insulated by means of amber. The electrodes were constructed after the specifications of MacInnes and Dole, using for the membranes the special Corning glass .015 manufactured for this purpose. Saturated calomel was used as a reference electrode. In all cases two glass electrodes were used and the connection to the grid was changed from one to the other by means of a long glass rod so as to avoid polarization effects while the electrode shielding cage was open. The electrodes were calibrated against standard buffers and it was found that a linear relation was approximated. The readings on any solution could be changed to pH by means of this calibration. That no drifting occurs may be seen from the determinations (see table 1) made of the pH of a solution of Eastman's isoelectric gelatin and distilled water at widely different times. These values were taken only with the idea in mind of getting an accuracy of about 0.1 pH. Therefore recalibration of the electrodes each day was not made as is essential in very accurate work. However, if the glass electrodes vary as stated by Hartman and Fleischer, it is hardly conceivable that they will vary together, therefore the authors give the following values, taken consecutively and without the added refinements that would go with determinations of pH in other connections. These are stated without regard for the content of gelatin acid or alkali, the pH having been changed by the addition of hydrochloric acid or sodium hydroxide.

TABLE 1

The pH of a solution of isoelectric gelatin

GEL	pH AS GIVEN BY ELECTRODE	
	1	2
per cent		
0.5	4.70	4.69
1.0	4.70	4.60
1.0	4.68	4.61
0.5	4.69	4.65

2.72	2.71
5.67	5.75
4.67	4.70
5.86	5.88
8.20	7.29
4.19	4.20
3.68	3.64
3.96	3.91

It would be possible to continue, as the authors have some hundred such determinations. In the list, there appears to be only one case where a pH disagreement of more than .1 is found, namely, with 7.08 and 6.96.

It has been found by Ferguson (4) and his students as well as by others that the pH values determined by the hydrogen electrode are reproducible and constant.

The authors are fully aware that mere agreement does not constitute a sound basis establishing the fundamental accuracy of a method. They do not at this time contend that the values obtained in gelatin solutions give the proper measure of the hydrogen-ion activity. They do however contend that, properly used, the glass electrode will give definite and reproducible values in gelatin solutions and, as contrasted with colorimetric determinations, the presumption of accuracy is in favor of the electrometric methods.

REFERENCES

(1) HARTMAN AND FLEISCHER: J. Phys. Chem. **36**, 1136 (1932).
(2) HILL: Science **73**, 529 (1931).
(3) MACINNES AND DOLE: Ind. Eng. Chem., Anal. Ed. **1**, 57 (1929).
(4) FERGUSON AND SCHLUCHTER: J. Gen. Physiol. **15**, 463–75 (1932).

CATAPHORESIS. AN IMPROVED CYLINDRICAL CELL

SANTE MATTSON[1]

New Jersey Agricultural Experiment Station, New Brunswick, New Jersey

Received October 13, 1932

In a previous issue of This Journal (2) the author described a cylindrical cataphoresis (electrophoresis) cell for the ultramicroscopic determination of the speed of electrical migration and of the isoelectric point of colloidal materials. A formula for calculating the electrosmotic velocity distribution of the liquid in the cylindrical tube was also given.

This cell has proven very useful in a series of investigations dealing with the isoelectric precipitation of a number of complex precipitates such as silicates, phosphates, humates, and proteinates of aluminum and iron (3); also ferrocyanides, sulfides and hydroxides, and a number of other amphoteric colloids (5, 3). In the course of this work it was found possible to improve the cell in regard to one important point. It is the object of this paper to describe the present construction of the cell and also, in response to several inquiries, to present the derivation of the formula expressing the electrosmotic flow of the liquid.

The new form of the cell is shown in figure 1. The cell represents an almost straight tube, the slope of the electrode compartments being merely sufficient to cause a free outflow of the liquid and to permit the latter of being sucked into the cell without leaving any air bubbles behind. The great advantage in this form is that the cell can be effectively cleaned, which is very important. This is done by pulling a thread through the cell by means of a thin copper wire covered with insulating material to prevent scratching. A little cotton is tied onto the thread, which is then pulled back and forth in the tube which has been filled with a soap solution or other cleaning liquid. This effectually removes any deposit on the glass.

To make this procedure possible the electrodes had to be so placed as to be out of the way. The writer is indebted to the Glass Blowing Department of Eimer and Amend for finding a way out of the difficulty. The electrodes, which must have a large surface to prevent the formation of gas bubbles up to as high a concentration as possible, have been fused on to the walls of the conically shaped electrode compartments. This has proven to be very satisfactory.

---

[1] Present address Båstad, Sweden.

The diameter of the tube is the same as that of the older type and should be about 2.5 mm. The distance between the electrodes should be such as to yield a potential gradient of about 10 volts per centimeter. At this potential and a magnification of from 100 to 150 diameters, the migration of the particles becomes sufficiently rapid for accurate measurements. A higher potential gradient is avoided because this lowers the upper limit of concentration of the electrolyte. Without the use of non-polarizable electrodes we are, even at this potential, limited to a salt concentration of about 0.02 normal. In the case of strong acids and bases this upper limit lies still lower. At higher concentrations gas is evolved at the electrodes and causes displacement of the liquid.

This limitation of the cell is however compensated for by its simplicity and the rapidity with which measurements can be made. Since the charge on colloidal particles is very sensitive to the influence of ions, it seldom happens that higher concentrations of electrolytes are employed. This is especially true of the amphoteric systems studied by the writer. These are precipitated from very dilute solutions and, except in the very rare cases where the system is isoelectric at very low or very high pH, no difficulties from the evolution of gas are encountered. Such difficulties can, however, within certain limits be overcome by reducing the potential gradient to five or less volts per centimeter. The particles then move more slowly in proportion and make the measurement less accurate.

FIG. 1. CYLINDRICAL CATAPHORESIS CELL

The cell is connected directly to the terminals of a D. C. generator, to a series of storage cells, or to dry cells. It can be ordered in any length according to the available voltage.

It is extremely important that the stopcock at the lower end of the cell be kept well greased so as to completely close the tube. The particles must show no movement when the circuit is open.

The optical combination consists of a Bausch and Lomb 8 mm. (21×) objective and a 5 or 7.5 ocular. The working distance of this objective is 1.6 mm., which is sufficient for a focus at the proper depth of the cell (see below). In measuring the diameter of the tube in terms of microscope scale divisions, a 16 mm. objective having a working distance of 7 mm. is employed as previously described.

In place of the more complicated system of illumination originally employed by the writer, a simple illumination unit consisting of a 16 mm.

objective, a system of condensing lenses, and a 6-volt Mazda lamp, all mounted in a single tube and adjustable by rack and pinion in three directions, has been adapted by the Arthur H. Thomas Company, Philadelphia, Pa., and by Eimer and Amend, New York City, for use in connection with the cell here described.

In the preceding article on this subject the electrosmotic flow of the liquid in a *closed* cylindrical tube of the type here described was explained and illustrated. At the boundary between the glass wall and the liquid there exists an electrical double layer. If the glass is negatively charged (as it usually is except when coated with positive colloids) then the liquid is positive and is attracted along the boundary to the negative electrode.[2]

Since now the cell is closed it is obvious that as much liquid as flows along the boundary in one direction must return through the center of the tube in the opposite direction. In an annular layer somewhere between the wall and the axis of the tube the liquid must therefore be at rest.

The following expression for the velocity V of the liquid in the different parts of the tube was given

$$V = c\left(r^2 - \frac{a^2}{2}\right)$$

where r = the distance from the axis of the tube,
a = the radius of the tube, and
c = a constant determined by the P D of the double layer.

From this expression it follows that $V = 0$ where

$$r = a\sqrt{\tfrac{1}{2}} = a \times 0.707$$

When we measure the cataphoretic movement of the particles in a closed cylindrical tube we must therefore focus the microscope at a depth of 0.3 (0.293) of the radius below the inner wall (or roof) of the tube, for only then will the observed velocity of the particles be equal to their true velocity. Owing to a steep velocity gradient of the liquid and to the depth of the focus, this condition is only approximately fulfilled. Thus the different particles visible in the field never move with exactly the same velocity.

The derivation of the formula for which the writer is indebted to Dr. Hilding Faxèn of the University of Upsala is as follows. The velocity distribution in a cylindrical tube obeys the law

$$V = c\,(r^2 - C) \qquad (1)$$

---

[2] In reality the layer of liquid immediately next to the glass does not move, as this constitutes the inner electrical layer and remains fixed to the glass. The thickness of this innermost layer is undoubtedly much less than a micron, probably only a few millimicrons. In a tube of 2.5 mm. diameter we can therefore ignore the thickness of this film.

where r = the distance from the axis of the tube, and c and C are constants (1, 4).

Where the motive force acts as a difference in pressure at the ends of the tube, as is ordinarily the case, then the movement is all in one direction and is greatest along the axis, whereas at the wall of the tube the liquid does not move at all. In this case $C = a^2$, where a = the radius of the tube.

But in electrosmose the motive force acts along the surface layer, causing a flow of liquid next to the wall of the tube. Since the tube is closed, the same amount of liquid must return through its center. This is mathematically expressed by the formula

$$\int_0^a Vrdr = 0 \tag{2}$$

The formula assumes this simple form through the rotation symmetry.

With the value of V inserted and integrated

$$c\left(\frac{a^4}{4} - C\frac{a^2}{2}\right) = 0 \tag{3}$$

we get

$$C = \frac{a^2}{2}$$

By putting $\frac{a^2}{2}$ in place of C in formula 1 we get

$$V = c\left(r^2 - \frac{a^2}{2}\right) \tag{4}$$

which is the expression employed.

For comparison the corresponding four expressions in the theory of Smoluchowski (6), which applies to a closed chamber between two plane parallel plates (the kind of cell used by all other investigators), will be given.

For a chamber the plates of which are the distance $d = 2a$ apart we have

$$V = c(x^2 - C) \tag{1a}$$

x = the distance from the middle

$$\int_{-a}^{+a} Vdx = 0 \tag{2a}$$

$$2c\left(\frac{a^3}{3} - Ca\right) = 0 \tag{3a}$$

$$C = \frac{a^2}{3}$$

$$V = c\left(x^2 - \frac{a^2}{3}\right) \tag{4a}$$

Hence in this type of cell $V = 0$ where

$$x = \frac{a}{\sqrt{3}} = a \times 0.577\ldots$$

These expressions take no account of the influence of the side walls of the chamber on the electrosmotic flow of the liquid. They are therefore only applicable when the sides of the chamber are very far apart in proportion to the depth. The cylindrical cell employed by the writer allows therefore a more exact mathematical expression of the velocity distribution.

REFERENCES

(1) LAMB, H.: Hydrodynamics, 5th edition No. 331, Cambridge University Press, London (1930).

(2) MATTSON, SANTE: J. Phys. Chem. **32**, 1532–52 (1928).

(3) MATTSON, SANTE: The laws of soil colloidal behavior. III. Soil Sci. **30**, 459–95 (1930). IV. Soil Sci. **31**, 57–77 (1931). V. Soil Sci. **31**, 311–31 (1931). VII. Soil Sci. **33**, 41–72 (1932). Isoelektrische Niederschläge und ihre Eigenschaften, in Kolloid-Z. **58**, 305–14 (1932).

(4) MISES, R. VON: Elemente der Theorie der Hydromechanik, Vol. I, pp. 36–40. Samml. math. phys. Schriften, von E. Jahnke, Leipzig (1914).

(5) PARBERY, N. H., AND MATTSON, SANTE: Soil Sci. **33**, 75–94 (1932).

(6) SMOLUCHOWSKI, M. VON.: Graetz, Handbuch Elektr. Magn. **7**, 383 (1921).

PERIODIC PRECIPITATION OF FERROUS CARBONATE

R. J. HARTMAN, E. W. KANNING, AND F. J. GALLION

Department of Chemistry, Indiana University, Bloomington, Indiana

Received August 22, 1932

INTRODUCTION

In a previous article of This Journal, "The Liesegang Phenomenon Applied to the Lake Superior Iron Formations" (1), a synthetic demonstration of the Lake Superior iron formation is presented. Silica gels were prepared by mixing ammonium carbonate and sodium silicate solutions. Over these gels were placed solutions of ferrous ammonium sulfate of various strengths. There resulted in the gel bands of ferrous carbonate. In the text of this article is cited the fact that the same banded structure might occur if a silica gel prepared from carbon dioxide and sodium silicate solution were employed. Also, it is proposed that with this gel ferrous sulfate might yield bands as good as those obtained with ferrous ammonium sulfate.

It is the purpose of this investigation to study further the periodic precipitation of ferrous carbonate in different gels, thus substantiating the theory of formation of the Lake Superior iron formations proposed in the previous article. The facts cited in this paper as well as those of the former article tend to support the geologic theories proposed by C. R. Van Hise and C. K. Leith (2) concerning the origin of this formation.

EXPERIMENTAL

From approximately one hundred different experimental preparations, the eighteen showing the most outstanding periodic precipitation are pictured in figure 1. Each tube was filled about two-thirds full with the gel and covered with about 7 cc. of iron salt solution.

The first horizontal row of test tubes (A) contains gels prepared from 4 per cent gelatin solution. The tubes, A1 and A2, contain 4 per cent gelatin solution made 0.1 *N* with respect to sodium carbonate; A3 and A4, 0.5 *N* with respect to ammonium carbonate; A5 and A6, 0.5 *N* ammonium carbonate and also containing 5 per cent glucose by weight. The tubes A1 and A2 were covered with 0.8 *N* and 0.4 *N* ferrous ammonium sulfate solution, respectively; A3 and A4 also with 0.8 *N* and 0.4 *N* ferrous ammonium sulfate solution, respectively; A5 with 0.4 *N* ferrous sulfate; and A6 with 0.4 *N* ferrous ammonium sulfate.

In the horizontal rows B and C the gels were prepared from sodium silicate solution (sp. gr. 1.03) by bubbling carbon dioxide gas through the silicate solution for varied lengths of time. This was accomplished by passing the gas through the silicate solutions contained in the test tubes (12 cc.) at the rate of 4.7 liters per hour. The carbonate content of the gels was governed by the length of time that the gas was allowed to bubble.

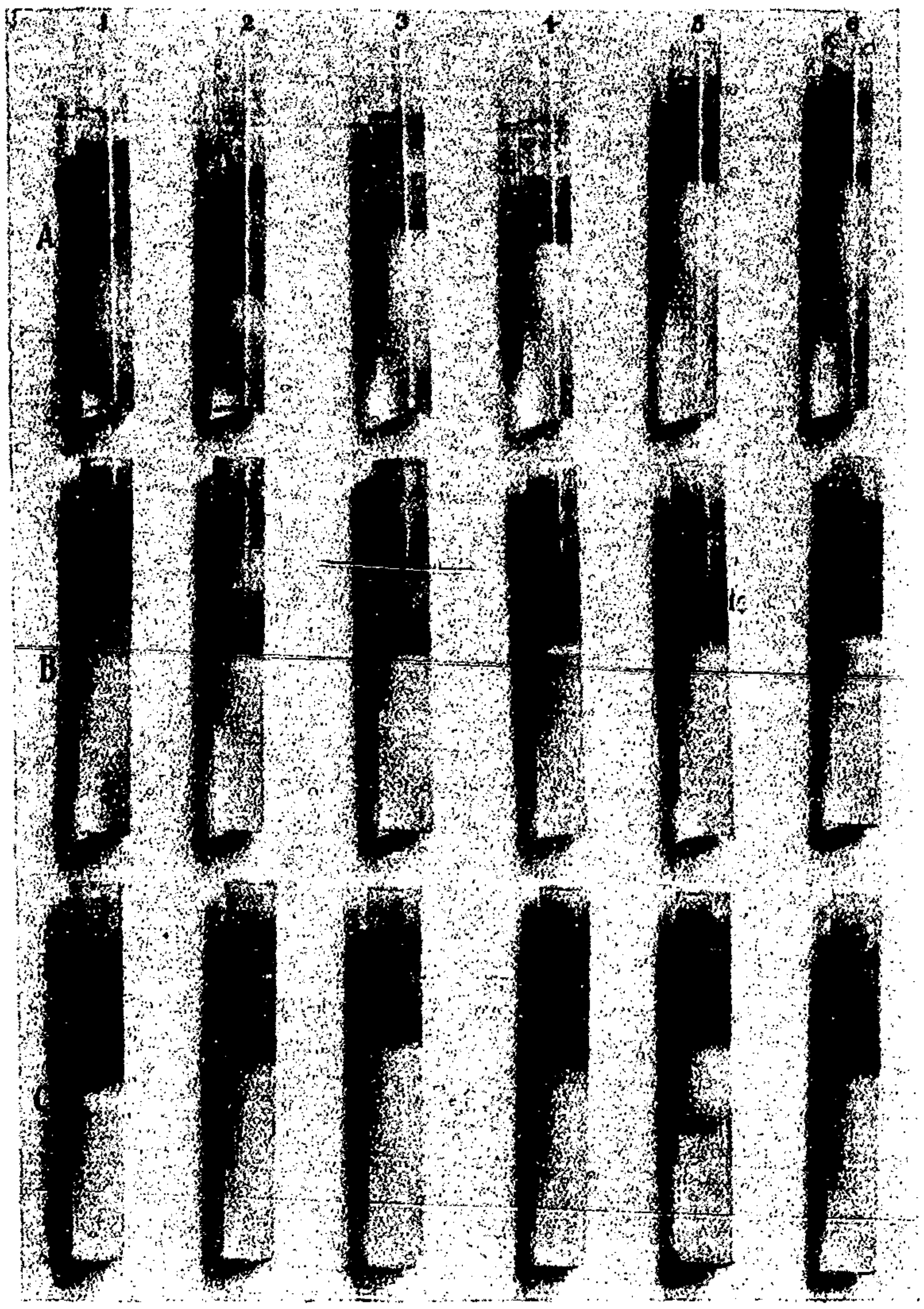


Fig. 1

The flow meter used to measure the rate of flow of the carbon dioxide gas was similar to that described in a previous article (3). In standardizing and using the flow meter, however, kerosene was used in place of water.

Gels B1, B2, and B3 were prepared by passing carbon dioxide gas at the rate of 4.7 liters per hour through sodium silicate solution (sp. gr. 1.03) for three, four, and five minutes, respectively; gels B4, B5, and B6 were prepared by bubbling the carbon dioxide gas for four minutes. In all cases in row B the gels were covered with ferrous ammonium sulfate solution. In B1, B2, and B3 the solution covering the gel was 0.3 *N* while the gels in B4, B5, and B6 were covered with *N*, 0.8 *N*, and 0.5 *N* solutions, respectively.

The gels in row C were prepared in a manner exactly analogous to the corresponding gels in row B. The gels in C1, C2, and C3 were each covered with 0.8 *N* ferrous sulfate solution; C4, C5, and C6 were covered with *N*, 0.5 *N*, and 0.3 *N* ferrous sulfate solutions, respectively.

All the ferrous salt solutions were changed each day for three days and then every other day until three more displacements had been made. Following this they were permitted to stand three weeks with a replacement of the solution once each week. The photograph was taken at this time.

DISCUSSION

A comparison of the bands produced in row A with either row B or C shows that the gels made from gelatin shown in row A were decidedly inferior for the production of bands. The gels made from gelatin (row A) produce less well-defined bands than those pictured in rows B and C where silica gel was the diffusing medium. This is probably due to the fact that gelatin offers a decidedly different diffusing medium than the silica gels. It appears, therefore, that the distinct banding of ferrous carbonate is specific for silica gels.

In comparing A1 and A2 in which the gels were made 0.1 *N* with respect to sodium carbonate and covered with 0.8 *N* and 0.4 *N* ferrous ammonium sulfate, respectively, it can be seen that the strength of the ferrous salt solution covering the gel seems to have no effect on the ferrous carbonate banding. This same conclusion may be drawn in A3 and A4, where the gels were made 0.5 *N* with respect to ammonium carbonate and covered with 0.8 *N* and 0.4 *N* ferrous ammonium sulfate solutions, respectively. Comparing A3 and A4 with A1 and A2 it is seen that ammonium carbonate in place of sodium carbonate in the gel tends to decrease the banding effect obtained in A1 and A2 and more even diffusion (A3, A4) occurs. The addition of 5 per cent glucose to a gel made from gelatin which is 0.5 *N* with respect to ammonium carbonate seems to decrease the formation of ferrous carbonate bands and to increase diffusion, as is evident in the comparison of tube A6 with A4.

A5, which is identical with A6 except that the gel is covered with ferrous sulfate in place of ferrous ammonium sulfate, demonstrated the same diffusion effect as is produced in A6.

Of the first three tubes in row B, the one containing the gel (B2) prepared by bubbling carbon dioxide for four minutes through the sodium silicate solution (sp. gr. 1.03) showed the deepest diffusion and the most distinct banding of ferrous carbonate. (B1, B2, and B3 were covered with 0.3 *N* ferrous ammonium sulfate solution.) For this reason gels prepared by bubbling carbon dioxide for four minutes were placed in tubes B4, B5, and B6 and were covered with *N*, 0.8 *N*, and 0.5 *N* ferrous ammonium sulfate solutions, respectively. Of these three gels (B4, B5, and B6) the gel covered with normal ferrous ammonium sulfate solution gave the best banding of ferrous carbonate.

A comparison of the tubes of row C indicates that gels covered with 0.8 *N* ferrous sulfate (C1, C2, and C3) give much better banding than the other tubes of that row. These experiments show conclusively that better banding is obtained when the carbon dioxide–sodium silicate gels are covered with solutions of ferrous sulfate (row C) rather than ferrous ammonium sulfate (row B).

A number of experiments were conducted using 2 per cent agar-agar gels made 0.5 *N* with respect to ammonium carbonate and sodium carbonate. Some of these gels also contained sucrose and glucose. These gels were covered with both 0.4 *N* and 0.8 *N* ferrous ammonium sulfate solutions. In all these experimental preparations very marked and rapid diffusion resulted with no banding whatsoever.

Carbon dioxide–sodium silicate gels were also prepared from sodium silicate solutions of specific gravity 1.06 and 1.10 and covered with the iron salt solutions of various strengths. A very dense impervious layer of ferrous carbonate was deposited on the surface of the gel after a very slight diffusion, thus preventing any further diffusion or banding. The gels made from these denser sodium silicate solutions were quite opaque.

Gels prepared from sodium silicate of densities less than 1.03 were not firm enough for any practical experiments. Likewise, iron salts of less than 0.3 *N* strength did not cause banding to any extent. Saturated solutions of these salts also resulted in no marked banding effect in the gels.

Tube C1 shows the best banding of ferrous carbonate of any herein pictured. The gel employed here was prepared by bubbling carbon dioxide through sodium silicate solution. Ferrous sulfate solution covered the gel. This, then, shows conclusively that the peculiar banding of the iron formations could have been brought about by the slow diffusion of ferrous sulfate (or, perhaps some other ferrous salt) as well as ferrous ammonium sulfate into a gel formed by the interaction of carbon dioxide, as well as basic nitrogenous substances or carbonates, with sodium silicate solution.

REFERENCES

(1) Hartman and Dickey: J. Phys. Chem **36**, 1129–35 (1932).
(2) Van Hise and Leith: U. S. Geol. Survey, Monograph 52.
(3) Hartman and Brown: J. Phys. Chem. **34**, 2651–65 (1930).

A METHOD FOR A MORE COMPLETE EXAMINATION OF BINARY LIQUID MIXTURES

W. ANDREW WRIGHT

Severance Chemical Laboratory, Oberlin College, Oberlin, Ohio

Received November 21, 1932

The customary examinations of liquid mixtures (either isothermal or isobaric) have been time-consuming and tedious enough, almost to prevent an exhaustive study of any particular mixture. Theoretical chemistry and the industries dealing with distillation and solvents have alike required an extension of the information available at the present. The study of zeotropic or azeotropic mixtures and their pressure-temperature-composition equilibria, requires a far greater fund of data than the literature affords. It would be desirable to have at hand not only a single isothermal investigation or two, but a "matte" of data from which we could construct at will any desired isobaric or isothermal diagram. Changes in the vapor pressure-temperature equilibria at constant composition in the liquid phase could be plotted from such data, and the heats of vaporization for any desired composition, pressure, and temperature combination could be calculated. Such a matte would allow an examination of the changes in the activity coefficients with the several variables of the system, and would permit predictions for any desired conditions or point (*P-T-N*). These predictions are one of the prime purposes of any investigation. It is the purpose of this paper to present a method of securing sufficient quantities for any system by a more simplified and direct means.

APPARATUS

Figure 1 illustrates the apparatus used by the author. The distillation flask was of somewhat new design, permitting a rapid equilibrium to be reached between the liquid and vapor phases. The flask, which contained the main volume of the sample being studied, was made from a 500-cc. round-bottomed Pyrex flask. The condenser was, as far as the author was able to ascertain, of new design. It consisted of an inner cooling tube against which the vapors impinged. This was sealed within the outer condenser wall but was left open at the top to permit of a variety of cooling methods. It was stoppered and a continual flow of water used, or if necessary, it could be filled with dry ice and ether. Various other refrigerants may also be used. This permits distillations even at fairly low temperatures. The condensate from the vapor phase flowed through a sampling trap and back into the liquid phase. The sampling tube for the liquid phase and the thermometer were placed in the ground glass stopper used for filling the flask. This stopper was securely held by a rubber-covered wire saddle. While no superheating was experienced in the apparatus, it can be prevented by etching the inside bottom of the flask with water glass (1). In order to prevent fractionation of the vapors before passing into the condenser, the upper half of the flask and the throat above it were insulated with asbestos rope wrapping. Control of the pressure was effected by a modified Victor Meyer mercury column regulator which could be rapidly changed in order to serve for control of pressures both above and below atmospheric. The pressure was adjusted to the desired point by raising or lowering the depth of the glass tubing in the mercury. Two large bottles of 4-liter capacity were included to increase the effective volume, thus preventing any noticeable fluctuation in the pressure during operation.

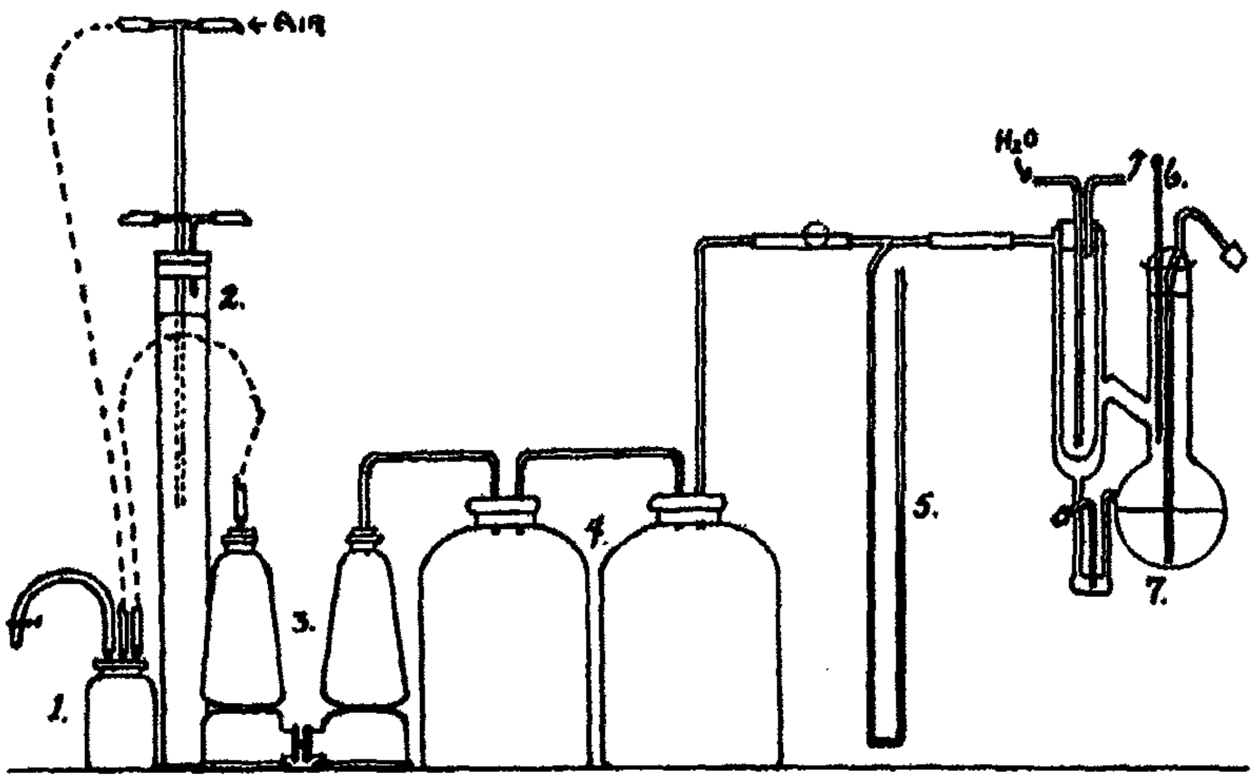


FIG. 1. APPARATUS USED IN THE EXAMINATION OF BINARY LIQUID MIXTURES
1, trap; 2, pressure regulator; 3, drying towers; 4, buffer bottles; 5, manometer; 6, thermometer; 7, distillation flask.

PROCEDURE

The system selected was toluene–ethyl alcohol. This selection was made partly because of previous work upon it (2), and because of the characteristics exhibited over the temperature range used and the ease with which it permitted the use of the refractometer as a means of analysis of the samples. Eleven samples, exclusive of the pure liquids and distributed over the range in composition, were made up from purified liquids. Each sample contained about 300 cc. The sample was placed in the flask and the pressure adjusted to the lowest value, the solution heated to boiling and given a half hour to reach equilibrium. Ordinarily, however, equilibrium was reached in five to ten minutes. A constant thermometer reading was taken as the criterion of equilibrium. The distillation rate was regulated and noted by counting the drops falling from the bottom of the cooling tube in the condenser. The rate was regulated until the condensate in the trap changed completely in a minute's time. The pressure and temperature were noted and the distillation stopped, and the pressure in the apparatus allowed to come to atmospheric level by use of the pinchcock. (Caution must be used when the pressure within the apparatus is greater than atmospheric. In this case the solution must be given time to cool sufficiently to prevent boiling when the pressure is released.) Dried air was forced into the apparatus to blow out samples of the condensed vapor phase and the liquid phase. These were analyzed by means of an Abbé refractometer and the remainder of the samples returned to the flask. The pressure was then adjusted 8 cm. higher and the process repeated on the same sample in the flask until the desired pressure range had been covered.

No trouble was experienced with changing composition of the liquid phase by removal of the samples for analysis. The relative amounts removed were too small to be of any consequence. The same procedure was followed, of course, for each succeeding mixture. This procedure gave the variations in the pressure and the temperature and the change in the composition in the vapor phase in equilibrium with a non-variant liquid phase. Variation in the liquid phase was accomplished only by changing the sample under investigation.

TREATMENT OF DATA

The changes in vapor pressure with temperature for each sample were plotted as shown in figure 2, the pressure in millimeters being given on the ordinate and the temperature on the abscissa. It will be seen that this curve is similar to the vapor pressure curve for a pure liquid. The dotted line represents the composition of the vapor phase in equilibrium, at the various temperatures, with a liquid phase of constant composition, the mole fraction being plotted on the ordinate. In the system of ethyl alcohol–toluene, the change in the vapor composition above any sample was slight, and linear in relationship to the temperature. Best line values were then read from the graph and used to construct tables 1 and 2.[1]

---

[1] While the data given in the tables are given to the nearest millimeter, a more recent study of the accuracy of the apparatus indicates that vapor pressures are correct to one-tenth of a millimeter.

From such a graph as figure 2, then, the vapor pressure and the composition of the vapor phase in equilibrium with the liquid phase for that sample can be determined at any desired temperature. Since this plot gives any minute variation in the pressure and the temperature, a plot such as figure 3 can be constructed. Figure 3 is a group of isotherms whose values were read from the graphs of type figure 2. The vapor phase curves in figure 3 have been omitted in all cases excepting that for the 80°C. isotherm.

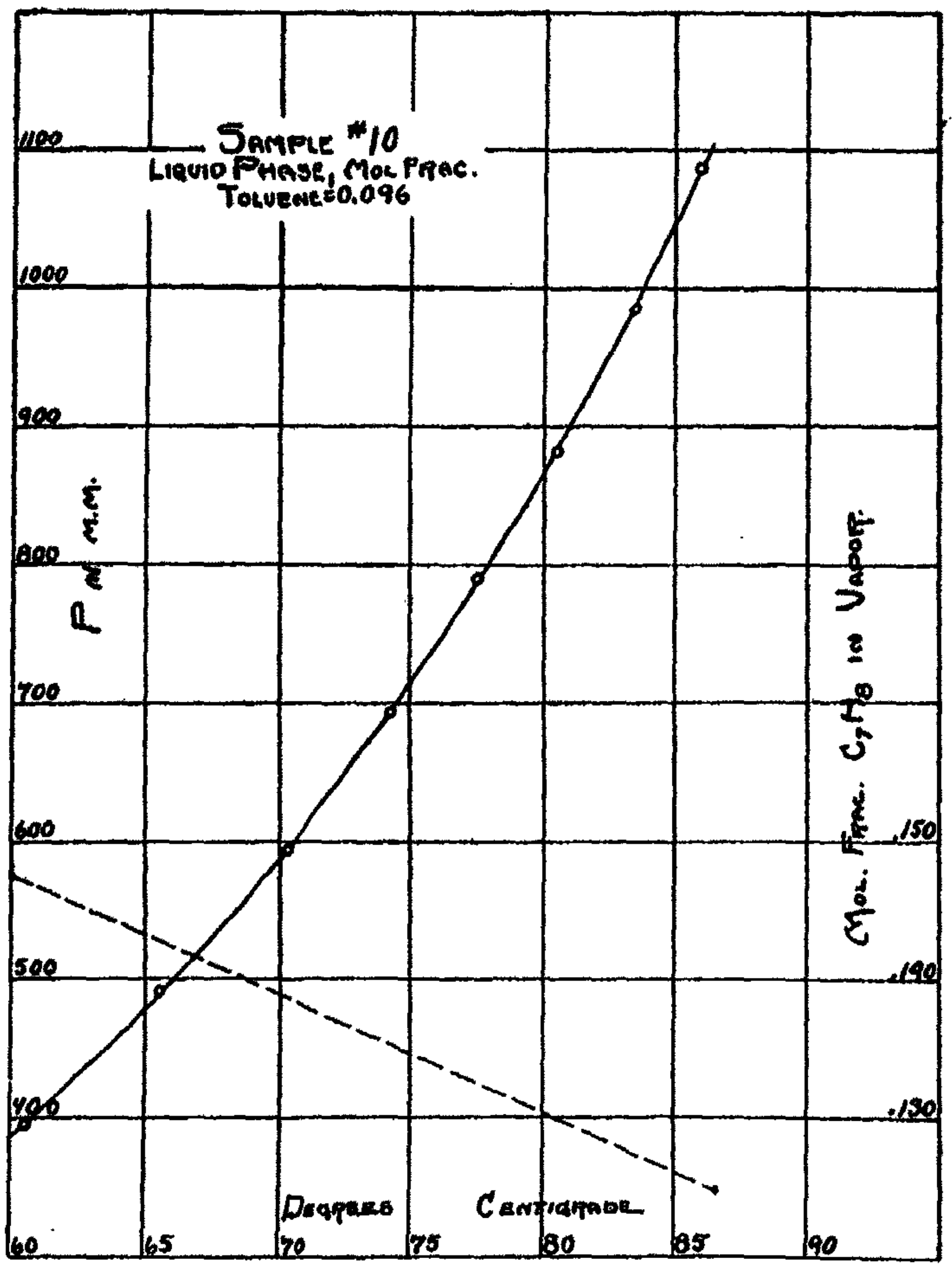


Fig. 2. Changes in Vapor Pressure with Temperature
Sample No. 10; mole fraction of toluene in liquid phase = 0.096

TABLE 1

Isotherms for the system toluene-ethyl alcohol

MOLE FRACTION TOLUENE		TOTAL PRESSURE	PARTIAL PRESSURE
Liquid	Vapor		
75°C.			
		mm.	
1.000	1.000	244	
0.893	0.380	444	169
0.769	0.307	677	208
0.648	0.286	688	197
0.557	0.280	698	195
0.457	0.269	707	190
0.375	0.253	715	181
0.274	0.232	722	167
0.233	0.217	724	157
0.155	0.180	724	130
0.096	0.135	716	96.7
0.043	0.075	699	52.4
0.000	0.000	666.1	0
80°C.			
1.000	1.000	289.7	
0.893	0.379	537	204
0.769	0.301	818	246
0.648	0.271	832	226
0.557	0.270	844	228
0.457	0.262	856	224
0.375	0.245	864	212
0.274	0.223	874	195
0.233	0.209	877	183
0.155	0.175	880	154
0.096	0.130	868	113
0.043	0.074	848	62.8
0.000	0.000	812.6	0
85°C.			
1.000	1.000	397.0	
0.893	0.379	642	243
0.769	0.294	990	291
0.648	0.266	1005	267
0.557	0.260	1016	264
0.457	0.257	1027	264
0.375	0.236	1037	245
0.274	0.215	1047	225
0.233	0.200	1052	211
0.155	0.169	1052	179
0.096	0.126	1047	132
0.043	0.073	1026	74.9
0.000	0.000	986.3	0

TABLE 2

Isotherms for the system toluene-ethyl alcohol

MOLE FRACTION TOLUENE		TOTAL PRESSURE	PARTIAL PRESSURE
Liquid	Vapor		
		60°C.	
		mm.	
1.000	1.000	139.5	
0.893	0.382	240	91.7
0.769	0.325	367	119
0.648	0.317	373	118
0.557	0.310	382	118
0.457	0.289	387	112
0.375	0.277	390	108
0.274	0.256	395	101
0.233	0.242	397	96.0
0.155	0.198	397	78.6
0.096	0.147	388	57.1
0.043	0.078	375	30.0
0.000	0.000	352.7	0
		65°C.	
1.000	1.000	166	
0.893	0.381	301	115
0.769	0.319	455	145
0.648	0.307	466	143
0.557	0.300	472	141
0.457	0.282	477	139
0.375	0.269	481	129
0.274	0.248	486	120
0.233	0.234	487	114
0.155	0.192	488	93.8
0.096	0.143	480	68.7
0.043	0.077	466	35.9
0.000	0.000	436.9	0
		70°C.	
1.000	1.000	202.4	
0.893	0.380	367	139
0.769	0.314	557	175
0.648	0.297	569	169
0.557	0.290	572	166
0.457	0.276	584	161
0.375	0.261	590	154
0.274	0.240	592	142
0.233	0.226	598	135
0.155	0.186	598	111
0.096	0.139	591	82.2
0.043	0.076	575	43.7
0.000	0.000	542.5	0

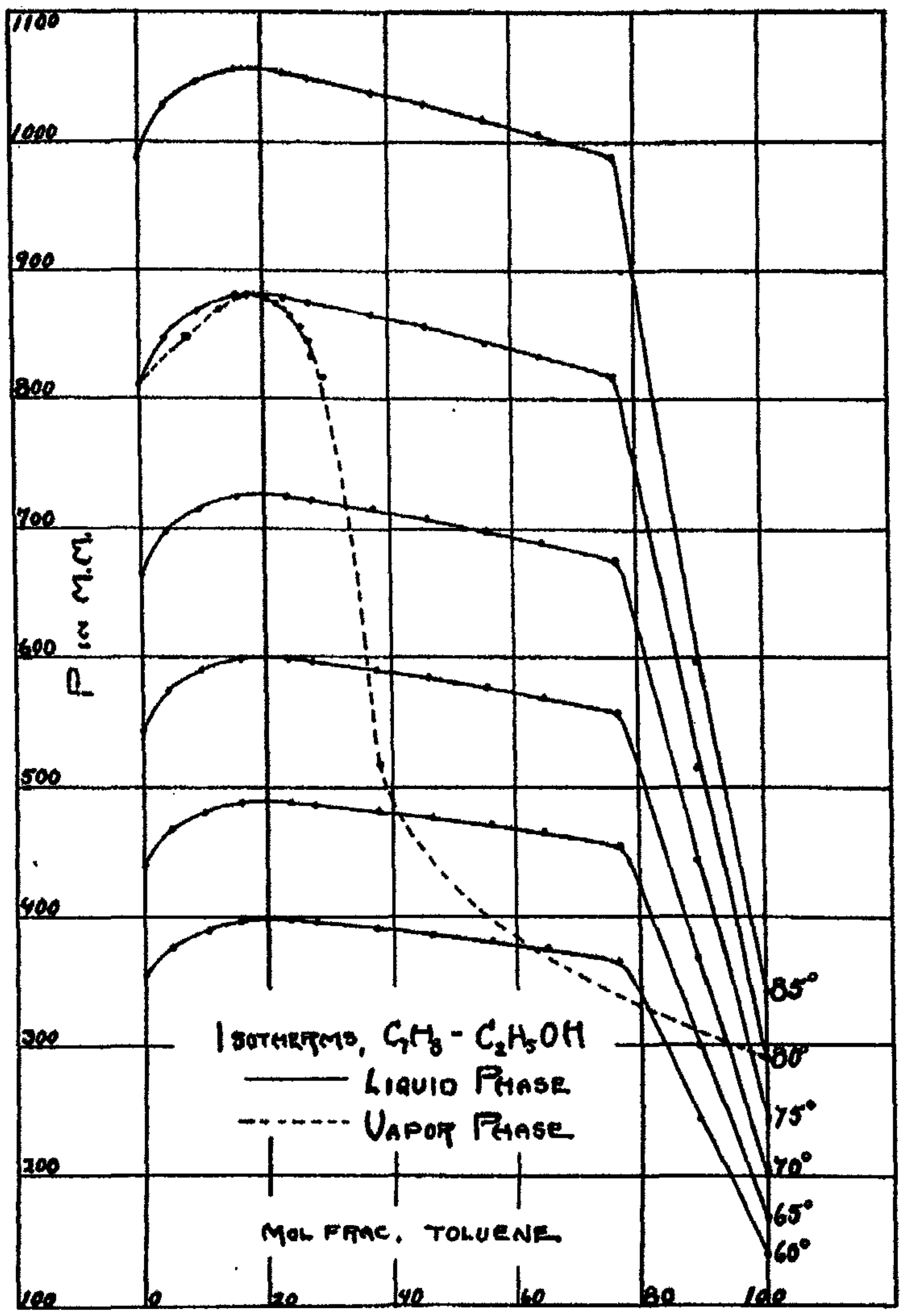


FIG. 3. ISOTHERMS FOR TOLUENE-ETHYL ALCOHOL

It would be advantageous to give an example of the above use of the graphs. If the isotherm at 80°C. is desired, we proceed as follows:

On figure 2, representing sample No. 10, we see that the composition of the liquid phase in mole fraction of toluene is 0.096. At 80°C., we find on referring to the curve that the total pressure on the system is

862.5 mm. This we plot on figure 3 for the isothermal diagram at 80°C., plotting the pressure against the mole fraction of toluene. The dotted line on figure 2 indicates that at the temperature of 80°C., the composition of the vapor phase in equilibrium with the liquid phase for sample No. 10 is 0.130. This, too, is then plotted on figure 3. We then proceed in a similar manner with each of the remaining samples distributed over the range of mixture, and thus determine the complete isothermal diagram for the system at that particular temperature.

DISCUSSION

If the logarithm of the vapor pressure is plotted against $1/T$ for each sample as shown in figure 4, the result is a straight line similar to the plot for a pure liquid. It will be recognized immediately that this is of great value, since the data can be extended by means of the straight line to any desired temperature or used for interpolation between values. The logarithms of the partial pressures of the constituents were then plotted against $1/T$ as in figure 5, and the straight line was again obtained. This is to be expected, for if the total pressure plot gives a straight line, the two partial plots must do likewise.

Data from Sameshima (3) and Cunaeus (4) for the system, acetone–ethyl ether, were plotted in a like manner and similar straight lines were found. Some data given by Schmidt (5) were also applied to such methods of plotting. In the system of benzene–carbon tetrachloride, the straight line relationships held true. The data for the system of benzene–toluene given by Schmidt were found to contain errors in the determination of the vapor pressures. The data given for the vapor pressures of pure toluene would not give a straight line when log P was plotted against $1/T$. Errors in the same direction were found to exist throughout the system at the same temperature.

In the case of toluene–ethyl alcohol, the system was azeotropic, while the system of acetone–ethyl ether and that for benzene–carbon tetrachloride were zeotropic. Evidently the principle holds for either type of liquid mixture. It becomes evident then, that the investigation of a binary liquid mixture requires only the determination of two pressure-temperature-composition diagrams to completely outline the system. This could be most rapidly accomplished by determining two isobaric diagrams.

Since the ethyl alcohol–toluene mixture is azeotropic, having a maximum in vapor pressure, a plot as in figure 4 gives some lines which are located higher than the line for the pure alcohol. However, the lines are not parallel, but vary between the slopes of the lines for the pure liquids and vary as the composition of the liquid phase is varied. Examination shows that the maximum occurs at a composition which changes with the temperature. If the straight lines were extended sufficiently, eventually all would lie within the lines for the pure liquids. At the temperature at which this occurs, the system becomes zeotropic. In this particular case, the maximum, or azeotropic point, is shifting so slowly that the temperature at which this would happen would be quite high. Predictions made by the extensions of the straight lines obtained are accurate throughout the

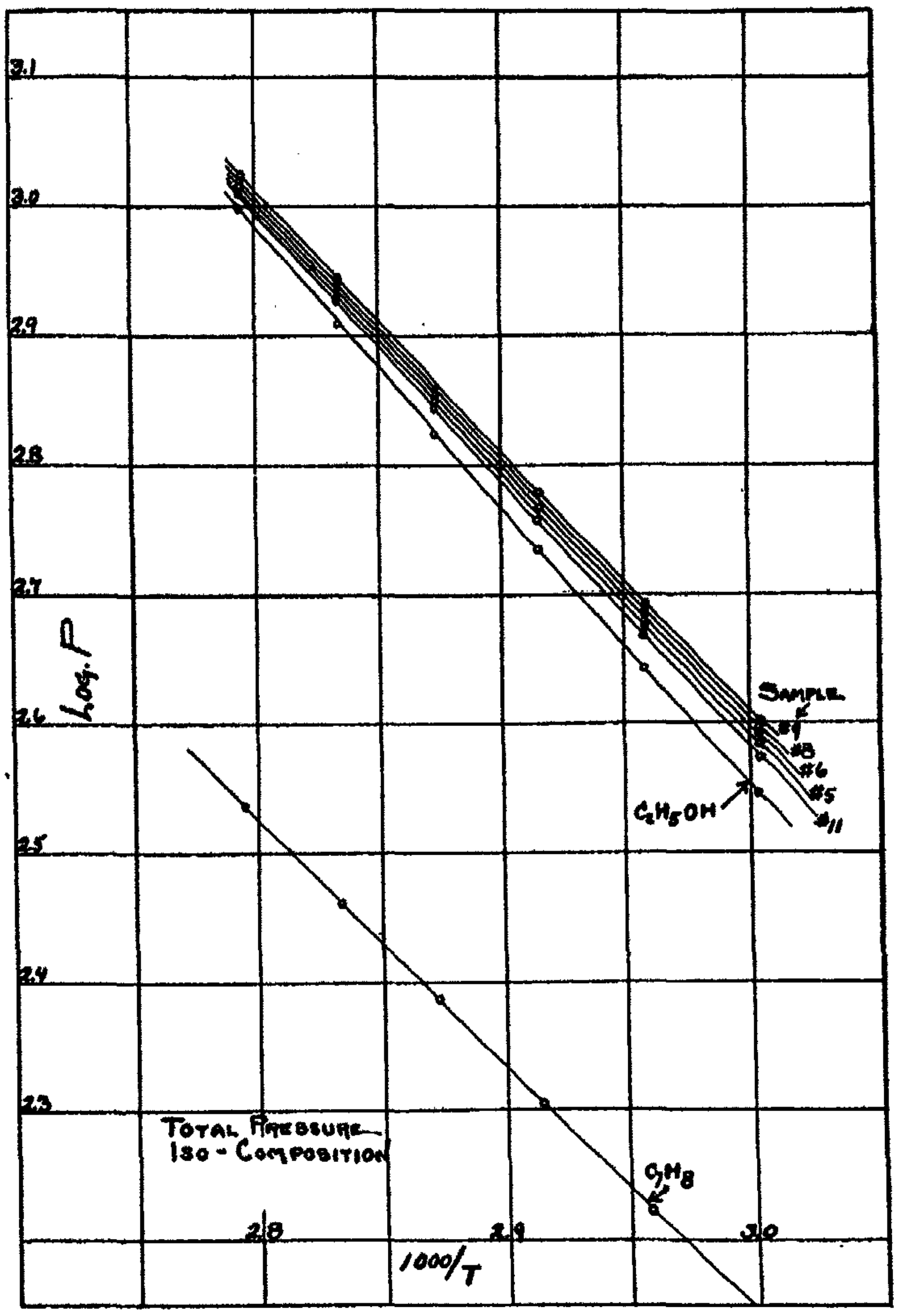


Fig. 4. Total Pressure Iso-composition

range where the pure liquids give a straight line when log P is plotted against $1/T$.

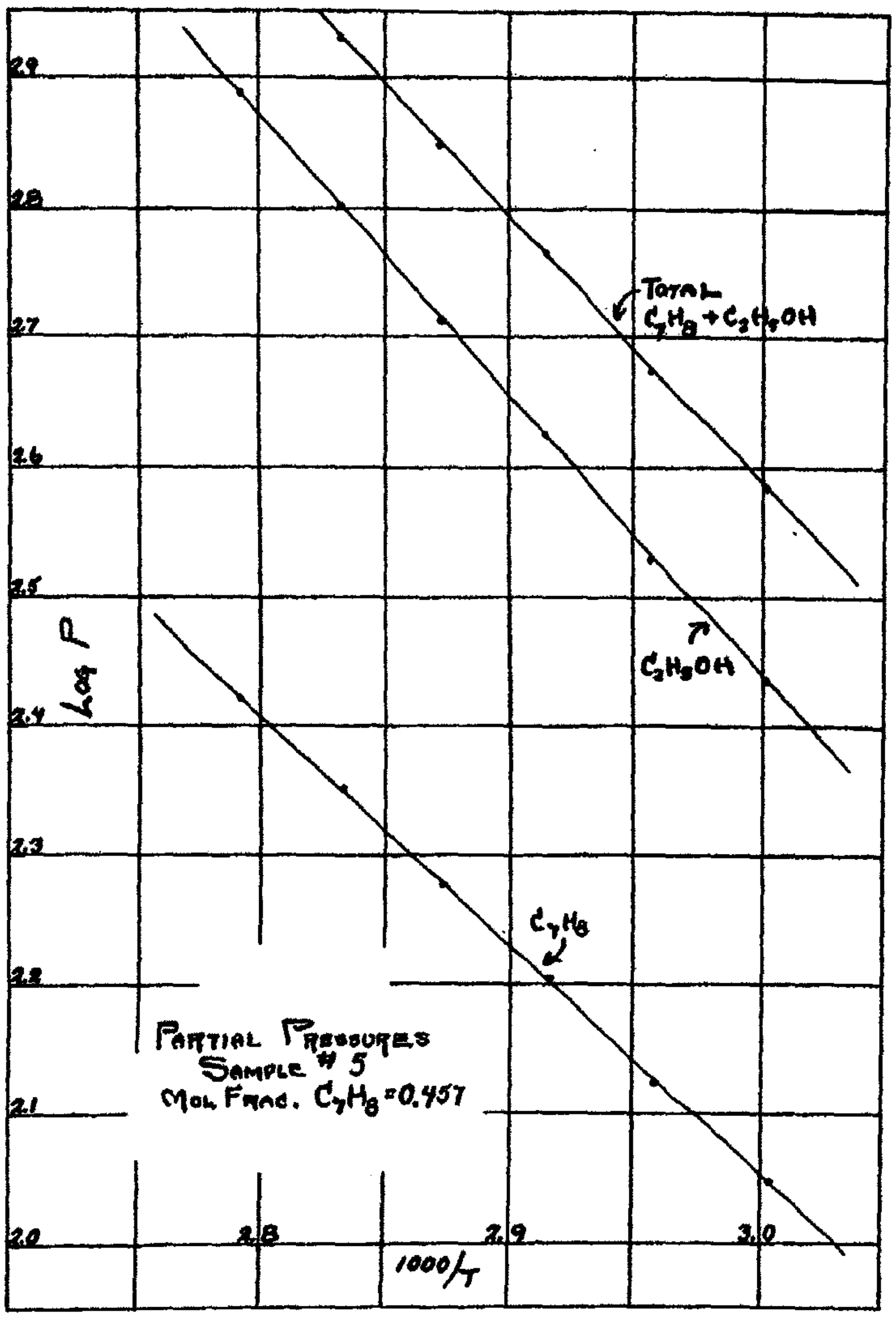


FIG. 5. PARTIAL PRESSURES
Sample No. 5; mole fraction of toluene = 0.457

A liquid mixture, when outlined as described, becomes a versatile source of data. Aside from the prediction of pressure, temperature, and composition equilibria, graphs of the type of figure 4 have been used to calculate the heats of vaporization at any desired temperature and composition.[2] Similarly, from the graphs of the type of figure 5 the partial heats of vaporization at any particular point were calculated. Studies on activities and activity coefficients can be made, prediction of the shift of the azeotropic point, etc.

SUMMARY

(1) In the study of liquid mixtures, the desirability of data in sufficient quantities to give a matte when plotted is pointed out.

(2) An apparatus is described and the procedure outlined for the determination of such data.

(3) A very complete examination of the system, toluene–ethyl alcohol, has been made over a pressure range of 700 mm. and its attendant temperature changes.

(4) As a consequence of the character of the data obtained, some generalizations are made on the laws of liquid mixtures, permitting equilibria predictions and calculations such as the heat of vaporization or the partial heats of vaporization at any point. The generalizations made in the paper have been tested with data from the literature and further confirmation obtained of their value.

REFERENCES

(1) Şwietoslawski: Bull. soc. chim. 50, 1568 (1931).
(2) Robinson, Wright, and Bennett: J. Phys. Chem. 36, 658 (1932).
(3) Sameshima: J. Am. Chem. Soc. 40, 1482, 1503 (1918).
(4) Cunaeus: Z. physik. Chem. 36, 232 (1901).
(5) Schmidt: Z. physik. Chem. 99, 71 (1921); 121, 221 (1926).

---

[2] These, together with some other similar calculations, may be discussed in a later paper.

DIFFUSION IN STANDARD CELLS

GEORGE A. HULETT AND R. B. ELLIOTT

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Received August 19, 1932

Our principal standards of electromotive force are: (1) the zinc (Clark) cell, $ZnAm/ZnSO_4 \cdot 7H_2O$, Hg_2SO_4/Hg; (2) the cadmium (saturated) cell, $CdAm/CdSO_4 \cdot 8/3H_2O$, Hg_2SO_4/Hg; and (3) the Weston (unsaturated) cell, $CdAm/CdSO_4$ solution (saturated 4C.)/Hg_2SO_4/Hg. All these cells are built about mercurous sulfate as depolarizer and it is the unique properties of this substance that have made these voltaic combinations useful standards (1). The mercurous sulfate has a solubility of about one gram in a liter in the cathode systems of these cells, while the amalgams of the anode system maintain the concentration of the mercury to something like 10^{-10} gram per liter at the amalgam electrode surfaces (2). Therefore these combinations may be looked on as concentration cells.

It is the function of the mercurous sulfate to maintain a definite concentration of mercury at the mercury cathodes, while the amalgams maintain an equally definite concentration of mercury at the amalgam anodes. These concentrations are widely different so that there must be a continual diffusion of mercury ions from cathode to anode, and this diffusion is an important factor in the slow changes that take place in the E.M.F. of the cadmium and Weston cells (3). It has been shown (4) that neutral cadmium sulfate solutions slowly hydrolyze mercurous sulfate but that the insoluble products of hydrolysis inhibit the reaction, and it is only as these products diffuse away to the anode that the hydrolysis becomes effective, so that it has become of interest to obtain more definite information on diffusion in standard cells.

Properly constructed cells show their normal E.M.F. immediately they are filled, so that the mercurous sulfate promptly establishes its proper concentration at the mercury electrode. The amalgam or anode electrolyte also promptly comes to equilibrium with a definite mercury ion concentration at the anode. The amalgam is able to maintain this concentration even when the mercury ions arrive by diffusion from the cathode, otherwise the arrival of the mercury ions at the anode would be accompanied by a change in the E.M.F. of the cell. The extended observations on zinc cells completely negative this proposition. It seemed of interest to have more information on the diffusion that actually takes place in standard cells. When a cell is freshly filled the electrolyte excepting that in the "paste" is quite free of mercury ions, but the cathode mercury ions begin at once to diffuse toward the anode. The potential of the electrolyte at any point toward a mercury electrode depends on its mercury ion concentration, so that if we determine this potential we have a measure of the mercury ion concentration at the particular point. Now, amalgamated platinum has exactly the same potential as mercury, so we may use a small amalgamated platinum point to explore the electrolyte of cells. We may measure it against the anode or cathode of the cell and so determine the mercury ion concentration at any point in the cells, provided that we know the relation between mercury ion concentrations and potentials in these solutions.

This information we have obtained as follows. A saturated cadmium sulfate solution was rotated at 25.00°C. together with $CdSO_4 \cdot 8/3H_2O$, mercury, and normal electrolytic mercurous sulfate (5) until no further change in concentration took place—two weeks. Two 100-cc. portions of the perfectly clear solution were removed for analysis and to each was added a very slight excess of 0.2 *N* HCl. Under these conditions Hg_2Cl_2 is one of our most insoluble precipitates. In the absence of mercury or a reducing agent the removal of the mercurous mercury does not disturb the mercuric mercury present. Instead of a tared filter paper disk previously employed (6) we used a small-sized Neubauer crucible with a minimum of sponge platinum filtering medium.[1] The Hg_2Cl_2 coagulates, filters, and washes very satisfactorily. The Hg_2Cl_2 is measurably volatile at 100°C. but may be satisfactorily dried in a vacuum desiccator at room temperature and the results are very exact (6). The two determinations checked quite closely, showing 1.122 grams Hg_2Cl_2 from a liter of the saturated $CdSO_4$ solution. This gives a calculated 0.9535 gram of mercurous mercury in one liter, or a concentration of 0.00238 molar.

The filtrates and wash waters were made acid with hydrochloric acid to keep cadmium sulfide in solution and then the mercuric sulfide was precipitated, vacuum desiccated in the Neubauer crucible, and was found to weigh exactly 4 mg. from the 200 cc. of the saturated solution or 0.00354 gram of mercuric mercury from 200 cc. of the saturated solution. This is 0.01725 gram of mercury in one liter, or 0.00086 molar. This indicated a ratio of

$$\frac{\text{Hg(ous)}}{\text{Hg(ic)}} = \frac{0.9535}{0.01725} = 55$$

A portion of the above solution (saturated with $CdSO_4 \cdot 8/3\ H_2O$, Hg_2SO_4, Hg) was brought onto a mercury electrode and joined to a cadmium amalgam–cadmium sulfate half-cell (7). The E.M.F. of this combination at 25.00°C. was 1.019614 volts, confirming previous observations on the

---

[1] The weight of a large sponge of platinum is not so reproducible on vacuum desiccation, but with our crucible we found the weight reliable to about 0.01 mg.

rotated cathode system of the cadmium cell (8). Now this voltage of 1.019614 corresponds to a concentration of 0.9535 gram of mercuric mercury and 0.01725 gram of mercuric mercury in a liter of the saturated cadmium sulfate solution at the mercury electrode. By diluting the original solution with known volumes of a saturated $CdSO_4 \cdot 8/3\ H_2O$ solution, we had solutions of known mercury concentration and we observed the potential of each of these on a mercury electrode combined with the cadmium amalgam half-cell. We thus had the cadmium cell combination with known concentrations of mercury at the cathodes. Obviously from E.M.F. values such a table (table 1) gives the mercury concentration at the cathode of any cadmium cell as accurately as we have knowledge of the mercury concentration of our original solution.

TABLE 1

SATURATION SOLUTION	Hg_2^{++} PER LITER	Hg^{++} PER LITER	E.M.F. OF CELL AT 25°C.
per cent	*grams*	*grams*	
100	0.9535	0.01724	1.019614
95	0.9057	0.01638	1.019050
90	0.8581	0.01552	1.018718
85	0.8104	0.01465	1.018082
80	0.7627	0.01378	1.017593
75	0.7151	0.01293	1.016828
70	0.6674	0.01207	1.018790
65	0.6197	0.01121	1.015093
60	0.0721	0.01035	1.014288
55	0.5244	0.00948	1.013208
50	0.4767	0.00862	1.01160
45	0.429	0.00776	1.010548
40	0.3814	0.00689	1.009058
35	0.3337	0.00603	1.004985
30	0.2860	0.00517	1.002533
25	0.2384	0.00431	1.001543
20	0.1907	0.00343	0.995340
15	0.143	0.00259	0.993793
10	0.09535	0.00172	0.988510
5	0.0477	0.00086	0.993793
4	0.0381	0.00068	0.979933
2	0.0191	0.00034	0.971973
1	0.0095	0.00017	0.962901
0.8	0.0077	0.000136	0.963453
0.6	0.0057	0.000102	0.961043
0.4	0.0038	0.000068	0.955143
0.2	0.0019	0.000034	0.950343

From table 1 it is of interest to note that the cadmium cell with an E.M.F. of 1.01808 volts at 25°C. has a solution next to the mercury electrode which had 0.8104 gram of mercurous mercury and 0.01465 gram of mercuric mercury to the liter. This is only 85 per cent of the concentration obtained by saturating a saturated solution of cadmium sulfate at 25°C. with normal mercurous sulfate in the presence of mercury. Here is further evidence that the cathode systems of our cadmium cells are not equilibrium systems. Indeed it is only necessary to stir the paste of any seasoned cadmium cell (9) to observe a marked increase in E.M.F. followed by a subsequent decrease with the E.M.F. dropping *below* the normal value, which is quite conclusive proof of the instability of this cathode system and confirms the conclusions drawn from the rotation experiments (7).

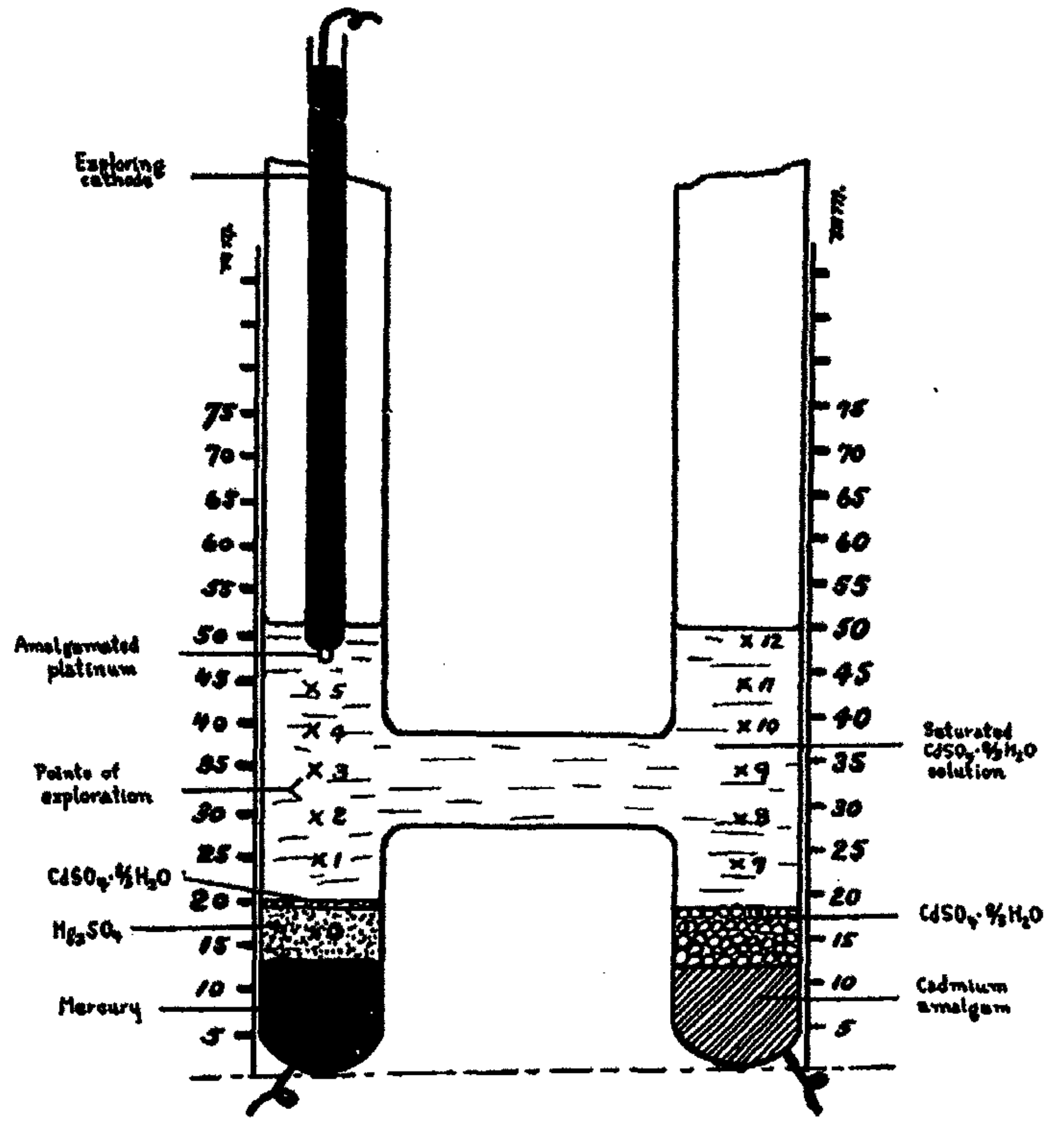


FIG. 1

With the information in table 1 we may unseal any cadmium cell and explore the mercury concentration at any point in the electrolyte or paste. Amalgamated platinum has the same potential as mercury. We only need a minute amalgamated platinum point. By placing such an electrode at the desired point in the cell and measuring its potential against the anode from this E.M.F. the table gives the exact concentration of mercurous and mercuric mercury at the point in question. It was of interest now to open cells of different ages and observe how diffusion had progressed. For this purpose two cadmium cells with electrolytic mercurous sulfate as depolarizers made up according to specifications developed in this laboratory were selected (10). One cell, A138, was made in 1914 and the other, G3, was made in 1928. These cells maintained at 25.00°C. were unsealed and the amalgamated point was placed at positions indicated in figure 1. The following observations (table 2) and deductions were made.

TABLE 2

LOCUS	E.M.F.	Hg_2	PER CENT NORMAL
		Cell G3	
		mg. per liter	
Cell itself	1.018140	817	102
0	1.01791	793	98
1	1.00812	372	45.7
2	1.00697	358	44.2
3	1.00659	354	43.7
4	1.00591	345	42.1
Cathode			
7	1.00437	323	40
8	1.00435	320	39.5
9	1.00431	320	39.5
10	1.00428	320	39.5
		Cell A138	
Cell itself	1.01804	807	99.5
Cathode			
0	1.01727	740	91.3
1	1.01737	745	92.1
2	1.01735	745	92
Anode			
7	1.01738	747	93.15
8	1.01735	745	93
9	1.01735	745	93
10	1.01739	749	93.1

It appears that diffusion does not attain a steady state in four years in the cadmium cell, but does inside of eighteen years. There is a distinct concentration gradient in the four year old cell but practically none in the eighteen year old cell. An interesting observation in cell A138 is that the concentration of mercurous mercury in the paste is less than that at the surface of the mercury electrode. This may well be due to the presence of much finely divided mercury in the paste, a factor we will consider in a subsequent article.

The above experiments do not give a very good idea of the rate of diffusion in newly constructed cells when it is a maximum. To get a clearer picture of this region we observed a cell constructed as follows. The usual mercury and 10 per cent cadmium amalgam electrodes were used but no paste or mercurous sulfate or cadmium sulfate was introduced into the cell. Instead, a saturated solution of these salts only was employed. The system ($CdSO_4 \cdot 8/3H_2O$, Hg_2SO_4, Hg, H_2O) was rotated at 25°C. for fourteen days and the clear solution taken to fill the cell. The observations are given in table 3. The cell had the high E.M.F. observed in the rotation experiments. Evidently the cadmium amalgam promptly reduced the mercury ions in its vicinity to the equilibrium concentration. Diffusion to

TABLE 3

TIME	E.M.F.	Hg_2	PER CENT NORMAL
days		*mg. per liter*	
0	1.019610	953.45	117.6
1	1.019053	905.72	111.7
2	1.018897	895.0	109.00
6	1.008719		47.0
7	1.005744		38.4
11	1.00120	236	29.1
20	0.99934	222	27.3
36	0.991857	124	15.3
53	0.980871	50	6.15
61	0.964187	9.53	1.08
74	0.956526	7.15	0.88
100	0.946194	2.38	0.29

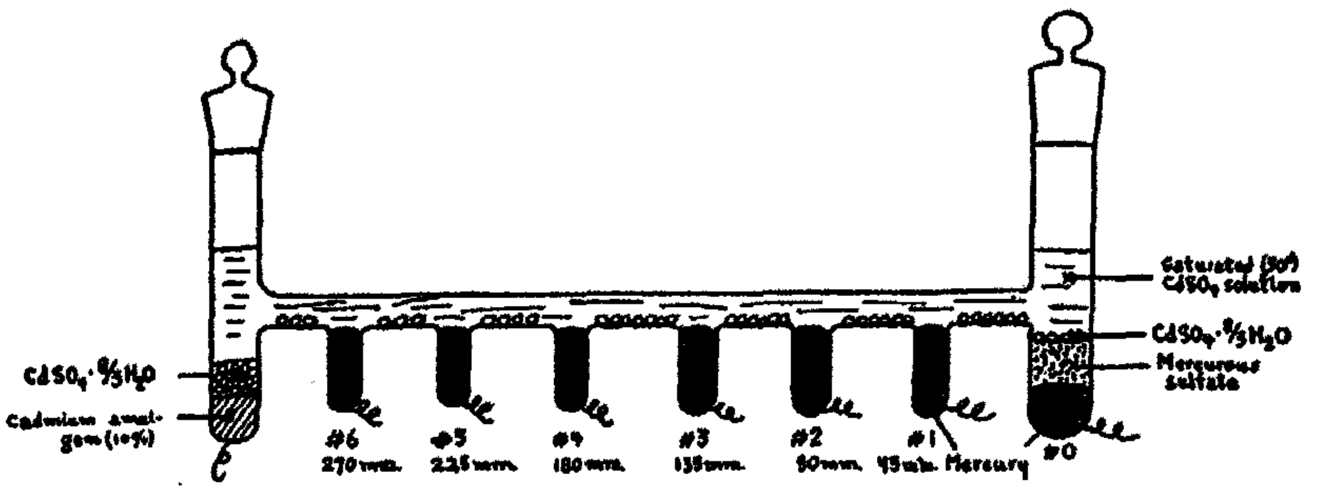


FIG. 2

TABLE 4

CELL		TIME	CATHODE NO. 6	CATHODE NO. 5	CATHODE NO. 4	CATHODE NO. 3	CATHODE NO. 2	CATHODE NO. 1	CATHODE NO. 0
Electrolytic Cell A	E.M.F. versus anode	1st day	0.97530	0.98477	0.98574	0.98641	0.98835	0.98890	1.018242
	Per cent normal		2.95	7.55	9.44	10.62	11.80	12.98	102.95
Crystalline Cell B	E.M.F. versus anode	1st day	0.97459	0.98279	0.98829	0.99181	0.99368	0.99493	1.01865
	Per cent normal		3.24	7.67	11.50	15.6	17.65	19.4	109.44
Electrolytic Cell A	E.M.F. versus anode	6th day	0.98442	0.98195	0.99910	0.9940	0.99968	0.99993	1.018157
	Per cent normal		8.55	7.05	26.5	27.1	27.7	28.5	102.06
Crystalline Cell B	E.M.F. versus anode	6th day	0.99852	0.99907	0.99965	0.99982	0.99982	1.00031	1.01849
	Per cent normal		24.6	26.2	26.7	27.6	27.7	28.2	107.1
Electrolytic Cell A	E.M.F. versus anode	65th day	1.00437	1.00438	1.00460	1.00511	1.00566	1.00664	1.01804
	Per cent normal		35.3	35.6	36.2	37.6	38.5	40.5	99.4

the anode began as soon as the cell was filled, and inside of twenty-four hours the diffusion began to affect the cathode potential, resulting in a decreased concentration at the mercury electrode. After six weeks the rate of this drop is pronounced, and in some three months there are exceedingly few mercury ions left about the cathode, so that this cathode potential is approaching the equilibrium value of mercury in saturated cadmium sulfate solution (11).

Further information was sought by observations on some special cadmium cells with a long connecting tube between anode and cathode, 31 cm. long and 10 mm. diameter (figure 2). This connecting tube carried small mercury electrode pockets spaced 45 mm. apart so that it was possible to observe the mercury ion concentrations at these various stations along the cross tube and so the changes with time. One cell was made up with the standard electrolytic mercurous sulfate as depolarizer and the other with our crystalline (12) mercurous sulfate as depolarizer. The electrolyte was saturated at above 25°C., so that it deposited some $CdSO_4 \cdot 8/3H_2O$ crystals along the cross tubes. The table given above gives the relation between E.M.F. and mercury ion concentration at the cathode. At 25°C. a cadmium cell with an E.M.F. of 1.01808 volts has a concentration of 810.43 mg. of mercurous mercury and 14.65 mg. of mercuric mercury to a liter of solution in contact with the mercury electrode. Taking these values as normal we have the observations given in table 4.

It appears from these experiments that the diffusion of mercury ions in standard cells is of considerable magnitude and appears to be greater when the depolarizer is crystalline mercurous sulfate than it is when the electrolytic, precipitate-like product is used for the paste. Evidently the crystalline product is able more rapidly to replenish the ions that diffuse away. When hydrolysis of the mercurous sulfate is possible (4), as in the neutral cadmium or Weston (unsaturated) cells, diffusion may well be an important factor in E.M.F. changes.

REFERENCES

(1) Hulett, G. A.: Trans. Am. Electrochem. Soc. **14**, 65 (1908).
(2) Hulett, G. A., and De Lury, Ralph E.: J. Am. Chem. Soc. **30**, 1805 (1908).
(3) Hulett, G. A.: Trans. Am. Electrochem. Soc. **58**, 299 (1930).
(4) Gardiner, W. C., and Hulett, G. A.: Trans. Am. Electrochem. Soc. **56**, 111 (1929).
(5) Hulett, G. A.: Phys. Rev. **23**, 175 (1906).
(6) Hulett, G. A.: Z. physik. Chem. **49**, 500 (1904).
(7) Hulett, G. A.: Phys. Rev. **23**, 176 (1906).
(8) Reference 7, page 180.
(9) Hulett, G. A.: Phys. Rev. **30**, 652 (1910).
(10) Hulett, G. A.: Phys. Rev. **32**, 257 (1911).
(11) Reference 2, page 1825.
(12) Elliott, R. B., and Hulett, G. A.: J. Phys. Chem. **36**, 2083 (1932).

SOME HEAT CAPACITY DATA FOR DURENE, PENTAMETHYLBENZENE, STILBENE, AND DIBENZYL

JOHN D. FERRY AND S. BENSON THOMAS

Department of Chemistry, Stanford University, Stanford University, California

Received December 5, 1932

A "radiation" calorimeter has been described in detail in a recent paper by Thomas and Parks (1). While this calorimeter was developed primarily for the measurement of the specific heats of boron trioxide glass at moderately elevated temperatures, it was later used very successfully in a study (2) of the heat capacities of eleven organic substances between room temperature and about 200°C. Continuing this latter application of the "radiation" calorimeter, we have now obtained specific heat and fusion data for the following four compounds: durene, pentamethylbenzene, stilbene, and dibenzyl.

MATERIALS

Durene and pentamethylbenzene

The samples of these two hydrocarbons were generously presented to us by Professor Lee Irvin Smith of the University of Minnesota. Details concerning them will not be given here, as their preparation and properties have been fully described elsewhere (3). The sharpness of their fusion curves indicated very satisfactory purity.

Stilbene and dibenzyl

These compounds were obtained from the Eastman Kodak Company. Two different samples of each compound were subjected to three or more fractional crystallizations from ethyl alcohol. The melting points of the best products were: stilbene, 124.4°C.; dibenzyl, 51.3°C.

EXPERIMENTAL RESULTS

Table 1 presents specific heat data for the solid and liquid states of the four hydrocarbons investigated. In each case a large number of individual determinations (forty to one hundred) of the specific heats were made. From a plot of these results a smooth curve was then constructed, and from this the values given in the table were taken. In no case were the actual experimental points more than two per cent off this curve. The absolute accuracy of the tabulated mean values is believed to be within two or three per cent.

The literature apparently contains no specific heat values for any of these substances within the temperature range of this investigation. However, our data fit fairly well with the results obtained in this laboratory at lower temperatures by use of the Nernst method with an aneroid calorimeter. Thus, for example, Huffman, Parks, and Barmore (4) report a value of 0.383 calorie per gram for durene at 24.0°C., while the curve for our present data, if extended, would lie about one per cent below this figure.

TABLE 1

Specific heat data for crystals and liquid

TEMPERATURE	DURENE	PENTAMETHYLBENZENE	STILBENE	DIBENZYL
degrees C.	*calories per gram*	*calories per gram*	*calories per gram*	*calories per gram*
30	0.384	0.431	.....	0.337
40	0.395	0.443	0.317	0.351
50	0.410	*m.p. 54.3°C.*	0.328	*m.p. 51.3°C.*
60	0.421	0.457	0.338	0.417
70	0.433	0.464	0.349	0.425
80	*m.p. 78.9°C.*	0.471	0.360	
90	0.487	0.478	0.370	
100	0.493	0.485	0.381	
110	0.499	0.494	0.391	
120	0.505	0.504	*m.p. 124.4°C.*	
130			0.466	

TABLE 2

Fusion and transition data

SUBSTANCE	NATURE OF CHANGE	TEMPERATURE	HEAT EFFECT
		degrees C.	*calories per gram*
Durene	Fusion	78.9	38.0
Pentamethylbenzene	Transition	23.2	2.9
Pentamethylbenzene	Fusion	54.3	19.9
Stilbene	Fusion	124.4	36.9
Dibenzyl	Fusion	51.2	29.6

The four fusion values for these compounds, together with a result for the heat of transition of the pentamethylbenzene in the solid state, are given in table 2. For durene our result is in good agreement with a value (37.5 calories per gram) calculated by Smith and MacDougall (3) from measurements of the freezing points of solutions of isodurene in durene and also with an experimental value (37.98 calories per gram) recently obtained by

Zeumer[1] in Professor Roth's laboratory at Braunschweig. Likewise, our heat of transition of pentamethylbenzene compares favorably with the result (3.19 calories per gram) obtained previously by Huffman, Parks, and Barmore (4) with a Nernst calorimeter which had been designed for low-temperature work. However, our fusion value for stilbene is considerably lower than the 40.0 calories per gram reported by Padoa (5) and our result for dibenzyl is also somewhat lower than the values of Padoa (5) (31.0 calories per gram) and of Bogojawlensky and Winogradow (6) (30.4 calories per gram).

Before concluding, the authors wish to thank Professor George S. Parks (under whose direction the investigation was carried out) and Dr. F. O. Koenig for their interest and advice during the progress of the work.

SUMMARY

Data for the specific heats (in both the solid and liquid states) and the heats of fusion of durene, pentamethylbenzene, stilbene, and dibenzyl have been obtained with a "radiation" calorimeter.

REFERENCES

(1) Thomas and Parks: J. Phys. Chem. **35**, 2091 (1931).
(2) Spaght, Thomas, and Parks: J. Phys. Chem. **36**, 882 (1932).
(3) Smith and Lux: J. Am. Chem. Soc. **51**, 2994 (1929).
Smith and MacDougall: J. Am. Chem. Soc. **51**, 3001 (1929).
(4) Huffman, Parks, and Barmore: J. Am. Chem. Soc. **53**, 3880 (1931).
(5). Padoa: Atti accad. Lincei **28**, 239 (1919).
(6) Bogojawlensky and Winogradow: Z. physik. Chem. **64**, 251 (1908).

---

[1] Private communication to Professor Parks from Dr. Hans Zeumer. This result was obtained by the use of a method of mixtures.

COMMUNICATIONS TO THE EDITOR

X-RAY STUDIES OF FATTY ACIDS AND OF MIXTURES OF FATTY ACIDS

In view of the time-consuming nature of this work a preliminary report is given at this time.

X-ray studies have been made of samples of the saturated normal fatty acids with ten to eighteen carbon atoms, and the large crystal spacings have been measured with great accuracy. (These samples, which represent the purest acids now available, were prepared by Dr. J. Ruhoff and Dr. J. D. Meyer with Professor E. E. Reid in this laboratory in the course of an investigation which will be published shortly.) In comparison with similar studies (Francis, F., Piper, S. H., and Malkin, T.: Proc. Roy. Soc. **A128,** 214 (1930)) made with the purest acids previously available, we find definite deviations which do, however, not exceed one per cent.

Francis, Piper, and Malkin have made a very interesting study of equimolar mixtures of fatty acids containing n and n + 1 carbon atoms. Their results, expressed as simply as possible, indicate that a characteristic long spacing is obtained for such mixtures and that the spacing is the mean value of the spacings the pure components would have if they crystallized in the same modification (same tilt of the fatty acid molecules, which are parallel to the C-axes of the crystals). Since the building elements of such crystals are double molecules they propose the following explanation. In the case of the mixtures the double molecules are obtained essentially by combination of a long and a short single molecule. This theory did not appeal to us for various reasons. The experimental test is given by a study of mixtures in non-equimolar proportions. In the case of the mixture of C_{10} and C_{11} for instance, we have studied the whole range in ten equal steps. We find the equimolar mixture to be the actual mean of the C_{10} and C_{11} spacings, but any of the other mixtures gives also single, sharp spacings, which follow roughly a linear relation with the composition. Thus, it is obvious that the theory proposed does not hold, but that the phenomenon is analogous to ordinary mixed crystal behavior, the relation being approximately expressed by Vagard's rule.

That our point of view is correct is also indicated by the fact that previous work on various non-equimolar mixtures of C_{16} and C_{18} gives definite spacings varying according to composition between the values of the two components. (Piper, S. H., Malkin, T., and Austin, H. E.: J. Chem. Soc. **1926,** 2310.) In this and other cases for mixtures of n and n + 2 we have found similar results.

For mixtures of the n and $n + 3$ acids we find, similar to Francis, Piper, and Malkin, mixed-crystal spacings. According to these authors such combination does not occur in mixtures of n and $n + 4$ acids. This is contrary to our results; the equimolar mixture of C_{14} and C_{18}, for instance, gives the spacing of the C_{16} acid.

For two-component mixtures of acids of still larger differences in chain length we have not been able as yet to obtain appreciable mixed-crystal formation.

It seemed of interest to study mixtures of a large number of components, for it was anticipated that in such cases mixed-crystal formation would be possible over a much wider range. Actually it was found that approximately equimolar mixtures of the acids with $n = 11, 13, 15,$ and 17, $n = 10, 12, 14, 16,$ and 18, and finally a mixture of $n = 10, 11, 12, 13, 14, 15, 16, 17,$ and 18 in each case gave rise only to one definite combination spacing, this value lying between the two corresponding extremes and closer to the higher one.

It seems that these experiments are important for the interpretation of x-ray diagrams of highly polymerized substances. Such bodies are in many cases assumed now to consist of chain-like molecules of varying lengths. Such systems were up to now not expected to yield any x-ray interferences connected with the chain length. Our results seem to indicate that this point of view must be modified. In an earlier paper (Ott, Emil: Z. physik. Chem. **B9**, 378 (1930)) it was shown that definite chain lengths could be assigned to certain polymer formaldehydes. Although the author was at that time inclined to his present outlook, it seemed safer to conclude, in agreement with the prevailing opinion, that the result indicated that such polymers were built up essentially of molecules of a given length only. At present it appears quite reasonable to consider the chain length mentioned as corresponding to an "average" length. This is of course in better agreement with the chemical experience. It is probably for the latter reason that Sauter (Z. physik. Chem. **B18**, 417 (1932)) attacks the view of the author; his evidence, however, is essentially negative. This point shall be tested further in due time. At present it seems to us most essential to increase the knowledge concerning x-ray diffraction of such well-defined systems, which may serve as a model for high polymers. The results thus far obtained in this direction seem to favor our point of view.

These investigations are being continued and with other coworkers extended to other groups of long-chain compounds.

EMIL OTT.
F. B. SLAGLE.

Department of Chemistry
Johns Hopkins University
Baltimore, Md.

BINARY SYSTEMS OF *m*-NITROTOLUENE AND *p*-NITROTOLUENE WITH NAPHTHALENE, *p*-TOLUIDINE, AND *o*-NITROPHENOL

In a continuation of the studies of the binary systems of the various nitrotoluenes with a second component which have been carried on in the Department of Chemistry of the University of North Carolina the following systems have been investigated: *m*-nitrotoluene–naphthalene, *m*-nitrotoluene–*p*-toluidine, *m*-nitrotoluene–*o*-nitrophenol, *p*-nitrotoluene–*p*-toluidine, and *p*-nitrotoluene–*o*-nitrophenol. The temperature-composition diagrams were determined by thermal analysis, using a calibrated mercury thermometer as the temperature-recording instrument. No compounds were obtained and the formation of solid solutions could not be detected. In plotting the logarithm of the mole fraction of solvent against the reciprocal of the absolute temperature straight lines were obtained, showing that the systems are ideal in nature. The calculated heats of fusion (accurate to about 2 per cent), the eutectic temperatures, and the eutectic composition in mole per cent are given in the following table.

SOLVENT	SOLUTE	HEAT OF FUSION		EUTECTIC TEMPERATURE	EUTECTIC COMPOSITION (SOLVENT)
		Solvent	Solute		
		calories per mole	*calories per mole*	*degrees C.*	
p-Nitrotoluene	*p*-Toluidine	3,970	4,158	15.9	46.5
p-Nitrotoluene	*o*-Nitrophenol	4,044	4,183	16.9	47.5
m-Nitrotoluene	*p*-Toluidine	3,365	4,012	−2.6	65.0
m-Nitrotoluene	*o*-Nitrophenol	3,432	4,133	−1.5	68.0
m-Nitrotoluene	Naphthalene	3,022	4,384	4.8	81.5

H. D. Crockford.
N. L. Simmons, Jr.

Department of Chemistry
University of North Carolina
Chapel Hill, N. C.

CORRECTIONS

The following corrections should be made in the article "Glass Electrode Determination of Sodium," appearing in This Journal, 35, 3058 (1931):

Page 3061, first line. For "mols NaOH" read "mols NaCl," and for "NaOH found" read "NaCl found."

Page 3061, second line. For "4%" read "4.0%."

Page 3061. For "Fig. 2" read "Fig. 3," and for "Fig. 3" read "Fig. 1."

Page 3062, eleventh line from the bottom. For "unchanged," read "uncharged."

Page 3063. For "Fig. 1" read "Fig. 2," and for "Fig. 2" read "Fig. 1."

F. Urban.
Alexander Steiner.

NEW BOOKS

Dans le champs solaire. By Paul Couderc. Encyclopédie Gauthiers Villars, 1932.

Written as a companion to the author's *Architecture de l'Univers*, the present volume deals, as the title expresses, with the solar system—a rather ungrateful, banal subject, in the author's opinion, when compared with the newer and wider vistas opened in stellar astronomy. In order to preserve the sense of unity with the previous volume, this one has been written with the guiding principle that the methods as well as the results of astrophysics should be accorded the principal emphasis, while furthermore the relationship between the sun and its planetary system and the stellar universe at large should be clearly realized.

It is natural, therefore, to find that the book differs considerably from most treatises on the same subject, and it is emphatically not a textbook. Some of these deviations render the book only more attractive—at least in the reviewer's opinion, such as the historical introduction, and the rather detailed exposition of the various theories for the origin of the system. Some other features would seem to have just the opposite effect, as, e.g., the unduly emphasized description of the earth and its atmosphere, and the very brief, almost hasty, résumé of the planets and their satellites which are accorded barely as much space as the subsequent description of the nearest stars, the motion of the sun among and with these, and that of the structure and motion of the galaxy as a whole—all of which would seem rather irrelevant in connection with the planetary system. More than one-third of the book is devoted to the sun, while comets and meteors, treated almost as an afterthought, coming *after* the description of the solar neighborhood, have no more than eleven pages allotted to them.

Probably all this is due to the desire already referred to, to treat the subject matter from the point of view of astrophysics, and always in relation to the stellar universe. With these limitations in view one must admit that the author has succeeded very well, for the book is clearly and interestingly written and attractively illustrated. I believe, however, that it is a fair criticism to say that it lacks unity; the various chapters are somewhat disjointed, and give the impression more of separate articles written for different purposes.

As to more specific criticisms: on page 36 one reads that it was *Bowen*, who cleared up the mystery of the *Aurora* line, while on page 81 one obtains the impression that, among others, the Harvard and Victoria Observatories concern themselves "more or less" with solar studies. The illustrations on the sun may well be called superb; several of those portraying lunar phenomena under high magnification, are, however, distinctly mediocre.

W. J. Luyten.

Hydrogen Ions. By F. T. S. Britton. 22 x 14 cm.; pp. xvi + 589. London: Chapman and Hall, 1932. Price 25 shillings (not 52 shillings as erroneously printed in the number for October, 1932). For review see volume 36, page 2687.

Treatise on Sedimentation. Second edition. By William H. Twenhofel and collaborators. pp. 960; 121 text figures: 8 chapters. Baltimore: Williams & Wilkins, 1932. Price: $8.00.

The book is a product of the work of the Committee on Sedimentation of the Division of Geology and Geography of the National Research Council. The first edition was published in 1926. The plan of the second edition follows closely that of of the first. Many specialists submitted manuscripts treating of the phases of sediments and sedimentation most familiar to each of them. Those manuscripts were organized and edited by Mr. Twenhofel and incorporated into a single volume. The result is a veritable mine of information on the various phases of sediments and sedimentary rocks. The chief advantage of this edition is that it gives a more complete list of footnote references, especially to foreign literature. The book thus provides in compact form, information that would otherwise require extended bibliographic search. It becomes a logical starting point for any investigation involving sediments and their relationship.

Many subjects of interest to the student of physical chemistry are presented. These include such matters as the stabilization of hydrosols of iron and manganese by organic colloids; colloidal calcium carbonate and its influence in the formation of limestone; the amount and nature of colloidal silica in ground water, streams, lakes and seas, and the various modes of its precipitation; the transportation of matter in the colloidal state; the flocculation of colloids in brackish water and marine environments and the electrolytes instrumental in producing the reaction; the behavior of gels of silicious dioxide, hydrated aluminum oxide, hydrated ferric oxide and humic acid compounds in clayey sediments and soils; the nature and causes of stratification in colloidal sediments; and the colloidal ground-mass of coal.

The reviewer considers this edition a more complete, better organized, and more authoritative contribution than the first edition. It contains few if any of the infelicities of expression, misspellings and typographical errors which marred the earlier volume. It is a compilation that does much to advance an understanding of the many intricate problems confronted by all students of sediments.

Geo. A. Thiel.

Organic Chemistry. By Perkin and Kipping. Fifth edition, Parts I and II, completely revised and rewritten, by F. Stanley Kipping and F. Barry Kipping. pp. 614 + xxix. Philadelphia: J. B. Lippincott Company, 1932.

This work comprises the first two of the three parts of the latest edition of an old, standard textbook on organic chemistry. In style and format, there is little change, but the subject material has been brought up to date and many of the chapters have been completely rewritten. There are useful summaries at the end of each chapter.

Parts I and II cover the important aliphatic and aromatic compounds and related material, while in part III it is planned to cover various special branches of organic chemistry such as *terpenes, cycloparaffins,* and the like.

The book is intended for use both as a text and a laboratory manual, but the directions for preparing substances in the laboratory are inserted in the text along with the descriptive matter. On page 614 there is a special index to these laboratory preparations, comprising about eighty laboratory experiments.

The printing is well done, the paper is excellent, and the book is very readable. The index is quite adequate.

Lee Irvin Smith.

An Introductory Course in Physical Chemistry. By Worth E. Rodebush. 22 x 14 cm.; pp. xiii + 421. New York: D. Van Nostrand Company, 1932. Price: $3.75.

"A generation ago physical chemistry was studied only by a few students who were particularly interested in the subject and who possessed some special aptitude for it. From such a modest beginning, this branch of chemistry has rapidly increased in popularity. During the last decade more than a thousand students have studied physical chemistry at the University of Illinois." Page v.

"The material presented is about the same as will be found in the average course in physical chemistry, although the order is somewhat novel in that chemical equilibrium is taken up early in the course. This is a tremendous advantage from the point of view of logic and involves no difficulty for the student since he has become familiar with reversible reactions in his inorganic chemistry." Page vi.

The headings of the chapters are: the atom and the molecule; the kinetic theory of matter—gases; the kinetic theory of matter—liquids; the crystalline state of matter; laws of chemical equilibrium; equilibrium between different phases of a pure substance; solutions; surface chemistry and solutions; equilibria involving ions in solution; conductivity; electrode potentials; the concept of entropy and the third law of thermodynamics; physical properties and molecular constitution; the rate and mechanism of chemical reaction; the atom; the molecule; the activation of atoms and molecules.

The reviewer approves highly of treating equilibrium before reaction velocity. It is the only rational way to do things because there is or should be a relation between the stoichiometrical and mass law equations, whereas the reaction velocity equations do not necessarily tie up with much of anything.

There are a number of other good things in the book. "There are certain rules governing the formation of mixed crystals. The substances must be of similar structure chemically. They must be isomorphous; that is, they must have the same crystal structure. The dimensions of the two lattices must be nearly the same. Sodium chloride and potassium chloride do not, to an appreciable extent, form mixed crystals at 25°C. because they do not satisfy the last condition. For miscibility in any proportion the difference between the dimensions of the two lattices can not exceed a few per cent. The tolerance is greater near the melting point." Page 74.

"In this chapter we have learned that chemical reactions do not take place between stable molecules, but between excited molecules, between fugitive aggregates such as hydroxyl, and often between atoms. For lack of a better term, we may characterize this branch of chemistry as the chemistry of the atom. It is still a comparatively unknown subject. We do not know very much about the chemical properties or reactions of the atoms. For example, atomic hydrogen may act as an oxidizing agent and atomic oxygen may act as a reducing agent. It is evident that the chemistry of the future will be very much the chemistry of the atom." Page 340.

"The metallic lattice is of the atomic type. Carbon forms an atomic crystal in diamond but diamond is not metallic in character. It is evident that one of the distinguishing characteristics of the metallic lattice is that it is primarily not a valence type of crystal. In general the atom in a metallic lattice is surrounded by too many other atoms for valences to have much significance." Page 398.

"It is of course rather naïve to suppose that any complicated set of phenomena in nature can be described exactly by a simple mathematical formula. Since van der Waals, literally hundreds of equations of state (any equation which gives the relation between pressure, volume, and temperature for any given mass of a substance is called an equation of state) have been proposed. Some of these are useful for specific cases but in general all are simply empirical formulas which fit the better the more adjustable constants they contain." Page 26.

"The summation of the quotients obtained by dividing each quantity of heat by the absolute temperature at which it was absorbed depends only upon the states of the system before and after the change and is independent of the path by which the change takes place. This is an experimental generalization that is just as important as that underlying the first law." Page 103.

The authors are a bit pessimistic over physical chemistry as chemistry. "As a matter of fact the 'normal' type of liquid consists chiefly of the common organic liquids with boiling points a little above room temperature, which are available in large numbers for experiment. One suspects that that is the reason they are called normal liquids." Page 55.

"Everything said so far has referred to association in the vapor phase. We know very little about association in the liquid phase, although some authors have attempted to explain all deviations from ideal solution by association. Solvents such as benzene are sometimes termed *associating solvents* on the theory that solutes have a tendency to polymerize in these solvents, but there is no evidence to support this view. In fact as we have been at great pains to point out, we have no means of determining the state of polymerization of solute or solvent in solution." Page 161.

"It is a tradition in physical chemistry textbooks that some space must be devoted to osmotic pressure, although osmotic phenomena are of much greater interest to the physiologist than to the chemist." Page 168.

"The typical strong electrolytes have certain characteristic physical properties such as high melting point and electrical conductivity in the pure liquid state. Hydrogen chloride is a gas at 25°C. and when condensed to a liquid at low temperatures it shows no conductivity; yet it is a typical strong electrolyte in solution. The explanation for this is that an ionized salt H_3O^+ Cl^- analogous to NH_4^+ Cl^- is formed in solution." Page 188.

"In order to simplify the notation and get around the difficulty of the various unknown factors which are involved in dealing with equilibria involving ions, G. N. Lewis invented the concept of activity. The activity of an ion is defined as the total molality of the ion multiplied by an experimentally determined correction factor, the activity coefficient. By the 'total molality' of an ion we mean the molality calculated on the assumption that all electrolytes present in solution which contain the ion are completely dissociated. The activity of an ion, e.g., Cl^-, is represented by the symbol $[Cl^-]$ and the activity coefficient will be represented by γ. The relation is then:

$$[Cl^-] = \gamma_{Cl^-} m_{Cl^-}$$

The activities are of course the effective concentrations which we shall use in the expression for the equilibrium constant of a reversible reaction involving ions.

"The student may wonder what is to be gained by the use of empirical correction factors to make a mathematical relation true. The justification is that of utility. If we have values of γ conveniently tabulated we can make accurate calculations of the equilibria where ions are involved." Page 193.

"When the concept of activity coefficient was introduced at the beginning of this chapter, it was expressly stated that only the mean activity coefficient for a pair of ions may be determined experimentally. This point needs to be recalled in connection with the foregoing discussion of hydrogen-ion activity. Regardless of the method used for the determination of hydrogen-ion 'concentration' the only thing that can be determined directly is the mean activity of the hydrogen-ion and associated anion. Any estimate of the individual activity of the hydrogen-ion involves assumptions." Page 218.

"It has been proposed to determine the true transference number by adding a non-electrolytic substance as a reference solute. The reference solute is assumed to remain stationary and from its concentration at the end of the run the difference in the amount of water transferred by the two ions may be calculated. The assumption that the reference solute remains stationary is very probably not justified. In dilute solution the transfer of water causes a negligible error in the transference number." Page 240.

"If a gradually increasing voltage is applied to a pair of inert electrodes in solution and the current plotted against voltage we obtain a curve such as is shown in figure 77. It has often been supposed that if the straight part of the curve were extrapolated back to zero current the corresponding voltage would be the 'decomposition potential.' There seems to be no particular significance to this voltage, however." Page 273.

"A fast dye is a contradiction in terms." Page 289. "It has been known for a long time that photographic plates could be sensitized to green and red light by certain dyes. The exact mechanism of this photosensitization is not known with certainty. Since fluorescent dyes do not show this effect especially, it seems that the mechanism is not one in which radiation is re-emitted by the sensitizing agent." Page 339.

"As we have learned more about the behavior of the atom we have been forced to the inevitable conclusion that the energy that is associated with lights exists in corpuscles that we call photons. . . . The number of photons in the beam is proportional to the intensity. If we know the original intensity of the beam and the characteristics of the grating we can calculate by the wave theory the intensity in the diffracted beam; but all we shall ever observe in the diffracted beam is the number of photons transmitted per second. Now if no medium exists for the transmission of light waves and we never observe these waves directly, the question arises naturally as to whether these waves really exist. This is a question, however, for the philosopher rather than the scientist. So far as the scientist is concerned, the electromagnetic theory of light is a mathematical theory which describes the behavior of light if one assumes a simple relation between the number of photons and the square of the amplitude of the wave; but the thing really observed is the number of photons." Page 335.

The reviewer doubts whether the student will grasp the fact that the 2 in the phase rule equation refers to pressure and temperature, page 126. The paragraph on flotation, page 185, is surprisingly obscure. On page 249 the authors prove that there is no potential difference between two metals. This is proving too much because there would then be no thermopiles. Cannizzaro's name is spelled wrongly on page 4.

"Pure water will dissolve a considerable amount of ether. If sodium chloride is added to the solution the ether will separate out as a second layer. This 'salting out effect' is easily explained in terms of dielectric constant. An electrical charge attracts a medium of high dielectric constant in the same way that a magnet attracts material of high permeability, e.g., iron. Since the dielectric constant of water is so much greater than that of ether, the water is pulled into the field existing between the ions and the ether is thrown out." Page 296.

This explanation does not seem to harmonise with the fact that if one added alcohol to a saturated sodium chloride solution, some of the salt is thrown out. The dielectric constant cannot always be on the job.

WILDER D. BANCROFT.

Recent Advances in Atomic Physics. By GAETANO CASTELFRANCHI. Translated by W. S. Stiles and J. W. T. Walsh. Vols. I and II. 20 x 13 cm.; pp. Vol. I xii + 372, Vol. II xii + 412. Philadelphia: P. Blakiston's Son and Co., 1932. Price: $4.00 each volume.

This is a translation of the third Italian edition with omission of the chapters on Brownian movement, relativity and mass, and astrophysics. In the first volume, which deals with atoms, molecules, and electrons, the chapters are entitled: atoms and molecules in physical chemistry; light; the kinetic theory of gases; fluctuations; electrons and positive rays; isotopes; x-rays and the atomic number; crystals;

radioactivity; the atomic nucleus. In the second volume, which deals with quantum theory, the headings are: thermal radiation and quantum theory; spectroscopy, Bohr's theory and the energy levels of the atom; Stark and Zeeman effects—multiplet lines—the spinning electron; specific heats; the photoelectric effect—the reverse effect—photoelectric cells and their applications; the Compton effect—light quanta; magnetism and the quantum theory; wave mechanics and quantum mechanics—applications; the new statistics—applications.

"The spherical electron, with the radius assumed above, is a pure supposition based on the hypothesis originally made; at present, however, it seems less necessary to consider the spherical electron with a fixed radius, since modern tendencies seem to lead to the conclusion—as we shall see in what follows—that the electromagnetic theory is no longer applicable to systems of atomic dimensions and therefore still less to electrons which are constituent parts of atoms; the structure of the electron is certainly one of the mysteries of contemporary physics." Volume I, page 146.

From Sommerfeld's theory one can deduce that "the ratio of the thermal to the electrical conductivity of a metal is independent of the nature of the metal and is proportional to the absolute temperature." Volume I, page 178.

"Thus, after the lapse of some years, the old hypothesis proposed by Prout at the beginning of the nineteenth century, viz., that the different elements are composed of a single primordial material, has been restored once more to a place of honour; thus science, through a new discovery, and by a road quite different from that followed for several decades, has found—and not for the first time—the confirmation of an idea which was originally put forward solely as a reasonable hypothesis." Volume I, page 203.

"Let us take a milligram of radium and observe its transformation. Why does one atom suddenly explode and die, why does another atom live for a day, another for a week, others for a month, a year, a century? If atoms are all alike, how is it that they are 'healthy' and 'unhealthy' ones? At the present time physics is unable to provide an answer to this question.

"However, since every fact is connected with some other, from which it results, by the chain of cause and effect, according to our rational line of thought (*determination*) we are led to think that, in reality, there must be a complex universe in every atom, and, by reason of the intervention of causes not known to us, the death of an atom is occasioned from time to time. Exactly similarly, in considering the incidence of mortality in a city, we cannot know *which individuals* will die on the morrow, but we can know *how many*, because the mathematics of probability has shown us how we may overcome our ignorance, our inability to take account of the extraordinary complication of elementary causes. We are here confronted with a practical problem which is insoluble, though perhaps not for ever." Volume I, page 302.

"Planck's bold hypothesis, deduced by an involved process of reasoning from statistics and thermodynamics, received very careful consideration at the hands of the more enlightened physicists, the more profound thinkers of the time; nevertheless in spite of the support of men like Einstein and Poincaré, it would probably have been relegated to the philosophy of physics and buried for all practical purposes, if certain experimenters had not been led to examine other phenomena, more simple and less abstruse, which indicated the existence of a discontinuity in nature which, until then, had been entirely unsuspected. While Planck in 1900 had simply asserted that the electrons emitted and absorbed energy in fixed finite quantities and shortly afterwards revised this new conception by restricting it to the process of emission, Einstein, in 1905, daringly proposed the theory that these fixed and finite quantities of radiant energy retained their separate identities throughout their journey from the instant of emission to the instant of absorption. In chapter VI we shall examine this reasoning, but for the present we shall confine ourselves to mentioning the fact that the latest developments of physics have confirmed the idea that in all *elementary* phenomena, i.e., those which concern a single atom, a single molecule, or a single electron, the discontinuity postulated by Planck is found to exist; in such elementary phenomena Nature proceeds by jumps or degrees; in macroscopic phenomena this discontinuity is hidden and it remained unsuspected by physicists for centuries." Volume II, page 28.

"Niels Bohr, with whose work we shall, in the main, be concerned in this chapter, is not one of those specialists who multiply experiments in a small field without regard to the close relations between the different branches of science. He possesses in high degree the research spirit, coupled with a mental audacity which has enabled him to throw off the old methods and worn-out conceptions, to find new approaches to a higher and more general view of phenomena. The experimental facts themselves are of course indispensable to the progress of science. They may in fact be regarded as the bony skeleton which resists the test of time. But, in the face of the mass and variety of observed phenomena, the intelligence would be overwhelmed and science would crack under the weight of material if it were not for the appearance from time to time, of a bold innovator with the theory which will harmonize and regroup the facts of experiment and predict new phenomena." Volume II, page 32.

"When a gas is irradiated with light of frequency greater than the resonance frequency, the return of the atom from the excited state to the normal may occur in stages. This is the phenomenon of fluorescence." Volume II, page 99.

"At low temperatures the atomic heat of solid substance is proportional to the cube of the absolute temperature, a result which Schrödinger has verified conclusively for various substances in a temperature range extending from 20° to 50° absolute." Volume II, page 153.

"Compton observed that, when a beam of X-rays fell on a body, the frequency of the scattered radiation remained unaltered in the direction of the incident rays, but became lower in other directions and depended on the angle of deviation." Volume II, page 196.

"If the luminous intensity is very high, the electromagnetic theory provides a means for calculating exactly both the luminous intensity at different points in space, and the variations produced by the superposition of the waves, variations which agree with those calculated directly from Planck's formula which, in its turn, is based upon and is in accordance with experiment. In the case of very low intensities, however, the formula giving the variations indicates that radiation must be regarded as composed of a collection of discrete particles, but nevertheless the electromagnetic theory—although of a kind which seems quite alien to the problem—enables the distribution of the light quants to be determined whether they be numerous or few. If, *then, we abandon any attempt to determine the path of a single light quant* between the moment and the place of its emission, and the moment and place at which it arrives at the measuring apparatus (the sensitive plate), the electromagnetic theory provides us with the means for determining *the average number of light quants* which reach a given point of an optical system however complicated. The luminous intensity, then, is simply the probable distribution of the photons." Volume II, page 222.

"It appears at first sight, therefore, that the observed magnetic moments should be multiples of the Bohr magneton. In reality they are much more complex, because the atom, in addition to the magnetic moment due to the orbital motion of the electrons, possesses also another magnetic moment which is the resultant of moments associated with the electrons themselves. We shall see, however, that the magneton theory is in fact valid and the magneton is obtained experimentally with the value just calculated." Volume II, page 245.

"Whilst de Broglie and Schrödinger had tried to discover the laws of atomic phenomena in the light of classical methods, and to bridge the gap separating the quantum mechanics of atoms from classical physics, Heisenberg—a few months before the appearance of Schrödinger's first paper—started out from the opposite idea. He considered that only a definite renunciation of the deeply-rooted classical representation could lead to a proper understanding of the *régime* obtaining in the atom. He was convinced that, as a fundamental principle in atomic physics, any attempt at *explanation* was pointless and without meaning, and that all magnitudes not susceptible to direct observation should be excluded from atomic theory." Volume II, page 314.

"One of the fundamental characteristics of the history of Science in recent years has been, strangely enough, to show that every explanation founded on the classical mechanics is quite untenable throughout the whole range of electricity, magnetism and optics, which latter has been proved by Maxwell and Hertz to be a branch of electromagnetism.

"The process of unification, although checked by this discovery, has not been entirely destroyed, but it has had to proceed in the opposite direction; relativity showed that it was not the simplest phenomena of mechanics (those that were studied and classified first of all) which were the most fundamental in character; after Einstein's genius had elucidated matters the opposite was seen to be the case: electrical and magnetic phenomena are the simplest and these lead to a mechanics which is more precise and more complete than the old mechanics.

"Another new and unexpected development of recent years is the discovery of discontinuity in every branch of atomic physics; it is the mysterious law of quanta which reigns supreme, and the discontinuity of atomic phenomena lies at the root of optics, electricity, magnetism and heat; Planck's constant, appearing as it does in the most diverse phenomena, has brought out new connections between different branches of physics. Through Heisenberg's principle it shows what is the region of error, of inaccuracy inevitable in human observation, when we are investigating atomic phenomena." Volume II, page 393.

WILDER D. BANCROFT.

Neure Forschungen über die optische Aktivität chemischer Moleküle. By G. KORTÜM. 25 cm. x 16 cm.; pp. 118. Stuttgart: Ferdinand Enke, 1932. Price: R.M. 11.10.

After more than a century of effort, the physical theory of optical rotation is still in the melting-pot. The fundamental basis for this theory was provided in 1824, when Fresnel showed that the optical rotatory power of media such as quartz or turpentine could be explained by postulating that the velocity of transmission of circularly-polarized light in the medium was not the same for circular polarizations of opposite signs. The unequal refraction of *right* and *left* circularly-polarized light, which results from these unequal velocities, was detected by direct measurements with a quartz prism of wide angle, compensated by two prisms of glass; and it is now a well-established practice that, in constructing optical apparatus, *d* and *l* quartz prisms must be used in pairs, in order to avoid the double images which would be produced if the circular double refraction were not compensated in this way.

The influence on optical rotatory power of variations in the wave-length of the light was investigated in the earliest experiments of Biot, who propounded an inverse square law, $a = k/\lambda^2$ as long ago as 1818. A theoretical foundation for these observations was, however, not provided until 1898, when Drude invented a model in which the electrons in an asymmetric medium were assumed to vibrate in spiral instead of linear paths. On this basis he deduced his well-known equation, $a = \sigma k_n/(\lambda^2-\lambda_n^2)$, where λ_n is a wave-length corresponding to one of the natural periods of the vibrating electron, and k_n is a constant which expresses the magnitude of the partial rotation thereby produced. This equation was checked by a comparison with the data for quartz; but the study of rotatory dispersion had fallen so completely into abeyance (as a sequel to the introduction of the sodium flame as an easy source of monochromatic light) that no data at all were available whereby the validity of the formula could be tested in the case of any of the thousands of optically-active organic compounds in which chemists had demonstrated the existence of optical rotatory power. It was this gap that the reviewer set out to fill by a series of studies of rotatory dispersion which have been in progress during the past twenty years. As a result it has been proved that Drude's formula expresses the rotatory dispersion of a large range of organic compounds with perfect accuracy over the range of wave-lengths to which they are transparent, and that anomalous rotatory dispersions can be represented with the same precision as normal rotatory dispersions, by making use of two terms of opposite sign.

In order to express the rotatory dispersion of a medium in the region of absorption, Drude in 1906 reintroduced a "damping factor" which he had omitted in the simplified equation cited above. He thus provided a theoretical basis for the well-known Cotton effect, which had been discovered in 1896, namely an unequal absorption of *d* and *l* circularly polarized light, which Cotton described as "circular dichroism," and a loop in the curve of rotatory dispersion within the same range of wave-lengths. More recently, Dr. Werner Kuhn, following up the work of Born and Oseen, has shown that a similar pair of equations can be deduced from a model in which optical rotatory power is attributed to an unsymmetrical coupling of electrons, such that when one electron moves in a north-and-south direction the other moves east-and-west. These equations, however, do not represent the real form of the experimental absorption curves, nor of the curves of circular dichroism and of rotatory dispersion in the region of absorption. A "damping factor" that can be used to interpret the effect of "forced vibrations" over a narrow range of frequencies, could in fact scarcely be expected to cover an absorption extending over a range of perhaps 1000 Å.

This difficulty was surmounted in 1915 by Bruhat, who obtained an approximation to the real form of the absorption-curve for carbon disulfide by combining *five* components of the "damped vibration" type, and was thus able to deduce the form of the curve of refractive dispersion in the region covered by the absorption band. By a similar process, Kuhn has deduced an equation for the rotatory dispersion produced by an active absorption band of a form which corresponds with a probability-distribution of frequencies in the band. This equation has been checked against his own experimental data; but, since absorption bands which are steeper on the side of shorter wave-lengths are so uncommon that the reviewer cannot recall any example of this type in a long experience of the absorption spectra of organic compounds, it is unlikely that an equation based on this type of absorption can represent the final goal in the investigations of rotatory dispersion.

The two models cited above lead to an identical numerical relationship between circular dichroism and rotatory dispersion in the region of absorption. Kuhn's equations, however, make it possible also to deduce numerical values for the distance between the coupled electrons, which are generally larger (and some times grotesquely larger) than the extreme diameter of the optically-active molecule. There can, indeed, be little doubt that both models are merely provisional, and are likely to be superseded in the near future by a wave-model which will provide a more realistic basis for the same equations. The present position, is, however, so interesting that there is a widespread demand for an expression in clear and simple terms of the fundamental principles involved in the theory of optical rotatory power. For this purpose the monograph now under review is altogether excellent, since the essential points are lucidly discussed, without introducing unessential equations, which would merely repel or confuse the non-mathematical reader. The monograph is indeed an almost ideal example of the way in which physical theory should be presented to chemical readers, and recalls the masterly way in which under similar conditions the greater physicists (it would be invidious to mention their names) are able to leave their tools in the workshop and display their finished work in clear and vivid outline to a lay audience.

In addition to the physical theory of optical rotatory power, the monograph gives an account of the way in which this property can be correlated with molecular structure and with other physical properties of the molecule, such as its dipole moment, its molecular refraction, and the dissociation constants of the acids used in preparing derivatives of a parent-substance. Here again, it is impossible to praise too highly the thoroughness with which the author has searched the original literature and reviewed impartially the many important contributions that have been made to the subject, especially since the modern period was initiated some thirty-six years ago, by the pioneer work of Drude and of Cotton on the physical side and of Pope on the chemical side. The bibliography of 234 entries will in fact be too useful to be overlooked by subsequent writers on this subject, and evidence of its usefulness as a guide to the literature is provided by the fact that two misprinted references from an earlier version of the bibliography have already been cited in a larger work on the same subject. The monograph may therefore be commended without reserve as an authoritative review of the present position of the fascinating topic with which it deals.

T. M. Lowry.

THE RÔLE OF FINELY DIVIDED MERCURY IN THE DEPOLARIZER OF THE STANDARD CELL

R. B. ELLIOTT AND G. A. HULETT

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Received September 13, 1932

THEORETICAL CONSIDERATIONS

Let us consider individually the chemical reactions capable of occurring at the cathode of a standard cell, in which both the mercurous and mercuric ions are present, and their corresponding E. M. F.'s:

$$\text{(a) } 2\text{Hg} = \text{Hg}_2^{++} + 2\text{E};\ \text{E.M.F.} = 0.75 + \frac{RT}{2F}\log(\text{Hg}_2^{++});\ \text{E}_0 = 0.75\text{ volt}$$

$$\text{(b) Hg} = \text{Hg}^{++} + 2\text{E};\ \text{E.M.F.} = 0.86 + \frac{RT}{2F}\log(\text{Hg}^{++});\ \text{E}_0 = 0.86\text{ volt}$$

$$\text{(c) } \text{Hg}_2^{++} = 2\text{Hg}^{++} + 2\text{E};\ \text{E.M.F.} = 0.91 + \frac{RT}{2F}\log\frac{(\text{Hg}^{++})^2}{\text{Hg}_2^{++}};\ \text{E}_0 = 0.91\text{ volt}$$

The value of the E.M.F. in all these cases is of necessity the same in the cathode limb of the cell but it does not necessarily follow that equilibrium prevails between all the ion species and the mercury. As we ordinarily consider the standard cell we assume that the cathode potential is governed by a very definite concentration of mercurous ions above the mercury surface. However it is far more complicated than this. We have seen (1) that if electrolytic mercurous sulfate is brought to equilibrium at 25°C. in a saturated cadmium sulfate solution in which mercury is present in large globules, the equilibriated solution contains a definite amount of mercurous and mercuric ion in the ratio

$$\frac{\text{Hg(ous)}}{\text{Hg(ic)}} = 55.3$$

Barring supersaturation it would be these concentrations of Hg_2^{++} and Hg^{++} which cause the standard cell as we know it to have its given voltage.

Let us digress a moment on the influence of the various mercury ion concentrations found experimentally (1) on the cathode potential. Normal catholyte contains 0.81043 gram of mercurous ion and 0.01465 gram of mercuric ion per liter, the normalities being respectively $N_{Hg^+} = 0.00404$ (as Hg^{++}, $N_{Hg_2^{++}} = 0.00202$) and $N_{Hg^{++}} = 0.00007303$. The former value is very accurate. If we substitute these values in the above equations we obtain

(a) for the mercury-mercurous potential:

$$\text{E.M.F.} = 0.75 + \frac{0.05915}{2}\log(0.00202)$$
$$= 0.75 + 0.0296\,(-2.69465)$$
$$= 0.75 - 0.0765$$
$$= 0.720 \text{ volt}$$

(b) for the mercury-mercuric potential:

$$\text{E.M.F.} = 0.86 + \frac{0.05915}{2}\log(0.00007307)$$
$$= 0.86 + 0.0296\,(-4.13694)$$
$$= 0.86 - 0.122$$
$$= 0.74 \text{ volt}$$

(c) for the mercurous-mercuric potential:[1]

$$\text{E.M.F.} = 0.91 + \frac{0.05915}{2}\log\frac{(0.00007307)^2}{(0.00202)}$$
$$= 0.91 + 0.0296\,((-4.13649)\,2 - 2.69465)$$
$$= 0.91 + 0.0296\,(-5.58233)$$
$$= 0.91 - 0.1645$$
$$= 0.745 \text{ volt}$$

For the present considerations let us consider that the normal electrode potential in (a) is correct. Since we know the exact concentration of Hg_2^{++} by experiment the electrode potential 0.7205 volt must be correct, and for equilibrium to prevail the potential in (b) and (c) must also be 0.7205 volt. Consequently we can substitute this value back into equation b,

$$\text{E.M.F.} = E_0 + \frac{0.05915}{2}\log(N_{Hg^{++}})$$

and determine the normality $N_{Hg^{++}}$.

$$0.7205 = 0.86 + 0.0296 \log(Hg^{++})$$
$$-0.1395 = 0.0296 \log N_{Hg^{++}}$$
$$\log N_{Hg^{++}} = -\frac{(0.1395)}{(0.0295)}$$
$$\log N_{Hg^{++}} = -4.73 = 5.27 - 10$$
$$N_{Hg^{++}} = 1.862 \times 10^{-5}$$

Therefore from these theoretical considerations the ratio of Hg(ous): Hg(ic) would have to be, for equilibrium,

$$\frac{N_{Hg^{+}}}{N_{Hg^{++}}} = \frac{4.039 \times 10^{-3}}{1.862 \times 10^{-5}} = 216.7 \text{ (not divalent} Hg_2^{++})$$

---

[1] The above normal electrode potentials have been taken from No. 8 of Der Abhandlung der deutschen Bunsengesellschaft, calculated presumably from thermochemical and free energy relations.

If the E_0 values are correct in all the above equations, the substitution of the adduced ratio $\frac{(Hg_2^{++})}{(Hg^{++})^2}$ in (c) above should give also the value 0.7205 volt.

$$
\begin{aligned}
\text{E.M.F.} &= 0.91 + \frac{0.05915}{2} \log \frac{(1.862 \times 10^{-5})^2}{(2.02 \times 10^{-3})} \\
&= 0.91 + 0.0296\ ((-4.73002)\ 2 - 2.69465) \\
&= 0.91 + 0.0296\ (9.46004 - 2.69465) \\
&= 0.91 - 0.1995 \\
&= 0.7105 \text{ volt}
\end{aligned}
$$

This value is in quite good agreement with that which we should expect from the afore deduced concentration of mercuric ions. These calculations nicely corroborate the theory of the diatomic mercurous ion, $Hg^+—Hg^+$.

Now the cathode potential in the standard cell will be governed by the highest of the three E.M.F. values calculated in (a), (b), and (c) preceding. To determine the relative importance of variations in concentration of mercurous and mercuric ions in the cathode let us inspect each equation separately. If the mercurous ion concentration changes tenfold either way, i.e., from 0.0040397 N to 0.040397 N or 0.00040397 N, the corresponding change in potential calculated from equation a would be $\pm \frac{0.05915}{2} \log 5.0$, since

$$(\tfrac{1}{2}N_{Hg^+} = N_{Hg_2^{++}}) \text{ or } \pm 0.0296\ (0.69897) = \pm 0.023 \text{ volt}$$

and its corresponding effect on the E.M.F. of (c) would be even less. Anyhow, a tenfold change in the mercurous ion concentration is quite impossible in view of the slight solubility of Hg_2SO_4. (A maximum increase in the Hg(ous) concentration to 117.6 per cent of its normal value has been recorded (1). If, however the mercuric ion concentration is changed tenfold either way, i.e., from 0.00007307 N to 0.0007307 N or 0.000007307 N (this is very possible in view of the high solubility of $HgSO_4$), the corresponding change in potential, calculated from equation b, would be

$$\pm \frac{0.0591}{2} \log \frac{(10)^2}{C} = 0.0296\ (1 \times 2) = \pm 0.05915 \text{ volt}$$

giving this effect preponderance over all others. Furthermore, any gain in the concentration of the mercuric ion would likely be at the expense of the concentration of the mercurous ion and a tenfold increase in the former would have an even greater effect on the ratio $\frac{(Hg^{++})^2}{(Hg_2^{++})}$ than $\frac{10^2}{1}$, and therefore on the electrode potential than 0.05915 volt.

EXPLORATION OF OLD CELLS BUILT UNDER OXIDIZING AND ANTI-OXIDIZING CONDITIONS

In 1928, cells were constructed by Dr. W. C. Gardiner (2), the contents of some of which were saturated with hydrogen and others of which were saturated with oxygen. The purpose of the cells was to determine whether or not the atmosphere oxidized the mercurous sulfate and changed the cell values. Two representative cells were carefully opened and the E.M.F. was explored at various points in the electrolyte by means of an amalgamated electrode (1). The cells showed only the usual concentraton-gradient of mercurous ion, the E.M.F.'s being practically identical through both solutions. If atmospheric oxidation were a factor the the E.M.F. throughout the solution saturated with oxygen would certainly be much greater than that throughout the solution saturated with hydrogen, owing to the greater Hg(ic):Hg(ous) ratio in the first one.

BEHAVIOR OF CELLS WITH FINELY DIVIDED MERCURY PRESENT

Theoretical considerations

That metallic mercury reduces mercuric mercury more or less completely to mercurous mercury can be proved by the formation of a white precipitate of mercurous chloride on the surface of clean mercury when the latter is introduced into a solution of mercuric chloride. In fact this is one of the laboratory methods of preparing calomel.

The ratio Hg(ous):Hg(ic) is controlled by the equilibrium of the reaction $Hg^{++} + Hg = Hg_2^{++}$. Mercury, being present in large quantities, is the stabilizing factor in this equilibrium but it can, by virtue of its globular size, change this ratio to an appreciable extent. We have already calculated the maximum ratio of Hg(ous):Hg(ic) as 216.7 from a thermodynamic standpoint entirely. This ratio corresponds to that created by a large body of liquid mercury and would be the same whether the equilibrium was approached from a solution of pure mercurous ion or mercuric ion.

Lewis and Randall (3) have deduced an equation,

$$F - F^0 = \frac{2\gamma V}{r}$$

showing the reciprocal relationship between the increase in free energy of a drop of liquid and its radius. In the equation F is the molal free energy of the drop, F^0 that of a large body of the liquid, γ is the surface tension of the large body of liquid, V is the molal volume, and r is the radius of the drop.

Qualitatively, thus, Hg would become increasingly more important in the equation $Hg^{++} + Hg = Hg_2^{++}$ as its state of subdivision increased, i.e., as its radius decreased, and we should expect a greater ratio of Hg(ous): Hg(ic) or a lower electrode potential as a result of this.

EXPERIMENTAL

By mechanical agitation one can obtain mercury in a sufficiently small state of subdivision to detect the change in E.M.F. resulting, but barely so. One has to resort to chemical means to obtain mercury globules of small enough radius to observe an appreciable effect.

To obtain mercurous sulfate absolutely free from mercury is a difficult task. The electrolytic and chemical preparations almost invariably contain some free mercury. The crystalline product should contain none but it is difficult to prepare by the usual recrystallization methods. A simple method (4) has recently been devised whereby gaseous sulfur dioxide is allowed to diffuse slowly into a sulfuric acid solution (1:6 acid) which is about 75 per cent saturated with respect to mercuric sulfate (about 350 grams per liter). If the sulfur dioxide diffusion is slow enough the Hg_2SO_4, which is formed by reduction and is comparatively insoluble in the acid, does not come out as a precipitate but grows into well-formed plates. This material must be well washed with 1:6 H_2SO_4 and the electrolyte to be used.

Cells, whether cadmium or zinc, built with this mercury-free crystalline mercurous sulfate have high E.M.F.'s (taking the E.M.F. of mercury-laden electrolytic mercurous sulfate as normal). There are two phenomena to consider with respect to the crystalline and electrolytic preparations. First, there is the effect of the particle size on the solubilities of two materials. The crystalline material has an average size of 500 microns, while the electrolytic material has a particle size of 1 micron. On the basis of this we should expect the solubility (5) of the former to be less than that of the latter, and, in view of equation a above we should expect the E.M.F. of the former to be smaller than that of the latter. However, just the contrary is true of the E.M.F., and so it is necessary to explain the difference by virtue of the effect the interspersed mercury in the electrolytic material has on the Hg(ous):Hg(ic) ratio and the consequent change in E.M.F. as calculated from equation c. This second phenomenon masks the first one quite completely.

The behavior of a typical saturated cadmium and zinc cell built with mercury-free crystalline mercurous sulfate, follows:

Time after construction	*Saturated cadmium cell*	*Saturated zinc cell*
1 day	1.018432 volts	1.420234 volts
5 days	1.018327 volts	1.420200 volts
25 days	1.018289 volts	
46 days	1.018255 volts	1.420214 volts
64 days	1.018229 volts	

The cadmium saturated cell shows the decline in E.M.F. characteristic of those cells made with large crystalline mercurous sulfate (6).

The above data can be contrasted with the following data for two cells built with electrolytic Hg_2SO_4:

Time after construction	*Saturated cadmium cell*	*Saturated zinc cell*
1 day		1.419980 volts
7 days	1.018122 volts	1.420000 volts
14 days	1.018114 volts	1.420004 volts
21 days	1.018113 volts	1.420031 volts
28 days	1.018114 volts	1.420034 volts

During the course of our exploration of the E.M.F. at various points in the electrolyte of old cells, the E.M.F. in the Hg_2SO_4 paste itself was examined and almost invariably it was lower than the E.M.F. of the large mercury electrode below. The mercurous sulfate in these cells was electrolytic product and contained much free mercury of small globule size, but at the cell's mercury electrode surface only a very large area of mercury of a small degree of curvature was existent. In the paste, therefore, we should expect the mercuric ion to be more repressed than at the surface of the mercury electrode and the E.M.F. to be smaller in the first case, which is observed.

	E.M.F. of cell	*E.M.F. in paste*
Cell G9 (4 years old)...................	1.018280 volts	1.017930 volts
Cell G17 (2 years old)..................	1.018140 volts	1.014790 volts
Cell G3 (4 years old)...................	1.018120 volts	1.017910 volts

The effect of very finely divided mercury on a cell's E.M.F. was emphasized by preparing a very black mercurous sulfate by a prolonged passage of sulfur dioxide into an acid solution of mercuric sulfate and using this product in cells which gave very low E.M.F.'s.

Time after construction	*Saturated cadmium cell*	*Saturated zinc cell*
1 day	1.017366 volts	1.418589 volts
4 days	1.018036 volts	
11 days	1.018036 volts	
32 days	1.018103 volts	
47 days		1.419734 volts

All of the cells built with this material show marked recuperative powers toward the normal E.M.F.

A very light coating of finely divided mercury was deposited on a sample of clear crystalline mercurous sulfate by running two 5-cc. portions of 1:6 H_2SO_4, 40 per cent saturated with sulfur dioxide at atmospheric pressure and room temperature, through the sample while on the filter. The crystals turned gray on the surface. Acid saturated cells were made of this material. The electrolyte was about 0.08 molar in H_2SO_4 to prevent effects due to hydrolysis. These cells likewise had low original values.

Time after construction	*E.M.F.*	*E.M.F. corrected to neutral solution*
1 day	1.016840 volts	1.016972 volts
3 days	1.017182 volts	1.017314 volts
2 days	1.017924 volts	1.018056 volts

The fact that cells built with finely divided mercury present in the depolarizer tend to increase in E.M.F. is quite concordant with theory. We have shown that the free energy of the spheroids of mercury and, therefore, their vapor pressure increases as the radius decreases. In obedience to the universal law that everything tends toward a state in which its free energy is a minimum, the smaller globules of mercury are continuously "distilling over" to larger ones of a smaller free energy. As this process continues the importance of the mercury in the equation $Hg^{++} + Hg = Hg_2^{++}$ becomes less, and the E.M.F. rises to the normal value. When the electrolytic method of preparing mercurous sulfate was developed (7), it was found that much finely divided mercury was formed at the mercury anode and attached itself to the mercurous sulfate, giving it a gray appearance. At that time it was our practice to stir the mercurous sulfate in the acid electrolyte together with excess mercury with the object of eliminating any finely divided particles of sulfate that might give an abnormal solubility. Now it seems that this procedure accomplished another important end. The very finest mercury globules also disappeared, as indicated above, and only those of a certain size remained, but these mercury globules appear to establish the equilibrium $Hg^{++} + Hg = Hg^{++}$ more rapidly and certainly than does the bulk mercury of the electrode, and this equilibrium determines the reproducibility of cells. Evidently much finely divided mercury should be present in the "paste," but it should be equilibriated by several hours (over night) stirring with sulfuric acid and excess mercury.

REFERENCES

(1) HULETT AND ELLIOTT: Diffusion in Standard Cells. J. Phys. Chem. **37**, 245 (1933).

(2) SUMMERS AND GARDINER: Trans. Am. Electrochem. Soc. **56**, 141–67 (1929).

(3) LEWIS AND RANDALL: Thermodynamics, pp. 251–2. McGraw-Hill Book Company, New York (1923).

(4) ELLIOTT AND HULETT: J. Phys. Chem. **36**, 2083 (1932).

(5) HULETT: The Solubility of Gypsum. J. Am. Chem. Soc. **24**, 667 (1902).

(6) GARDINER AND HULETT: Trans. Am. Electrochem. Soc. **56**, 111–28 (1929). The Hydrolysis of Mercurous Sulfate.

(7) CARHART AND HULETT: Trans. Am. Electrochem. Soc. **5**, 59 (1904).

ON THE FORMATION, SIZE, AND STABILITY OF EMULSION PARTICLES. I

A New Method of Emulsification

C. G. SUMNER

58 St. Thomas' Road, Chorley, Lancashire, England

Received December 9, 1932

I. GENERAL METHODS OF EMULSIFICATION

In general, the formation of a disperse system may be achieved in two distinct ways: (a) by mechanical disintegration of bulk material into the fine particles forming the disperse phase, (b) by condensation of molecules of the disperse phase into larger aggregates, either process taking place in the presence of the dispersion medium. This fact is fully recognized in general colloid chemistry, where both types of method are in use, although condensation methods are there of chief importance. On the other hand, in the study of emulsions little attention has been paid to the possibility of utilizing condensation methods of preparation, mechanical dispersion being almost invariably employed. We shall here consider chiefly emulsions containing an emulsifying or stabilizing agent; since in such systems the added substance produces an interfacial phase between the two liquids, these emulsions will be described as "three-phase" emulsions, in contrast with "two-phase" systems where only the pure liquids are present.

Two modifications of the dispersion method are possible in emulsification: (a) the whole of the two liquids forming the emulsion may be agitated together for a suitable time in the presence of an appropriate emulsifying agent, either in one operation or with gradual addition of the liquid which is to form the disperse phase; (b) the latter liquid may be injected into the medium containing a stabilizing agent as a stream of fine droplets. The former means is almost invariably used, although it is theoretically inefficient and open to grave objections; it has been criticized by Clayton (1).

The processes taking place in the agitation method have been considered by Stamm and Kraemer (2). The formation of the emulsion is the net result of two opposing forces: the effect of agitation in disrupting the liquids, and the tendency to re-coalescence with the formation of bulk phases. Both liquids are broken up, and the degree of subdivision of each will be conditioned by mechanical factors such as the mode of agitation, the volume ratio, densities, and viscosities of the liquids, and the interfacial tension. Formation of an emulsion depends on the re-coalescence of only one liquid to a continuous phase, the second liquid remaining subdivided after agitation ceases. The chief function of the emulsifying agent is to inhibit coalescence of the internal phase during and after emulsification, although in so far as its presence affects the mechanical properties of the liquids, it will affect the dispersion process. In particular, the reduction in interfacial tension which is produced by substances capable of acting as emulsifying agents will assist disintegration of the phases. Either an oil-in-water or a water-in-oil emulsion may be obtained as a stable system, by suitable choice of the emulsifying agent.

For the description and critical discussion of the various methods of agitation or stirring used for emulsification, reference should be made to Clayton's publications (1). It may be mentioned that according to recent experiments (3, 4), agitation by mechanical means may be replaced by irradiation by ultrasonic waves of the order 200 to 500 kilocycles per second, many different emulsions having been prepared in this way.

Since in the final emulsion only one liquid is subdivided, energy expended in breaking up the medium is entirely wasted, and greater efficiency is to be obtained in emulsification by injection of the internal phase, already broken up into droplets, into the bulk of the medium containing the stabilizing agent (3a). "The whole work of dispersion can thus be made on the internal phase and adsorption at the dineric interface can be reached without the interfering adsorption at the gas-liquid boundary common to the usual agitation or stirring methods" (Clayton 1b). In this method the degree of dispersity or particle size will be fixed by the method of breaking up the internal phase, and the function of the stabilizing agent will lie mainly in preserving the individuality of the particles introduced into the medium.

Three possible methods may be considered for the formation of emulsion particles by condensation from a state of molecular subdivision, according as the molecules are derived from (1) a vapor phase, (2) true solution, (3) chemical action. The two latter methods, when applicable, introduce complications, owing to the presence of unwanted solvents or reaction products. Lewis (4) obtained a dilute emulsion of mineral oil in water by pouring an alcoholic solution of the oil into water. No stabilizing agent was used, the product being a two-phase emulsion or oil hydrosol, but the same method could be employed for obtaining a more concentrated three-phase emulsion. Chemical methods are of considerable importance in general colloid chemistry, being often the only means of obtaining certain sols, but this is not the case with emulsions. A case of interest is the formation of an oleic acid-in-water emulsion by the addition of mineral acid to a solution of sodium oleate. If the acid is not in excess, the residual soap acts as a stabilizing agent.

Methods involving condensation from a vapor phase fall into two types, according as (a) the vapors of both disperse and continuous phases are brought into admixture and condensed, or (b) the vapor of the disperse phase is injected below the surface of the bulk of the medium. These correspond roughly with the two types of dispersion method. Both have been applied to the production of sols and two-phase emulsions. Roginsky and Shalnikoff (5) obtained sols of the alkali metals in organic liquids by condensing the vapors of liquid and metal on a surface cooled with liquid air, subsequently allowing liquefaction to take place. Lewis (4) obtained dilute two-phase emulsions (oil hydrosols) by boiling oil and water together under a reflux condenser, and by steam distilling aniline. As with the agitation method of emulsification, formation of a disperse system depends on the coalescence of only one component to a continuous phase. Method b has been employed by Nordlund (6) for the production of mercury hydrosols, and by Gutbier (7) for sols of sulfur, selenium, and mercury. The so-called "electrical dispersion" method of preparing metallic sols is essentially similar, the production of metallic vapor by an electric arc below the surface of the medium replacing injection from an external source.

Hitherto, the preparation of three-phase emulsions by condensation of vapor of the internal phase in the presence of a stabilizing agent has not been investigated. For this purpose method b is required, and in the next section the study of such a method of emulsification will be described. The results show that it is of considerable theoretical interest, and where it can be applied, it is of practical value in obtaining emulsions of very uniform grain.

II. A VAPOR CONDENSATION METHOD OF EMULSIFICATION

Emulsification being the preparation of a disperse system, the particle size or degree of dispersity is the criterion by which must be measured the efficiency of the process and the influence of various factors on it. In these experiments emulsification was effected by forcing oil vapor through a single capillary jet dipping below the surface of the aqueous phase contained in a beaker. The emulsion system was benzene in water, the stabilizing agent being sodium oleate. The size distribution of particles in each emulsion was determined by an improved sedimentation method based on those of Kraemer and Stamm (8) and of Lambert and Wightman (9), a sedimentation tube being used in conjunction with an automatic photographic recorder. The technique of this method has been fully described in a separate paper by the present author (10).

The dispersity of an emulsion made by passing a stream of oil vapor into an aqueous liquid may be influenced by factors of two kinds: (1) the conditions of injection, (2) the physico-chemical properties of the emulsion components. Factors of the first kind include the temperature and pressure of the vapor on entry, and the dimensions of the orifice through which it issues. The pressure of the vapor and the dimensions of the jet control the velocity of the vapor, and in this connection two quantities must be considered, viz., the linear velocity imparted to the molecules, and the mass or volume of vapor passing per second. The effects of all these conditions have been studied. In addition, the temperature and volume of the medium and the shape of the container may be relevant. Factors of the second kind include the chemical nature and physical properties of the liquids and stabilizing agent, the volume ratio of the liquids in the final emulsion, the concentration of stabilizing agent, etc. As indicated, the experiments cited have been confined to a single system, and of the conditions named, the concentration of sodium oleate has received chief attention.

Apparatus

In order to control the conditions of injection of the vapor, the apparatus shown in figure 1 has been developed. Benzene is boiled by means of the heating coil A in the vessel B, which is provided with a trap bulb C. The vapor passes through the delivery tube D, jacketing the cylindrical bulb E which is filled with nitrogen, to the bulb F. For clearness of drawing, the apparatus has been dissected in figure 1; in actual front view D is immediately behind F, the connecting tube (shown dotted) being about 8 cm. long so as to leave a clear space below the jet. The vapor finally emerges via the trap G through the jet H. From C nearly to H, the tube is wound with nichrome wire on asbestos paper. All parts of the apparatus which are subjected to heat are lagged by winding with asbestos string. The temperature of the vapor is read on the thermometer J cemented into the bulb F, and the pressure on the manometer K, both values being measured as near as possible to the jet.

The bulb E forms a nitrogen thermoregulator, and operates a mercury contact L controlling the relay M, which in turn controls the current through the superheater coil. The temperature at which the regulator works is determined by adjustment of the nitrogen pressure by means of the mercury column N, the whole arrangement being essentially a constant volume gas thermometer. In this way the temperature of the issuing vapor may be maintained at any arbitrary constant value. Automatic regulation of the pressure is provided by adjusting the contact P of the manometer to the desired value. This controls the current through the heating coil A by means of the relay Q. Since the rate of vapor formation governs the rate of efflux, equilibrium being reached at a pressure such that these two rates are equal, maintenance of a constant pressure is dependent on a steady rate of boiling, and this is achieved by the arrangement described. Power is taken from the mains (200 volts, D.C.), and a relay circuit already described by the author (11) is used; except that whereas the relay Q brings extra resistance into the heating circuit when contact P is closed, as in the published arrangement, relay M does so when contact L is opened.

Taps are included in the apparatus at suitable points, for filling and draining the boiling vessel, for setting up and also for isolating the two manometric systems, and for draining distilled benzene from the bulb S. No tap is exposed directly to vapor.

A special device is used for introducing the beaker of dispersion medium quickly and accurately beneath the efflux jet. This comprises a stage T which is moved vertically by means of a rack and pinion U, and may be held in any desired position by a quick-release pawl (not shown). The beaker is placed on the stand, and the latter is quickly raised until the jet just dips into the liquid. After the required amount of vapor has been passed, the pawl is released, the stand quickly lowered, and the beaker withdrawn.

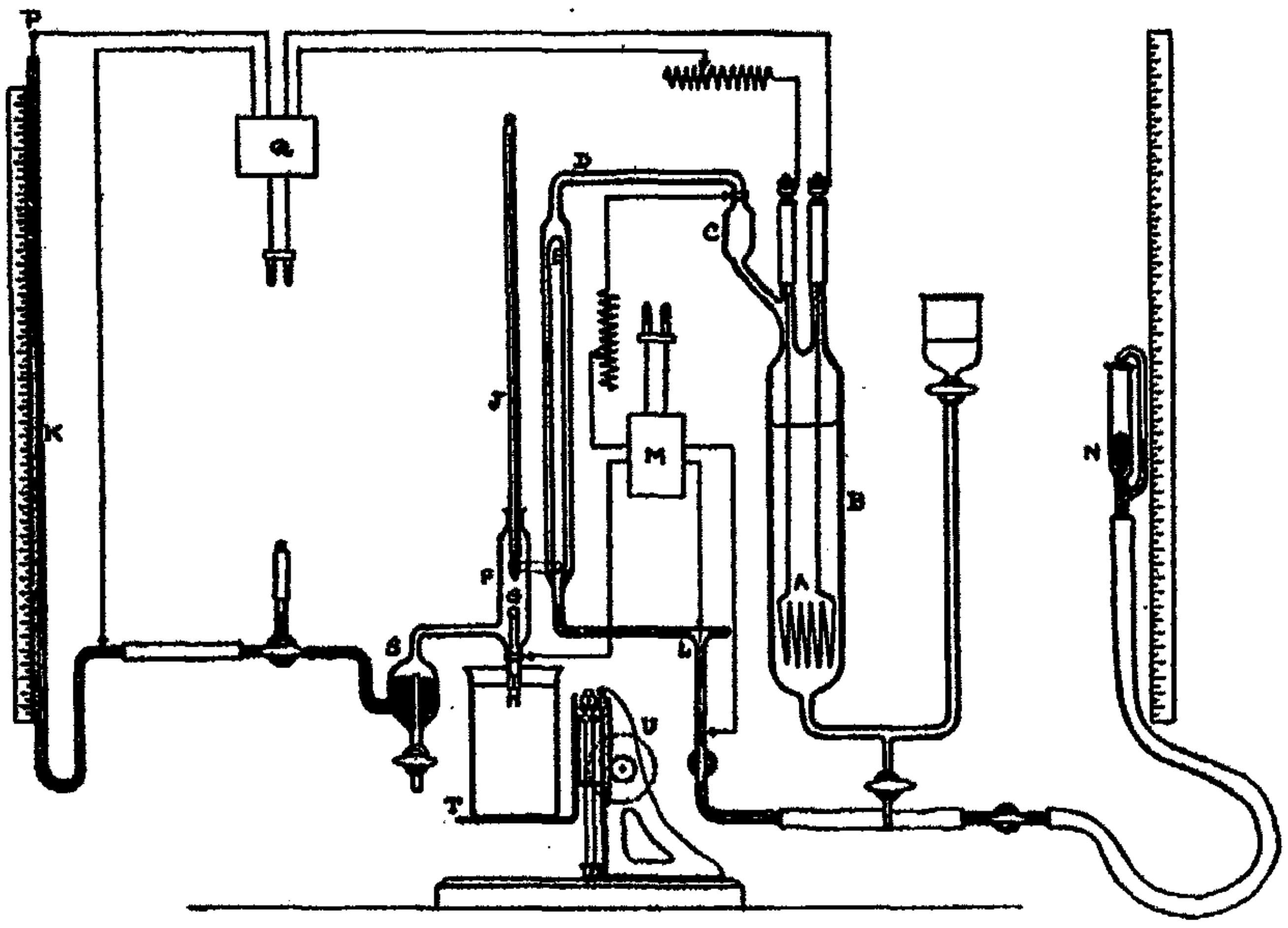


FIG. 1. EMULSIFICATION APPARATUS

The procedure in an experiment was as follows. The emulsification apparatus was started up and the oil vapor allowed to issue into pure water until a steady state was reached, under the desired conditions of temperature and pressure. A known volume of the dispersion medium, at a known temperature, was then quickly substituted for the water, and vapor was allowed to pass for the required time. The temperature of the emulsion having been noted, the beaker was then transferred to a special device in a water thermostat at 25°C., where the emulsion was kept stirred without free access of air. When temperature equilibrium was reached, a quantity of the emulsion was rapidly transferred to the sedimentation tube, previously set up in an air thermostat at 25°C. Another portion of the fresh emulsion was utilized for a pycnometric determination of its density (also at 25°C.), whence its composition was calculated from the known densities of oil and medium.

Materials

The benzene used was Kahlbaum's "crystallized thiophene-free" quality, without further treatment. It was recovered after use by allowing the emulsions to settle out, shaking the separated "cream" with water and benzene in bulk. The water phase was run off and replaced by pure water after each separation, and by repeating the treatment the concentration of soap was progressively reduced until the cream was entirely broken. The separated benzene was dried over sodium sulfate and redistilled, after which it was used in further experiments.

Sodium oleate was made from Kahlbaum's oleic acid, further purified by formation of the lead salt and extraction with ether, followed by hydrolysis and distillation of the acid *in vacuo*. The first sample of the sodium salt was prepared by neutralization of the acid in alcoholic solution with a slight excess of solid anhydrous sodium carbonate; the soap was extracted by repeated hot filtration, crystallization, and resolution in absolute alcohol. Superior results were obtained by the method of Harkins and Beeman (12); sodium ethylate made by dissolving sodium in alcohol was added to the acid (also in alcohol) until neutrality to phenolphthalein was reached. The salt was recrystallized from alcohol and finally dried for two days at 25°C. A 0.01 molar solution was made up in the cold and diluted as required; only a small quantity (100–250 cc.) was prepared at a time, in order to avoid waste due to deterioration on standing. Conductivity water was used throughout.

Conditions of emulsification

The capillary jet employed throughout had a diameter of 0.7 mm., giving a cross-section of 0.0038 sq. cm., and the length of the cylindrical portion was about 9 mm. With these dimensions, the times required under various pressures for the injection of 15 cc. of benzene into 135 cc. of solution, to form 150 cc. of a 10 per cent emulsion, were found to be as follows.

Pressure (mm. of mercury)	25	50	100	150
Time (minutes)	8¼	5	3	2⅓

The velocity was thus not a linear function of the pressure, and since any substantial increase in velocity would evidently require a considerable increase of pressure, experiments were limited to the range given.

In one series of experiments, the orifice was reduced in diameter by cementing over the end of the capillary a disc of thin zinc foil, pierced with a fine hole. A solution of celluloid in amyl acetate was used for this purpose, so that the disc was readily removable. The diameter of the orifice was then 0.48 mm., the cross-section being 0.0018 sq. cm. The corresponding pressure-time relation was as follows.

Pressure (mm. of mercury)	50	100
Time (minutes)	11	6½

For a given pressure, the times with the two orifices were very nearly in the ratio of the respective areas, so that the linear velocity of the vapor was practically unaltered by reducing the opening. This fact enabled the effects of orifice diameter and linear velocity to be separated.

The temperature of the vapor remained constant to within ±1.5°C. during each experiment; in separate experiments the mean temperature corresponding with a given nitrogen pressure was not exactly reproducible, varying over a range of about 5°C. In order to control this as far as possible, the technique was standardized. First the superheater was switched on, and left for 30 minutes before heating of the benzene was begun. A further 15 minutes was allowed for equilibrium to be reached before the vapor was allowed to pass into the experimental solution.

Determination of size distribution

The results of the sedimentation analysis were plotted with time as abscissa and the reading of the index as ordinate. The size distribution was derived by drawing tangents to the curve, as described in the paper cited (10). In most of the following data, radius intervals of 1μ have been taken; the intercepts cut off the vertical axis by tangents drawn at the calculated points were read from the curve, and the results tabulated as the fractions of the total mass of disperse phase lying between given size limits. This fraction was obtained as the ratio between the intercept corresponding with the given interval, and the length cut off the axis by the limiting tangent, i.e., the tangent to the curve where the movement of the index became the steady drift due to evaporation. (It had been found that a linear relation held between the movement of the index and the mass of particles sedimented.) Any error involved in assuming that sedimentation was complete when the movement of the index became uniform would be slight, since observation of the sedimented emulsion after the experiment showed that the mass of any fine particles not included in the cream must be extremely small. A certain number of failures in sedimentation analysis were registered, through stoppage of the automatic mechanism, temperature irregularities due to faulty working of the thermostat, or bubbles in the index tube.

Reproducibility

The first experiments were carried out under the following conditions: vapor temperature 95–100°C., pressure 50 mm. of mercury, concentration of sodium oleate 0.0005 *M*, volume of solution 135 cc., time of passage of vapor 5 minutes. These constants proved to be convenient and were used to test the reproducibility of the emulsions, and also at various times as a check on the experiments. In consequence, this group of experiments forms the largest series corresponding with one set of conditions. The results are collected in table 1.

TABLE 1

EXPERIMENT	ΔS				
	$< 4\mu$	$4–5\mu$	$5–6\mu$	$6–7\mu$	$> 7\mu$
1	8	21	32	21	18
2	–	38	32	13	17
3	8	34	29	16	13
4	4	31	32	15	18
13	11	36	32	12	9
15	10	28	35	12	15
17	5	40	29	13	13
Mean......	6	32	32	15	15

In table 1 ΔS represents the percentage of the total mass of particles corresponding with the radius intervals shown. Considering the nature of the process under investigation, the concordance of these results is excellent. The distribution varies slightly, but in all cases about 80 per cent of the mass of particles corresponds with the range 4μ to 7μ (the limits being 75 to 83 per cent). For an emulsion this is an extremely uniform dispersion, but it will be seen that even greater homogeneity has been obtained by the use of a higher vapor velocity.

Influence of conditions of injection

(*a*) *Vapor pressure.* The results obtained under various pressures, using the same orifice, vapor temperature, solution concentration, and oil concentration (10 per cent by volume) as before, are shown in table 2.

Table 2 would appear to show a progressive decrease in the mean particle radius with increase of pressure, but examination shows that this is due to a closing up of the limits of size, radii less than 4μ in no case passing the lower limit 3.5μ. The effect of an increase of pressure was therefore to produce a more uniform dispersion. It is remarkable that with pressures of 100 mm. and over, about 80 per cent of the mass of particles lay within the range 4μ to 6μ; moreover, at 100 mm. substantially the whole range of sizes was from 3.5μ to 6.8μ (approximately), and at 150 mm. from 3.5μ to 6μ.

TABLE 2

EXPERIMENT	PRESSURE	ΔS				
		< 4μ	4–5μ	5–6μ	6–7μ	> 7μ
	mm.					
11	25	–	11	18	18	53
14	25	3	10	30	21	36
Mean		1½	10½	24	19½	44½
Mean*	50	6	32	32	15	15
6	100	16	52	27	5	–
7	100	11	54	26	9	–
Mean		13½	53	26½	7	–
9	150	19	55	26	–	–
10	150	17	50	33	–	–
Mean		18	52½	29½	–	–

* *From* table 1.

TABLE 3

EXPERIMENT	PRESSURE	TEMPERATURE	ΔS				
			< 4μ	4–5μ	5–6μ	6–7μ	> 7μ
	mm.	*degrees C.*					
15	50	100	10	28	35	12	15
16	50	115	10	33	34	12	11
18	50	135	7	38	27	19	9
19	50	156	8	22	34	27	9
Mean			9	30	32	18	11
Mean*	100	96	13½	53	26½	7	–
22	100	117½	17	45	33	5	–
20	100	134	14	46	33	7	–
21	100	156	14	49	32	5	–
Mean			15	48	31	6	–

* From table 2.

(*b*) *Vapor temperature.* Experiments were carried out over the range of temperature 96°C. to 156°C. (16°C. to 76°C. above the boiling point of benzene), using steps of from 15 to 20 degrees, for each of the pressures 50 mm. and 100 mm. The results are given in table 3.

It is evident from the figures in table 3 that the temperature of the vapor was without effect on the distribution of particle sizes.

(*c*) *Orifice diameter.* In these experiments the capillary jet was as before, except that the orifice was reduced by cementing over the end a perforated disc of zinc foil. The results are shown in table 4.

By comparison of table 4 with table 2, it is seen that the efficiency of emulsification with the higher pressure was not considerably altered by a reduction in the cross-section of the orifice, the size range of the particles remaining about the same. A somewhat higher percentage of the total mass corresponded with the interval 4μ to 6μ, but of this a larger proportion lay in the interval 5μ to 6μ, while there was a decrease in the fraction between 3.5μ and 4μ, and an increase in that between 6μ and 7μ. With the lower pressure, there was a reduction in the fraction lying between 4μ and 7μ, owing to an increased proportion of large particles.

TABLE 4

EXPERIMENT	PRESSURE	ΔS				
		< 4μ	4-5μ	5-6μ	6-7μ	> 7μ
	mm.					
23	100	7	48	35	10	–
24	100	–	45	43	12	–
Mean		3½	46½	39	11	–
25	50	–	23	30	17	30
26	50	3	27	29	16	25
Mean		1½	25	29½	16½	27½

The effect of orifice diameter, therefore, became less noticeable as the pressure was increased.

Since it was found that the linear efflux velocity of the vapor was not greatly affected by a reduction in the size of the orifice, it would appear that the linear velocity was of more importance than the mass or volume velocity. This suggests that the uniformity of dispersion was largely dependent on an efficient distribution of vapor throughout the condensation zone rather than on the actual amount injected per second. With a view to obtaining some idea of the conditions of mixing, the linear and volume velocities under the experimental conditions have been calculated from the observed mass velocity and orifice diameter (see table 5). Since the gas laws have been used for this purpose in default of empirical information as to the specific volume of benzene vapor at various temperatures and pressures, the figures are necessarily very approximate, and useful only for comparison purposes.

The figures in table 5 show clearly the predominant importance of the linear velocity. Thus the larger jet in conjunction with a pressure of 50 mm. gave roughly the same momentum as the smaller jet and a pressure of 100 mm., while the actual mass of volume of vapor emerging per second was greater in the former case; notwithstanding this, the higher pressure gave more efficient dispersion. The uniformity of the dispersion clearly increased as the linear velocity of the vapor rose, but had no obvious connection with any of the other factors.

(*d*) *Other conditions.* The volume of solution and the shape of the container might be expected to influence the condensation process through their effect on the conditions of mixing, if condensation of the vapor occurred throughout the liquid. Actually, it was observed that condensation occurred in the neighborhood of the jet, the drops formed then distributing themselves throughout the whole volume of liquid. Thus as far as the actual condensation was concerned, the liquid was effectively without limit, so that the actual boundaries were unimportant.

TABLE 5

ORIFICE	PRESSURE *mm.*	m*	V	u	mu
I	25	0.025	9.2	2400	59
	50	0.044	16	4200	190
	100	0.074	26	6700	500
	150	0.085	28	7200	600
II	50	0.020	7.1	3900	778
	100	0.033	11	6400	210

* Here m = mass of vapor passing per second, in grams (observed), V = volume of vapor per second, in cubic centimeters (calculated), u = linear velocity at orifice, in centimeters per second (calculated), $mu = m \times u$ = momentum at orifice, in gram centimeters per second (calculated).

The influence of the initial or mean temperature of the solution has not been studied experimentally, but may be inferred. The effect of raising the temperature may be expected to depend chiefly on the consequent reduction in viscosity and in interfacial tension. The former will facilitate the passage of vapor or of drops through the liquid, and so will have the effect of a higher linear velocity, while the latter will probably have a similar effect to that of an increased concentration of soap. It may be mentioned that in the experiments described, the temperature of the solution during emulsification rose by about 10–12°C.

Influence of soap concentration

(*a*) *Initial concentration.* In these experiments the concentration of soap in the solution was varied over the range 0.0005 *M* to 0.0025 *M*. For each of the concentrations 0.0010, 0.0015, 0.0020, 0.0025 *M*, two experiments were performed; one of the records for 0.0015 *M* showed a disturbance of the sedimentation, but as it gave good qualitative agreement with the satisfactory record, the experiment was not repeated. The figures for 0.0005 *M* are from previous experiments. In all cases the unobstructed jet was used, the pressure being 100 mm. and the vapor temperature 95–100°C. As in previous experiments the concentration of benzene in the emulsion was as nearly as possible 10 per cent. The results are shown in table 6, a more detailed analysis of the size distribution being given in order to bring out clearly the effect of the concentration of solution used in the emulsification process.

TABLE 6

EXPERIMENT	CONCENTRATION	ΔS								
		2–2.5	2.5–3	3–3.5	3.5–4	4–4.5	4.5–5	5–5.5	5.5–6	> 6μ
	M									
6	0.0005	–	–	–	16	21	31	17	10	5
7	0.0005	–	–	–	11	24	30	18	8	9
Mean		–	–	–	13½	22½	30½	17½	9	7
28	0.0010	–	–	5	24	32	26	10	3	–
29	0.0010	–	–	4	19	35	20	14	8	–
Mean		–	–	4½	21½	33½	23	12	5½	–
32	0.0015	–	5	22	20	30	14	9	–	–
30	0.0020	–	20	24	29	17	10	–	–	–
31	0.0020	–	16	25	30	18	11	–	–	–
Mean		–	18	24½	29½	17½	10½	–	–	–
27	0.0025	5	34	36	11	9	5	–	–	–
33	0.0025	6	23	41	15	15	–	–	–	–
Mean		5½	28½	38½	13	12	2½	–	–	–

It is evident from table 6 that with increasing concentration there was a continuous downward trend of the mean particle radius. This effect is quite distinct from that due to increasing pressure, for in this case the range of sizes was not reduced appreciably, but was shifted as a whole. The phenomenon was shown very clearly by even a qualitative inspection of the sedimentation records, since the time of sedimentation varies inversely as the square of the particle radius.

Over the range of concentration investigated, the optimum interval was reduced from 4.5–5μ to 3–3.5μ. There is no indication in these results as to the limiting size obtainable by further increase in concentration; extension in this direction became difficult owing to the greatly increased time required for sedimentation, in accordance with the relation (Stokes' law) mentioned above. For 0.0005 *M* solutions, a complete sedimentation record covered a period of twenty to twenty-four hours; for 0.0025 *M*, about fifty hours. The fact that dispersions having distinct size limits within such a small range could be reproduced at will is an indication of the accurate definition of conditions which is possible in this method of emulsification.

(*b*) *Effect of additions of soap after emulsification.* It was noticed that on standing for a day or so, an emulsion formed as above showed a coarsening of the dispersion. With 0.0005 *M* soap solution, the cream in the sedimentation tube had almost invariably broken to some extent by the end of the experiment. Over the same period the emulsion filling the pycnometer tube showed no breaking, but on redistributing the cream throughout the liquid, the uniform emulsion was less opaque than originally. Similar coarsening without breaking was found when a stoppered cylinder completely filled with the emulsion was left to stand, so that the behavior in the sedimentation tube must be ascribed to the presence of an air phase above the liquid, other conditions being the same. This is in agreement with the fact noted by Clayton (1b), that emulsions can be broken by shaking if a gaseous phase is present.

In explanation of the observed decrease in dispersity, it was supposed that the amount of soap present, while able to promote emulsification, must be insufficient to prevent coalescence of the oil droplets over a prolonged period, especially when the emulsion was allowed to cream so that the droplets came into close contact. This suggested that enhanced stability might be achieved by further addition of soap, and a series of experiments was carried out, in which was examined the effect of increasing the soap concentration *after* emulsification.

A known volume, *V*, of 0.0005 *M* sodium oleate solution was used to prepare an approximately 20 per cent emulsion, under fixed conditions of temperature and pressure, and to this emulsion was added an equal volume, *V*, of x molar sodium oleate solution, x being variable. A 100-cc. stoppered cylinder was completely filled with the resulting emulsion of 10 per cent benzene in $\frac{1}{2}(x + 0.0005)$ *M* solution, and left to stand in a thermostat at 25°C. for from forty-four to forty-eight hours. The emulsion was then mixed uniformly again and a sedimentation analysis carried out. For comparison purposes were taken 10 per cent emulsions in 0.0005 *M* solution, made not directly but by dilution of a 20 per cent emulsion with the same medium. One such emulsion was sedimented immediately, and a similar one after two days. This gave directly the effect of ageing on the original emulsion, while additions of 0.0015, 0.0025, 0.0035, 0.0075 *M* solution showed the behavior in contact with concentrations of 0.0010, 0.0015, 0.0020, and 0.0040 *M*, respectively.

The results may be shown best, not by analysis of the sedimentation curves but by plotting these directly on the same graph, as in figure 2. This shows time as abscissa, and the percentage of the total mass of particles which have settled out, as ordinate. It will be seen that the original emulsion showed a great increase in the velocity of sedimentation (and hence in particle size) as the result of standing, but that with increasing soap concentration the sedimentation velocity of an aged emulsion decreased and the curve approached that of a fresh emulsion. Over the range examined, however, this curve was not reproduced for an aged emulsion.

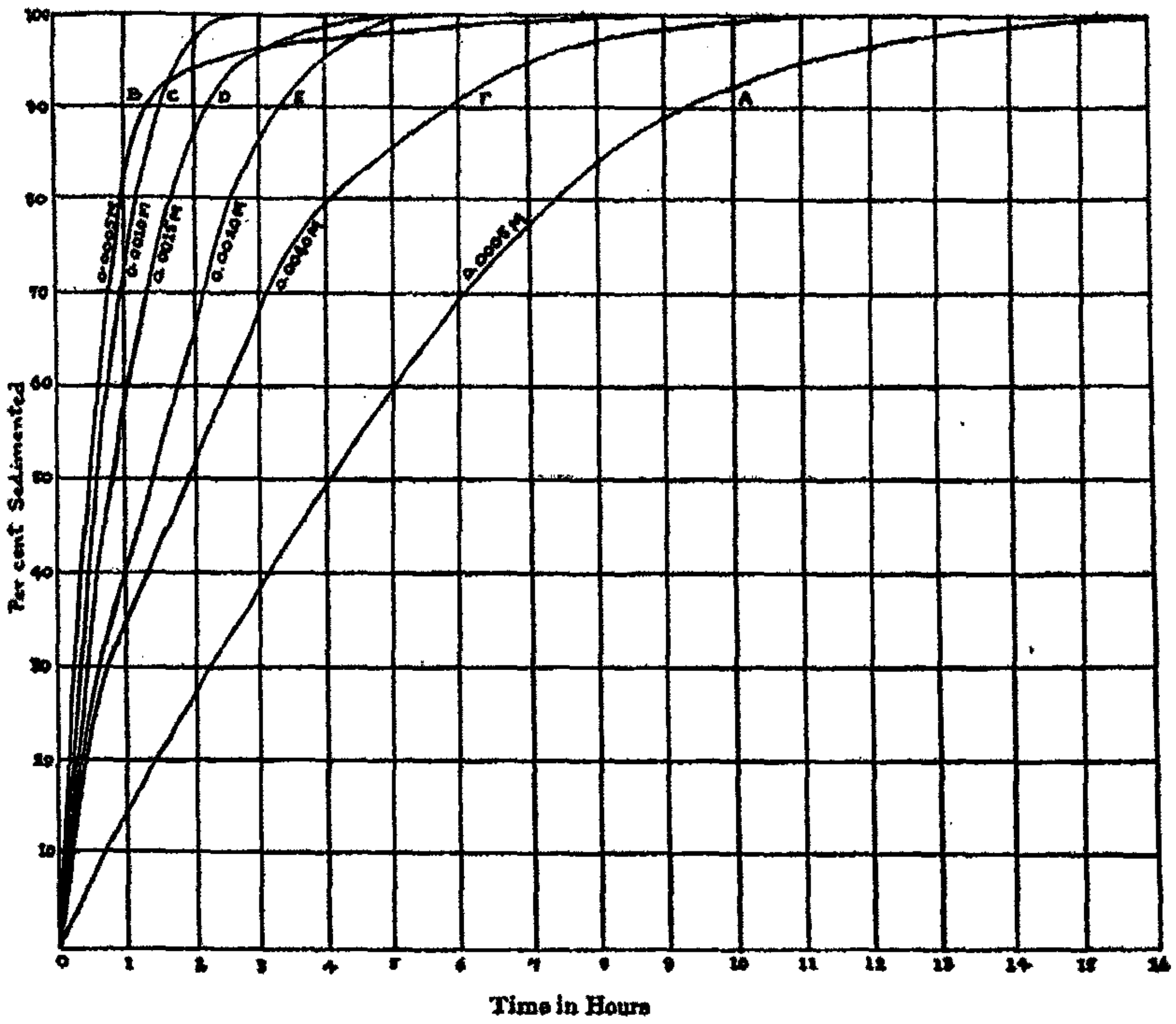


FIG. 2. SEDIMENTATION CURVES OF EMULSIONS
A, fresh emulsion; B, C, D, E, F, aged emulsions

Consideration of the effect of soap concentration on the stability of emulsion particles is reserved for a later paper. For the present purpose it is sufficient to notice that in this condensation method of emulsification, it is of prime importance whether the final soap concentration is fixed before or after the emulsion is made. The dispersity of the emulsion is governed by the initial concentration. It is evident that the size and number of the particles formed in the emulsification have no direct relation with the area of interface which may be maintained over a prolonged period of time, for on raising the initial soap concentration the dispersity (and hence the interfacial area) increases, in spite of the fact that at the lower concentration this area is too great for stability. Thus in passing from 0.0005 *M* to 0.0025 *M* solution, the interfacial area was augmented by about 50 per cent; nevertheless a concentration of 0.0040 *M* was insufficient to keep the lower area stable for two days. It must be concluded that the soap exercises two distinct functions: (1) in the formation of the emulsion; (2) in the stabilization of the emulsion. The second function does not depend on the method of preparation, and will be the same for an emulsion of given properties (dispersity, volume ratio, soap concentration), however it is made. On the other hand, the first function is characteristic of the method of emulsification. In the present method the soap concentration has a direct influence on the dispersity of the emulsion, and a physcochemical equilibrium in the condensation process must be postulated. The question then arises: what is the function of the emulsifying agent in other methods of emulsification? This function, and the influence of the emulsifying agent on emulsion stability, will be considered in a later paper.

III. THEORY OF THE CONDENSATION PROCESS

Possible mechanisms

In an attempt to ascribe a mechanism to the formation of emulsion particles by this method, two possibilities must be examined: (1) bubbles of vapor may be produced by the breaking up of a cylinder of vapor formed by the jet, these bubbles then condensing to liquid droplets; (2) particles may be produced by the growth of nuclei spontaneously formed in a supersaturated system of oil molecules. The latter case may be further subdivided, according as condensation takes place in the vapor or in the liquid phase, i.e., oil vapor may condense within water vapor, the droplets being then taken up by the medium, or oil molecules may aggregate to particles in direct contact with the aqueous liquid.

The observed results do not support the first hypothesis. The stability of a cylinder of fluid was investigated by Plateau (13), who showed that when the length exceeded the circumference, instability set in, a long cylinder breaking into drops, the distance between whose centers was equal to the circumference of the cylinder. A small globule was formed between each pair of large drops. Neglecting the volume of the small drop, the radius of the large drop is seen to be $a\left(\frac{3}{2}\pi\right)^{1/3}$, a being the radius of the cylinder. The drop radius should be directly dependent, therefore, on the jet radius, which was found not to be the case. Moreover, it may be calculated that of the orifices used, the larger should give liquid droplets having radii of the order 80μ, and the smaller one radii of the order 60μ, both of which values are considerably larger than the observed size. Still more does this latter fact exclude the alternative explanation that the break-up of the cylinder might form primary particles which would grow under conditions dependent on the properties of the medium, and we are led to the conclusion that the mechanism is of the second type.

The observed effect of soap concentration on particle size may be reasonably assumed to be due to the decrease in interfacial energy produced by the soap. If condensation to the final droplets occurred in the vapor phase, however, the only interface coming into account would be that between liquid oil and the mixed vapor of oil and water, whose surface tension would be independent of the soap concentration. There remains the possibility that primary particles might be formed in the vapor phase and might be taken up by the solution, there growing by coalescence with one another. This would mean that nucleus formation would be independent of the soap concentration but growth would not, since the ease of coalescence would depend on the interfacial tension. The variation in dispersity (which means the production of varying numbers of particles from a given mass of oil) must then depend on the degree of aggregation of primary particles.

On the other hand, the hypothesis that the whole process of condensation takes place in direct contact with the aqueous phase presents more analogy with the processes known to take place in other supersaturated systems, since the mechanism would then consist in the formation of primary particles or nuclei, which grow by accretion of other oil molecules independently of collision between the particles themselves. A variation in dispersity may then be caused by an alteration in the process of nucleus formation or in the rate of growth. Since the interface concerned is that between oil and aqueous solution, it is readily understandable that both the formation and growth of nuclei may be conditioned by the composition of the solution. This view of the process has been adopted provisionally, and will now be considered in some detail.

Nucleus formation

The experiments described differ from the ordinary case of condensation or crystallization in a supersaturated system, where the process starts from a certain initial supersaturation and goes to completion without the introduction of further material, for here there is a continuous addition of molecules to the system. It has been mentioned that the actual condensation takes place in a limited zone near the jet, so that the particles leaving the zone probably take no further part in the process. A steady state will therefore be set up, in which as much material leaves the zone in the form of particles as enters in the same time in the form of individual molecules. This will correspond with a certain degree of supersaturation in the condensation zone. Considering a single particle, the process may be regarded as comprising two stages, viz., the appearance of a nucleus, and its growth as it passes through the zone. The average size which a particle attains will depend on the velocity of growth and the time spent in the zone.

The formation of a nucleus means the collision and union of a number of molecules to an aggregate having the properties of surface, and this involves the generation of surface energy, which must be provided by the energy of condensation. Two conditions are therefore necessary: (1) a number, n, of molecules must be mutually so situated that they may condense together; (2) the condensation of these molecules to a particle must involve a net decrease in free energy. We will take the latter condition first. The formation of nuclei in any supersaturated system (vapor, solution, undercooled melt) will depend on similar factors, but for purposes of calculation the case of condensation in the vapor phase is the simplest to take, and will now be considered. In what follows the vapor is assumed to behave ideally.

It is shown readily that there is a minimum radius, which must be reached before a drop of liquid can grow by condensation of molecules upon its surface. W. Thomson (14) showed that the vapor pressure over a curved liquid surface increases with the curvature, the relation between p_x, the pressure over a spherical drop of liquid of radius x, and p_∞, the pressure over a plane surface of the same liquid, being

$$RT \ln \frac{p_x}{p_\infty} = \frac{2\sigma M}{d} \tag{1}$$

where M is the molecular weight, σ the surface tension, and d the density of the liquid. Following Gibbs, Volmer and Weber (15) point out that in consequence of this relation, in a vapor having a supersaturation pressure p_r, a drop having a certain radius r will be in equilibrium. Drops of smaller radius have a higher vapor pressure and are consequently unstable, while for radii greater than r the vapor pressure will be less than p_r and condensation on the drop will occur. A drop having the "characteristic radius" r corresponding with the supersaturation pressure p_r is defined by Volmer and Weber as a "nucleus," since under the given conditions it represents the lower limit of size for a drop capable of spontaneous growth. The work necessary to form such a drop within the vapor is shown to be

$$W = \frac{4}{3}\pi r^2 \sigma \tag{2}$$

or by substitution from equation 1

$$W = \frac{16\pi\sigma^3 M^2}{3R^2T^2d^2\left(\ln \frac{p_r}{p_\infty}\right)^2} \tag{3}$$

This work is taken as a measure of the stability of the supersaturated vapor.

Adopting this definition of a "nucleus," Farkas (16) has calculated the number of nuclei which overstep the characteristic radius r per second and grow to larger sizes. In the present writer's view, the production of drops having the "characteristic radius" is of secondary importance where the condensate is highly disperse, since the molecules forming such a drop must have energy above the average. The formation of a large number of nuclei[1] is only possible if molecules of average energy can condense together, and this may be achieved if groups containing a sufficient number of molecules are available. The idea of the "characteristic radius" may, however, be utilized in deriving the condition under which condensation of "average" molecules will occur.

Consider first the condensation of vapor on a plane surface of its own liquid, of constant area; let the vapor pressure of the liquid be p_∞ and the actual pressure of the vapor p_r. Since no surface work is involved in the change of state, the increase in free energy per molecule will be

$$w_\infty = kT \ln \frac{p_\infty}{p_r} \tag{4}$$

where k is Boltzmann's constant. Condensation will occur if w_∞ is negative, i.e., if $p_r > p_\infty$, while evaporation will occur if $p_r < p_\infty$. The condition $w_\infty = 0$ is realized when $p_r = p_\infty$, and corresponds with equilibrium.

When the liquid surface is curved, surface work is involved in the change of state, and this must be taken into account in the calculation. Consider the formation of a drop of liquid containing n molecules and having a radius x. The net increase in free energy is given by

$$\begin{aligned} W &= nw_\infty + 4\pi x^2\sigma \\ &= nkT \ln \frac{p_\infty}{p_r} + 4\pi x^2\sigma \end{aligned} \tag{5}$$

Now

$$nkT \ln \frac{p_\infty}{p_r} = -\frac{2\sigma}{r}\cdot\frac{M}{d}\cdot\frac{n}{N} = -\frac{2\sigma}{r}\cdot\frac{4}{3}\pi x^3 \tag{6}$$

where N is Avogadro's number, so that

$$W = 4\pi x^2\sigma\left(1 - \frac{2}{3}\frac{x}{r}\right) \tag{7}$$

---

[1] This term is used to denote a primary particle of any size, and not in the above limited sense.

This equation reduces to equation 2 when $x = r$. W is negative when $x > \frac{3}{2}r$, and this is the condition for the formation of a nucleus by molecules of average energy.[2]

It is to be noted that when n is small, the drop cannot be regarded as spherical, and in order to apply these equations the idea of an "equivalent radius" must be introduced, i.e., x and r are then not actual dimensions of the drops but the radii which the respective drops would have if they were spherical. An uncertainty remains, in that the value of σ for such small drops is not necessarily the same as for larger drops.

A similar calculation may be applied to the case of a supersaturated solution. It has been found (17) that the solubility of small crystals is greater than that of large ones, in analogy with the vapor pressure of liquid drops, and an equation similar to equation 1 may be used, solubility or solution pressure being substituted for vapor pressure. In fact, in any change of state where surface energy is generated, there will be a critical radius below which particles cannot be formed by molecules of average energy.

The probability, P_n, that a group of n molecules will be formed, at a given temperature, is a function of the concentration (of uncondensed molecules) and of the number n, such that (a) for a given value of n, P_n will increase with the concentration, (b) with a given concentration, P_n will diminish as n is increased, both rates of change being greater than proportionality. To each concentration, therefore, two numbers may be assigned, where (1) n_1 is the least number of molecules in an aggregate, the probability for whose formation is less than a given very small quantity (and therefore representing the upper limit of size for a group), and (2) n_2 is the number of molecules in an aggregate for which the net change in free energy in condensation is zero, for molecules of average energy. If $n_1 < n_2$, nuclei will not be formed with such molecules. At low supersaturations n_1 will be small and n_2 large, but since P_n increases with rising concentration, n_1 will also increase, whereas it is evident from equations 1 and 7 that n_2 will decrease. With increase of supersaturation, n_1 and n_2 will therefore approach one another, until the condition $n_1 = n_2$ is reached. Beyond this state n_1 will become greater than n_2, and nuclei formed by molecules of average energy will then appear. The "nucleus formation velocity" $\frac{dv}{dt}$ may be defined as the number of nuclei formed per second in

---

[2] The condition $W = 0$ does not correspond here with a true equilibrium between vapor and liquid. Once a drop of radius $\frac{3}{2}r$ is formed, it will grow indefinitely, since a decrease in free energy occurs in condensation on a surface of radius greater than r. The condition involved is different, therefore, according as the formation or growth of the drop is considered. Equilibrium between vapor and a surface actually formed holds when $x = r$.

unit volume; the part of $\frac{dv}{dt}$ corresponding with the nuclei considered will depend on P_n and on the range n_2 to n_1. Since all groups for which $n > n_2$ will condense, the relation may be expressed

$$\left(\frac{dv}{dt}\right)_{av} = \sum_{n = n_2}^{n = n_1} f(P_n) \tag{8}$$

This number includes all nuclei having from n_2 to n_1 molecules, but not nuclei of number less than n_1 (i.e., having radii between n and $\frac{2}{3} r$), formed by molecules of more than average energy. P_n and n_1 rise and n_2 falls with increasing concentration, and $\left(\frac{dv}{dt}\right)_{av}$ will increase rapidly with the supersaturation above the critical value. The optimum size of a nucleus will be that nearest the critical size, since on kinetic grounds the probability of formation increases as the size considered diminishes. The average size of a nucleus will therefore diminish as the concentration increases.

Nucleus growth

The growth of the nucleus depends on the rate of deposition of molecules on its surface and on the time spent in the condensation zone. The "specific velocity of growth" may be defined as $\frac{dm}{dt}$, where m is the mass of material deposited per unit area of surface. Now the number of molecules deposited per second on unit area is the difference between the number impinging on the surface and the number leaving it during this time. For a given solution pressure of the particle, therefore, $\frac{dm}{dt}$ will increase with the concentration of uncondensed molecules in the system. With a given supersaturation, $\frac{dm}{dt}$ will depend on the size of the particle, since the solution pressure increases as the radius diminishes.

If $\frac{dq}{dt}$ is the mass of material entering the condensation zone per second, V the volume of the zone, and μ_p the average size of a particle leaving the zone, then for equilibrium,

$$\frac{1}{v}\frac{dq}{dt} = \mu_p \frac{dv}{dt} \tag{9}$$

Let μ be the average mass of a nucleus, t_∞ the average time spent by a particle in the zone, and α the average area of the particle at any instant. Then we shall have

$$\mu_p = \mu + \int_0^{t_\infty} \alpha \frac{dm}{dt}\, dt \tag{10}$$

At the beginning of growth, $\frac{dm}{dt}$ will relate to the surface of the nucleus; since $\frac{dv}{db}$ and μ are fixed by the supersaturation, the initial value of $\frac{dm}{dt}$ for an average nucleus will be fixed also. The time t_∞ is determined by the relation of the path through the zone to the velocity of the particle. Hence as long as the conditions of injection are maintained, μ_p will be constant, i.e., successive "batches" of the dispersion will be similar.

Influence of pressure

In the emulsification method described, it is found experimentally that if the pressure of the vapor is raised and the cross-section of the jet is diminished in such a way as to keep $\frac{dq}{dt}$ constant, μ_p is reduced, so that by equation 9, $V\frac{dv}{dt}$ is increased. This means that on raising the pressure there must be an increase in either the volume of the zone or the equilibrium concentration, or (as probably happens) in both. An increase in concentration will reduce the average size of a nucleus but will increase the total mass of the nuclei formed per second; the diminution in μ_p therefore means a reduction in the time spent by a particle in the zone, in relation to the velocity of growth, i.e., an appropriate increase in the velocity of the particle relative to its path. Other things being equal, the velocity of the particle is determined by the entering linear velocity of the vapor, which is proportional directly to $\frac{dq}{dt}$ divided by the density of the vapor, and inversely to the cross-section of the jet. It may be concluded that for a constant value of $\frac{dq}{dt}$, with rising pressure the linear velocity of the vapor increases in relation to the depth of the condensation zone. This will mean a more efficient "sweeping" of the zone by the vapor, while the times spent in the zone by individual particles formed at different points will vary less; both these factors will tend towards greater homogeneity in the particle sizes, as actually observed. The zone will probably have approximately the form of a cone with the jet at the apex.

To a first approximation, the zone produced by the column of vapor entering the liquid may be regarded as the additive effect of a number of columns of smaller cross-section, i.e., with a given pressure the equilibrium will be practically independent of the cross-section of the jet. This was found to hold when the pressure was not too low. The above conclusions may be applied, therefore, to the influence of increasing pressure with a given jet, instead of with a fixed value of $\frac{dq}{dt}$.

Influence of soap concentration

Suppose that with fixed conditions of injection, $\frac{dm}{dt}$ is decreased. This means that in passing through the zone a particle will grow less than before, i.e., μ_p will be reduced. In order to maintain $\frac{dq}{dt}$ constant, $\frac{dv}{dt}$ must be increased, and conditions will therefore alter in such a way that this is effected. A given mass of the condensate will then comprise a larger number of smaller particles than before. The effect of an increasing concentration of sodium oleate in the aqueous phase of the emulsion may be ascribed to this phenomenon, since $\frac{dm}{dt}$ will be reduced progressively by addition of a surface-active colloid, through formation of a film round the particle which obstructs the access of further molecules. Now if the soap had no influence on $\frac{dv}{dt}$ at a given supersaturation of oil, the requisite increase in $\frac{dv}{dt}$ would necessitate a rise in the equilibrium supersaturation. It has been shown, however, that nucleus formation is conditioned by the interfacial tension, and since the latter is diminished by addition of soap, the reduction of $\frac{dm}{dt}$ is accompanied by a fall in the critical number of molecules, n_3. The range of group sizes available for nucleus formation by molecules of average energy is thereby extended, so that $\frac{dv}{dt}$ will rise independently of an increase in supersaturation. It does not follow that the latter will not take place, but the rise necessary will be less than if $\frac{dv}{dt}$ were independent of the soap concentration.

CONCLUSION

No claim is made for the experiments described, that they are exhaustive even over the limited field investigated, but the results obtained warrant the conclusion that an important new avenue of research has been opened. The study of emulsification by this new method is of interest in connection both with emulsions and with general condensation processes. An important feature of the work is quantitative specification of the experimental conditions and results.

SUMMARY

1. The possible means of preparing emulsions are discussed briefly in relation to the general methods of colloid chemistry, on the basis of the division into dispersion methods and condensation methods.

2. An experimental condensation method of preparing emulsions by injection of oil vapor into an aqueous liquid is described, and results obtained with the system benzene–sodium oleate solution are correlated on the basis of the particle size distribution, as determined by a sedimentation method. It is found that over the range of conditions investigated, the dispersion is independent of the vapor temperature, and of the cross-section of the jet if the pressure is not too low, but is made more homogeneous (without considerable alteration of the mean size) by increasing the pressure. Increase of the sodium oleate concentration effects a progressive shift in the range of particle sizes in a downward direction. The emulsions are reproducible and very homogeneous, practically the entire disperse phase lying between radius limits of which the higher is about twice the lower. Emulsions so formed are unstable if the initial soap concentration is low, but may be made more stable by the addition of more soap afterwards, and from the data it is concluded that the function exercised by the soap and emulsification is independent of its stabilizing action.

3. The mechanism of this process of emulsification is considered, and the experimental results are correlated by postulating the formation and growth of nuclei in the liquid phase.

In connection with the research, grateful acknowledgments are due to the following: The Department of Scientific and Industrial Research, for a Senior Research Award which enabled the work to be undertaken; Mr. D. C. Henry (Director of the Thomas Graham Colloid Research Laboratory in the University of Manchester), for laboratory facilities and for encouragement; Dr. W. Clayton, for his interest in the research and assistance in connection with publication.

REFERENCES

(1) (a) CLAYTON: The Theory of Emulsions, 2nd Edition. P. Blakiston's Son and Company, Philadelphia (1928).
(b) CLAYTON: J. Soc. Chem. Ind. (Chemistry & Industry) **51**, 129 (1932).
(2) STAMM AND KRAEMER: J. Phys. Chem. **30**, 992 (1926).
(3) WOOD AND LOOMIS: Phil. Mag. [7] **4**, 417 (1927).
RICHARDS AND LOOMIS: J. Am. Chem. Soc. **49**, 3086 (1927).
RICHARDS: Ibid. **51**, 1724 (1929).
FREEDMAN: British patent 332,533 (1930).
(3a) BENDIXEN: German patent 466,353 (1925).
(4) LEWIS: Kolloid-Z. **4**, 211 (1909); Trans. Faraday Soc. **28**, 597 (1932).
(5) ROGINSKY AND SHALNIKOFF: Kolloid-Z. **43**, 67 (1927).
(6) NORDLUND: Kolloid-Z. **26**, 121 (1920).
(7) GUTBIER: Z. anorg. Chem. **152**, 163; **155**, 199; **158**, 99 (1926).
(8) KRAEMER AND STAMM: J. Am. Chem. Soc. **46**, 2709 (1924).
(9) LAMBERT AND WIGHTMAN: J. Optical Soc. Am. **11**, 393 (1925).
(10) SUMNER: Trans. Faraday Soc. **28**, 20 (1932).

(11) Sumner: J. Sci. Instruments 7, 398 (1930).
(12) Harkins and Beeman: J. Am. Chem. Soc. 51, 1674 (1929).
(13) Plateau: Statique des Liquides, Vol. II, pp. 209, 254 (1873).
(14) Thomson, W.: Phil. Mag. [4] 42, 448 (1871).
(15) Volmer and Weber: Z. physik Chem. 119, 277 (1926).
(16) Farkas: Z. physik. Chem. 125, 236 (1927).
(17) Ostwald: Z. physik. Chem. 34, 495 (1900).
Hulett: Z. physik. Chem. 37, 385 (1901).

THE FUSION CURVES FOR THE SYSTEMS AMMONIA-PROPYL ALCOHOLS AND AMMONIA-BUTYL ALCOHOLS

H. P. CADY AND ETHEL ANN JONES[1]

Department of Chemistry, University of Kansas, Lawrence, Kansas

Received August 19, 1932

INTRODUCTION

Baume and Perrot (1) used the phase law method to investigate the system methyl alcohol–ammonia. Broderson (2) used the same method with the system ethyl alcohol–ammonia. Baume and Perrot found that the compound $CH_3OH \cdot NH_3$ was formed in the ammonia–methyl alcohol system. Broderson found the compounds formed in the ammonia–ethyl alcohol system to be $C_2H_5OH \cdot NH_3$ and $2(C_2H_5OH) \cdot NH_3$.

The object of this work was to apply the phase law method to systems of ammonia and some of the other alcohols of this series.

APPARATUS

The melting points were determined using a nickel–iron thermocouple, the potential differences being measured with a potentiometer.

The thermocouple was constructed by joining the junctions with bronze solder. The copper–nickel and the copper–iron junctions were kept surrounded by chipped ice from which the water drained away. The nickel–iron junction was placed in the melting point apparatus.

Calibration of the thermocouple

Table 1 gives the data used in plotting a curve from which melting points in degrees centigrade were read.

Melting point tube

The melting point tube used is shown in figure 1. The samples of alcohol and ammonia were introduced through A. C is a constriction in the glass tubing. The glass rod D carried a short piece of rubber tubing, B, at the lower end. The rod D has a constriction underneath the rubber tubing B, so that the tubing is held in place by means of a platinum wire wrapped around the tubing just over the constriction in the glass rod.

---

[1] From a thesis submitted by Ethel Ann Jones to the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The rod D was held in place at the upper end at E by a short piece of rubber tubing. When the rod was raised the rubber tubing at B closed the melting point tube at the constriction C.

F is a glass tube, closed at the lower end, and sealed into the larger tube. The small tube F was used to carry the thermocouple to the lower end of the melting point tube. G is a hollow cylinder of iron with coils of steel wire attached at H and H′.

These steel coils served two purposes: first, to stir the ammonia alcohol system, and second, to break the rise and fall of the iron cylinder, thus protecting the glass tube.

Method of stirring the alcohol-ammonia systems

The melting point tube carrying the iron cylinder and coils was slipped through a coil made from a large number of turns of copper wire carrying an intermittent D. C. current which alternately magnetized and demagnetized the iron cylinder, causing it to move upward and downward, resulting in the coil H stirring the system in the lower part of the melting point tube.

TABLE 1

Calibration of thermocouple

CALIBRATING SUBSTANCES	POTENTIOMETER READINGS	TEMPERATURE
	volts	*degrees C.*
Ammonia	0.001033	b.p. −33.4
Chlorobenzene	0.001412	f.p. −45.2
Chloroform	0.001955	f.p. −63.5
Ammonia	0.002362	f.p. −78
Carbon dioxide (solid)	0.002405	s.p. −78.92
Carbon disulfide	0.003252	f.p. −111.6
Ethyl ether	0.003552	f.p. −116.3

The D. C. current was made intermittent by a motor-driven interrupter making contacts at intervals of about one per second. Contact was about one-tenth of a second in duration.

In figure 2, J is a large test tube. L is a tube ending under mercury at Q with water above the mercury. The tube L takes care of any excess pressure developed in J. The tube K connects J with the melting point apparatus M through a short rubber connection at X. O is a Dewar flask containing liquid air. The Dewar flask was supported in a glass cylinder with cotton plugs holding it in place.

MATERIALS

The liquid ammonia used was dried by distilling from contact with sodium. The alcohols were of Eastman grade dried with metallic calcium.

METHOD

The melting point tube M, figure 2, was cleaned by connecting as shown in figure 2 with the valve at B pushed down. The test tube J contained liquid ammonia in contact with sodium. The melting point tube M was about one half immersed in liquid air, resulting in ammonia condensing in M. When about 20 cc. of ammonia had distilled into the tube, the connection at X was broken. The rubber tubing was left on the tube K and was closed with a screw clamp S. The melting point tube M was then removed from the liquid air and the ammonia allowed to melt. The liquid ammonia passed rapidly out of the tube A on inversion of the melting point tube. The above procedure was repeated three times. The melting point tube was then connected at A to the vacuum pump. After several minutes the

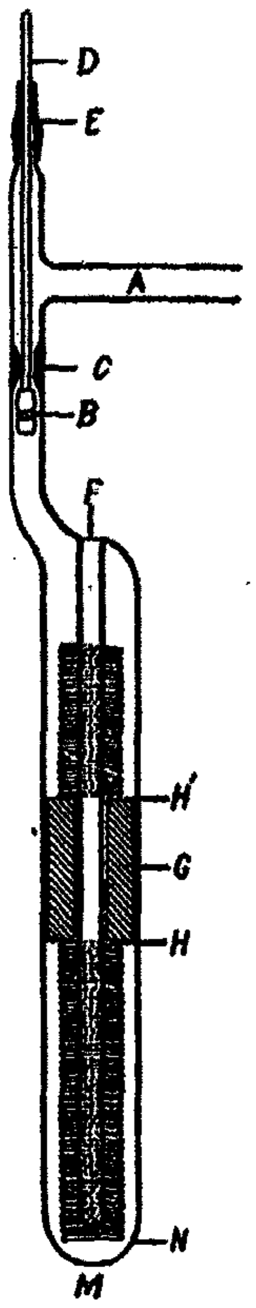


Fig. 1

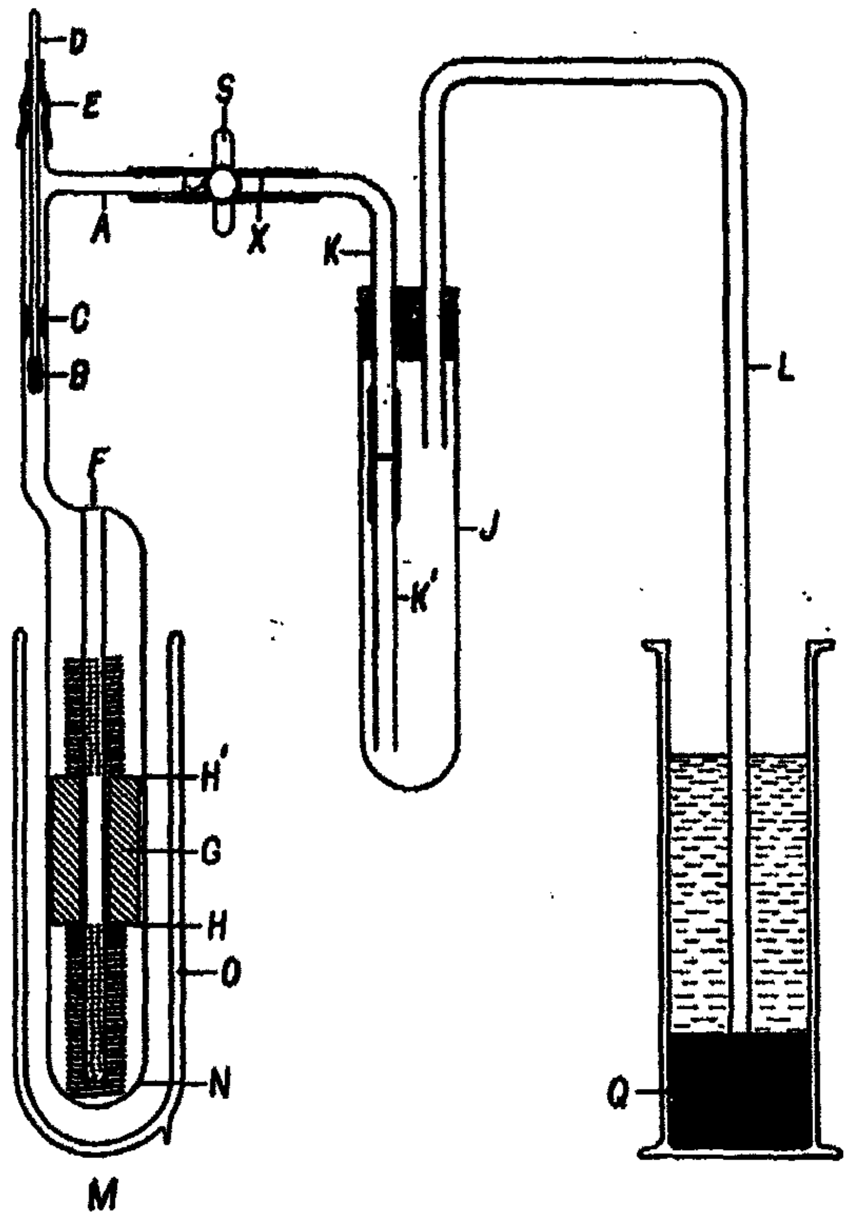


Fig. 2

Fig. 1. Melting Point Tube
Fig. 2. Apparatus for Melting Point Determinations

tube was closed at A with a rubber tube and screw clamp, disconnected from the vacuum pump, and weighed. All weighings were made in a silvered Dewar flask. The melting point tube M was then evacuated again and connected as shown in figure 2 to a clean test tube J containing the sample of alcohol to be introduced into M. On opening the screw clamp S the alcohol flowed up through K′ and K into M. The tube K′ was used only when alcohol was being transferred from J to M. A rubber tube and screw clamp was then placed on A and the melting point tube M, containing the alcohol, was weighed, and then connected again to the test tube J containing liquid ammonia in contact with sodium. After the desired quantity of ammonia had distilled into M, the valve B was closed and the melting point tube M was allowed to stand above a small quantity of liquid air in the Dewar flask, so that the ammonia melted from the upper surface downward and before the alcohol; this was done in order to prevent the melting of the alcohol first with its resulting expansion causing breaks in the melting point tube at F and N. After the ammonia and alcohol had melted, the melting point tube was placed in the magnetizing coil, the thermocouple was introduced into the small tube at F, and a melting point determination made as follows. The potentiometer was balanced against a standard cell so that a spot of light reflecting from a galvanometer mirror rested on zero of a scale. A switch was then turned bringing the thermocouple into the potentiometer circuit. The motor for breaking the D. C. current was then started, resulting in the thorough stirring of the solution as it was cooled with liquid air. As soon as the solution was partly solidified the flask of liquid air was lowered and the temperature of the mixture allowed to rise slowly. When only a few crystals remained in the thoroughly stirred solution the potentiometer was balanced, read, and the above procedure repeated. The melting point tube was then prepared for weighing again so that the weight of ammonia in the system could be calculated.

RESULTS

Measurements of molecular percentage compositions and freezing points were made with the results given in tables 2 to 7 (see figures 3 to 8).

Normal propyl alcohol did not crystallize but solidified as a clear glass. Mixtures of the alcohol and small quantities of ammonia also gave glasses. At 21.74 mole per cent of ammonia distinct crystallization occurred.

The fusion curve for the system normal propyl alcohol-ammonia indicates: (1) There is formed one compound of ammonia and normal propyl alcohol, composed of one mole of ammonia and one mole of alcohol. The melting point is about −77.1°C. (2) The compound formed is relatively slightly dissociated into ammonia and the alcohol, since the change in direction of the curve at its maximum point is sharp. (3) One eutectic is distinctly indicated at about −90°C., having a composition of 73.5 mole

TABLE 2

Data for the fusion curve of ammonia and normal propyl alcohol

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0.0	−127.1 (not definite)	66.95	−86.2
21.74	−99.0	68.73	−87.1
29.39	−91.0	70.79	−88.6
31.39	−88.8	72.42	−89.3
36.69	−83.7	75.55	−88.2
37.8	−82.8	77.29	−87.0
42.87	−79.3	78.3	−86.7
44.65	−79.0	79.32	−85.7
46.21	−78.2	83.18	−83.5
49.66	−77.1	85.12	−82.6
50.73	−77.1	89.66	−81.1
51.66	−77.3	95.54	−79.1
53.58	−78.0	96.12	−78.9
55.12	−79.6	97.17	−78.1
56.15	−80.1	99.25	−77.5
60.89	−81.4	100.00	−77.4
63.3	−84.5		
65.67	−85.1		

TABLE 3

Data for the fusion curve of ammonia and isopropyl alcohol

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0.0	−86.6	64.25	−74.0
0.31	−87.4	68.51	−75.5
13.82	Glass	72.19	−77.8
21.82	−88.1	73.57	−79.1
27.11	−85.0	76.97	−82.1
36.75	−81.1	80.55	−85.1
43.33	−76.3	82.6	−85.6
46.79	−73.9	87.07	−85.2
48.66	−72.8	88.06	−84.8
49.98	−72.0	89.16	−83.6
50.98	−71.9	91.28	−83.0
54.28	−71.9	92.78	−82.0
56.60	−71.9	97.87	−79.7
59.16	−72.2	98.51	−78.8
60.62	−72.9	100.00	−77.4
61.84	−72.9		

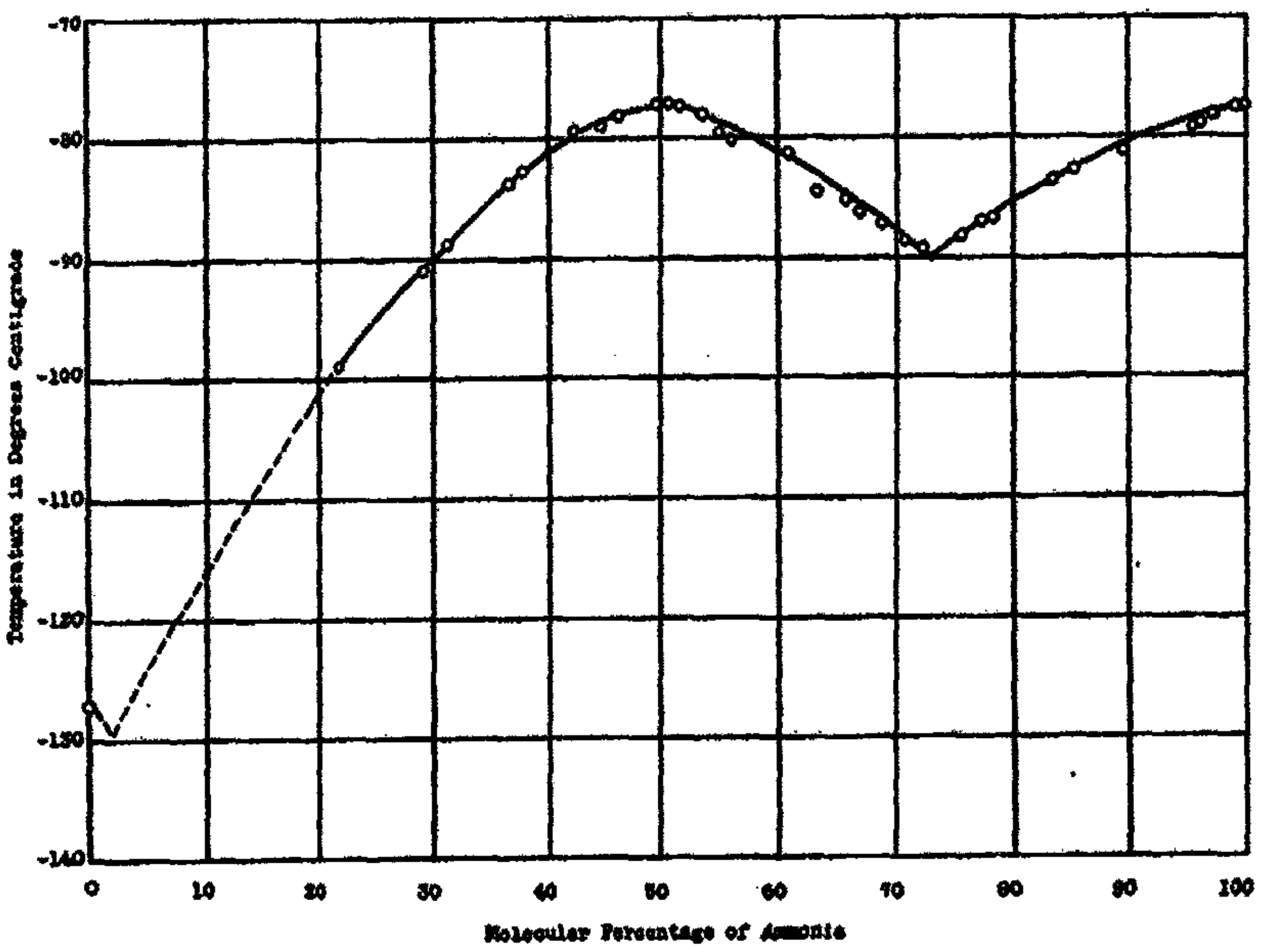


Fig. 3. Ammonia-*n*-Propyl Alcohol

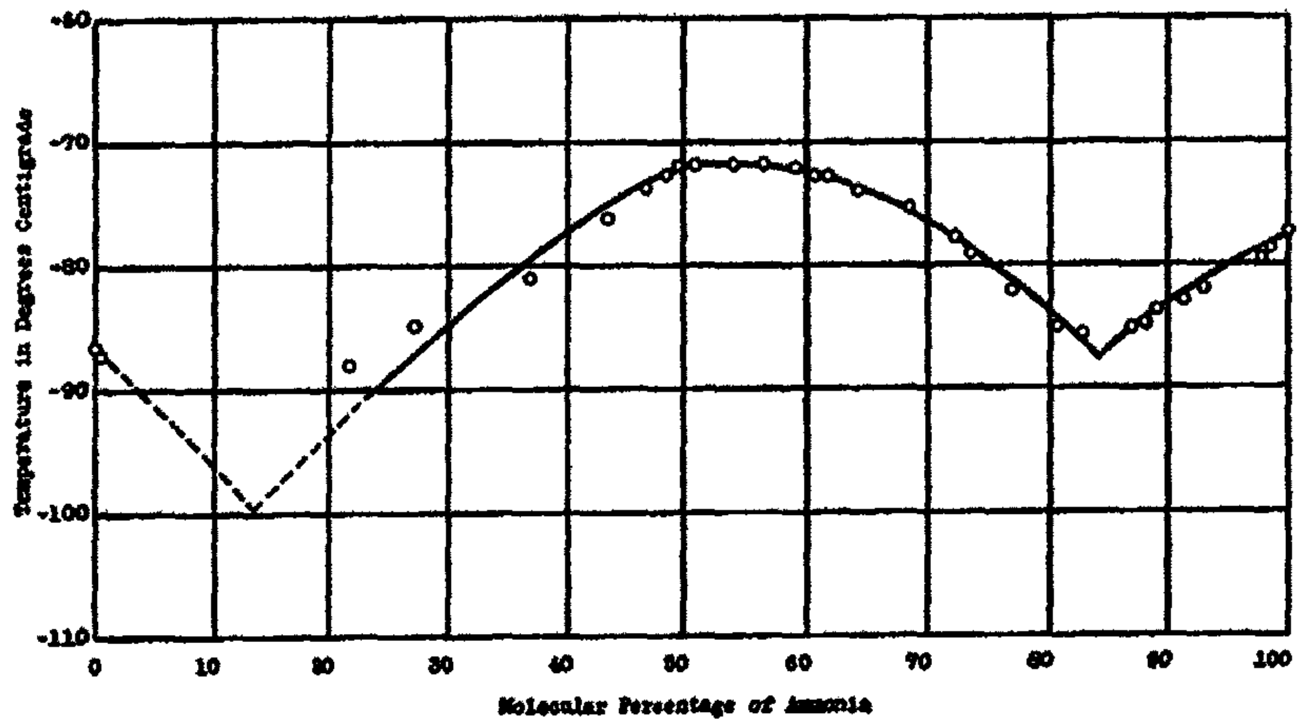


Fig. 4. Ammonia-Isopropyl Alcohol

per cent of ammonia. There is probably another one below −127°C., which could be definitely located if the system could be made to crystallize in this region.

The fusion curve for the system ammonia-isopropyl alcohol indicates:

(1) There is one compound of ammonia and isopropyl alcohol formed, composed of one mole of ammonia and one mole of the alcohol. The melting point of the compound is about −71.9°C. (2) The compound is relatively more dissociated than the one in the ammonia-normal propyl alcohol system. This is indicated by the flattened portion of the curve at its maximum. (3) There are two eutectic mixtures, one in the region having the composition between zero mole per cent of ammonia to 21.82 mole per cent and below −87°C. Owing to the formation of a glass this eutectic could not be definitely located. The other eutectic was in the region of 85 mole per cent of ammonia and at about −86°C.

TABLE 4

Data for the fusion curve for the ammonia-normal butyl alcohol system

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0.00	−90.4	67.31	−66.7
1.8	−91.9	69.32	−67.7
13.95	−80.6	71.22	−68.4
15.66	−77.4	74.08	−68.9
17.69	−74.2	77.4	−71.8
22.70	−72.8	78.05	−71.6
29.56	−69.4	80.31	−72.7
32.53	−66.6	83.12	−72.9
39.38	−61.9	83.42	−72.6
39.98	−62.3	86.95	−75.2
43.77	−61.3	89.7	−76.6
47.62	−60.1	91.76	−77.1
50.44	−60.2	93.16	−77.3
52.24	−60.6	95.5	−77.5
56.43	−62.0	96.16	−78.2
57.53	−62.1	96.7	−78.3
59.59	−63.1	97.0	−78.4
62.51	−63.6	100.0	−77.4

The fusion curve for the system ammonia-normal butyl alcohol indicates: (1) There is one compound of ammonia and normal butyl alcohol formed. It is composed of one mole of ammonia and one mole of normal butyl alcohol and melts at about −60°C. (2) The compound formed is but relatively slightly dissociated; this is indicated by the fact that the curve is relatively sharp at the maximum. (3) There are two eutectic mixtures indicated, one in the region having the composition between 1 mole per cent of ammonia and 13.95 mole per cent and below −90.4°C. The other one is in the region having a composition of about 97 mole per cent of ammonia and a temperature of −78.4°C.

The fusion curve for the system ammonia–isobutyl alcohol indicates: (1) There is one compound of ammonia and isobutyl alcohol formed. It is composed of one mole of ammonia and one mole of isobutyl alcohol, and melts at −59.1°C. (2) The compound formed is but slightly dissociated, since the curve is relatively sharp at the maximum. (3) The pure isobutyl alcohol solidifies forming a glass so that the composition and temperature for the eutectic mixture in the region of 100 mole per cent alcohol was not determined. On the other hand, in the region of 97 mole per cent of ammonia a eutectic mixture formed at −78.5°C.

TABLE 5

Data for the fusion curve for the ammonia–isobutyl alcohol system

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0.00	−108.0	64.85	−66.4
	value given in	66.32	−67.0
	critical tables	69.37	−68.4
12.52	−83.4	71.39	−68.9
17.17	−78.1	71.42	−69.4
27.92	−71.2	73.63	−71.2
30.88	−68.1	76.5	−72.3
37.16	−65.0	78.61	−73.2
39.57	−62.6	80.42	−74.6
43.25	−59.6	81.25	−74.9
43.63	−60.0	82.84	−76.0
46.07	−59.6	84.2	−76.0
48.16	−59.3	86.92	−77.5
50.13	−59.1	90.96	−77.3
51.12	−60.2	92.2	−77.9
51.89	−59.5	93.77	−78.6
54.91	−61.6	95.21	−78.2
55.05	−60.3	95.85	−78.1
57.44	−62.9	96.28	−78.5
61.62	−64.3	97.29	−78.5
64.06	−65.4	100.00	−77.4

The fusion curve for the system ammonia–*secondary* butyl alcohol indicates: (1) There is one compound of ammonia and *secondary* butyl alcohol formed, composed of one mole of ammonia and one mole of the alcohol. Its melting point is −60°C. (2) The compound formed is but relatively slightly dissociated, since the curve is relatively sharp at its maximum. (3) There are two eutectic mixtures possible but, since the alcohol solidified to a glass at −114.7°C. and did not give crystals until about 13 moles per cent of ammonia were added, the exact composition of this eutectic was not determined. The other eutectic is in the region of about 97 mole per cent of ammonia and about −79°C.

The fusion curve for the system ammonia-*tertiary* butyl alcohol indicates: (1) There is one compound of ammonia and *tertiary* butyl alcohol formed, composed of one mole of alcohol and one mole of ammonia, and melting at −43.9°C. (2) The compound formed is relatively more dissociated than the compound formed between ammonia and the other butyl alcohols.

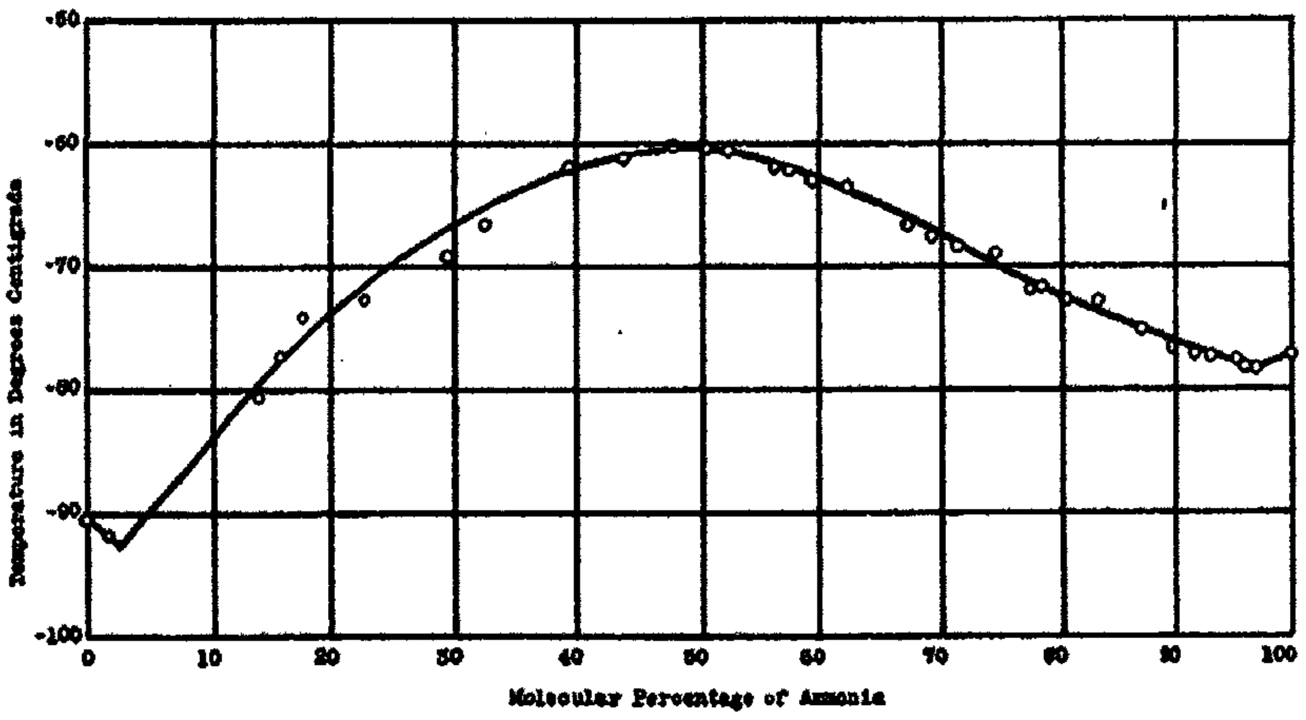


FIG. 5. AMMONIA-*n*-BUTYL ALCOHOL

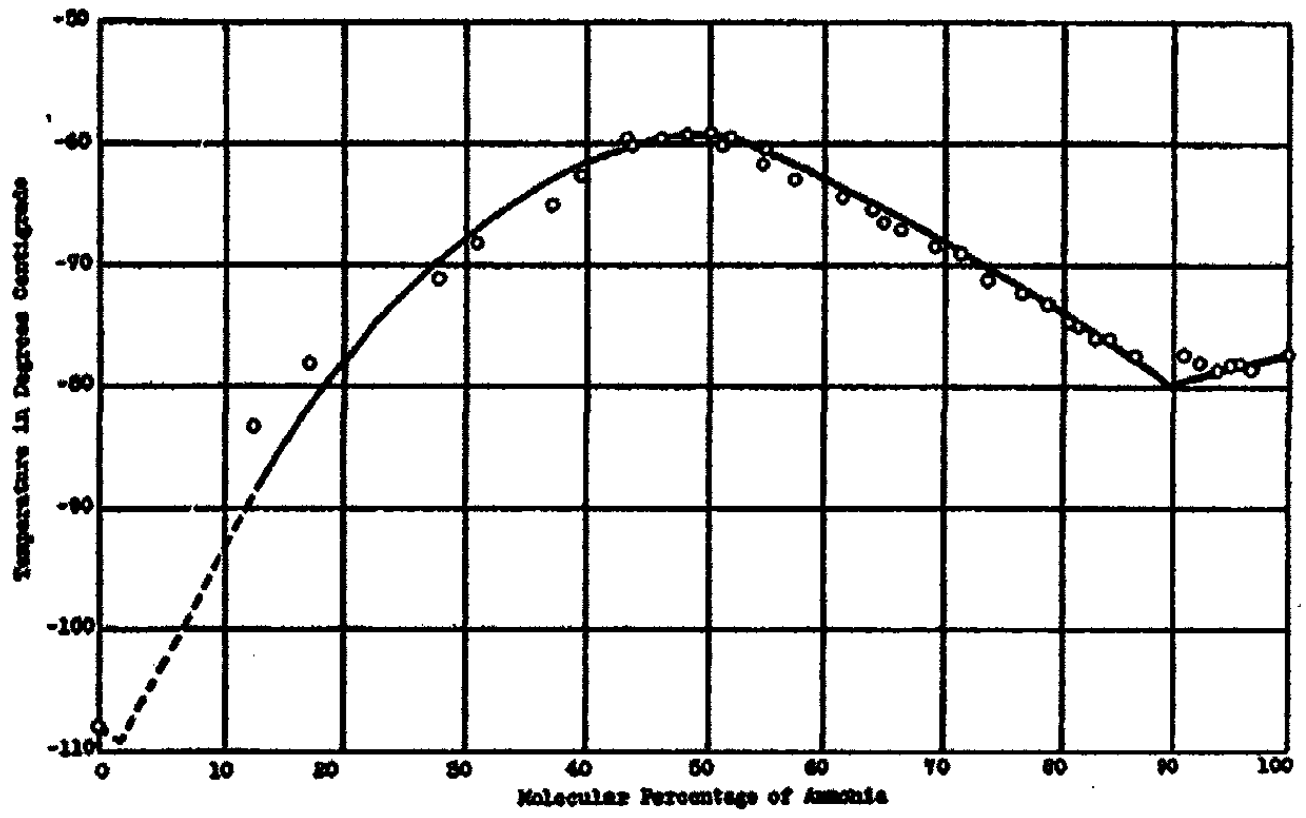


FIG. 6. AMMONIA-ISOBUTYL ALCOHOL

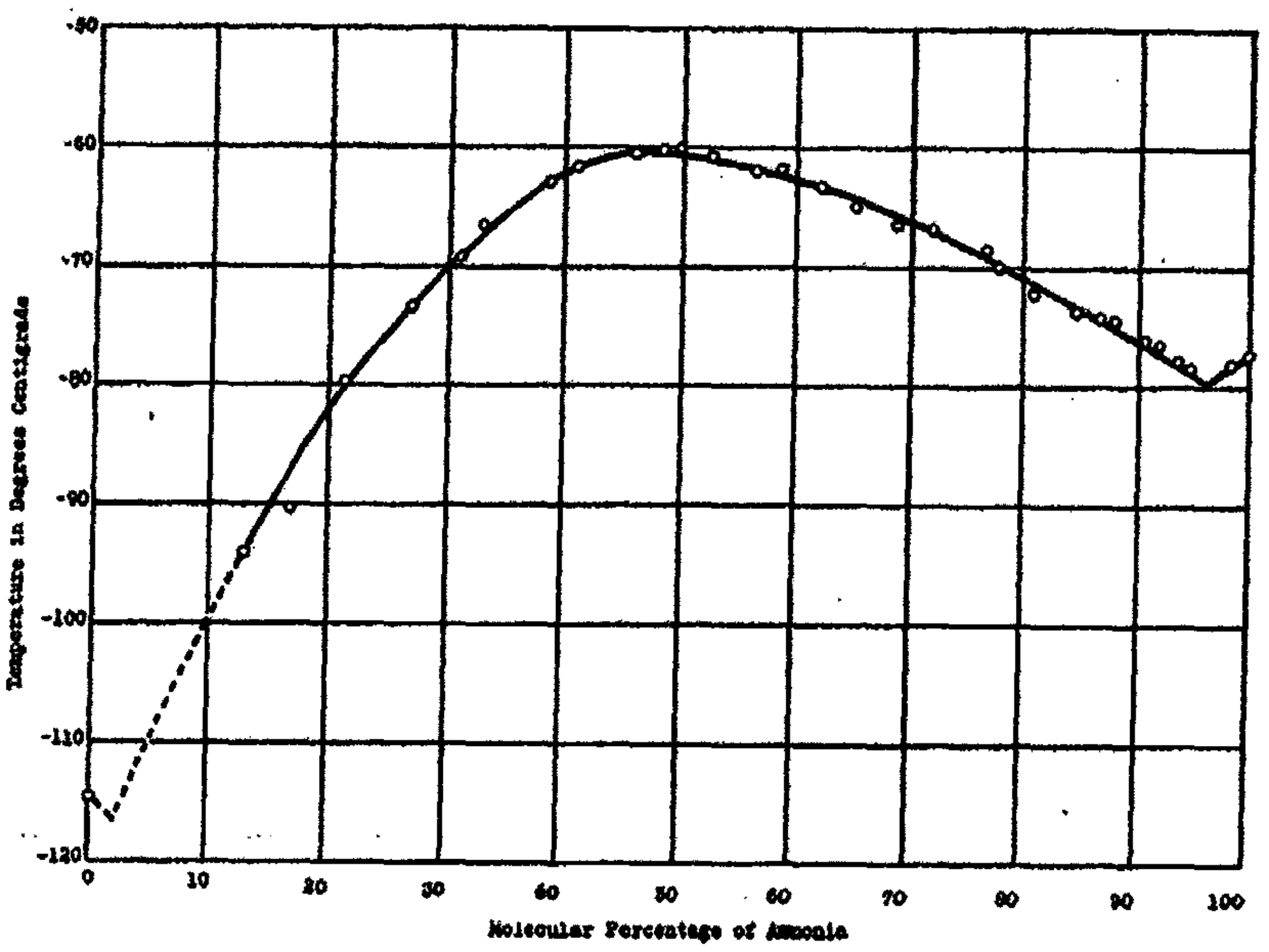


FIG. 7. AMMONIA-*secondary* BUTYL ALCOHOL

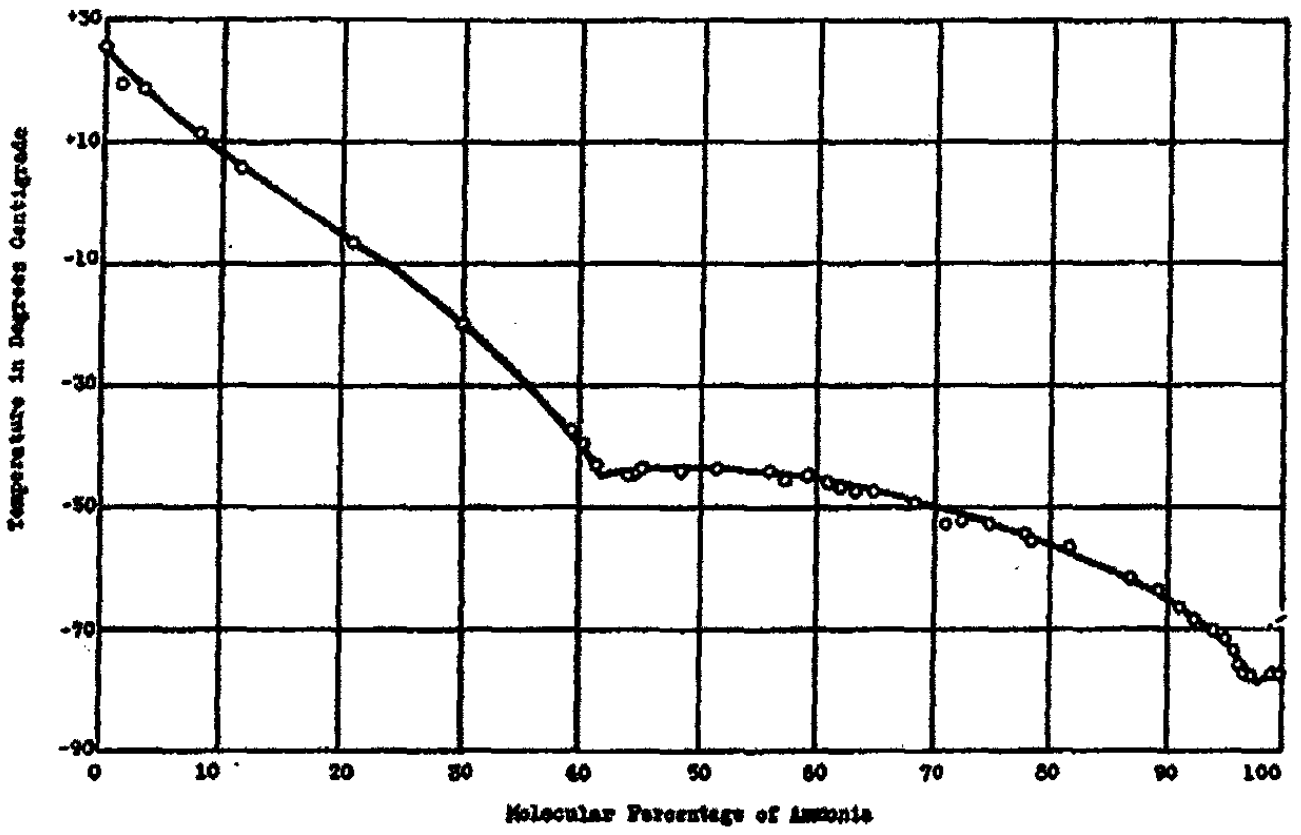


FIG. 8. AMMONIA-*tertiary* BUTYL ALCOHOL

TABLE 6

Data for the fusion curve for the ammonia-secondary butyl alcohol system

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0.0	−114.7	62.17	−63.3
13.0	−94.2	68.86	−66.4
16.78	−90.4	71.83	−66.9
21.36	−79.9	76.63	−68.6
26.91	−73.4	77.86	−70.0
30.95	−69.4	80.93	−72.1
32.9	−66.6	84.91	−73.6
38.94	−62.8	86.63	−74.2
41.06	−61.7	88.23	−74.4
45.72	−60.5	90.61	−76.1
48.19	−60.2	91.87	−76.5
49.83	−60.1	93.69	−77.9
52.63	−60.7	94.73	−78.5
56.43	−62.0	98.67	−78.1
58.62	−61.9	100.00	−77.4

TABLE 7

Data for the fusion curve for the ammonia-tertiary butyl alcohol system

MOLE PER CENT OF AMMONIA	MELTING POINT	MOLE PER CENT OF AMMONIA	MELTING POINT
	degrees C.		*degrees C.*
0.0	25.7	63.22	−47.4
1.3	19.6	64.93	−47.3
3.33	18.8	68.45	−49.5
8.01	11.1	70.93	−53.0
11.53	5.9	72.39	−52.3
20.81	−6.7	74.85	−52.7
29.98	−20.1	77.88	−54.5
39.45	−37.6	78.53	−55.9
40.19	−39.6	81.77	−56.5
41.31	−43.0	87.04	−61.7
43.98	−44.8	89.31	−63.7
44.4	−44.7	91.08	−66.7
44.99	−43.3	92.34	−68.5
48.45	−44.3	94.09	−69.9
51.47	−43.9	95.15	−71.8
55.93	−44.2	96.02	−73.6
56.13	−44.1	96.45	−76.0
57.37	−45.5	96.84	−77.1
59.3	−44.8	97.49	−77.5
60.92	−46.1	99.12	−77.1
62.04	−46.9	100.00	−77.4

TABLE 8

OBSERVER	AMMONIA MELTING POINT	ALCOHOLS				COMPOUNDS			EUTECTICS			
		Composition	Melting point	Melting point in Critical Tables	Type of solid	Composition	Melting point	Qualitative indication of dissociation	Composition	Melting point	Composition	Melting point
	degrees C.		*degrees C.*	*degrees C.*			*degrees C.*			*degrees C.*		*degrees C.*
Jones	−77.4	Normal propyl alcohol $CH_3 \cdot CH_2 \cdot CH_2OH$	−127.1	−127	Glass (1)	$CH_3 \cdot CH_2 \cdot CH_2OH \cdot NH_3$	−77.1	Relatively slight	Less than 21.74 mole per cent ammonia	Less than −127	73.5 mole per cent ammonia	90
Jones	−77.4	Isopropyl alcohol $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$	−86.6	−85.8	Crystals	$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH \cdot NH_3$	−71.9	More than in the preceding case	Less than 21.82 mole per cent ammonia	Below −87	85.0 mole per cent ammonia	−86
Jones	−77.4	Normal butyl alcohol $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$	−90.4	−89.8	Crystals	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH \cdot NH_3$	−60	Relatively slight	Less than 13.95 mole per cent ammonia	Below −90.4	97 mole per cent ammonia	−78.4
Jones	−77.4	Isobutyl alcohol $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH \cdot CH_2OH$	−108	−108	Glass (1)	$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH \cdot CH_2OH \cdot NH_3$	−59.1	Relatively slight	Less than 12.52 mole per cent ammonia	Below −108	97 mole per cent ammonia	−78.5
Jones	−77.4	*secondary* Butyl alcohol $CH_3 \cdot CH_2 \cdot CHOH \cdot CH_3$	−114.7	Not given	Glass	$CH_3 \cdot CH_2 \cdot CHOH \cdot CH_3 \cdot NH_3$	−60	Relatively slight	Less than 13 mole per cent ammonia	Below −114.7	97 mole per cent ammonia	−79
Jones	−77.4	*tertiary* Butyl alcohol $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH$	25.7	25.5	Crystals	$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH \cdot NH_3$	−43.9	Relatively high	42.5 mole per cent ammonia	−43	97 mole per cent ammonia	−77.5
Baume and Perrot (2)		Methyl alcohol CH_3OH		−97.8		$CH_3OH \cdot NH_3$	+55	Relatively slight				
Broderson (3)	−76.5	Ethyl alcohol C_2H_5OH	−112	−117.3		$C_2H_5OH \cdot NH_3$ $(C_2H_5OH)_2NH_3$ Transition point −89.5°C.	−74.2	Relatively slight				
Briner and Agathon (4)		Phenol C_6H_5OH		41		$C_6H_5OH \cdot NH_3$	Near 0	Relatively high	36 mole per cent ammonia	0	65 mole per cent ammonia	−20

(1) Gazz. chim. ital. **33**, 331–43 (1903).
(2) Baume and Perrot: Compt. rend. **151**, 528 (1910).
(3) Broderson: The Fusion Curve of Ammonia and Ethyl Alcohol. Master's thesis, University of Kansas, 1911.
(4) Briner and Agathon: Helv. Chim. Acta **9**, 905 (1926).

(3) Two eutectic mixtures are indicated; one having a composition of about 42.5 mole per cent of ammonia and melting at about −43°C., the other at about 97 mole per cent of ammonia and melting at −77.5°C.

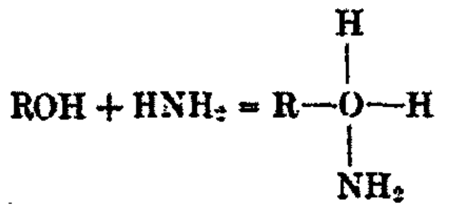
These data are summarized in tables 8 and 9.

DISCUSSION

There are two possibilities to be considered in attempting to explain the mechanism of addition reactions between oxygen compounds and nitrogen compounds. In the systems of anhydrous ammonia and alcohols described by the fusion curves previously given, the question is whether the compounds are formed by ammonia adding to the oxygen of the alcohol as represented by this general reaction:

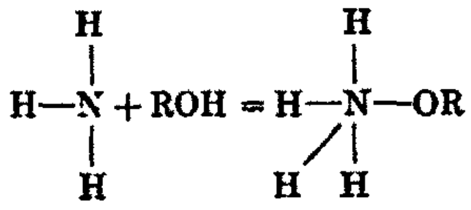
TABLE 9

ALCOHOL		MELTING POINT OF ALCOHOL	MELTING POINT OF COMPOUND	*T*(50 MOLE PER CENT AMMONIA)−*T*(55 MOLE PER CENT AMMONIA)	QUALITATIVE INDICATION OF DISSOCIATION OF COMPOUND
		degrees C.	*degrees C.*		
Primary	Propyl	−127	−77.1	1.4	Relatively slight
	Butyl	−89.8	−60	1.3	Relatively slight
	Isobutyl	−108	−59.1	1.9	Relatively slight
Secondary	Isobutyl	−85.8	−71.9	0.1	Relatively more than in preceding case
	secondary Butyl	−114.7	−60	0.8	Relatively more than in preceding case
Tertiary	*tertiary* Butyl	25.5	−43.9	Less than 0.1	Relatively high



$$\mathrm{ROH + HNH_2 = R{-}\overset{H}{\underset{NH_2}{O}}{-}H}$$

or whether the alcohol adds to the nitrogen of the ammonia in this manner:



$$\mathrm{H{-}\overset{H}{\underset{H}{N}} + ROH = H{-}\overset{H}{\underset{H\ H}{N}}{-}OR}$$

It has been thought by several workers (3) in the field that compounds are formed between a number of types of oxygen compounds such as alcohols, ethers, aldehydes, ketones, and acids combining with both organic and inorganic acids.

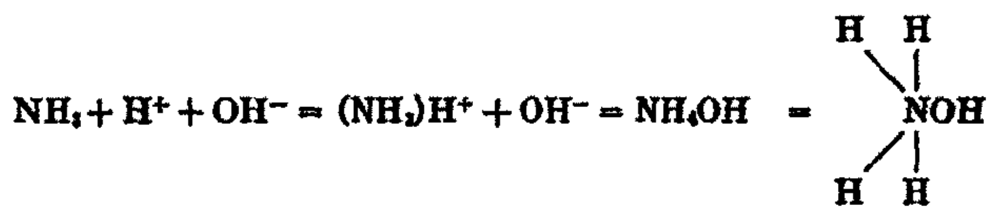
The oxonium theory attempts to explain the mechanism of compound formation in these cases by considering that combination may be due to the basic properties of oxygen. The ending "onium" indicates basic properties. Many oxygen reactions can be explained if the valence of oxygen is considered greater than two.

Elements near oxygen in the periodic system show basic properties, for example, iodine in phenyl iodide is able to add another mole of phenyl iodide forming diphenyl iodonium iodide, which on being treated with silver hydroxide gives diphenyl iodonium hydroxide, a strong base. Sulfur gives a basic substance in the compound $(CH_3)_3SOH$. These facts help support the oxonium theory by indicating that the elements near oxygen in the periodic table show basic properties.

In the systems studied, consisting of alcohols and anhydrous ammonia, we have in the alcohols oxygen which may function as oxonium oxygen and in the ammonia nitrogen which may react as ammonium nitrogen.

Ammonia (4) in some cases behaves as a saturated substance, since it does not combine with more hydrogen to form NH_4 or NH_5. In some cases it shows unsaturated properties, in that it combines directly with water to form ammonium hydroxide.

Rupert (5) shows that ammonia forms with water two compounds both freezing at −79°C. One compound is formed by the addition of one mole of ammonia and one mole of water. The properties of a solution of ammonia in water indicate that these properties would be represented by a substance having the formula NH_4OH. This compound could be considered to be formed in this manner:

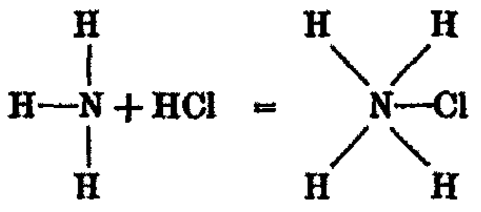


$$NH_3 + H^+ + OH^- = (NH_3)H^+ + OH^- = NH_4OH = \overset{H\ \ H}{\underset{H\ \ H}{NOH}}$$

Rupert's second compound has the composition, $2NH_3 \cdot H_2O$ or $(NH_4)_2O$ and could be called ammonium oxide. Addition in this compound can be represented as follows:

$$NH_3 + HOH + NH_3 = NH_4ONH_4$$

Ammonia (4) also combines with hydrochloric or other acids to form salts.



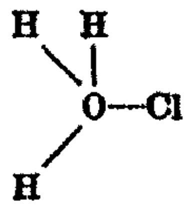
$$\overset{H}{\underset{H}{H—N}} + HCl = \overset{H\ \ H}{\underset{H\ \ H}{N—Cl}}$$

In this type of reaction ammonia is able to add only pairs of unlike atoms or groups which show a contrast to each other. It is not able to add a pair of chlorine atoms or a pair of hydrogen atoms. One of the characteristics of this type of valence change is that one of the atoms or groups added is always capable of splitting off as a negative ion, leaving the other atom or group as a part of the positive ion. Another characteristic property is the fact that the addition reaction can be easily reversed. In the case of ammonium hydroxide the reversal to ammonia and water takes place so readily that it is impossible to isolate the ammonium hydroxide above −79°C.

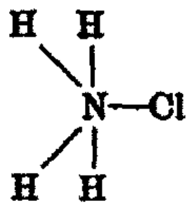
In the case of ammonium chloride the union is much more stable and dissociation into ammonia and hydrogen chloride takes place appreciably only at higher temperatures.

This type of valence change shown by nitrogen in ammonia compounds is not generally shown by other elements, but is definitely shown by several members of the nitrogen family, also by oxygen, sulfur, and iodine.

Water forms with hydrogen chloride three (6) unstable hydrates. The monohydrate may be indicated as



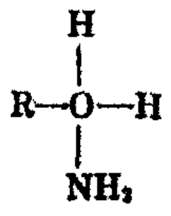
This is analogous to the formula for ammonium chloride



The hydrate of hydrogen chloride is much more easily decomposed than is ammonium chloride. It may be that the only difference between the unsaturation shown by ammonia and the unsaturation shown by water is in the degree of stability of the products. That is, the salts formed by the action of acids and ammonia are stable and form an important class of compounds. But the products formed by the addition of acids to water and similar oxygen compounds are so unstable that they have been neglected.

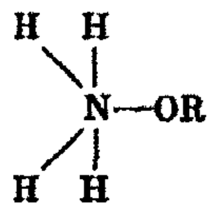
Combinations formed then by additions to ammonia are called ammonium compounds; the corresponding oxygen compounds which are much less stable are known as oxonium compounds. Other substances which show similar properties are known as phosphonium, arsonium, stibonium, sulfonium, and iodonium compounds. As a group they are referred to as "oxonium" compounds. All have the general characteristics shown by the ammonium compounds in that: (1) they are formed by the addition of a positive and a negative group to some compound; (2) one of the groups added breaks off as a negative ion; (3) the addition products are unstable and may dissociate again into two definite compounds.

In order to prove the type of addition of alcohols with anhydrous ammonia some of the properties of the compounds would have to be determined in order to decide whether the compounds are of the general type

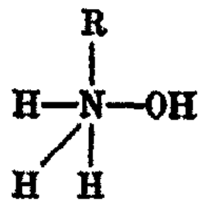


$R{-}\overset{\displaystyle H}{\underset{\displaystyle NH_3}{O}}{-}H$

or



or possibly,



The primary alcohols resemble each other in properties more than they resemble either the secondary or tertiary alcohols, that is, each member of a class resembles other members of the same class. Therefore, it is not surprising to find some differences in the relative dissociation of the alcohol ammonia compounds formed with the three classes of alcohols. As shown in table 9, the relative dissociation of the compounds formed between anhydrous ammonia and the primary, secondary, and tertiary alcohols used in these studies is in the following order: primary alcohols–ammonia, relatively slight dissociation; secondary alcohols–ammonia, slightly more dissociated; tertiary alcohols–ammonia, dissociation relatively high.

SUMMARY

1. The fusion curves for systems of ammonia–propyl alcohols and ammonia–butyl alcohols, together with similar curves previously obtained for the systems ammonia–methyl alcohol and ammonia–phenol, indicate very definitely the formation of a compound in each case consisting of one mole of the alcohol and one mole of ammonia, each compound having a congruent melting point.

2. The curve for the ammonia–ethyl alcohol system indicates definitely a compound $C_2H_5OH \cdot NH_3$ with a congruent melting point and seems to indicate another $(C_2H_5OH)_2 \cdot NH_3$(2), but this was not definitely determined.

3. The fusion curves for the systems ammonia–*tertiary* butyl alcohol and ammonia–phenol are not as smooth as the others. At some places it cannot be definitely stated whether other compounds are indicated.

4. The dissociation of the ammonia-alcohol compounds formed is in the order: primary alcohol-ammonia, relatively undissociated; secondary alcohol-ammonia, slightly more dissociated; tertiary alcohol-ammonia, relatively highly dissociated.

5. A value for the melting point of *secondary* butyl alcohol was not found in the literature. The melting point as determined by the method used in this work is −114.7°C.

6. The ammonia-alcohol compounds may be oxonium or ammonium complexes.

REFERENCES

(1) BAUME AND PERROT: Compt. rend. **151**, 528 (1910).
(2) BRODERSON: The Fusion Curve of Ammonia and Ethyl Alcohol. Master's thesis, University of Kansas, 1911.
(3) COLLIE AND TICKLE: J. Chem. Soc. **75**, 710 (1899).
KENDALL: J. Am. Chem. Soc. **36**, 1222, 1722–34 (1914); **37**, 149 (1915).
MAASS AND MCINTOSH: J. Am. Chem. Soc. **34**, 1273–90 (1912); **35**, 535 (1913).
(4) WILLIAMS, R. J.: Introduction to Organic Chemistry. D. Van Nostrand Co., New York (1928).
(5) RUPERT: J. Am. Chem. Soc. **31**, 866 (1909).
(6) RUPERT: J. Am. Chem. Soc. **31**, 851 (1909).

STUDIES ON SILICIC ACID GELS. III

THE EFFECT OF THE ADDITION OF SOME SOLUTES ON THE TIME OF SET

CHARLES B. HURD AND DANIEL H. CARVER

Department of Chemistry, Union College, Schenectady, New York

Received July 22, 1932

INTRODUCTION

The setting of a gel of hydrated silica, or a silicic acid gel as it is commonly called, is affected, among other things, by the concentrations of the solutions, the type of silicate, the temperature, the pH of the mixture, and the presence of additional soluble materials. Several investigations are being conducted in this laboratory upon the effects of some of these factors upon the time of set. In connection with a study of the effect of the pH of the mixture, the idea suggested itself that measurements be made upon the pH of mixtures containing certain additional solutes such as ammonia, the amines, pyridine, and certain others.

In this paper are presented some of our typical results. The effect of the change in the pH of the mixture and the specific effects of certain substances are shown. An attempt has been made to explain certain of these results.

The gel mixtures were prepared by mixing solutions of sodium silicate with dilute acetic acid. Such a process produces in the mixture sodium acetate together with excess acetic acid. A possible, though not practicable, way of avoiding the presence of these soluble materials has already been pointed out by Hurd and Letteron (1), that is, to start with a pure suspension of colloidal silicic acid in water. The results of Werner (2) and Kröger (3) show that the removal of the last traces of electrolytes is impossible. It is also obviously impossible to determine the time of set correctly.

The results of various studies reported in the literature on the effects of added materials on the time of set of the gel are difficult to interpret, because in general the specific effect of the solute has not been distinguished from the indirect effect due to a change in the pH of the mixture. We may mention here only a few of the results reported.

The addition of strong bases has been found to prevent the formation of a gel, in fact, solutions of sodium hydroxide will peptize an already formed silicic acid gel. The effect of weak bases is less pronounced than that of strong bases. The effect of ammonia was studied by Bhatnagar and Mathur (4). Various compounds, including ammonia and pyridine, were studied by Prasad and Hattiangadi (5). The latter determined the pH of their mixtures. These compounds were found to accelerate setting.

The effect of excess acid has been considered by many workers. We may mention Holmes (6), Prasad and Hattiangadi (7), Maschke (8), and Pappada (9). Excess acid has been found to increase the time of set, although Holmes, and later Hurd and Letteron, have shown that at high acid concentrations the time of set decreases rapidly, until at very high acid concentrations sodium silicate solutions cannot be mixed with the acid to give a clear solution.

The effect of salts on the time of set has been considered by a number of workers, including Prasad and Hattiangadi, Pappada, and Werner.

The effects of various unionized solutes have been studied, among them the alcohols, studied by Prasad and Hattiangadi, and certain gums and sugars, investigated by Wulf and Praetorius (10).

The general impression received from a survey of the literature is that the addition of bases to an acid gel mixture hastens the setting and that excess acids retard the setting. The effects of other solutes have not in general been divided into their effect on the pH of the mixtures and their specific effects.

EXPERIMENTAL

The determination of the pH in colloidal solutions has been the subject of much study and of voluminous discussion. The system under investigation here involves a colloidal material, namely colloidal silicic acid. In similar systems Prasad and Hattiangadi (7) have measured the pH by means of an indicator method. They note in their discussion, however, that the turbidity of the gel mixture caused difficulty in determining the color of the indicator, and also that the alcoholic solution affected the setting of the gel.

A study of the various methods has led us to the belief that the quinhydrone method would prove the most applicable, especially since no alkaline gels were to be studied. A study of gels formed from alkaline mixtures has led us to believe that such gels differ considerably from the gels produced from acid mixtures. We have, accordingly, limited our study to acid gels.

A series of determinations of the pH of gel-forming mixtures from the time of mixing until after the time of set, using the quinhydrone method,[1] has shown that only a negligible change, if any, in the pH of typical acid

---

[1] These experiments were performed by Mr. D. P. Roehm at Union College in 1931–1932.

mixtures of various sodium silicate solutions with excess acetic acid occurs from the time of mixing until after the gel has set. As a further check on the quinhydrone method, comparisons were made of the pH values obtained on portions of the same mixture by the quinhydrone method and by the use of a special glass electrode-vacuum tube potentiometer circuit, using a McInnes and Dole electrode.[2] The agreement was within the limits of experimental error. No doubt there is a possibility that the quinhydrone may have a specific effect on the time of set. The time of set and the pH were accordingly determined on portions of the same mixture, no quinhydrone having been added to the portion upon which the time of set was determined.

The time of set was determined as follows. The correct amounts of solutions were drawn from bottles which had been standing for at least several hours in a water thermostat. They were mixed in a 100-cc. Pyrex Griffin beaker which was standing in the thermostat. The time of set was determined by the tilted rod method described by Hurd and Letteron (1). The method consists of inserting a small stirring rod into the gel at an angle of about 20° to the vertical until the gel is stiff enough to hold the rod in its tilted position. The glass rod is about 3 mm. in diameter and about 8 cm. long, drawn out to a stubby point and fire-polished.

The effects of ammonium hydroxide, of methyl-, dimethyl-, and trimethylamines, of pyridine, and of aniline were studied. The sodium silicate was "E" brand, Philadelphia Quartz Company silicate.[3] It was diluted with distilled water. The concentration was determined by titration with standard sulfuric acid using methyl orange, giving the sodium hydroxide equivalent. From this and the soda–silica ratio supplied by the maker, the concentration in equivalents of sodium hydroxide and gram-moles of silica per liter were calculated. The acetic acid was prepared from J. T. Baker C.P. acetic acid by dilution with distilled water. Its strength was determined by titration with standard sodium hydroxide, using phenolphthalein as an indicator.

The ammonium hydroxide was prepared by diluting Grasselli C.P. ammonium hydroxide (sp. gr. 90). The methylamine was prepared and purified in our laboratory. The other amines were purchased from the Eastman Kodak Company, the dimethylamine in the form of the hydrochloride. This amine was set free by distillation from a solution of the hydrochloride with excess sodium hydroxide. The strengths of the

---

[2] By the courtesy of Mr. B. W. Nordlander of the Research Laboratory of the General Electric Company. The special apparatus employed in this determination is described in an internal report of the Research Laboratory.

[3] The writers wish to thank the Philadelphia Quartz Company for their courtesy in supplying not only the silicate used in this research but also information concerning analysis, composition of the silicate, and other valuable data.

diluted ammonium hydroxide and the amine solutions were determined by titration with standard sulfuric acid, using methyl orange as an indicator. The aniline and pyridine were freshly redistilled and made up accurately by weight.

TABLE 1

The effect of weak bases on the time of set and the pH of mixtures of sodium silicate and acetic acid at 25°C.

Concentrations constant throughout are as follows: NaOH, 0.395; SiO_2, 0.664; CH_3COOH, 0.454.

CONCENTRATION OF BASE	TIME OF SET	pH	CONCENTRATION OF BASE	TIME OF SET	pH
Effect of ammonium hydroxide, NH_4OH			Effect of methylamine, $CH_3NH_2 \cdot HOH$		
gram-moles per liter	*minutes*		*gram-moles per liter*	*minutes*	
0	22.60	5.52	0	22.75	5.52
0.00422	20.50		0.00422	20.25	
0.0105	18.00		0.0105	17.75	
0.0169	15.75		0.0169	15.00	
0.0211	14.00	5.63	0.0211	13.50	5.67
0.0316	10.25		0.0316	9.75	
0.0422	7.25	5.97	0.0422	6.50	5.97
Effect of dimethylamine, $(CH_3)_2NH \cdot HOH$			Effect of trimethylamine, $(CH_3)_3N \cdot HOH$		
0	22.50	5.52	0	22.75	5.52
0.00422	19.80		0.00422	19.30	
0.0105	17.00		0.0105	16.00	
0.0169	14.50		0.0170	12.75	
0.0211	12.50	5.67	0.0211	11.00	5.67
0.0316	9.00		0.0316	7.50	
0.0422	5.60	6.00	0.0422	4.50	5.99
Effect of pyridine, C_5H_5N			Effect of aniline, $C_6H_5NH_2$		
0	22.75	5.52	0	23.00	
0.00422	20.75		0.00422	22.75	
0.0105	18.75		0.0105	22.50	
0.0170	16.75		0.0170	22.00	
0.0211	15.75	5.63	0.0211	21.50	
0.0316	12.50		0.0316	21.00	
0.0422	10.50	5.87	0.0422	20.50	

The results obtained on the time of set of the mixtures of sodium silicate and acetic acid with varying amounts of ammonium hydroxide or the various amines are given in table 1. The values for the pH of the mixtures as determined by the quinhydrone method are also tabulated.

The results shown in table 1 are plotted in figure 1. The effect of the six weak bases is shown graphically, the decrease in the time of set being greatest for trimethylamine and least for aniline. From the four curves for the trimethylamine, dimethylamine, methylamine, and ammonia, together with the pH data, there is a small, though easily evident, specific effect here. The effect of the trimethylamine is evidently the greatest.

We have not found aqueous solutions of pyridine to show an effect as noticeable as that reported by Prasad and Hattiangadi. We were unable to make pH determinations by means of the quinhydrone electrode in the case of the addition of aniline, because the aniline and the quinhydrone apparently react chemically.

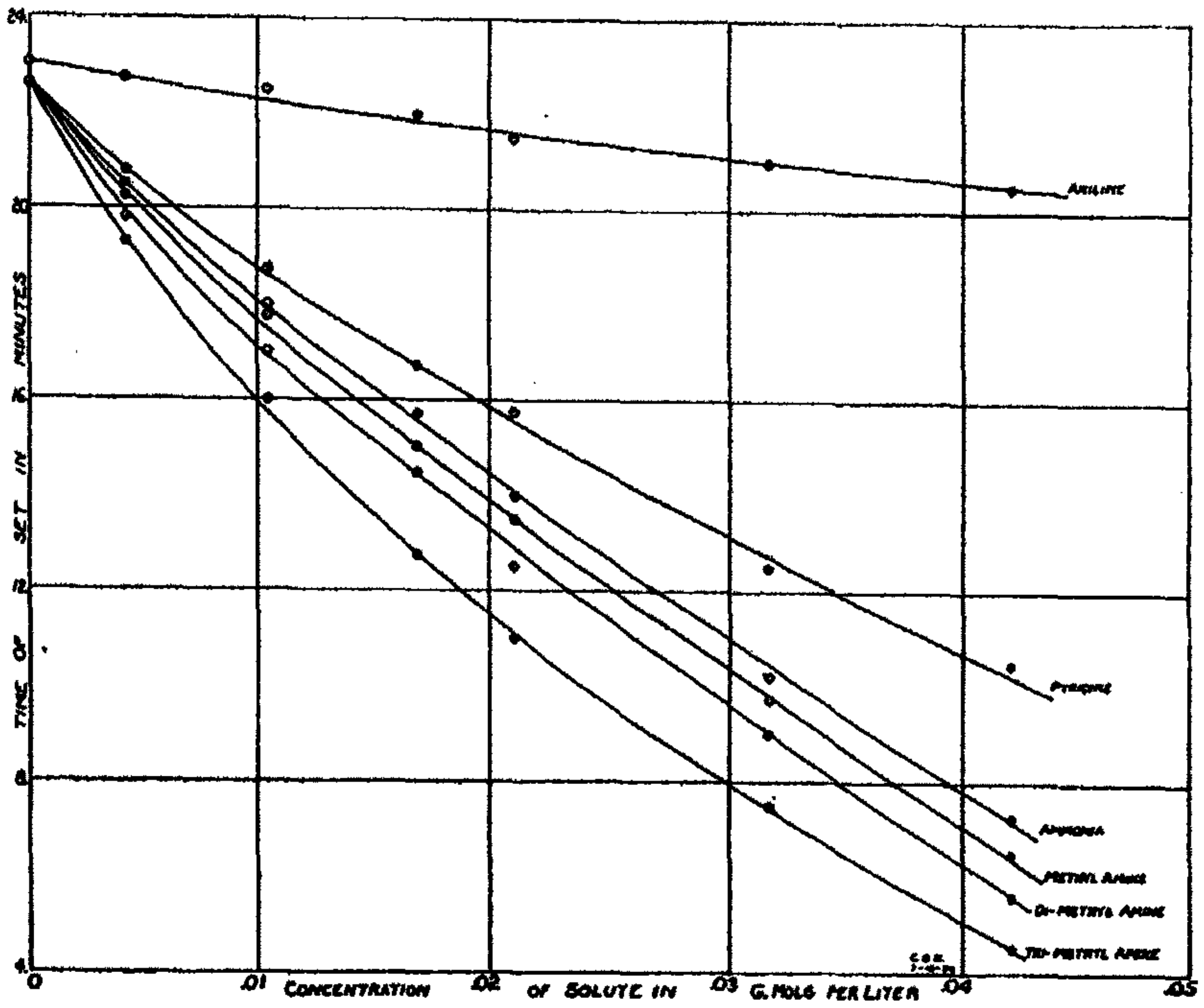


FIG. 1. EFFECT OF VARIOUS WEAK BASES UPON THE TIME OF SET

We have also attempted to analyze the effect of a typical ester, ethyl acetate, which was found to retard the setting of a silicic acid gel. Four series of determinations of the time of set were made, all at 22°C., and all using the same amounts of sodium silicate and acetic acid. The first series, table 2 (1), contained increasing amounts of ethyl acetate; the second contained extra amounts of acetic acid equivalent in concentration to the ethyl acetate of table 2 (1); the third series contained amounts of alcohol equivalent to the ethyl acetate of table 2 (1); and the fourth contained amounts of alcohol and extra acetic acid each equivalent to the ethyl acetate of table 2 (1), in other words, the products of the complete hydrolsis of the ethyl acetate of table 2 (1).

The results in table 2 show the effect of the addition of ethyl acetate and the products of its hydrolysis separately and together. The effect of the ethyl alcohol is obviously practically negligible at these concentrations. The extra acetic acid has the effect of greatly increasing the time whether alone or in the presence of its equivalent of alcohol. The ethyl acetate, therefore, apparently supplies extra acid, being hydrolyzed in the acid environment, the extra acid increasing the time of set.

TABLE 2

The effect of ethyl acetate and the products of the hydrolysis of ethyl acetate at 22°C.

Concentrations constant throughout are as follows: NaOH, 0.395; SiO_2, 0.664; CH_3COOH, 0.454.

CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET	CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET
(1) Effect of ethyl acetate		(2) Effect of extra acetic acid	
gram-moles per liter	*minutes*	*gram-moles per liter*	*minutes*
0	28.50	0	29.50
0.0166	30.00	0.0166	38.00
0.0416	36.50	0.0416	51.00
0.0830	44.00	0.0830	69.00
0.125	52.25	0.125	89.00
0.166	60.00	0.168	110.00
(3) Effect of ethyl alcohol		(4) Effect of the products of hydrolysis of ethyl acetate	
0	30.50	0*	29.50
0.0166	30.50	0.0166	37.50
0.0416	31.50	0.0416	51.75
0.0830	31.00	0.0830	69.00
0.1250	31.00	0.1250	89.00
0.1665	31.00	0.1665	109.00

* Both ethyl alcohol and extra acetic acid are added and the concentration of each is as given in this column.

We have an example here, therefore, of a type of compound which causes a change in the time of set because it supplies more acid to the gel mixture. Whether the ethyl acetate as such gives a specific effect is impossible to say.

In the next portion of the work, a study was made of the effect of a series of typical organic compounds upon the time of set. An aliphatic alcohol, an aldehyde, a ketone, a hydrocarbon, a sugar, and glycerine were investigated. These substances were added to the acetic acid before mixing with the sodium silicate. Table 3 shows the effects of these substances. It will be noted that the hydrocarbon, benzene, is present in very small amount, because of its slight solubility in water. It will also be noted that the alcohol concentrations here are much higher than those involved in the study of the effect of ethyl acetate.

TABLE 3

Effect of various organic compounds on the time of set and on the pH at 25°C.

Concentrations constant throughout are as follows: NaOH, 0.395; SiO_2, 0.664; CH_3COOH, 0.454.

CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET	pH	CONCENTRATION OF ADDED SUBSTANCE	TIME OF SET	pH
Effect of ethyl alcohol			Effect of acetaldehyde		
gram-moles per liter	*minutes*		*gram-moles per liter*	*minutes*	
0	20.50	5.52	0	20.5	5.55
0.1910	21.25		1.02	24.0	
0.955	25.00		2.04	28.5	5.55
1.910	28.75	5.52	3.06	32.0	
2.865	33.25		4.08	36.0	5.55
3.810	37.00	5.52			
Effect of acetone			Effect of benzene		
0	21.25	5.52	0	22.00	
0.1515	24.25		0.00001	22.25	
0.7575	27.75		0.00005	22.00	
1.515	31.50	5.52	0.00010	22.00	
2.278	36.50		0.00015	22.25	
3.030	42.50	5.52	0.00020	22.00	
Effect of cane sugar			Effect of glycerine		
0	21.00	5.55	0	21.00	5.55
0.065	21.25		0.152	21.25	
0.130	21.25	5.55	0.760	21.75	
0.195	21.50		1.520	22.00	5.55
0.260	21.25	5.55	2.280	22.25	
			3.040	22.50	5.55

The results of these six sets of data in table 3 are shown graphically in figure 2.

An analysis of the effects of ethyl alcohol, acetaldehyde, acetone, benzene, cane sugar, and glycerine may be attempted as follows. The benzene may only be added in such minute quantities that it is not surprising that we have found no apparent effect. It may be concluded, however, that benzene, if it possesses any specific effect on the time of set, does not possess a large one. The cane sugar shows an effect which is practically negligible. Glycerine shows a slight effect. It should be noted that the maximum concentration of cane sugar obtained was 0.26 molar, while the glycerine reached 3.04 molar. The effect on the pH by these compounds was also shown to be very slight. The effects of ethyl alcohol, acetaldehyde, and acetone upon the pH of these sodium silicate–acetic acid mixtures when added up to concentrations of 3 to 4 molar are seen to be negligible when measured by the quinhydrone method. The effects on the time of set, however, are perfectly evident. Each one lengthens the time of set, and the effect of the acetone is greater than the effects of the other two. The effects of these compounds are apparently specific, since no change of pH could be detected.

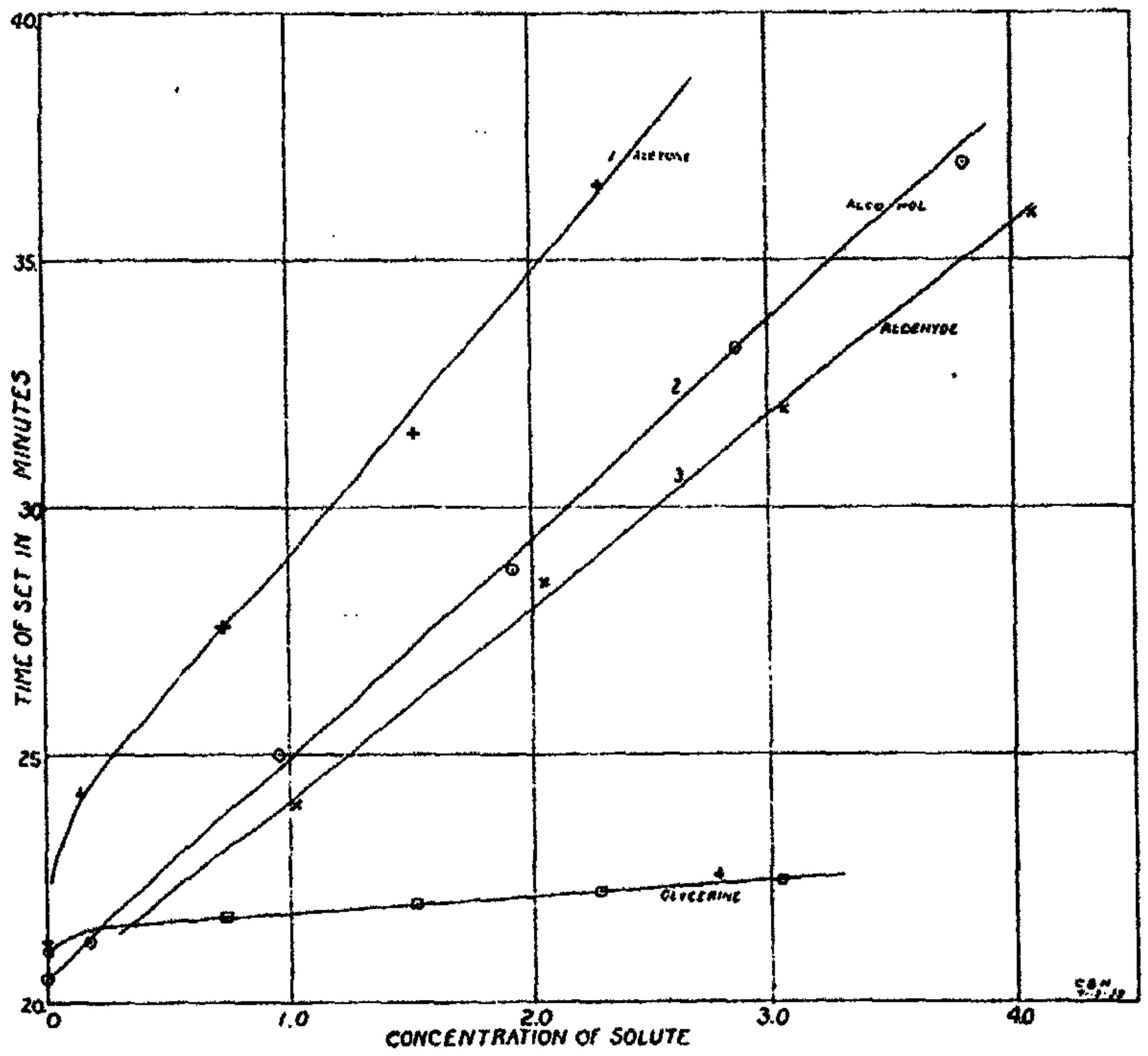


FIG. 2. EFFECT OF SOLUTES UPON THE TIME OF SET

It will perhaps be possible in the future to correlate these results with the results of other investigators on other properties of these gel mixtures.

SUMMARY

The effects of added solutes on the time of set of gel mixtures produced by mixing solutions of acetic acid and sodium silicate have been studied. An attempt has been made to separate the specific effects of the compounds themselves from the effects which they produce by changing the pH of the mixtures.

Ammonium hydroxide, methyl-, dimethyl-, and trimethyl-amines, pyridine, and aniline up to 0.04 *M* decrease the time of set mainly by increasing the pH of the mixture. There is, however, a specific effect apparent, greatest in the case of trimethylamine.

A typical ester, ethyl acetate, apparently increases the time of set chiefly because of acetic acid set free during acid hydrolysis of the ester.

Cane sugar and glycerine have little effect either on the time of set or on the pH. Benzene shows no effect, although its very low solubility practically precludes any save a very unusual effect.

Ethyl alcohol, acetaldehyde, and acetone show practically no effect upon the pH, but show considerable specific effects in increasing the time of set.

REFERENCES

(1) Hurd and Letteron: J. Phys. Chem. **36**, 604 (1932).
(2) Werner: J. Am. Pharm. Assoc. **9**, 501 (1920).
(3) Kröger: Kolloid-Z. **30**, 16 (1922).
(4) Bhatnagar and Mathur: Kolloid-Z. **30**, 368 (1922).
(5) Prasad and Hattiangadi: J. Indian Chem. Soc. **6**, 653, 893, 991 (1929).
(6) Holmes: J. Phys. Chem. **22**, 510 (1918).
(7) Prasad and Hattiangadi: J. Indian Chem. Soc. **6**, 893 (1929).
(8) Maschke: Ann. Physik. **222**, 90 (1872).
(9) Pappada: Gazz. chim. ital. **33**, 272 (1903); **35**, i, 78 (1905).
(10) Wulf and Praetorius: Rec. trav. chim. **49**, 582 (1930).

THE SOLUBILITY OF OXYGEN IN GOLD AND IN CERTAIN SILVER-GOLD ALLOYS

F. J. TOOLE AND F. M. G. JOHNSON

Department of Chemistry, McGill University, Montreal, Canada

Received August 4, 1938

INTRODUCTION

In earlier papers on the subject of the solubility of gases in metals, one of us (F. M. G. J.) (1), in collaboration with E. W. R. Steacie, has discussed the solubility of oxygen and of hydrogen in silver. The present paper is concerned with the solubility of oxygen in gold and in certain gold-silver alloys.

Little is known of the solubility of oxygen in gold. The early work of Graham (2) indicated an absorption of 0.006 volume of oxygen per volume of metal. Later workers (3) obtained contradictory results, which may be partly explainable by surface effects. Bone and his coworkers (4) obtained some evidence of the occlusion of oxygen by gold wire, but the experimental conditions were such that the conclusion that appreciable amounts of oxygen are absorbed appears somewhat doubtful.

The solubility of oxygen in alloys of the noble metals has received small attention. Some observations of a qualitative nature are to be found in the early literature. Sieverts and Krumbhaar (3) studied quantitatively the solubility of oxygen in alloys of gold and silver, in the molten state, at 1123°C. So far as is known to us, no quantitative work on the solubility of this gas in solid silver-gold alloys has been published.

APPARATUS

The experimental method was the same in principle as that described in detail in previous communications. A known volume of gas is introduced into a calibrated silica bulb of about 10 cc. capacity, which contains the metal foil under investigation and which is connected to a mercury manometer. At any temperature the pressure of the gas in the bulb can be calculated by the gas laws. If any absorption takes place, the observed pressure will be less than the calculated value and the difference between the two pressures will be a measure of the amount of gas which has been dissolved by the metal.

At the conclusion of an experimental run, the gas is pumped out of the bulb and measured. This procedure affords a check on the apparatus and eliminates errors due to incomplete evacuation of the metal. All experiments in which the volume of recovered gas differed from that originally admitted to the bulb were discarded.

Temperatures were measured by a constant-volume nitrogen thermometer consisting of a silica bulb of approximately the same size as that containing the metal under observation. The two bulbs were placed side by side in the furnace, any temperature variations in different regions being thus automatically compensated.

When a fresh sample of metal was placed in the bulb the temperature was raised to 850–900°C. and kept there for six hours while the bulb was evacuated by means of a condensation pump backed by a Toepler pump. Thereafter during the succeeding experiments, extending in most cases over months, the temperature varied between that of the room and 850–900°C. Any crystal strain caused by the cold-rolling of the metal into foil must have been destroyed by this treatment.

With the exception of some minor changes the apparatus was identical with that already described (1a).

MATERIALS

Commercially pure gold was further purified by the method of Krüss (5). The metal was then fused under borax in a silica tube, cleaned by scrubbing with sand, and rolled into sheets about 0.15 mm. thick. Two samples of gold were employed, having volumes of 1.32 and 2.89 cm.^{3} respectively.

The silver used for the preparation of the alloys was purified by a method due to Stas (6) and prepared in the same form as the gold.

The alloys were prepared by weighing out the calculated quantities of purified gold and silver and fusing the mixture in a silica tube. When fused, the metal was thoroughly stirred with a silica rod, allowed to solidify, cooled, cleaned with sand, and rolled into sheets. Alloys of 5, 10 and 20 per cent of gold were employed, the volume of metal being 2.65, 2.76, and 3.60 cm.^{3} respectively. One sample of each alloy was investigated.

Nitrogen and oxygen, obtained from cylinders of the compressed gas, were purified by the usual methods and stored over phosphorus pentoxide.

EXPERIMENTAL RESULTS

At the conclusion of the experiments the various metals showed, on examination, little evidence of change. No surface changes could be observed in the *gold* (second sample), although it had lost 0.03 gram in weight. The edges of the foil had sintered together and the probability is that the small loss in weight is due to evaporation. The silver–gold alloys had developed a crystalline surface and the evaporated silver from the alloy containing 5 per cent of gold had imparted a slight brownish tinge to the silica. A small loss in weight occurred, with partial sintering of the edges of the foil.

Solubility of nitrogen

No measurable absorption of nitrogen either by gold or by the three alloys of gold and silver, over the temperature range 200–900°C., was found.

Solubility of oxygen

A. In gold. Preliminary experiments using a Pyrex bulb indicated a small solubility, of the order of 0.01 volume at 500°C. and under a pressure of 60 cm. of mercury. The solubility decreased with decreasing temperature and pressure, but the magnitude of the absorption was too close to the experimental error of the apparatus to allow of satisfactory measurement. It appeared possible that at higher temperatures and pressures the effect might become measurable, and accordingly further experiments were carried out, using a silica bulb. In this second series of twelve experiments, the pressure varied from 10 to 70 cm. of mercury and the temperature from 300°C. to 900°C. The solubility as measured by these experiments was small, in no case exceeding 0.014 volume, but varied irregularly with temperature and pressure, owing, in part, to the high percentage error of the apparatus. The results are given in table 1.

TABLE 1

Solubility of oxygen in gold (sample 2) in a silica apparatus

TEMPERATURE	PRESSURE	ABSORPTION	TEMPERATURE	PRESSURE	ABSORPTION
degrees C.	*cm. Hg*	*volumes per volume*	*degrees C.*	*cm. Hg*	*volumes per volume*
900	14.0	0.002	750	63.9	0.007
	19.4	0.000		68.4	0.005
	30.7	0.005	700	28.1	0.006
850	13.9	0.002		33.3	0.010
	30.1	0.005		58.5	0.003
	66.7	0.010		61.2	0.007
800	29.5	0.005	600	55.3	0.002
	35.1	0.010		57.9	0.006
	61.0	0.005		63.2	0.007
	64.5	0.004	550	11.9	0.009
	65.3	0.008		25.9	0.014
	70.0	0.003	500	51.0	0.003
750	18.2	0.002		55.4	0.007
	28.8	0.005	400	27.7	0.011
	34.2	0.002		50.5	0.002
	59.5	0.005	320	45.2	0.001

These figures indicate that oxygen is absorbed by gold to a small extent,

TABLE 2

Values of k at different values of P and Q

Alloy No. 3: 20 per cent gold, 80 per cent silver

Temperature 900°C. log a = 1.135

P	Q	k (CALCULATED)
10.7	0.043	0.486
14.9	0.050	0.486
24.9	0.063	0.478
54.3	0.090	0.473
68.2	0.099	0.478
93.6	0.117	0.474

TABLE 3

Solubility (volumes per volume of metal) of oxygen in silver–gold alloys

Alloy No. 1: 5 per cent gold, 95 per cent silver

PRESSURE	T = 200	300	400	500	600	650	700	750	800	850°C.
	k = 0.328	0.286	0.183	0.309	0.334	0.397	0.548	0.554	0.543	0.533
cm.										
10	0.039	0.040	0.043	0.043	0.048	0.049	0.043	0.047	0.060	0.076
20	0.049	0.049	0.049	0.053	0.061	0.065	0.062	0.072	0.088	0.110
30	0.055	0.055	0.053	0.060	0.070	0.076	0.078	0.089	0.109	0.138
40	0.061	0.060	0.056	0.066	0.078	0.085	0.090	0.105	0.127	0.160
50	0.065	0.064	0.059	0.071	0.083	0.093	0.102	0.119	0.144	0.180
60	0.069	0.067	0.061	0.074	0.088	0.100	0.113	0.132	0.150	0.198
70	0.073	0.070	0.063	0.078	0.092	0.107	0.123	0.144	0.172	0.215
80	0.076	0.073	0.065	0.081	0.096	0.112	0.132	0.154	0.185	0.236

TABLE 4

Solubility (volume per volume of metal) of oxygen in silver–gold alloys

Alloy No. 2: 10 per cent gold, 90 per cent silver

PRESSURE	T = 200	300	400	500	600	650	700	750	800	850°C.
	k = 0.045	0.037	0.042	0.178	0.280	0.462	0.583	0.573	0.536	0.545
cm.										
5	0.044	0.043	0.039	0.033	0.029	0.022	0.018	0.022	0.029	0.039
10	0.045	0.043	0.040	0.037	0.036	0.031	0.027	0.033	0.042	0.056
20	0.046	0.044	0.042	0.042	0.043	0.043	0.040	0.049	0.061	0.083
30	0.046	0.044	0.042	0.045	0.048	0.052	0.050	0.062	0.076	0.103
40	0.047	0.045	0.044	0.047	0.052	0.059	0.059	0.072	0.088	0.120
50	0.048	0.045	0.045	0.049	0.055	0.065	0.068	0.082	0.100	0.136
60	0.049	0.046	0.046	0.050	0.058	0.071	0.075	0.091	0.110	0.150
70	0.049	0.046	0.047	0.052	0.061	0.077	0.082	0.100	0.119	0.164
80	0.049	0.046	0.047	0.053	0.063	0.082	0.089	0.107	0.128	0.176

which probably does not exceed one-hundredth of a volume at 900°C. and under atmospheric pressure, and is consequently not much larger than the experimental error of the method (0.002 volume). The results obtained are not wholly consistent with each other, and although many experiments were made in an endeavor to obtain greater precision, it was found impossible to reproduce results at a given temperature within the known experimental error. The difficulty cannot be wholly ascribed to the large percentage error of the measurements; there appears to be some other factor entering into the solubility relationship. Whether, however, this is a surface phenomenon, or hysteresis due to the thermal history of the metal or to some other obscure cause, cannot be elucidated without further investigation.

TABLE 5

Solubility (volume per volume of metal) of oxygen in silver–gold alloys

Alloy No. 3: 20 per cent gold, 80 per cent silver

PRESSURE	$T = 200$	300	400	500	600	650	700	750	800	850	900°C.
	$k = 0.121$	0.124	0.094	0.084	0.156	0.236	0.415	0.395	0.498	0.474	0.480
cm.											
10	0.053	0.049	0.049	0.050	0.047	0.041	0.028	0.025	0.026	0.034	0.041
20	0.058	0.053	0.052	0.053	0.052	0.047	0.037	0.033	0.037	0.047	0.057
30	0.061	0.056	0.055	0.055	0.056	0.053	0.044	0.039	0.045	0.057	0.070
40	0.063	0.058	0.056	0.056	0.059	0.057	0.050	0.043	0.051	0.065	0.080
50	0.065	0.060	0.057	0.057	0.061	0.060	0.055	0.047	0.057	0.072	0.089
60	0.066	0.061	0.058	0.058	0.062	0.063	0.059	0.051	0.062	0.079	0.097
70	0.061	0.062	0.059	0.058	0.064	0.065	0.063	0.054	0.067	0.085	0.106
80	0.069	0.064	0.060	0.059	0.066	0.067	0.067	0.057	0.071	0.090	0.113

The results show, however, that there is a small absorption of oxygen by gold, although nothing can be deduced as to the variation of the solubility with temperature and pressure. The comparative insolubility of oxygen in gold established by these measurements is in agreement with the results of Sieverts and Krumbhaar (3).

B. In silver–gold alloys. The solubility of oxygen in silver has been shown to be proportional, at any fixed temperature, to the square root of the pressure, and this relationship can be represented by the equation

$$Q = aP^{\frac{1}{2}}$$

where Q is the solubility, expressed as volumes of gas per volume of metal, P is the pressure, and the coefficient a depends on the temperature.

The solubility of oxygen in silver–gold alloys has been found to conform to this equation only at higher temperatures, but the expression

$$Q = aP^k$$

adequately expresses the results over the whole temperature range investigated. In this equation, the exponent k is equal to $\frac{1}{2}$ at all temperatures above a certain "critical" temperature (700–750°C.), which appears to be independent of the composition of the alloy. Below this temperature, k decreases with decreasing temperature. The experimental results were obtained by fixing the temperature at the desired point and measuring the solubility under pressures of oxygen varying from 5 to 80 cm. of mercury. If the logarithm of the solubility is then plotted against the logarithm of the pressure, the slope of the resultant straight line gives the value of k for that temperature, while the intercept on the y-axis is a measure of log a. By inserting these values in the equation, the solubility at pressures of 5, 10, 20, etc., cm. can be calculated.

Tables 3, 4, and 5 give the values of the solubility of oxygen in the three alloys investigated. To illustrate the constancy of k, table 2, in which P is the actual pressure of the gas and Q the corresponding solubility, is inserted.

DISCUSSION OF RESULTS

Solubility of oxygen in silver–gold alloys

The variation of the solubility with the pressure of oxygen is illustrated in figures 1 and 2, taken from the results obtained with an alloy containing 10 per cent of gold. At temperatures above 700°C., the solubility is approximately proportional to the square root of the pressure ($k = \frac{1}{2}$), while below this temperature the exponent k decreases, although the curve remains a straight line. This statement applies to all three alloys investigated, with the reservation that in the case of the alloy richest in gold (20 per cent) the "critical" temperature is higher, viz., at 750°C.

The variation of solubility with temperature is shown in figures 3, 4, and 5. In figure 3 is included, for purposes of comparison, the curve of solubility of oxygen in pure silver under a pressure of 80 cm. of mercury. It will be seen that the solubility curves of oxygen in this alloy show a general resemblance to those of the system oxygen–silver, but only at the higher pressures and for temperatures above 400°C. Below this temperature the solubility does not increase so markedly as in the latter system. Inspection of the curves for the pressures 40, 30, 20, and 10 cm. reveals the gradual appearance of a minimum at 700°C. in the solubility curve, which at 40 cm. is a mere inflection in the curve, but at 10 cm. is strongly marked. It will also be noticed that the minimum found to exist in the solubility of oxygen in silver is indicated, in the case of this alloy, at the higher pressures, but disappears as the pressure of the gas diminishes.

The curves of solubility versus temperature for the second alloy (90

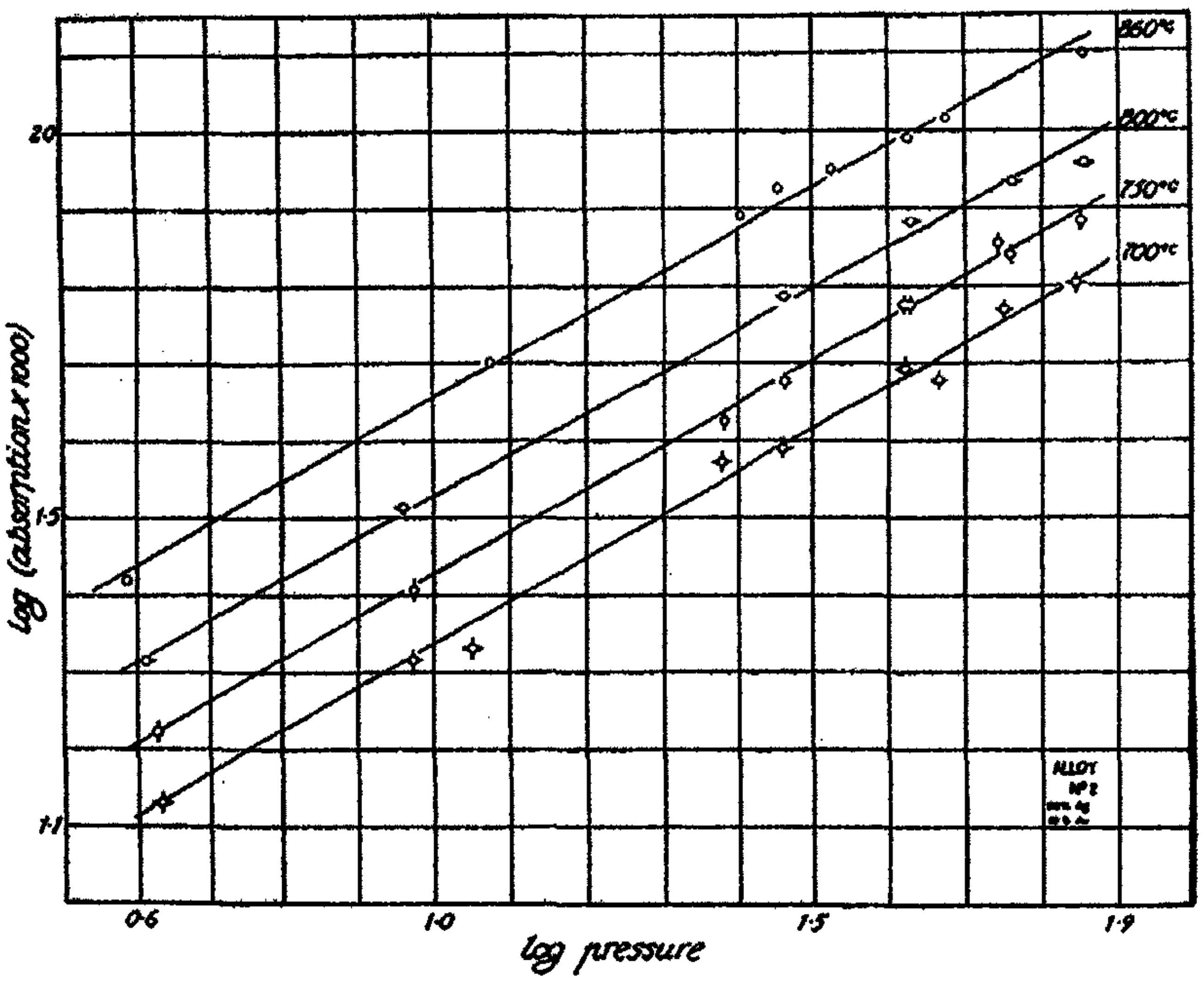


FIG. 1. VARIATION OF SOLUBILITY WITH PRESSURE AT TEMPERATURES ABOVE 700°C. Silver 90 per cent; gold 10 per cent

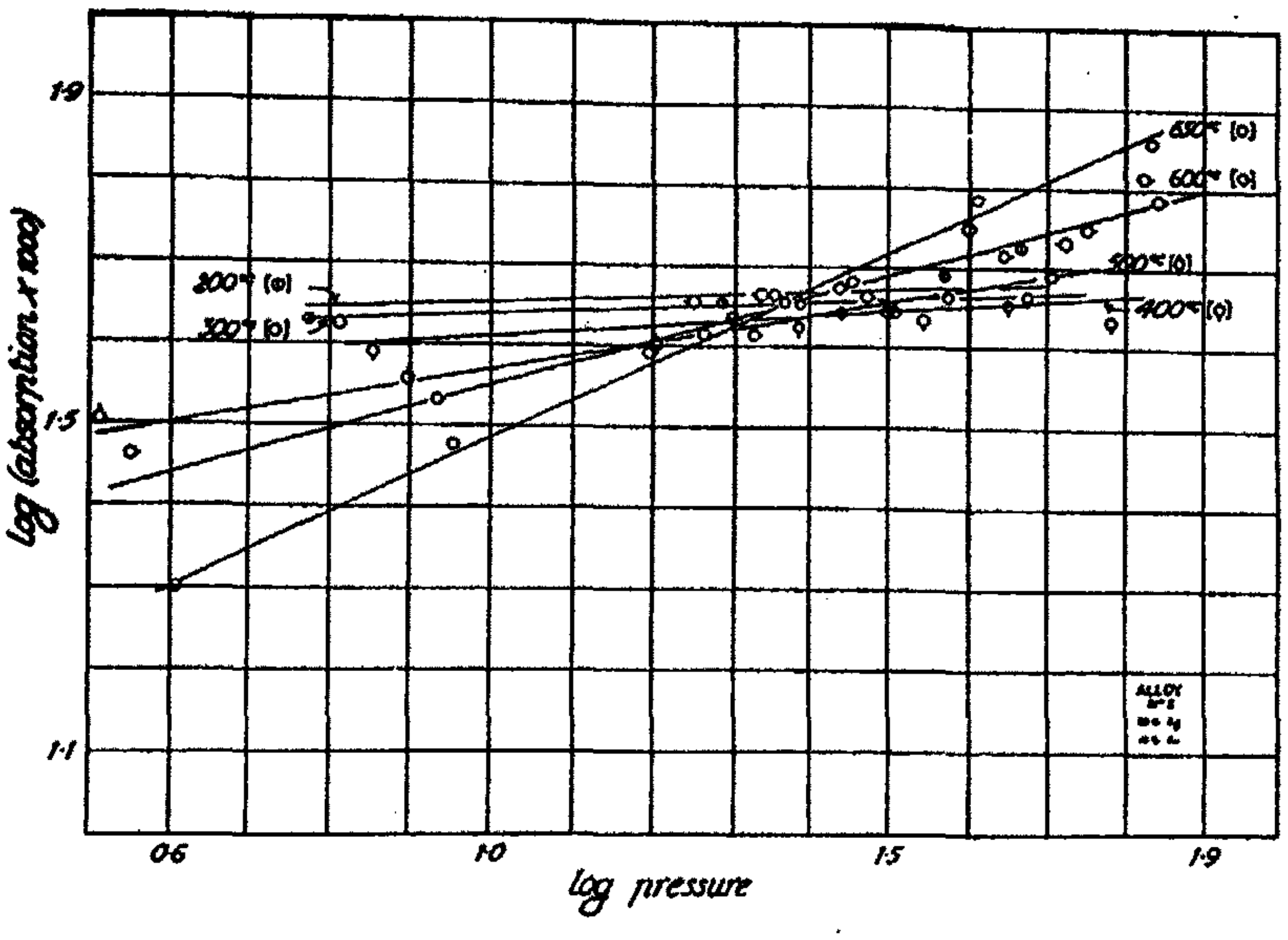


FIG. 2. VARIATION OF SOLUBILITY WITH PRESSURE AT TEMPERATURES BELOW 700°C. Silver 90 per cent; gold 10 per cent

per cent Ag, 10 per cent Au; figure 4) exhibit a minimum at 700°C. in a more strongly marked form, and here it does not disappear at the higher pressures. The drawing-together of the curves at low temperatures is also more pronounced than in the alloy richer in silver, and there is no indication of the minimum at 400°C., even at a pressure of 80 cm. With the

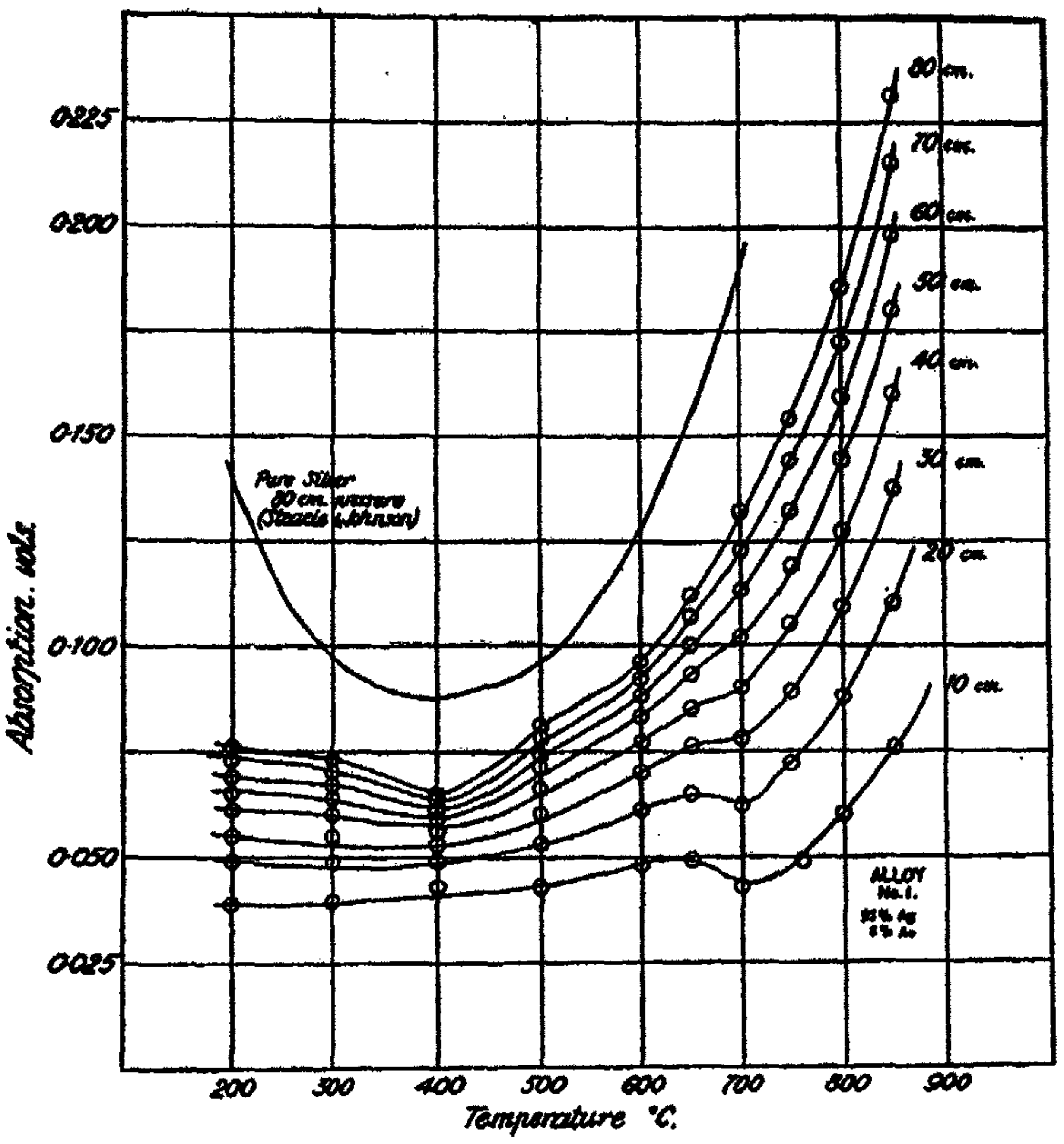


FIG. 3. VARIATION OF SOLUBILITY WITH TEMPERATURE
Silver 95 per cent; gold 5 per cent

TABLE 6

ALLOY NUMBER	COMPOSITION	A	MELTING POINT
		degrees C.	*degrees C.*
1	95 per cent silver: 5 per cent gold	1040	970
2	90 per cent silver: 10 per cent gold	980	980
3	80 per cent silver: 20 per cent gold	1025	1010

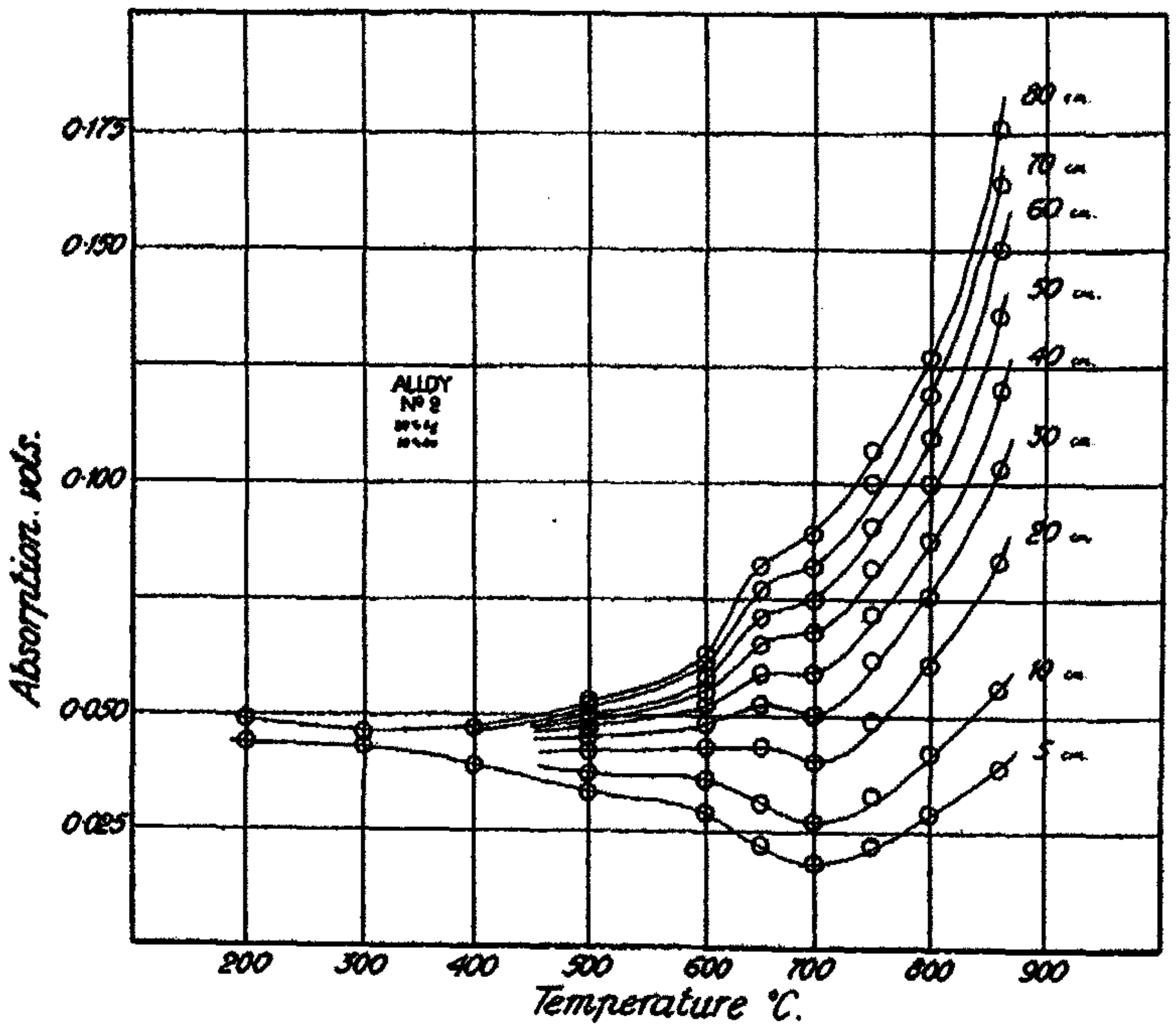


FIG. 4. VARIATION OF SOLUBILITY WITH TEMPERATURE
Silver 90 per cent; gold 10 per cent

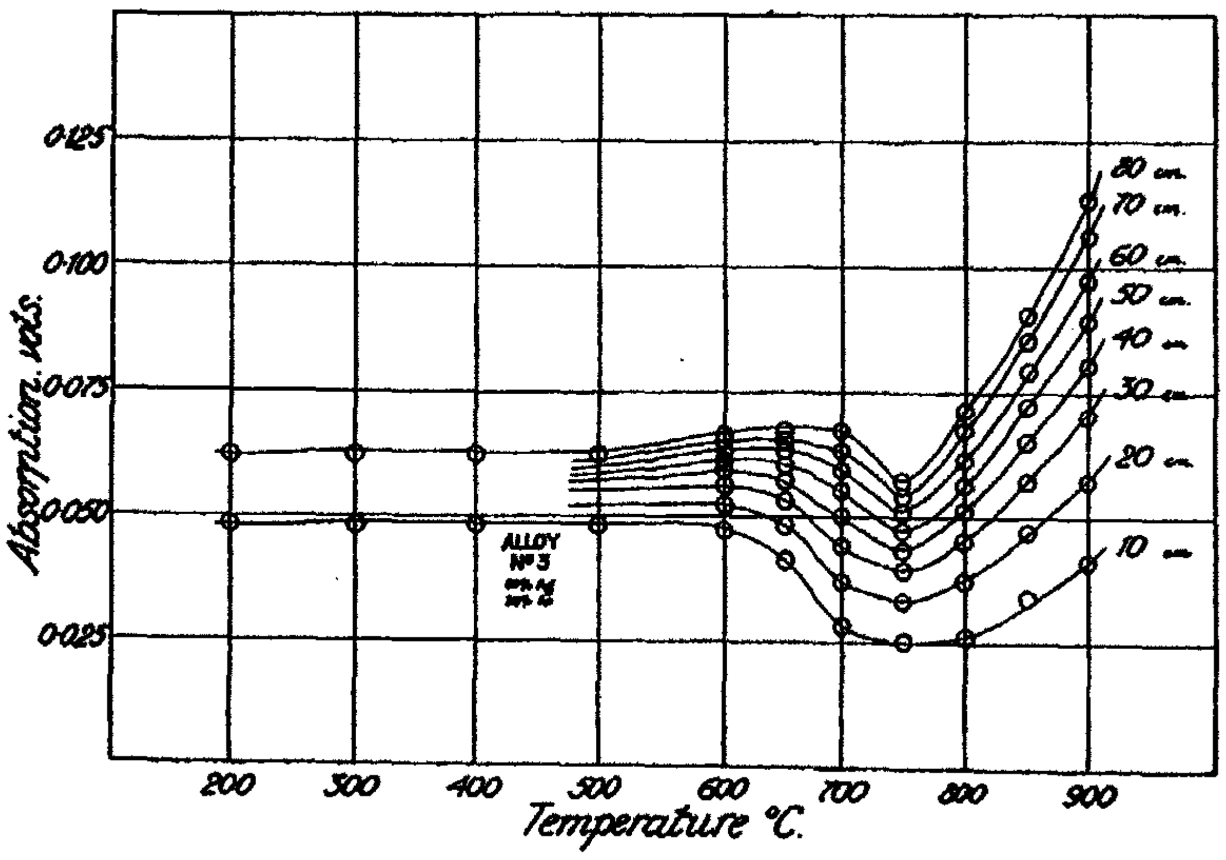


FIG. 5. VARIATION OF SOLUBILITY WITH TEMPERATURE
Silver 80 per cent; gold 20 per cent

third alloy (80 per cent Ag, 20 per cent Au; figure 5), the 400°C. minimum is also completely absent. The inflection in the curves at the higher temperature, however, has developed still more strongly. The curves below 500°C. are here represented as parallel to the temperature axis, which means that for the temperatures 500–200°C. the solubility results for each pressure are the same for all these temperatures within the experimental error.

As mentioned before, the difficulties of establishing the log absorption versus log pressure curve for temperatures below 400°C. have made these results less reliable than those at higher temperatures; for this reason only the extreme pressure values are drawn in the curves representing the variation of solubility with temperature, the other values lying within these limits. At these temperatures, the most that can be said is that with the two alloys richer in gold (alloy No. 2, alloy No. 3), the solubility appears to approach a value of about 0.05 volume, which is the same for both alloys. With the alloy richest in silver there is some indication that for higher pressures of oxygen an increase in the solubility value takes place from 400°C. to 200°C., a behavior which is similar to that of pure silver (figure 3). The effect, however, is very much less, even in this case, than was found with silver.

The relationship between solubility and temperature for the three alloys of silver and gold examined is thus a complicated one. Above the temperature at which the minimum occurs, the curves for all pressures, in the range investigated, are parallel for each alloy. Below this temperature complications are added, and it is hence not possible to express the results for all temperatures by a concise equation. For temperatures above the "critical" temperature, the equation

$$\frac{1}{Q} = K_1 (A - t)$$

has been found to hold. Here, Q is the solubility, t the temperature in degrees Centigrade, K_1 a coefficient specific for each pressure and each alloy, and A varies between 980°C. and 1040°C. as shown in table 6. The value of A thus approximates to the melting point of the alloy. This is in agreement with results for the system oxygen–silver (1).

The variation of solubility with concentration of gold in the alloy is shown for the temperature 800°C. in figure 6, in which the values for the solubility of oxygen in pure silver are taken from Steacie and Johnson's results. The change of solubility with concentration for the eight pressures 10 to 80 cm. forms a family of smooth curves which, for this temperature, can be expressed by the equation

$$\frac{1}{Q} = K_2 (C + 5.7)$$

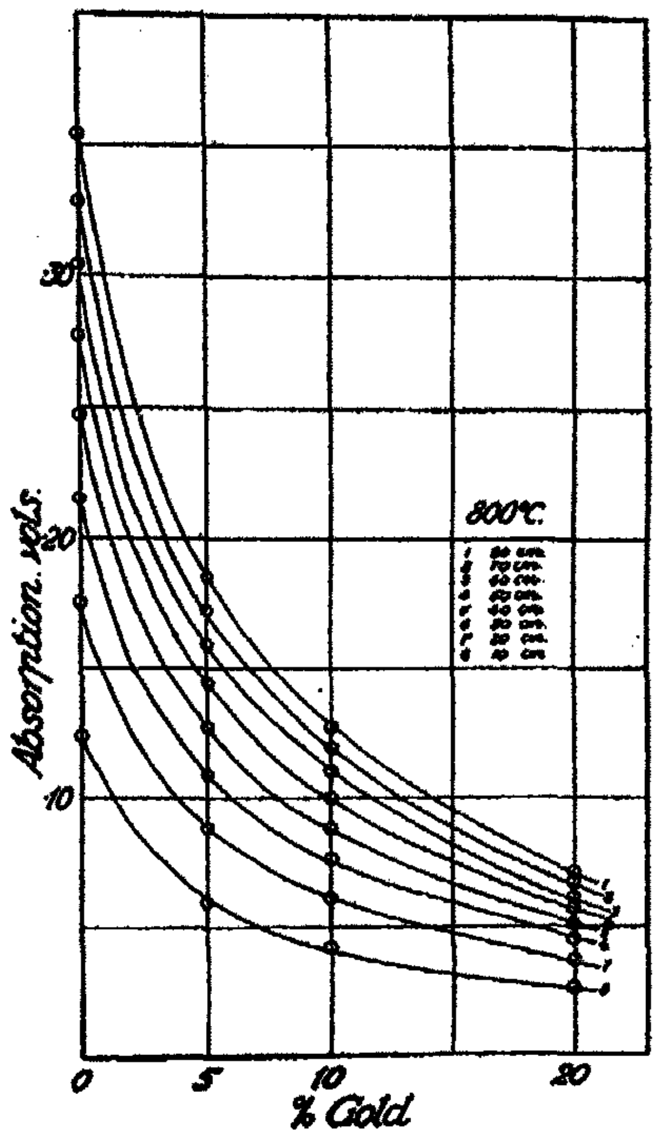


Fig. 6. Variation of Solubility with Concentration at 800°C.

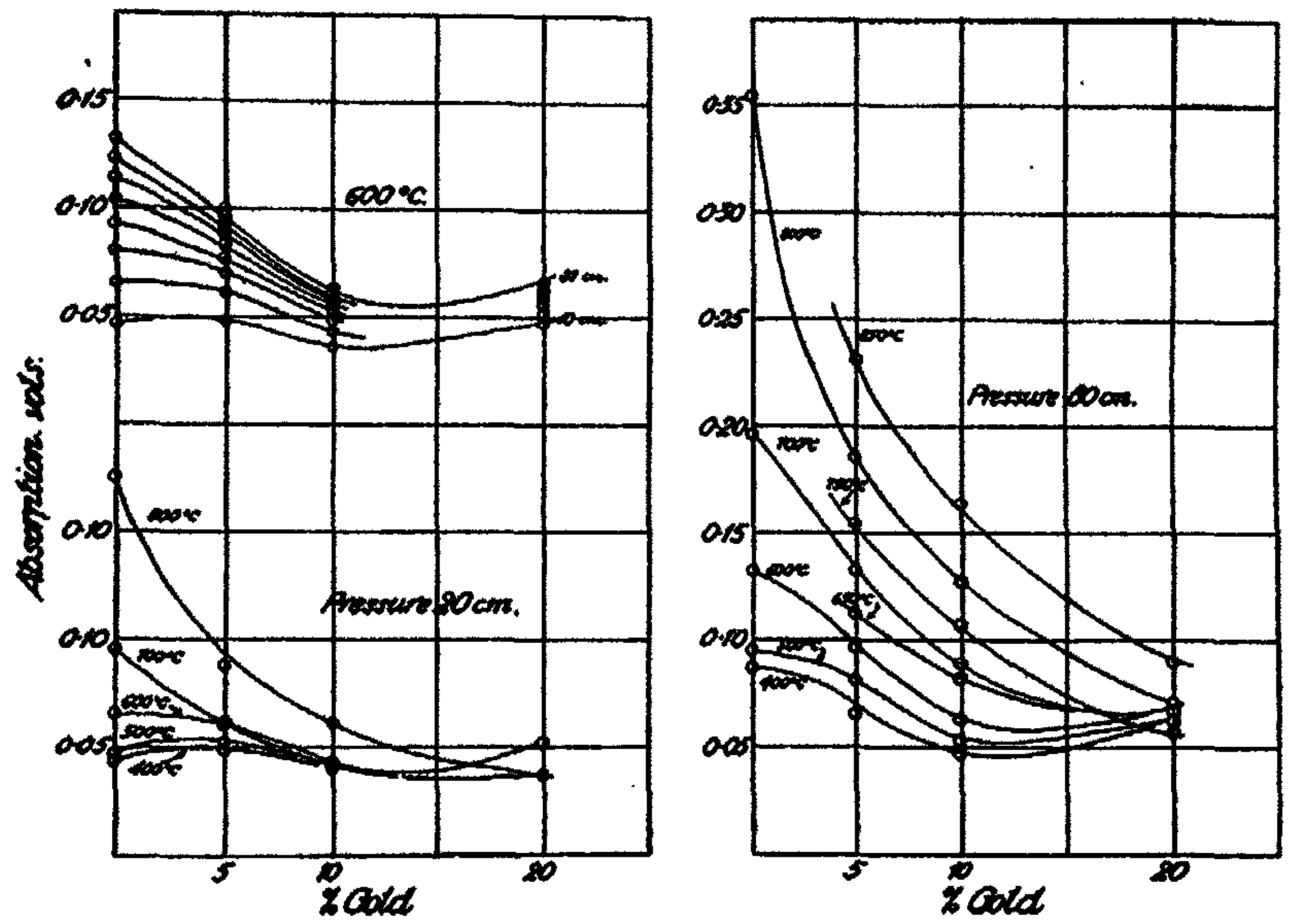


Fig. 7. Variation of Solubility with Concentration at Various Temperatures and Pressures

where C is the concentration (per cent) of gold, and the coefficient K_2 varies with the pressure.

Similar curves for other temperatures and pressures are given in figure 7.

GENERAL DISCUSSION

Solubility of oxygen in silver–gold alloys

The experimental results have been summarized in the foregoing section, and the effect of various factors on the solubility has been discussed. Above a certain "critical" temperature, which apparently varies with the concentration of gold, the factors affecting the solubility of oxygen in the three alloys examined appear to be the same as those previously found to condition the solubility of the gas in pure silver, i.e., the solubility is proportional to the square root of the pressure. As the temperature is reduced below the critical temperature, however, this relationship no longer holds; the exponent k in the equation

$$Q = aP^k$$

becomes less than ½ and decreases with decreasing temperature to an extent varying with the composition of the alloy.

The behavior of the solubility-pressure relationship is reflected in the solubility-temperature curves, and is partly responsible for the inflection in the curves at the so-called critical temperature. This dip is most marked at low pressures and becomes more strongly defined with increasing concentration of gold. The curves representing the solubility-temperature relationship for the solubility of oxygen in silver exhibit a minimum at 400°C.; below this temperature and above it, the solubility increases, but remains for all temperatures related to the pressure by the expression $Q = aP^{\frac{1}{2}}$; no trace of any variation in the exponent of P with temperature was found. It appears to be established, therefore, that the form of the curves connecting solubility and temperature for these three alloys is due to the presence of gold.

The measurements of the solubility of oxygen in pure gold show that a small absorption of the gas occurs, which appears to decrease with decreasing temperature and pressure. Any admixture of this practically inert metal with silver would therefore be expected to diminish the solubility of oxygen according to some simple function of the concentration of gold. That it actually does so at high temperatures is shown by the equation

$$\frac{1}{Q} = K_2 (C + 5.7)$$

which applies only at temperatures above those at which irregularity appears in the solubility-temperature curves for the different alloys.

It has been suggested that the minimum in the solubility-temperature curves for oxygen and silver might perhaps be due to the change from one allotropic form of silver to another, or to a change in the manner of combination with oxygen. In a similar way, it could be argued that the form of the solubility-temperature curves for oxygen in these alloys is caused by the formation of some compound of gold and silver which is stable only at temperatures below 750°C. To this suggestion, however, there is the objection that all the measured properties of gold–silver alloys show a gradual change as the concentration changes, and give no indication of any interruption in the curve, such as would be caused by the existence of a compound. Thus Holgersson (7) in an x-ray study of gold–silver alloys by the Debye-Scherrer method, found that the length of side of the unit cube is very nearly a linear function of the atomic composition. Measurements of the physical properties of the alloys, such as specific heat, electrical conductivity, etc., all support the conclusion from freezing point data that these two metals form no compound.

The view that the existence of this "critical" temperature is due to change in the crystal state of the metal is not accepted. Any strains in the crystal lattice caused by cold-working of the metal would be eliminated by the heat treatment incidental to the experiments; and the completely reproducible results below this critical temperature show that gradual recrystallization can have little effect on the solubility of oxygen in these alloys.

The effect of surface

It is possible that the irregularities in the solubility-temperature curves are due to surface effects.

If it be assumed that the true solubility falls off uniformly with the temperature, in the manner indicated by the solubility of oxygen in silver, that is, with a minimum at 400°C., below which the solubility increases, and if it be further assumed that, as the temperature is decreased below 750–700°C., surface effects begin to appear, rapidly increasing below 700°C. until 500°C. or so is reached, then an apparent solubility curve of the form actually obtained would result. This is shown diagrammatically in figure 8.

Lack of time has prevented the investigation of more than one sample of each alloy. Certain deductions can, however, be made from the results obtained. The metal was used in the form of foil, rolled to a thickness of 0.1 mm. The surface can therefore be calculated from the mass of metal, its density, and the thickness of the foil, but many factors affect the calculation. (1) The thickness of the foil varies in different places. (2) The foil, after being used for a time, develops a crystalline appearance, which indicates a largely increased surface. (3) Distillation of the metal takes place to some extent to the walls of the silica bulb.

The surface of the metal as calculated from the volume and the thickness is affected by these uncertainties to an extent which is quite unknown, and which might easily vitiate any attempted control of the surface area. If, however, these uncertain factors are neglected, a numerical calculation will show that the surface of the metal may account for a considerable apparent solubility of oxygen in the alloy. In the experiments on alloy No. 3, the volume of metal was 3.60 cm.^{3}, its thickness 0.01 cm.; hence its calculated surface was 720 cm.^{2} The volume of the bulb and dead space was approximately 10 cm.^{3} If we adopt Langmuir's theory of a unimolecular layer as the maximum amount of gas which the metal can adsorb on its surface and assume that at the lower temperatures the surface is saturated, then the number of molecules adsorbed on the surface can be calculated.

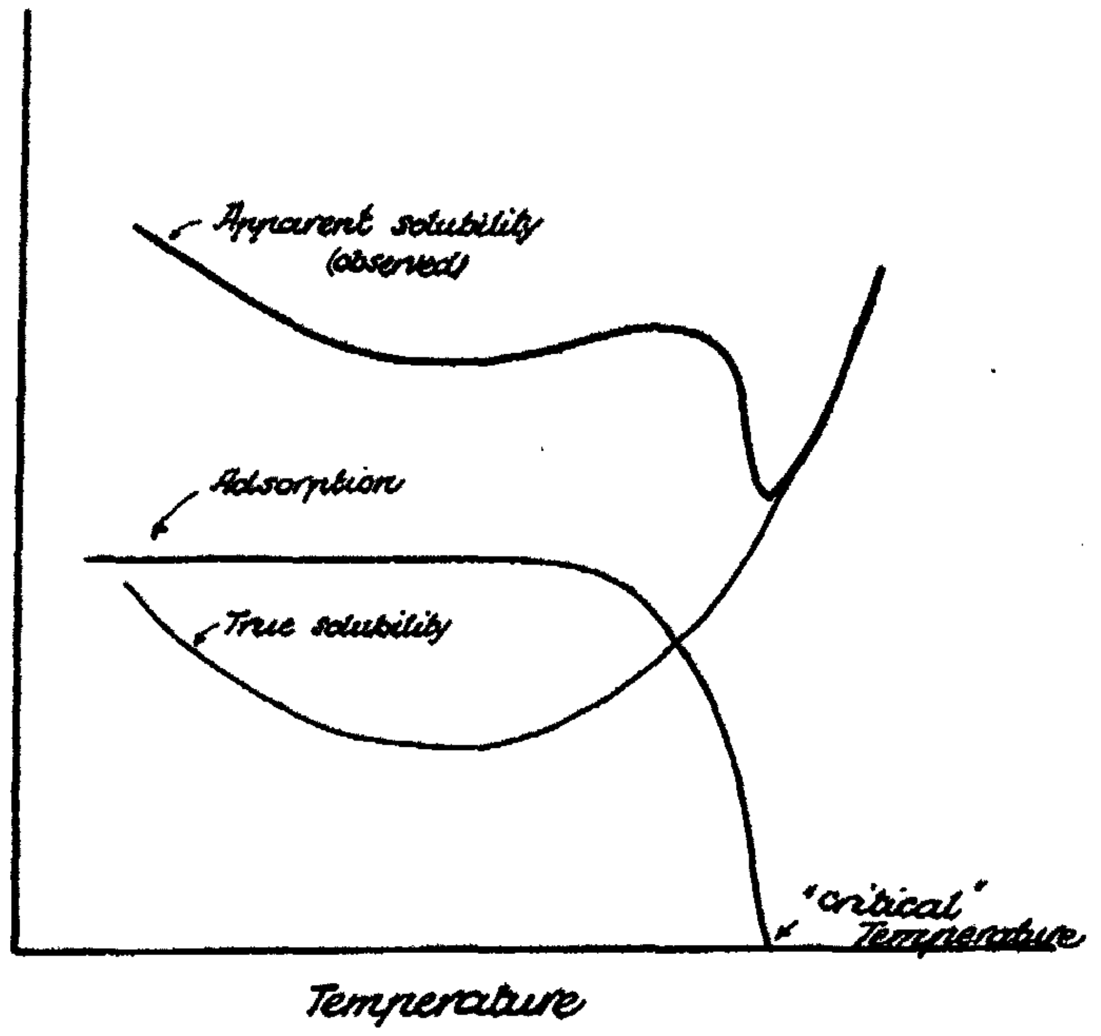


FIG. 8

The radius of the oxygen molecule is 1.5 × 10^{-8}cm.; hence its (projected) area is 7 × 10^{-16} cm.^{2} The number of oxygen molecules adsorbed on a surface of 720 cm.^{2} in a unimolecular layer is, therefore, 10^{18}. By the gas laws, this number of molecules, in a space of 10 cm.^{3} in volume, would exert, at 0°C. a pressure of 0.28 cm. At higher temperatures the pressure would vary according to the law of Charles, and at 200°C. would be approximately 0.5 cm. Hence, at 200°C. the gas molecules adsorbed in a complete unimolecular layer on the surface of the metal would cause a pressure drop of 0.5 cm. This corresponds, using the constants of the apparatus in the case of this particular alloy, to an apparent solubility of 0.01 volume of gas per volume of metal. The apparent solubility as measured is about 0.05 volume, which, taking into account the very approximate nature of the calculated value and the fact that part of this apparent solubility is undoubtedly due to true solution, is of the same order of magnitude. Furthermore, the crystallization of the metal surface, and the distillation of the metal to the walls of the bulb, would have the effect of largely increasing the surface area of the metal, and hence the pressure drop due to the adsorbed molecules.

The form of the true solubility curve below 400°C. would affect the observed curve to an increasing extent as the pressure is increased, while the effect of adsorption would remain constant for the range of temperature where the surface is completely covered with a layer of molecules of oxygen. In the most favorable case, the increased solubility due to increasing pressure might eventually, at higher temperatures, mask the surface effect altogether. This is apparently so in the case of alloy No. 1, where the minimum at 700°C. disappears at higher pressures; while that at 400°C., on the other hand, develops as the pressure is increased.

It may perhaps be mentioned that the assumption of the persistence of surface effects up to the comparatively high temperature of 750°C. is not without corroboration. Langmuir (8) found that tungsten wire adsorbs appreciable amounts of oxygen up to a temperature of 3000°C., while at 1200°C. the surface of the metal is saturated.

SUMMARY

The solubility of oxygen in gold has been measured over a wide range of temperature at various pressures, and has been found to be of the order of 0.010 volume per volume of metal at the highest temperature (900°C.) and pressure (70 cm. of mercury) employed.

The solubility of oxygen in three silver-gold alloys containing 5, 10, and 20 per cent of gold has been measured at temperatures between 850°C. and 200°C., and under pressures of from 5 to 80 cm. Above a certain temperature the solubility is proportional to the square root of the pressure and is related to the temperature by the equation $1/Q = K_1(A - t)$, where Q is the solubility, t the temperature in degrees Centigrade, and A the melting point of the alloy; the solubility is a function of the concentration which, for each temperature, can be expressed by the equation $1/Q = K_2\ (C + 5.7)$, where C is the percentage concentration of gold in the alloy. Below this "critical" temperature the apparent solubility is related to the pressure by the equation $Q = aP^k$, in which k diminishes with decreasing temperature; the relation between solubility and temperature, and that between solubility and concentration of gold, are complicated by the appearance of minima in the curves.

An explanation of the solubility phenomena at temperatures below the so-called "critical" temperature has been advanced which depends on the assumption of surface effects. This effect of surface first becomes apparent, as the temperature is decreased, at the "critical" temperature.

Nitrogen is insoluble in gold and in silver–gold alloys of the composition investigated.

REFERENCES

(1) (a) Steacie and Johnson: Proc. Roy. Soc. London **A112**, 542 (1926).
    (b) Steacie and Johnson: Proc. Roy. Soc. London **A117**, 662 (1928).
(2) Graham: Phil. Mag. [4] **32**, 503 (1866).
(3) Neumann: Monatsh. **13**, 40 (1892).
    Sieverts and Krumbhaar: Ber. **43**, 893 (1910).
    Benton and Elgin: J. Am. Chem. Soc. **49**, 2426 (1927).
(4) Bone and coworkers: Trans. Roy. Soc. London **A206**, 1 (1906); **A109**, 459 (1925).
(5) Krüss: Ann. **238**, 30 (1887).
(6) Stas: Mem. acad. Belg. **33**, 1 (1865).
(7) Holgersson: Ann. Physik **79**, 35 (1926).
(8) Langmuir: Phys. Rev. **8**, 149 (1916); Chem. Rev. **6**, 473 (1929).

SOLID POLYIODIDES OF THE ALKALI METALS[1]

NORMAN S. GRACE[2]

Department of Chemistry, University of California, Berkeley, California

Received September 6, 1932

INTRODUCTION

In an earlier paper (1) evidence has been presented for the existence of three solid solvated polyiodides of potassium: $KI_3 \cdot H_2O$, $KI_7 \cdot H_2O$, and a compound containing benzene. Each of these compounds contains solvent molecules which are apparently part of the constitution of these polyiodides, for on the removal of combined solvent the polyiodides decompose, e.g., the dehydration of the triiodide by P_2O_5 (2).

$$KI_3 \cdot H_2O \longrightarrow KI + I_2 + H_2O$$

This, and other experiments, beside indicating that the combined solvent is part of the constitution of these polyiodides, show that solid *unsolvated* polyiodides of potassium are unstable, and do not exist at 25°C. and 1 atmosphere pressure.

While the earlier paper was in the press, Bancroft, Scherer and Gould (3), from a survey of the literature and additional experiments, concluded that potassium polyiodides definitely do not exist at 25°C. They failed, however, to consider the possibility of solvation, which is apparently the key to the problem, and their results when interpreted in this light are actually largely in agreement with the existence of *solvated* polyiodides and in complete agreement with ours as to the non-existence of unsolvated polyiodides of potassium.

Some of their most critical experiments may be reinterpreted. That (4) in which potassium triiodide, prepared by Johnson's method, is shown to exist in equilibrium with an aqueous solution of potassium iodide containing 65.19 per cent iodine, is in excellent agreement with our results (5), which show $KI_3 \cdot H_2O$ to exist in equilibrium with aqueous potassium iodide solutions whose iodine content may be varied between 62 and 66 per cent. This experiment indicates that $KI_3 \cdot H_2O$ is a stable phase in this system under these conditions.

---

[1] The experimental part of this paper was carried out as part of the requirements for the degree of Doctor of Philosophy at the Royal College of Science, University of London, and completed in July, 1931.

[2] Commonwealth Fellow.

Bancroft and his associates (6) quote some analyses on three different preparations of potassium triiodide, from which mother liquor had been removed by drying between filter papers and which gave a potassium iodide to polyiodide iodine ratio of 1.002 and totalled ($KI + I_2$) 94.78 per cent (which is very close to $KI_3 \cdot H_2O$). After obtaining these results which indicate $KI_3 \cdot H_2O$, they quote two analyses on wet solid which had not been dried between filter papers and which gave a different potassium iodide to iodine ratio than the above. It is then suggested that drying between filter papers is responsible for this difference and that a large error is introduced by following such a procedure for the preparation of samples for analysis and that this error affects all previous analyses which had indicated the existence of solid potassium triiodide. However, their analyses of the undried wet solid only total ($KI + I_2$) 79.3 and 76.2 per cent, or over 20 per cent of water (by difference). Our results (1) show that $KI_3 \cdot H_2O$ does not exist in equilibrium with more than 8 per cent of water at 25°C., so that it appears very probable that the above wet solid was only potassium iodide wet with solution. This indicates that the difference in potassium iodide to iodine ratios, for the dried and undried samples, did not lie in the difference in treatment, but that in the first case $KI_3 \cdot H_2O$ was the solid phase while in the other the solid was only potassium iodide, so that Johnson's method of analysis is not discredited.

The failure of their x-ray measurements (7) to show any lines other than those due to potassium iodide is difficult to understand and the experiments should be repeated employing analysed samples under very carefully controlled conditions, for, as has been shown earlier, the triiodide decomposes at a low temperature, and potassium iodide is the solid decomposition product.

OTHER SOLVATED POLYIODIDES

Other solid solvated polyiodides of the alkali metals are known: $KIBr_2 \cdot H_2O$, $NaICl_4 \cdot 2H_2O$, $LiICl_4 \cdot 4H_2O$, and $HICl_4 \cdot 4H_2O$ (a hydrogen polyhalide) have been reported by Wells and Weeler (8), Cagliotti (9), Cremer and Duncan (10), and others. The first two of the above polyhalides have been shown to exist in both the hydrated and anhydrous states, while the hydrogen compound and the polyiodides of potassium appear to exist only in the solvated state (i.e., the combined solvent appears to be essential for the existence of these compounds in the solid state). In view of these solvated polyhalides it seemed of interest to investigate further the alkali polyiodides which have been reported in the literature, paying particular attention to the possibility of solvation and the conditions which favor the formation of such solvated compounds.

THREE SOLID POLYIODIDES OF CESIUM

Two solid polyiodides of cesium have been prepared from water solution and their composition studied by Wells and his associates (11) and others. One compound was definitely shown to be the triiodide, while the other was first believed to be a pentaiodide. Briggs, Greenawald, and Leonard (12a), and Briggs (12b) from studies of the ternary system iodine–cesium iodide–water, and of the binary system iodine–cesium iodide have shown the higher polyiodide to be a tetraiodide (CsI_4) and not a pentaiodide.

Rae (13) from a study of the rate of loss of iodine from a fused mixture of iodine and cesium iodide, over sodium hydroxide, finds a sharp change in the loss curve when the composition of the solid corresponds with CsI_4.

Abegg and Hamburger (14) studied the ternary system iodine–cesium iodine–benzene at 25°C., employing methods similar to those adopted with potassium iodide. Three ternary invariant solutions were found which were considered to be in equilibrium with (1) CsI and CsI_3, (2) CsI_3 and CsI_5 (or CsI_7) (3) CsI_5 (or CsI_7) and CsI_9. These results, while agreeing with those of other workers for the triiodide, *disagree regarding the composition of the polyiodide intermediate in iodine content, and an enneaiodide is reported, which has not been found by other investigators.*

The experimental data from which Abegg and Hamburger deduce the composition of the intermediate polyiodide are in reality in favor of this compound being a tetraiodide rather than a penta-or hepta-iodide. In their table 12 (15) the most concentrated ternary invariant (0.563 *N*) was shown to exist in equilibrium with solids whose composition might be varied between $CsI_{4.8}$ and CsI_9. When the solid phase had reached the composition of the enneaiodide no further change in its composition was noted while the solution was raised to 1.04 *N* (saturation with respect to iodine being 1.09 *N*). This indicates cesium enneaiodide as the highest polyiodide present at the invariant 0.563 *N*. This invariant was, however, obtained when the solid phase had a composition $CsI_{4.8}$, which indicates that the intermediate polyiodide contains less iodine than a pentaiodide (since no mixture of CsI_9 and CsI_5 could produce a composition of $CsI_{4.8}$). Their tables 13 and 14 (reference 14, pages 423 and 424) are similar, and show that at the next lower invariant (0.170 *N*) the two solids present are CsI_3 and a compound richer in iodine than the triiodide. These experiments therefore indicate that the intermediate polyiodide contains more iodine than a triiodide and less than a pentaiodide—i.e., is a *tetraiodide*, which agrees with the conclusions of Briggs and his associates.

Abegg and Hamburger appear to have been influenced in the interpretation of their own results regarding the composition of this polyiodide, partly by the work of Wells and his coworkers (8), who had reported a pentaiodide, and also by the analogy with rubidium and potassium (since they had obtained heptaiodides of these two metals). They therefore assumed that the cesium compound must be either a penta- or hepta-iodide, without considering the possibility of a tetraiodide. Indeed a tetrahalide does not seem probable, for in the analogous compounds the total number of halogen atoms is odd—e.g., CsI_3, $CsBr_3$, $CsIBr_2$, $CsICl_2$, $CsICl_4$, etc.; this tetraiodide is the first compound which apparently contains an even number. Although Rae (16) has reported evidence indicating the existence of cesium tetrabromide, Cremer and Duncan (17) in experiments similar to those of Rae found no evidence for a polybromide[3] more complex than $CsBr_3$. Considering the apparent uniqueness of the tetraiodide it seemed desirable to study it further and in particular to determine whether it contained combined solvent (as this seemed a possible explanation of its unusual composition), and at the same time to check the tri- and ennea-iodides.

PREPARATION OF CESIUM IODIDE

Cesium chloride was prepared from finely ground pollucite, following the procedure described by Harned and Schupp (18). The chloride was converted to the acid sulfate by heating strongly with sulfuric acid in a platinum dish. The sulfate was removed by the addition of the calculated quantity of freshly recrystallized $2BaI_2 \cdot 15H_2O$. Evaporation of the filtrate yielded cesium iodide, which was further purified by one recrystallization from water. This product was dried, at first gently and then at 200°C., and ground to a powder. Duplicate analyses (as silver iodide) gave an iodine content corresponding to 99.81 and 99.87 per cent of that of pure cesium iodide.

CESIUM TRI- AND TETRA-IODIDES

Samples of cesium tri- and tetra-iodides were prepared from water solution by the methods outlined by Briggs, Greenawald, and Leonard (12a). Samples of each, plus a minimum quantity of mother liquor, were placed in weighing bottles and loss of moisture over phosphoric oxide determined. In each case a steady loss (about 0.1 gram per day) was maintained as long as mother liquor was present and then the loss dropped suddenly to practically nothing (0.0002 gram per day) at which point specimens were analyzed for moisture by the complete method described earlier (1). The results in neither case showed more than 0.10 per cent moisture to be present, which indicates that these two polyiodides exist unsolvated and that they do not form stable hydrates. The mean of two analyses for the higher polyiodide gave CsI, 40.68 per cent; polyiodide I_2,

---

[3] Since this work was completed Harris (J. Chem. Soc. 1932, 1694) has demonstrated the existence of the interesting compound $2KBr_6 \cdot 3H_2O$, which contains an even number of halogen atoms.

59.24 per cent (0.08 per cent H_2O); and a CsI to I_2 ratio of 1:1.49, which is in good agreement with $CsI \cdot 1.5\ I_2$.

THE SYSTEM IODINE–CESIUM IODIDE–BENZENE AT 25°C.

Experiments were carried out in a manner similar to those with potassium iodide (reference 1, page 605), with the exception that the containing bottles were not rotated, but merely immersed up to the neck in a thermostat; the lack of stirring, caused by the absence of rotation, did not appear to materially affect the rate of attainment of equilibrium, since rate of reaction at the solid liquid interphase seems to be the governing factor in this respect. The state of subdivision of the solid phase was found to be the chief factor influencing the rate of reaction. The alkali iodide was therefore ground to a very fine powder before the experiments were commenced.

TABLE 1

The formation of solid polyiodides of cesium by the removal of iodine from benzene solution

DAYS	NORMALITY	DAYS	NORMALITY
Experiment No. 1 CsI, 3.04 grams	Benzene, 50 cc. I_2, 7.05 grams	Experiment No. 2 CsI, 2.01 grams	Benzene, 100 cc. I_2, 16.57 grams
0.2	0.950	7	0.936
11	0.475	12	0.872
18	0.435	19	0.812
24	0.415	25	0.782
36	0.400	40	0.740
50	0.399*	55	0.710
		70	0.705*
Experiment No. 3 CsI, 2.00 grams	Benzene, 50 cc. I_2, 12.50 grams		
12	0.770		
22	0.747		
33	0.743*		

* Equilibrium value.

The invariant solutions in equilibrium with the solid phases (1) CsI, CsI_3 and (2) CsI_3, CsI_4 were redetermined and values of 0.00338 N and 0.170 N, respectively, obtained at 25°C. These values are almost identical with those obtained by Abegg and Hamburger. ($N/100$ thiosulfate was employed in determining the lower value).

Table 1 (see also figure 1) contains the data concerning the preparation of the cesium polyiodides. In experiment 1 when equilibrium was established the solid phase had a composition $CsI \cdot 1.5\ I_2$ (by synthesis), while in experiments 2 and 3 the solid phase present at equilibrium had an iodide to iodine ratio very close to 1:4.0. Samples of each of the polyiodides prepared in this manner were placed in isoteniscopes (described earlier) and the benzene pressures maintained at 25°C. determined. Neither the tri- nor the tetra-iodide maintained a constant benzene pressure, while analyses of the samples showed no combined benzene to be present. The tetraiodide gave CsI 40.32 per cent and polyiodide iodine 59.52 per cent, or CsI : 1.51 I_2, which confirms the composition of the unsolvated tetraiodide. The enneaiodide, on the other hand, maintained a constant benzene pressure of 32 mm., showing the presence of combined benzene. This pressure was maintained until nearly all the benzene had been removed, for as soon as the pressure fell appreciably analysis showed the sample to contain 99.8 per cent iodine plus iodide.

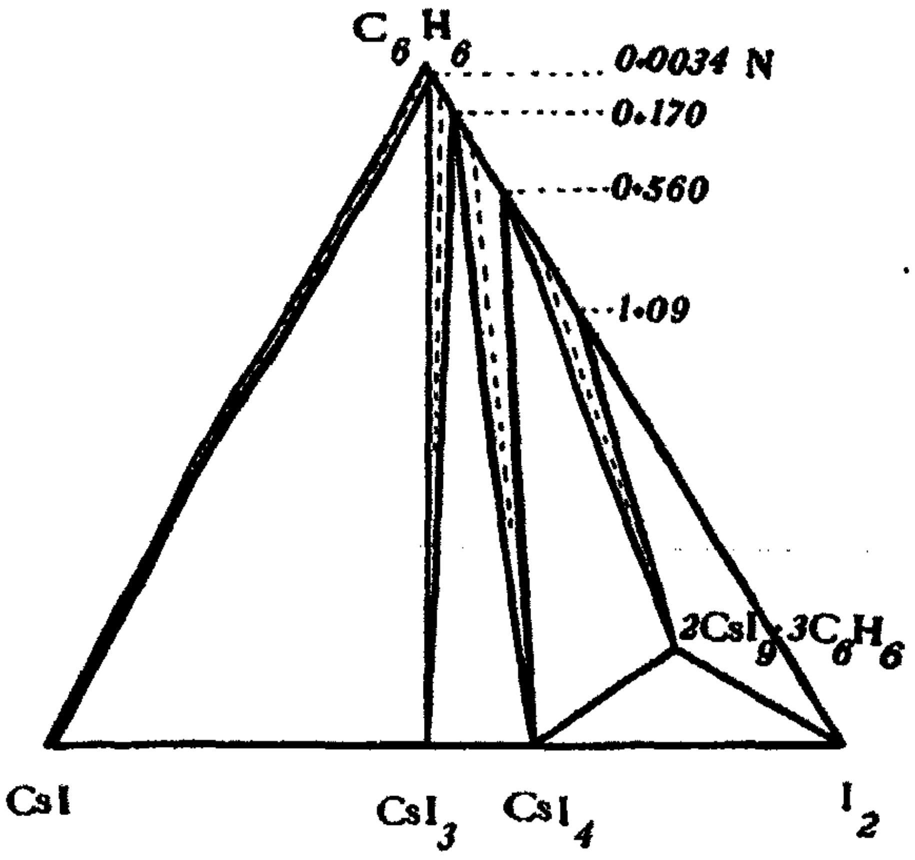


FIG. 1

To determine the number of molecules of combined benzene, samples of the enneaiodide were placed in isoteniscopes and benzene slowly removed until the constant pressure of 32 mm. was first reached, and then the isoteniscopes were opened and the samples rapidly transferred for analysis. Five analyses on the two preparations of the enneaiodide (experiments 2 and 3, table 1) gave concordant results, indicating this compound to have the composition $CsI_9 \cdot 1.5C_6H_6$, i.e., $2CsI_9 \cdot 3C_6H_6$. Two typical analyses, by the usual method, gave for the per cent of CsI, 18.61 and 18.65, mean 18.63; polyiodide iodine 73.58 and 73.26, mean 73.42 and (by difference) 7.95 per cent benzene; this corresponds with CsI:4.03I_2:1.42C_6H_6.

These results support the existence of two unsolvated polyiodides of cesium, CsI_3 and CsI_4, and the enneaiodide solvated with benzene. The equilibrium conditions at 25°C. of these three compounds in the ternary system in which benzene is the solvent are indicated in figure 1.

SOLID POLYIODIDES OF RUBIDIUM

Wells and Wheeler (8) prepared rubidium triiodide from aqueous solution, while Foote and Chalker (19), from a study of the ternary system iodine–rubidium iodide–water at 25°C. found only the triiodide. Abegg and Hamburger (14) studied the ternary system iodine–rubidium iodide–benzene at 25°C. and found three invariant solutions which they considered to be in equilibrium with (1) RbI and RbI_3, (2) RbI_3 and RbI_7, and (3) RbI_7 and RbI_9 respectively. From analogy with the results obtained with cesium and potassium it seemed most probable that the rubidium hepta- and ennea-iodides, which had not been reported in the aqueous system, would be found to contain combined benzene, and that they owed their existence to this fact.

TABLE 2

The preparation of polyiodides of rubidium at 25°C.

DAYS	NORMALITY	DAYS	NORMALITY
Experiment No. 1 RbI, 0.80 gram	Benzene, 50 cc. I_2, 3.50 grams	Experiment No. 3 RbI, 1.30 grams	Benzene, 50 cc. I_2, 12.54 grams
10	0.400	11	1.070
20	0.400*	18	1.050
		25	1.030
Experiment No. 2 RbI, 1.188 grams	Benzene, 50 cc. I_2, 9.02 grams	35	1.025
		50	1.023*
3	0.900		
10	0.804		
17	0.774		
30	0.768		
40	0.767*		

* Equilibrium value.

Rubidium iodide of reagent quality was obtained from Hopkins and Williams and an attempt was made to prepare the three polyiodides reported by Abegg and Hamburger, employing a method similar to that used in the case of 2 $CsI_9 \cdot 3C_6H_6$ (details in table 2). In experiment No. 1 at equilibrium the solid phase consisted of RbI and I_2 in the ratio 1:1.00, i.e., RbI_3. Some of this material in an isoteniscope maintained no constant benzene vapor pressure, while analysis showed no combined benzene. (By analysis this solid had the composition $RbI \cdot 0.99I_2$.)

Experiments 2 and 3 (table 2) are in agreement with the results of Abegg and Hamburger and indicate rubidium hepta- and ennea-iodides, respectively, as the solid phases present at equilibrium. Measurements at 25°C.

showed these two compounds to have very nearly the same benzene dissociation pressures, being 61.5 and 60.0 mm., respectively; however, measurements over a temperature range indicated that these two compounds had independent dissociation pressure curves. From the equilibrium diagram, figure 2, it is seen that the heptaiodide, on the removal of benzene, breaks down into triiodide plus enneaiodide, which accounts for the heptaiodide having the higher benzene dissociation pressure at 25°C., although at this temperature it has the lower iodine dissociation pressure.

Combined benzene was determined by difference by the usual method. For the heptaiodide were found RbI, 18.52 and 18.67, mean 18.59; I_2, 68.40 and 68.71, mean 68.55; total 87.14; benzene, 12.86 per cent; this

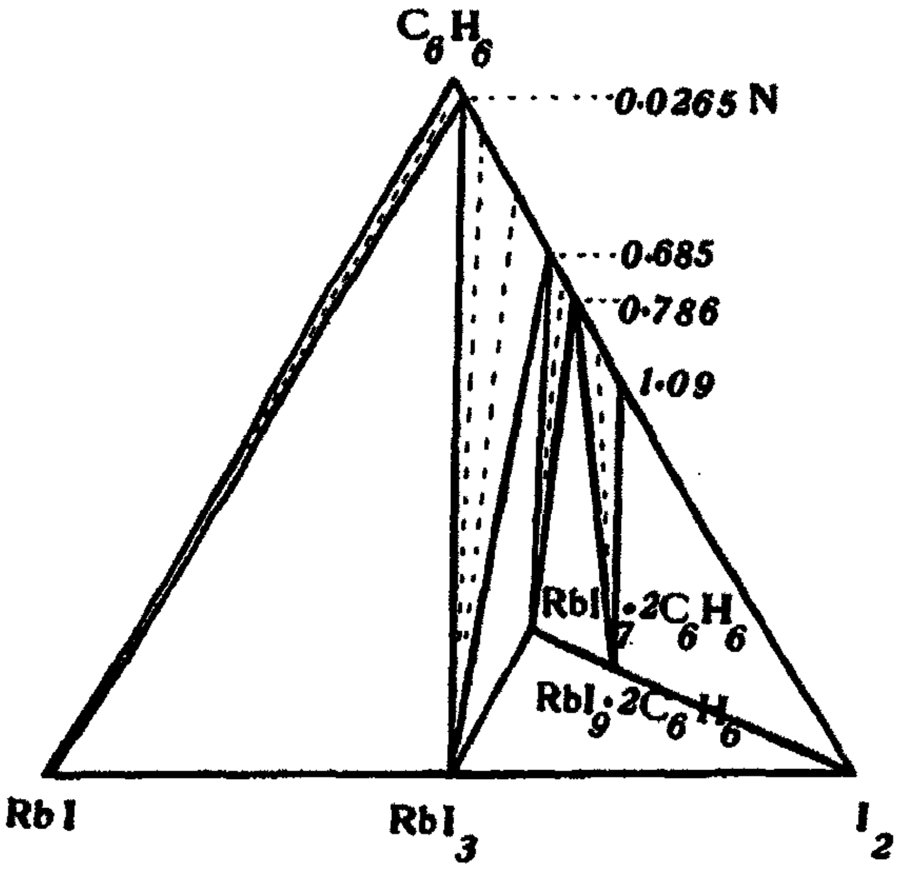


FIG. 2

corresponds with $RbI:3.08I_2:1.88C_6H_6$, or $RbI_7 \cdot 2C_6H_6$. The enneaiodide gave on analysis RbI, 15.53 and 15.31, mean 15.42; I_2, 73.12 and 73.68, mean 73.40; benzene, 11.18 per cent; this corresponds with $RbI:3.98I_2:1.97C_6H_6$ or $RbI_9 \cdot 2C_6H_6$.

The invariant solutions when (1) RbI_3 and $RbI_7 \cdot 2C_6H_6$ and (2) $RbI_7 \cdot 2C_6H_6$ and $RbI_9 \cdot 2C_6H_6$ were the solid phases, were redetermined and mean values of 0.680 and 0.782 respectively obtained, which do not agree too well with 0.690 and 0.790 *N* of Abegg and Hamburger. We may take a mean of the two different sets of observations as the best values which would give 0.685 and 0.786 *N*.

These results indicate three solid polyiodides of rubidium, one unsolvated, RbI_3, and two solvated with benzene, $RbI_7 \cdot 2C_6H_6$ and $RbI_9 \cdot 2C_6H_6$.

The equilibrium conditions of these compounds at 25°C. are shown in figure 2.

The results obtained indicate the existence of *only three unsolvated* polyiodides of the alkali metals, the triiodides of rubidium and cesium and a tetraiodide of the latter. This shows the tetraiodide to be the highest unsolvated polyiodide formed by the alkali metals at 25°C.

POTASSIUM ENNEAIODIDE

The results obtained with rubidium and cesium confirm Abegg and Hamburger that enneaiodides of these two metals exist at 25°C. (both compounds containing combined benzene). Abegg and Hamburger consider the heptaiodide to be the highest polyiodide of potassium stable at 25°C. and indeed give some evidence that an enneaiodide does not exist; however, a close examination of their work shows that their experiments were not sufficiently critical to justify a definite conclusion on this point.

The existence of enneaiodides of cesium and rubidium suggested that a similar compound of potassium might be formed. In one experiment containing 1.66 grams of potassium iodide, 16.16 grams of iodine, and 50 cc. of benzene, the normality of the solution (after approaching equilibrium for two months) was 1.03, so that the solid present had an iodide to iodine ratio of 1 to 3.9, while the same material gave on analysis (mean of three) KI, 11.53, I_2, 72.56, and benzene (by difference) 15.90 per cent, which corresponds with $KI:4.11I_2:2.94C_6H_6$ or $KI_9 \cdot 3C_6H_6$. This material at 25°C. had a benzene dissociation pressure of 52 mm.

The composition of this polyiodide agrees with that obtained by Foote and Bradbury (20). Foote and Bradbury found only one solid ternary compound $KI_9 \cdot 3C_6H_6$ in the system iodine–potassium iodide–benzene at 25°C. and 6°C.; however, the author has obtained some evidence indicating two ternary compounds. The strongest evidence in favor of two ternary compounds comes from dissociation pressure measurements where two different constant benzene pressures were observed on removal of benzene (one at 52 mm. and the other at 50 mm. at 25°C.). Further work is necessary on this point.

It should be mentioned that the experimental method employed by Foote and Bradbury, where they used glass beads or porcelain chips which in a shaker greatly hastened attainment of equilibrium, is probably superior to the method of the author, for they found equilibrium attained in three days (or less) whereas in the work described here often a matter of a month or more was necessary and even then one could not be quite sure that true equilibrium was actually reached, the difficulty being greatest in dealing with the equilibrium conditions of the most complex polyiodides.

POLYIODIDES OF SODIUM AND LITHIUM

The work of Abegg and Hamburger (14), in which neither solid sodium nor lithium iodide remove iodine from a nearly saturated solution of iodine in benzene at 25°C., indicates that no solid polyiodides of these two metals, either unsolvated or solvated with benzene, exist at this temperature. From the general trend of the polyiodides of the metals of higher atomic weight it is not surprising to find no unsolvated polyiodides of either sodium or lithium (since there appear to be none of potassium, one of rubidium, and two of cesium). However, potassium enneaiodide solvated with benzene is just a little more stable than that of rubidium, so that it would appear significant that this stability is not continued with sodium or lithium.

In dilute solution the presence of sodium triiodide has been deduced by J. S. Carter (21) at 25°C., while in more concentrated solutions higher polyiodides are considered also to be present. In our study an aqueous solution, saturated with both sodium iodide and iodine at 25°C., was evaporated slowly. Two distinct types of crystal separated; the one less dense than the solution was shown to be $NaI \cdot 2H_2O$, while the other which was more dense was iodine alone. Similar results were obtained with lithium iodide. These experiments indicate that any polyiodides present in solution at 25°C. are not stable in the solid phase. Possibly one might express this another way by saying that at 25°C. the stable form of sodium and lithium hydrated polyiodides may be not solid but liquid. This viewpoint is supported by the fact that $KI_3 \cdot H_2O$ begins to melt at about 31°C.; so that above 31°C. and atmospheric pressure solid potassium triiodide would not be found. Consequently, experiments with sodium iodide were tried at lower temperatures where it was thought that a hydrated polyiodide might be stable in the solid phase.

TABLE 3

Analyses of sodium triiodide

TEMPERATURE OF PREPARATION	SOLID PLUS ADHERING MOTHER LIQUOR			MOTHER LIQUOR		
	NaI	I_2	H_2O	NaI	I_2	H_2O
degrees C.						
10.6	30.40	53.80	15.79	30.15	53.45	16.31
10.6	30.32	53.81	15.90	30.10	53.41	16.51
11.6	31.02	53.47	15.63	30.42	53.72	15.89
11.6	31.12	53.40	15.53	30.42	53.72	15.89
Theory for $NaI_3 \cdot 4H_2O$	31.51	53.36	16.13			

An aqueous solution saturated with both sodium iodide and iodine was gradually cooled from room temperature; little change was apparent till a temperature of 11.8°C. was reached, when the solution became filled with fine blue-black needles, while the temperature remained nearly constant. By first cooling the solution down to 12°C. and removing any iodine or sodium iodide which separated, it was found possible to prepare a fairly homogeneous sample of the needles. After being freed as much as possible from mother liquor (the complete removal of mother liquor being impossible due to its viscosity and the very fine nature of the crystals) the needles melted almost completely at 11.8°C. The analyses (by complete method) for some preparations are given in table 3.

These results show that at 11.6°C. mother liquor and the solid separating have very nearly the same composition; however the solid is slightly richer in sodium iodide and poorer in water content. The mean composition of the solid separating at 11.6°C. corresponded to $NaI:1.02I_2:4.18H_2O$, which is quite close to $NaI_3 \cdot 4H_2O$.

Definite proof of the existence (and composition) of solid hydrated sodium polyiodides was sought in a phase rule study at 0°C. This study was attempted without using a mechanical shaker because of the difficulties involved at that temperature and since the equilibrium solutions were very much less concentrated than in the case of potassium polyiodides it was hoped that shaking would be unnecessary; however, equilibrium in the solutions richest in iodine was approached too slowly to permit an accurate study in the time available. The results obtained are therefore not quantitative, but in a qualitative manner support the existence of at least one solid polyiodide of sodium at 0°C., the composition of which is possibly $NaI_3 \cdot 4H_2O$.

Similar even more preliminary experiments with lithium iodide indicated the existence of at least one solid hydrated polyiodide of lithium which melts about 10°C. The results with sodium and lithium, while not being sufficiently definite to stand alone, are of interest since they fit in well with the trend shown by the polyiodides of the alkali metals of higher atomic weight, for potassium forms low-melting hydrated polyiodides, while rubidium and cesium form no such hydrated compounds. In this connection one might be permitted to speculate regarding the existence of polyiodides of hydriodic acid. Their existence in solution has been demonstrated by many workers. In the solid state, however, none have been isolated. Considering the general behavior of the polyiodides of the alkali metals one might predict that at a very low temperature solid hydrated polyiodides of hydrogen may be isolated.

ENNEAIODIDES THE HIGHEST POLYIODIDES

Enneaiodides of potassium, rubidium, and cesium have been kept in contact with iodine solutions in benzene which are nearly saturated (1.09 *N*) without any indication of a polyiodide higher than an enneaiodide being formed. However, in the nearly saturated solutions it would be difficult to detect a slow change. The evidence is therefore not quite conclusive, but indicates strongly that the enneaiodides are the most complex solid polyiodides of these three metals under the above conditions.

The work of Strömholm (22), Geuther (23), Chattaway and Hoyle (24), and others, seems to show that enneaiodides are the highest solid polyiodides of the quaternary ammonium salts such compounds as $N(CH_3)_4I_9$, $N(C_2H_5)(CH_3)_3I_9$ and $N(C_2H_5)_4I_7$ being reported. These compounds are also of interest in that they are apparently unsolvated (although no complete analyses are given), while the higher polyiodides of the alkali metals do not exist unless they contain combined solvent molecules. This difference between polyiodides of the alkali metals and those of the quaternary ammonium salts may be explained on the *hypothesis of relative ionic size*. This hypothesis (discussed in detail in a later publication) suggests that in ionic crystals (both ions monovalent) one of the factors influencing stability is relative ionic size—greater stability occurring when anion and cation are nearly equal in radius rather than when they are very unequal. In the substituted ammonium polyiodides there is a large cation (e.g., $N(CH_3)_4^+$) and also a large anion I_9^-, whereas in unsolvated polyiodides of the alkali metals there would be a very great difference between a small metal ion (K^+) and the very large I_9^- ion. This difference in size might be more or less made up by the packing of benzene molecules around the cation. This hypothesis is supported by CsI_9 containing one and one-half, RbI_9 two, and KI_9 three molecules of benzene, so that the smaller the cation the greater the number of benzene molecules. However, sodium and lithium (which ions usually most readily form solvated compounds) do not form stable polyiodides solvated with benzene. This failure of sodium and lithium would indicate that the formation of polyiodides solvated with benzene by the other alkali metals did not occur through the formation of covalent links between alkali ion and benzene molecules, but that the benzene molecules are only necessary to fill in the space lattice. Energies of formation of these compounds have been measured by dissociation pressure methods and found to be very nearly zero, which is further evidence that the benzene present is merely filling in the space lattice, i.e., that these solid polyiodides (solvated with benzene) are *lattice compounds*.

This study shows that potassium (as is usual) occupies a position intermediate between rubidium and cesium on the one hand and sodium and lithium on the other. For potassium forms solid polyiodides solvated with either water or benzene (none unsolvated), rubidium and cesium form polyiodides both unsolvated and solvated with benzene (none with water), while sodium and lithium probably form (at temperatures below 12°C.) solid polyiodides solvated with water (none unsolvated or solvated with benzene at 25°C.). In the interpretation of these differences there are two distinct factors to be considered: (a) the size or mass of the alkali ion,

(b) the nature of the solvent. It is not inconceivable that some such method as this may be of use in studying the properties of different solvents. An x-ray study of those polyiodides containing benzene would be useful and might lead to interesting results.

SUMMARY

1. At 25°C. and 1 atmosphere there are only three true binary polyiodides of the alkali metals, RbI_3, CsI_3, and CsI_4; the tetraiodide of cesium is the most complex binary compound.

2. The other solid polyiodides of the alkali metals reported have been shown to contain combined solvent and the presence of solvent is essential for the existence of these polyiodides in the solid state.

3. Ternary compounds in the systems iodine–alkali iodide–benzene have been shown to be: $2CsI_9 \cdot 3C_6H_6$, $RbI_9 \cdot 2C_6H_6$, $RbI_7 \cdot 2C_6H_6$ and that of the highest polyiodide of potassium $KI_9 \cdot 3C_6H_6$. The most complex ternary compounds appear to be enneaiodides.

4. Neither sodium nor lithium form solid polyiodides, unsolvated or solvated with water or benzene at 25°C., while evidence is presented that at temperatures lower than 25°C. these two metals probably form solid polyiodides solvated with water.

5. At 25°C. potassium forms solid polyiodides solvated with either water or benzene (none unsolvated), rubidium and cesium form polyiodides both unsolvated and solvated with benzene (none with water), while sodium and lithium probably form solid polyiodides solvated with water (at temperatures below 12°C.) and none unsolvated or solvated with benzene.

6. It is suggested that these differences may be correlated with (a) relative ionic size and (b) the nature of the solvent (third component).

The author wishes to express his sincere gratitude to Professor H. B. Baker, C.B.E., D.Sc., F.R.S., for his kindly interest during the work and to Mr. G. H. Cheeseman, B.Sc., for valuable suggestions. Grateful acknowledgment is made of a Beit Scientific Research Fellowship, during the tenure of which the experimental part of this paper was carried out.

REFERENCES

(1) Grace: J. Chem. Soc. **1931**, 594.
(2) Reference 1, page 596.
(3) Bancroft, Scherer, and Gould: J. Phys. Chem. **35**, 764 (1931).
(4) Reference 3, page 772.
(5) Reference 1, page 602.
(6) Reference 3, page 774.
(7) Reference 3, page 778.
(8) Wells and Wheeler: Z. anorg. Chem. **1**, 442 (1892).
(9) Cagliotti: Atti accad. Lincei **9**, 563 (1929).
(10) Cremer and Duncan: J. Chem. Soc. **1931**, 2243.

(11) Reference 8, pages 86 and 442.
(12) (a) BRIGGS, GREENAWALD, AND LEONARD: J. Phys. Chem. **34**, 1951 (1930).
(b) BRIGGS: J. Phys. Chem. **34**, 2260 (1930).
(13) RAE: J. Phys. Chem. **35**, 1800 (1931).
(14) ABEGG AND HAMBURGER: Z. anorg. Chem. **50**, 422 (1906).
(15) Reference 14, page 423.
(16) RAE: J. Chem. Soc. **1931**, 1578.
(17) CREMER AND DUNCAN: J. Chem. Soc. **1931**, 1865.
(18) HARNED AND SCHUPP: J. Am. Chem. Soc. **52**, 3886 (1930).
(19) FOOTE AND CHALKER: Am. Chem. J. **39**, 561 (1908).
(20) FOOTE AND BRADBURY: J. Phys. Chem. **36**, 673 (1932).
(21) CARTER: J. Chem. Soc. **133**, 2227 (1928).
(22) STRÖMHOLM: J. prakt. Chem. **66**, 423, 517 (1902); **67**, 345 (1903).
(23) GEUTHER: Ann. **240**, 66 (1887).
(24) CHATTAWAY AND HOYLE: J. Chem. Soc. **124**, 654 (1923).

A NEW METHOD FOR OBTAINING DATA FOR THE SORPTION OF VAPORS BY SOLIDS

J. L. PORTER

Department of Chemistry, Stanford University, Stanford University, California

Received December 11, 1932

A technique for obtaining sorption data more simply and rapidly than those ordinarily used has been developed for the sorption of vapors by solids. It arose by following up an idea suggested by two sentences found in papers by Cude and Hulett (1) and by Tryhorn and Wyatt (2), respectively. Cude and Hulett filled charcoal with water to get the pore space, not the sorption. Tryhorn and Wyatt noticed that the weight of benzene in charcoal when the visible liquid surface had just disappeared by evaporation was the same as that obtained by exposure to fully saturated vapor. However, the significance of their results is left uncertain, since in both cases capillary liquid might equally well have been present. The only test would be to compare the values obtained by wetting and superficial drying of so microporous a body as charcoal with values obtained for the sorption isotherm for distinctly unsaturated vapor. The same comment applies to any powder.

EXPERIMENTAL METHOD

The solid was placed in a commercial microfilter tube[1] with a sintered glass filter from which the excess liquid could be removed by suction or by centrifuging. As the liquid must be introduced on to the evacuated solid, the filter, A in figure 1, was placed in a bulb B with a ground glass joint C to the stopcock D through which the liquid could be introduced. The bulb and tube with stopcock was joined to the vacuum line by a ground glass joint E.

About a gram of the material to be used was placed in the filter and in certain cases washed with water, which was removed by suction and centrifuging. Weighings were taken of the bulb, tube, and filter separately and of the filter and the solid material. The solid was evacuated with heating by an electric furnace around the lower part of the bulb. The tube and bulb were detached at E and weighed, giving the weight of the evacuated solid. The liquid to be introduced was placed in the upper part

---

[1] Jena Geräte glass, size 12, porosity 4, 1 centimeter inside diameter, Fish-Schurman Corporation, New York City.

of the tube and slowly admitted through the stopcock. In order to prevent the liquid from washing any stopcock grease down on to the solid, the lower bulb was cooled and the upper tube warmed so that the liquid vaporized into the bulb and condensed on the solid in the lower part of the bulb. When the solid was covered with liquid, the bulb was opened at C, the filter removed, and the excess liquid centrifuged off. In certain cases suction was applied for a few seconds to remove liquid from the sintered glass. The filter with the solid and the sorbed liquid was weighed in a weighing bottle and from these values the amount sorbed at saturation was calculated. An isotherm was determined by evacuating to a definite pressure and reweighing. The solid could be reëvacuated and the experiment repeated with the same or other liquids.

TABLE 1

Maximum amount of various liquids retained at 23°C. by dehydrated chabasite in the centrifugal method

SUBSTANCE	a/m	CUBIC CENTIMETERS PER GRAM	MOLECULAR VOLUME
Water	0.323	0.324	18
Formamide	0.088*		33
Formic acid	0.473†	0.386	37
Methyl alcohol	0.268‡	0.339	40
Ethylene oxide	0.056		49
Methyl cyanide	0.048		51

* Mean of 0.078, 0.099, and 0.087.
† Mean of 0.485 and 0.461.
‡ Mean of 0.268, 0.272, 0.270, and 0.263.

EXPERIMENTS WITH CHABASITE[2]

It was most interesting to begin with a crystalline solid containing no pores in the ordinary sense of the word. The zeolites (3) are hydrated calcium aluminum silicates which can give up their water of hydration on evacuation or heating without destroying the crystal form of structure. The spaces left by the water may be filled indifferently by any molecule small enough to enter. They then form, as McBain (4) pointed out and as is now generally accepted, almost perfect molecular sieves or semipermeable membranes of great regularity. Evans (5) quotes Taylor (6) to the effect that the water molecules in chabasite lie on non-intersecting triagonal axes of the cubic space group. No other atoms lie on these axes, so there are long channels passing through the structure wide enough to accommodate fairly large molecules and empty of everything but water molecules.

---

[2] $CaAl_2Si_4O_{12} \cdot 6H_2O$ subject to slight variation due to base exchange. Theory gives 21.3 per cent of water, but G. Friedel (Bull. soc. franç. minéral. **22**, 5 (1889)) found 22.28 per cent.

The chabasite crystals were washed with water before weighing, as in the routine described. It was found that evacuation for twenty-four hours at 350°C. brought the chabasite to constant weight at 10^{-6} cm. of mercury. The average of nine values gave 24.4 per cent of water lost by the chabasite. Expressed as ratio of weight of water to weight of dehydrated chabasite, $x/m = 0.323$. The results with liquids are summarized in table 1.

As is seen from table 1, the two substances with the largest molecular volume are taken up only to a small fraction of the extent of water, methyl alcohol, and formic acid. The small amount of formamide indicates that mere molecular volume is not the sole determining factor. The shape and composition of the molecule must also be of importance.

Formic acid has a small molecular volume, but it also attacks the chabasite and a deposit is observed on the filter. A sample of chabasite, used first with formic acid, was used again with water, which it took up to the extent of 28.5 per cent as compared with the original 24.4 per cent. This enlargement of the sorption space is fully adequate to account for the higher value of formic acid sorbed.

The heat of sorption of methyl alcohol by chabasite is considerable, the filter and glass bulb being observed to heat up to above 60°C., a much greater effect than was observed with charcoal and far too great to be explained as heat of compression.

Rapid sorption of methyl alcohol vapor by chabasite disintegrates the crystals to a powder, owing to the sudden unequal heating and expansion.[3] The heat on rapid sorption may decompose the alcohol and change the colorless crystals to yellowish-black. It was found impossible to desorb all the alcohol, and if the temperature were raised above 400°C. during evacuation, the crystals became yellow or black.

EXPERIMENTS WITH CHARCOAL

The charcoal was highly active (82 per cent)[4] air and steam activated charcoal made from especially pure sugar. It was covered with two thicknesses of silver foil pierced with fine holes and was evacuated for several days at 500°C. and 10^{-5} cm. of mercury. The volumes of liquid sorbed at 28°C. at saturation pressure or just below were 0.59 cc. of benzene, 0.6 cc. of water, and 0.61 cc. of acetic acid per gram of charcoal.

ISOTHERMS

It is possible to obtain isotherms by this method, especially on desorption, as a manometer in the vacuum system gives the pressure after partial

---

[3] Compare the observation of M. G. Evans (Proc. Roy. Soc. London **A134**, 97 (1931)) on the disintegration by ammonia vapor.

[4] One gram of 200 mesh charcoal sorbs in three minutes from 50 cc. of a 0.2 *N* aqueous solution of iodine in 0.27 *N* potassium iodide, 82 per cent; method of N. K. Chaney, A. B. Ray, and A. St. John (Ind. Eng. Chem. **15**, 1244 (1923)).

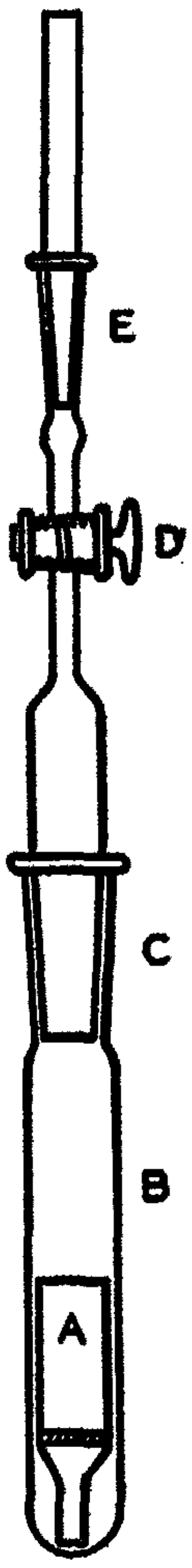


Fig. 1

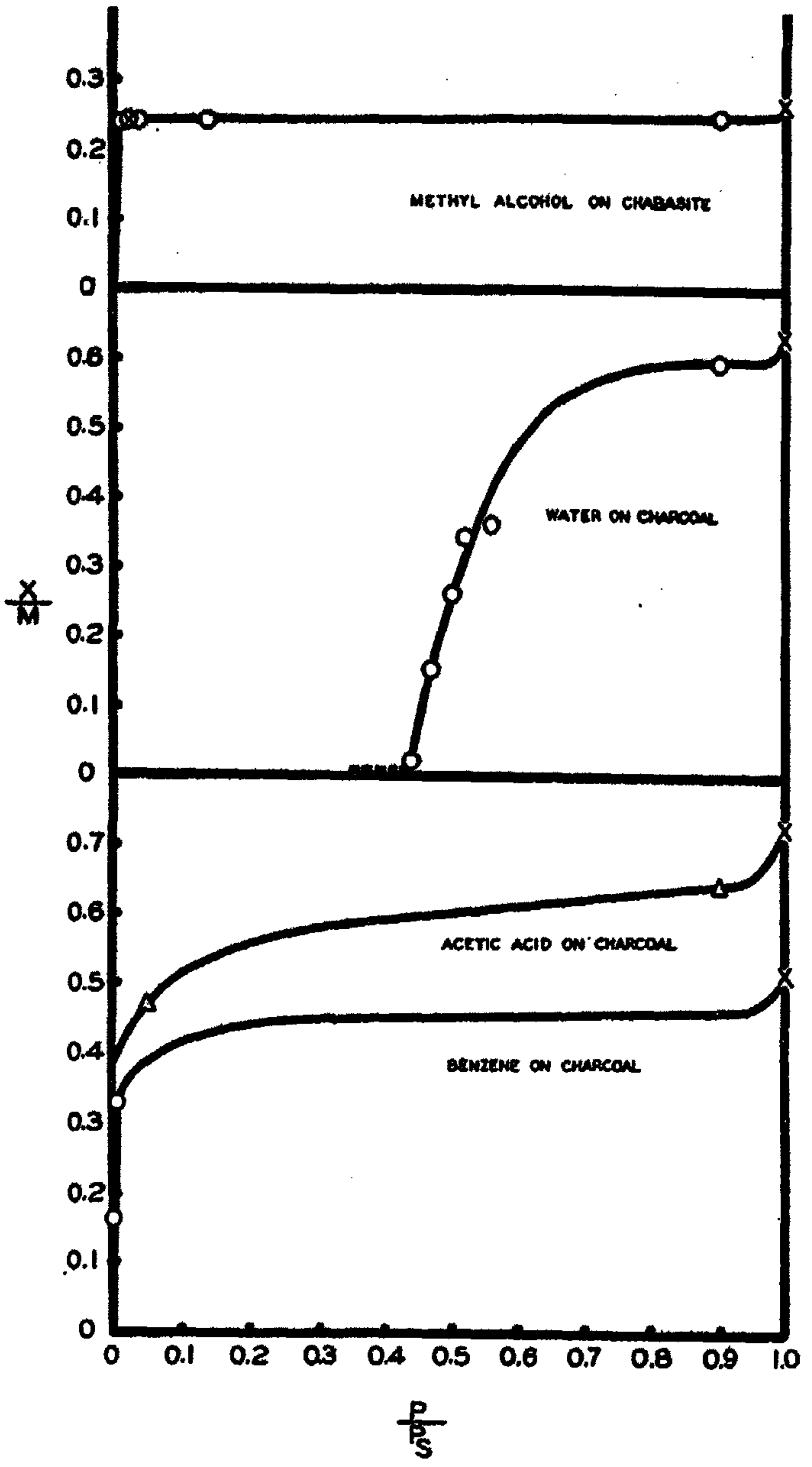


Fig. 2

Fig. 1. The Filter Tube Apparatus for Measuring Sorption
Fig. 2. Isotherms by the Filter Tube Method

evacuation, and at any stage the stopcock in the tube may be closed and the bulb, tube, and filter removed and weighed without exposing the solid to the atmosphere.

The results are shown in figure 2. Inspection of the isotherms for methyl alcohol and the crystalline chabasite reveals the ideal form of isotherms for uniform "surfaces."[5] It is even more rectangular than those obtained with highly evacuated, active charcoal (7). Here, therefore, is most definite proof of persorption and not condensation of capillary liquid. The isotherms for acetic acid and benzene on charcoal likewise show that sorption is far advanced at infinitesimal pressures.

The isotherms for the sorption of water by charcoal are of a wholly different type, owing to formation of a two-dimensional liquid permeating the charcoal, the water molecules being held as much by mutual polarization as by attachment to the charcoal (8). Comparison of these isotherms with those for organic vapors on the same charcoal shows them to be due to sorption, or rather persorption, in both cases and that the isotherms with water cannot be interpreted as measuring the volume and distribution of the assumed pores of the charcoal. Inspection of the extreme right hand of each diagram in figure 2 shows the small additional amount of liquid held by capillary condensation in each case, an amount which is only a minute fraction of the total sorption.

SUMMARY

A simple method for the rapid and moderately accurate study of sorption of liquids and vapors by solids is described. Sorption isotherms obtained with a molecular sieve, dehydrated chabasite, are nearly rectangular, even more so than those for organic vapors with highly activated charcoal where the sorption goes largely to completion at infinitesimal pressures. The sorption of water, although of a different type, is likewise interpreted as persorption and definitely not as capillary condensation.

In conclusion my thanks are due to Professor J. W. McBain at whose suggestion this work was undertaken.

REFERENCES

(1) Cude, H. E., and Hulett, G. A.: J. Am. Chem. Soc. 42, 398 (1920), footnote 1.
(2) Tryhorn, F. G., and Wyatt, W. F.: Trans. Faraday Soc. 22, 137 (1926).
(3) For more complete references and discussion, see McBain, J. W.: The Sorption of Gases and Vapours by Solids, Chapter V, page 167. George Routledge and Sons, Ltd., London (1932).

---

[5] A. S. Coolidge (J. Am. Chem. Soc. 49, 712 (1927), figure 3) has published a very similar result, ascribed to J. C. Woodhouse, for the sorption of water by chabasite.

(4) McBain, J. W.: Colloid Symposium Monograph **4**, 1 (1926); Kolloid-Z. **40**, 1 (1926).
Schmidt, O.: Z. physik. Chem. **133**, 280 (1928).
(5) Evans, M. G.: Proc. Roy. Soc. London **A134**, 97 (1931).
(6) Taylor, W. H.: Z. Krist. **74**, 1 (1930). See also Pauling, L.: Proc. Nat. Acad. Sci. **16**, 453 (1930).
(7) McBain, J. W., Lucas, H. P., and Chapman, P. F.: J. Am. Chem. Soc. **52**, 2668 (1930).
McBain, J. W., Jackman, D. N., Bakr, A. M., and Smith, H. G.: J. Phys. Chem. **34**, 1439 (1930).
McBain, J. W., and Britton, G. T.: J. Am. Chem. Soc. **52**, 2198 (1930).
(8) For much further evidence, see McBain, J. W., Porter, J. L., and Sessions, R. F.: Communicated to J. Am. Chem. Soc.; also reference 3, p. 143.

THE INTERACTION OF ETHYL ALCOHOL AND OXYGEN PHOTOSENSITIZED BY HYDROGEN PEROXIDE

A Contribution to the Haber-Willstätter Mechanism of Enzyme Reactions

HUGH S. TAYLOR AND AUSTIN J. GOULD

Frick Chemical Laboratory of Princeton University, Princeton, New Jersey

Received February 6, 1933

For the enzymotic oxidation of ethyl alcohol, Haber and Willstätter (1) postulate the following mechanism:

$$CH_3CH_2OH + \text{Enzyme} = CH_3\overset{/}{C}H(OH) + \text{Monodesoxy-enzyme} + H^{\cdot} \tag{a}$$

$$CH_3\overset{/}{C}H(OH) + CH_3CH_2OH + O_2 = 2CH_3CHO + OH + H_2O \tag{b}$$

$$OH + CH_3CH_2OH = CH_3\overset{/}{C}H(OH) + H_2O \tag{c}$$

Some light may be thrown upon the possibility of such a mechanism by a study of the effect of the introduction of OH radicals into an aqueous alcohol solution in the presence of oxygen. If the postulated mechanism is the correct one, the chain would then be started at step (c) and the reaction continue as a chain reaction. Since Haber and Willstätter also give a similar mechanism for the oxidation of acetaldehyde in which the OH radical is again the active link in the chain,

$$CH_3CHO + \text{Enzyme} = CH_3\overset{/}{C}O + \text{Monodesoxy-enzyme} + H^{\cdot} \tag{a'}$$

$$CH_3\overset{/}{C}O + CH_3CHO + H_2O + O_2 = 2CH_3COOH + OH \tag{b'}$$

$$OH + CH_3CHO = CH_3\overset{/}{C}O + H_2O \tag{c'}$$

it is to be expected that the oxidation of the acetaldehyde formed in the alcohol oxidation will occur as a secondary process.

One convenient method for introducing OH radicals is to decompose photochemically hydrogen peroxide which has been added to the alcohol solution. The question as to whether the first step in the hydrogen peroxide decomposition is the formation of OH or of HO_2 is not pertinent in this connection (2). In either case OH is ultimately one of the products of the decomposition. If HO_2 is formed in the first step, OH is formed in the next step.

$$HO_2 + H_2O_2 = H_2O + OH + O_2$$

The evidence will tend to favor the mechanism of Haber and Willstätter if the oxidation process under these conditions is found to be a chain reaction.

EXPERIMENTAL

The apparatus used has been described elsewhere (3). It consisted of a quartz reaction vessel mounted on a horizontal shaker running at 265 oscillations per minute, immersed in a water thermostat. With the exception of those for the determination of the temperature coefficient, all runs were made at 25 ± 0.05°C. The reaction vessel was connected by a short piece of suction tubing to a Hulett gas burette (4) filled with water. The source of illumination was a horizontal, air-cooled, laboratory model, Hanovia mercury arc operating at 60 ± 1 volts and 4 ± 0.05 amperes mounted outside the thermostat directly in front of a quartz window in the side of the thermostat.

The general procedure was to fill the apparatus with oxygen, add 25 to 30 cc. of the liquid sample to the shaker, shake a few minutes until temperature equilibrium was attained, and then to start the reaction by removing the shutter from in front of the quartz window. Tank oxygen was used. The hydrogen peroxide was obtained by diluting "Superoxol" with water. Since check runs using 95 per cent alcohol obtained by diluting absolute ethyl alcohol with water gave the same rates of reaction as those made with commercial 95 per cent ethyl alcohol, the commercial alcohol was used in the experiments without further purification. Unless otherwise specified, all data refer to 95 per cent ethyl alcohol.

When the reaction products were to be determined, the liquid product was removed from the shaker, diluted to 250 cc. with water, and analyses made on aliquot portions. The amount of acid was determined by titration with 0.05 *N* NaOH, peroxide by titration with 0.1 *N* thiosulfate of the iodine liberated from acid potassium iodide solution, and aldehyde by the Ripper method (5) after the solution from the determination of peroxide had been made neutral with sodium hydroxide solution. Appropriate blank analyses were made in every case.

RESULTS

Photochemical oxidation of alcohol

It was first necessary to determine if alcohol itself was oxidized photochemically in the presence of oxygen. Reports in the literature by various workers differ on this point. Several workers (6) have found that alcohol and oxygen do not react when illuminated, while Dhar and Sanyal (7) report that a small amount of acetaldehyde was formed when moist alcohol and oxygen were exposed to sunlight for an hour. In some preliminary experiments made with an aged, water-cooled Kromayer mercury arc, it was found that no appreciable amount of oxygen was taken up on illuminating alcohol with oxygen over a period of ten hours. When the Hanovia lamp was used as a source of illumination, however, the absorption of oxygen was marked, as shown by curve A of figure 1. The analysis of the product is given in table 1. The product gave a blue color with chromic acid and ether. Since Clover and Richmond (8) have shown that neither peracetic acid nor organic peroxides give this test, hydrogen peroxide must have been formed in the oxidation. All attempts to find peracetic acid according to the method of D'Ans and Frey (9) and to that described by

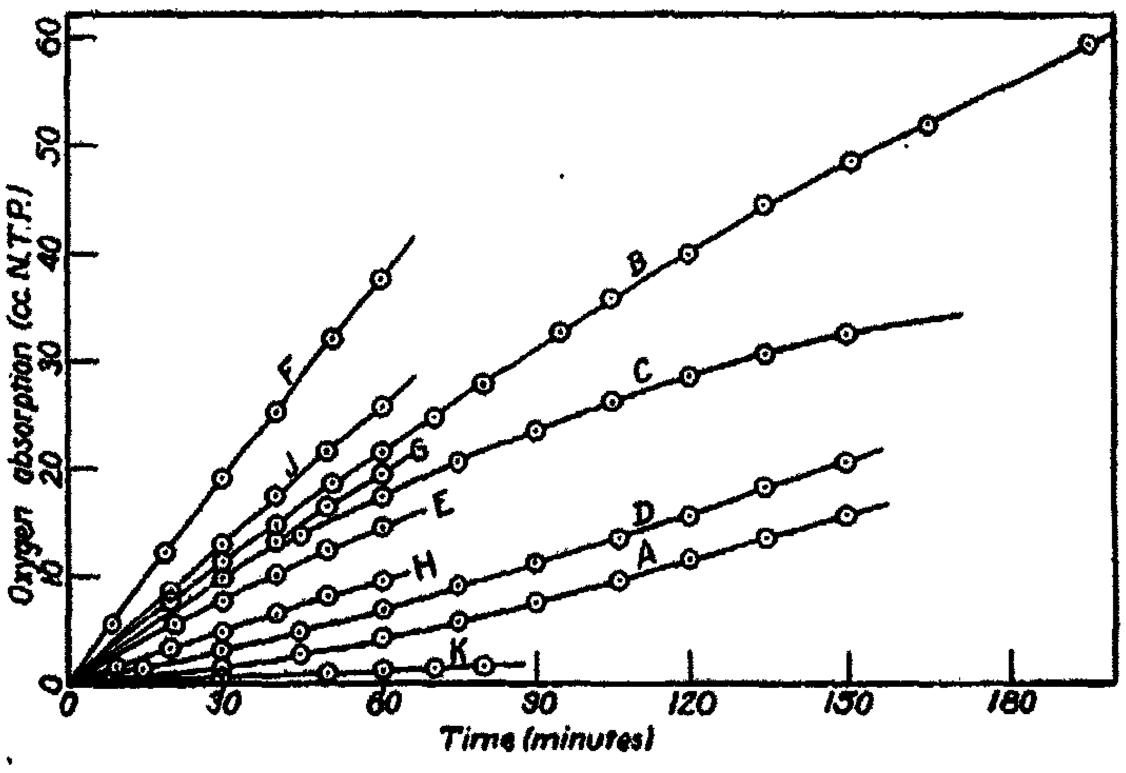


FIG. 1. RATE OF OXIDATION OF ETHYL ALCOHOL

A. 25 cc. alcohol.
B. 25 cc. alcohol and 0.81 millimole hydrogen peroxide.
C. B − A.
D. 25 cc. alcohol and 1.98 millimoles acetaldehyde.
E. 25 cc. alcohol and 0.48 millimole hydrogen peroxide.
F. 25 cc. alcohol and 4.75 millimoles hydrogen peroxide.
G. 25 cc. alcohol, 4.75 millimoles hydrogen peroxide, and 0.074 millimole ethylamine.
H. 25 cc. alcohol, 4.75 millimoles hydrogen peroxide, and 0.74 millimole ethylamine.
J. 25 cc. 50 per cent alcohol and 4.75 millimoles hydrogen peroxide.
K. 25 cc. alcohol and 0.74 millimole ethylamine.

Bäckström (10) gave negative results. As may be seen from the rate curve, the rate was autocatalytic in nature. To determine if this increasing rate were due either to the accumulation of acetaldehyde or of acetic acid, runs were made with alcohol to which had been added acetaldehyde and acetic acid separately in quantities comparable to those formed in the oxidation with alcohol alone. The rate with added acetic acid was practically the same as with alcohol alone, while, as may be seen from curve D, figure 1, the rate with added acetaldehyde is somewhat faster, but is also increasing with time. As before, hydrogen peroxide was identified in the product. The autocatalytic rate, therefore, is probably due to the formation and accumulation of hydrogen peroxide.

Oxidation of alcohol photosensitized by hydrogen peroxide

In order to be sure that the photochemical oxidation of alcohol with added hydrogen peroxide was a true photosensitized process and not one of direct oxidation of the alcohol by the peroxide, it was necessary to show that hydrogen peroxide, alcohol, and oxygen do not react unless illuminated. Although Renard (11) had shown that such a reaction does not occur, the reaction was tried using 0.81 millimole of hydrogen peroxide and 25 cc. of alcohol without illumination. No appreciable absorption of oxygen was noted over a period of eight hours.

TABLE 1

Analyses of products (millimoles)

	A 25 CC. ALCOHOL	B 25 CC. ALCOHOL + 0.81 MILLIMOLES HYDROGEN PEROXIDE	C 25 CC. ALCOHOL + 1.98 MILLIMOLES ACETALDEHYDE
Acid	0.39	2.10	0.58
Aldehyde	0.60	2.01	2.07
Peroxide	0.14	0.50	0.25
Oxygen absorbed	0.70	2.95	0.92

When alcohol–hydrogen peroxide solutions were illuminated, the rate of oxygen absorption was rapid (curves B, E, and F of figure 1) and decreased with time. As shown in column B of table 1, the amount of peroxide found in the product was less than that initially added.

With 4.75 millimoles of added hydrogen peroxide, the rate of oxygen absorption was not so fast with 50 per cent alcohol solution as it was with 95 per cent alcohol solution (compare curves F and J of figure 1).

The determination of the rates of reaction with 4.75 millimoles of added peroxide at 0°, 25°, and 35°C. gave temperature coefficients for this reaction of 1.06 and 1.13 per 10° rise.

Effect of inhibitors on the alcohol oxidation

Chain reactions are characterized by the marked decrease in rate produced by the addition of small quantities of inhibitors. For this reason, the effect of inhibitors on the reaction was studied. The addition of 0.74 millimole of ethylamine decreased the rate of the photochemical oxidation of alcohol in the absence of peroxide to about one-fourth (curve K, figure 1) and 2.2 millimoles of benzene reduced it to about one-half.

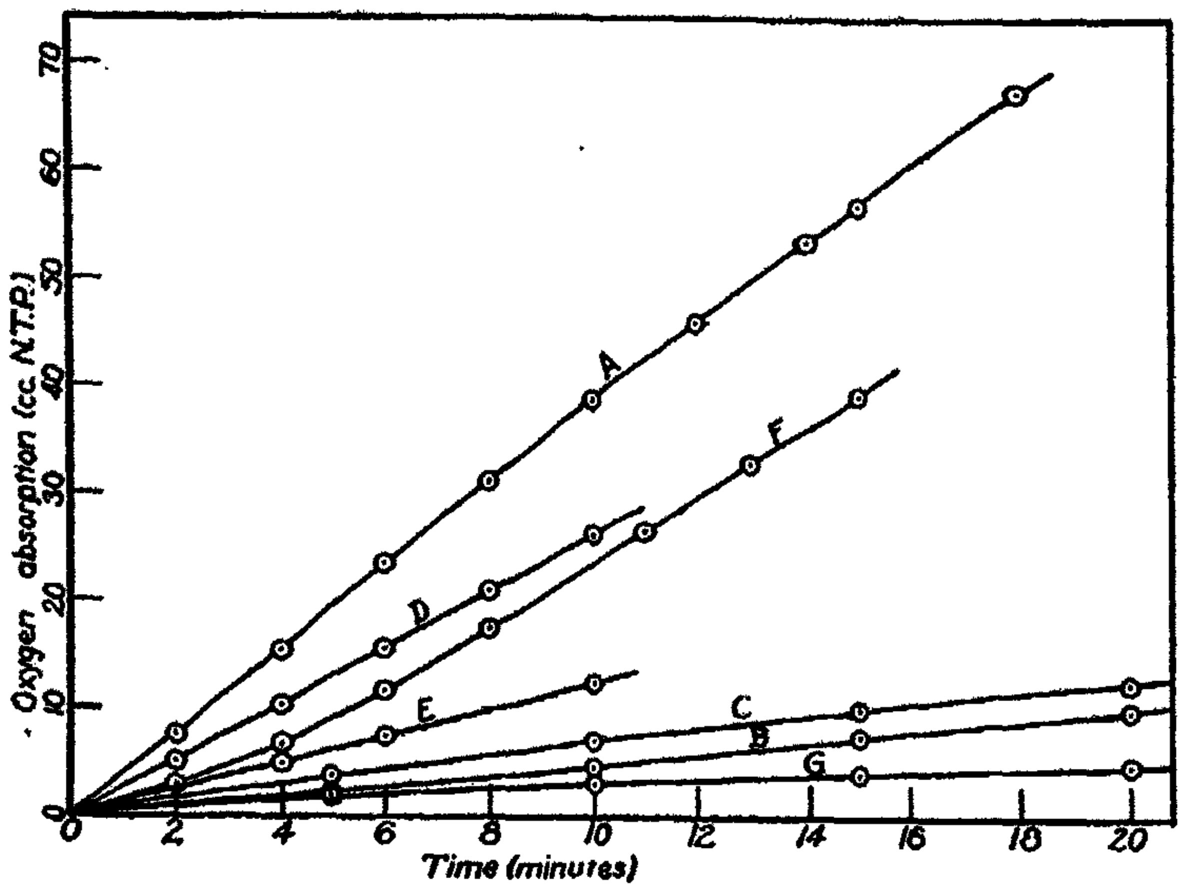


FIG. 2. RATE OF OXIDATION OF AQUEOUS ACETALDEHYDE SOLUTIONS

A. 25 cc. 10 per cent acetaldehyde.
B. 25 cc. 1 per cent acetaldehyde.
C. 25 cc. 1 per cent acetaldehyde and 0.9 millimole hydrogen peroxide.
D. 25 cc. 10 per cent acetaldehyde and 1 cc. 95 per cent alcohol.
E. 25 cc. 10 per cent acetaldehyde and 5 cc. 95 per cent alcohol.
F. 25 cc. 10 per cent acetaldehyde and 0.074 millimole ethylamine.
G. 25 cc. 10 per cent acetaldehyde and 0.74 millimole ethylamine.

As curves F, G, and H of figure 1 show, the addition of 0.07 millimole of ethylamine to 25 cc. of alcohol solution containing 4.75 millimoles of hydrogen peroxide reduced the rate to about one-half, while the addition of 0.74 millimole of ethylamine reduced the rate to about one-fourth of its original value.

Using 0.95 millimole of hydrogen peroxide in 25 cc. of alcohol, the addition of 0.1 millimole of benzylamine reduced the rate to about one-fifth and 0.5 millimole of benzylamine reduced the rate to about one-tenth of its original value. Like quantities of hydroquinone, ethylamine, diphenylamine, and benzene were found to exhibit similar inhibitory effects.

When the oxidation with 0.95 millimole of hydrogen peroxide was allowed to proceed for about an hour before the inhibitor was added, the rate was markedly retarded as before, but in this case the rate slowly increased until it had practically reached its original value at the end of another hour.

Oxidation of aqueous acetaldehyde solutions

The photochemical oxidation of aqueous acetaldehyde solutions was studied in order to determine what effect the acetaldehyde formed might have on the alcohol oxidation. With 25 cc. of a 10 per cent (by volume) solution, the rate of oxidation was very rapid (figure 2). The addition of 0.9 millimole of hydrogen peroxide did not increase the rate. With a 1 per cent solution of acetaldehyde, the rate was much slower. In this case the addition of 0.9 millimole of hydrogen peroxide did increase the rate.

Ethylamine and ethyl alcohol inhibited the oxidation, the alcohol being much less efficient as an inhibitor than the amine (figure 2).

DISCUSSION

Since no photochemical oxidation of alcohol was noted when the Kromayer lamp was used, but a marked reaction found with the Hanovia lamp, the variation in the results reported by different workers on the photochemical oxidation of ethyl alcohol may probably be ascribed to differences in the intensities of the light sources used.

Curve C of figure 1 was obtained by subtracting curve A from curve B and represents, therefore, the amount of oxygen absorption due to the added 0.81 millimole of hydrogen peroxide. This curve may be seen to be approaching an asymptotic value of some 40 cc. of oxygen, which is equivalent to about 1.8 millimoles. Since the ratio of moles of oxygen absorbed to moles of hydrogen peroxide used is greater than two, this result indicates a minimum chain length greater than one, assuming that two OH radicals are obtained from each hydrogen peroxide molecule decomposed and that every OH initiates a chain. These assumptions obviously may be incorrect, but such a calculation does give a minimum value for the chain length. If the first step in the hydrogen peroxide decomposition is HO_2, the minimum chain length is then increased by a factor of four. At the time when the slopes of curves A and B become equal, the concentration of hydrogen peroxide will have reached a steady state at which its rate of formation is equal to its rate of decomposition.

Since ethylamine absorbs light only very weakly and that in a region between 2190 and 2480 Å. (12), the possibility that the inhibitory action of this substance might be due to a light screening effect is excluded.

Furthermore, the effect cannot be due to a destruction of the hydrogen peroxide by the amine because of the large ratio of the amount of peroxide present to that of the amine (4.75 to 0.074). Such marked decrease in rate of reaction can only be due to the existence of a chain reaction. The amount of inhibition is not great enough, however, to indicate a long chain. This conclusion is concordant with the previous calculation of minimum chain length. The observation that no retardation occurs when an otherwise efficient inhibitor is added to the system after reaction has proceeded for some time is not new (13). Such behavior is usually ascribed to the formation during the oxidation of peroxides which destroy the inhibitor.

The fact that the addition of 0.9 millimole of hydrogen peroxide to a 10 per cent solution of acetaldehyde did not increase the rate of oxidation is as one would expect. Since acetaldehyde has a high absorption coefficient over a wide range (14), one would expect the hydrogen peroxide to be well screened in such a concentrated solution of acetaldehyde. That the rate of oxidation of the 1 per cent solution is increased by the addition of peroxide indicates that, at this concentration, some of the light is being absorbed by the hydrogen peroxide molecules which decompose and enter into the oxidation. As shown by curves F and G of figure 2, the effect of ethylamine as an inhibitor is great. Curves D and E of figure 2 show that ethyl alcohol is an inhibitor of the aldehyde oxidation, but not a very good inhibitor. This fact explains why it is that the acetaldehyde formed in the alcohol oxidation is not immediately oxidized, but rather accumulates and may be identified in the product.

Bowen and Tietz (15) concluded that an organic peroxide, probably diacetyl peroxide, is formed when gaseous, liquid, or dissolved acetaldehyde is exposed in presence of oxygen to ultra-violet light, but that in aqueous solutions the peroxide will have reacted and disappeared at the end of twenty seconds. They also showed that the oxidation of acetaldehyde was a chain reaction and found that alcohol acted as an inhibitor when added to hexane solutions of acetaldehyde. From their results one would expect that, even if a peroxide were first formed in the oxidation of acetaldehyde in a 95 per cent aqueous alcohol solution, the peroxide would immediately react to form acetic acid which would be the oxidation product found.

All of the experimental evidence indicates that the oxidation of alcohol photosensitized by hydrogen peroxide is a chain reaction, but that the chains are short ones. It is of interest to note that Alyea and Bäckström (16) in their work on the inhibitory action of alcohols on the sodium sulfite oxidation found that their data could best be explained by assuming that if the oxidation of alcohol were a chain reaction, the chains were short ones. Under their experimental conditions the chain length of the alcohol oxidation would be even shorter than in the present case.

It is clear that these considerations do not prove that the Haber-Willstätter mechanism is correct. They do show, however, that the concept of a chain mechanism for the oxidation of ethyl alcohol is a justifiable one. Moreover, all of the experimental results reported in this paper may be satisfactorily interpreted by this mechanism.

SUMMARY

1. With an intense source of light, and in contact with oxygen, ethyl alcohol is oxidized photochemically, the process being auto-accelerating in nature.

2. The oxidation of alcohol by oxygen may be photosensitized by hydrogen peroxide.

3. Such an oxidation is a chain reaction with short chain length.

4. The photo-oxidation of aqueous acetaldehyde solutions is a chain reaction with longer chain length.

5. A chain mechanism such as that of Haber and Willstätter involving hydroxyl radicals as intermediates in the chain is compatible with the experimental results.

REFERENCES

(1) Haber and Willstätter: Ber. **64**, 2844 (1931).
(2) Urey, Dawsey, and Rice: J. Am. Chem. Soc. **51**, 1371 (1929).
Allmand and Style: J. Chem. Soc. **1930**, 596, 606.
(3) Alyea: Thesis, Princeton University.
(4) Taylor and Burns: J. Am. Chem. Soc. **43**, 1274 (1921).
(5) Kingscott: Methods of Quantitative Organic Analysis, p. 118, Longmans, Green and Company, London (1914).
(6) Ciamician and Silber: Ber. **46**, 3894 (1912).
Sernagiotto: Atti accad. Lincei, **28**, I, 432 (1919); Chem. Abstracts **14**, 1672 (1920).
(7) Dhar and Sanyal: J. Phys. Chem. **29**, 926 (1925).
(8) Clover and Richmond: Am. Chem. J. **29**, 179 (1903).
(9) D'Ans and Frey: Ber. **45**, 1848 (1912).
(10) Bäckström: Medd. Vetenskapsakad. Nobelinst. **6**, No. 15, 9 (1927).
(11) Renard: Ann. chim. phys. [5] **16**, 289 (1880).
(12) Bielecki and Henri: Compt. rend. **156**, 1861 (1913).
(13) Wagner and Brier: Ind. Eng. Chem. **23**, 49, 662 (1931).
(14) Bielecki and Henri: Compt. rend. **155**, 456 (1913).
(15) Bowen and Tietz: J. Chem. Soc. **1930**, 234.
(16) Alyea and Bäckström: J. Am. Chem. Soc. **51**, 90 (1929).

THE AUTOXIDATION OF STANNOUS CHLORIDE. III

The Photochemical Reaction[1]

ROBERT C. HARING and JAMES H. WALTON

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received January 4, 1933

In the preceding paper (1) the thermal reaction of stannous chloride with atmospheric oxygen was discussed, and evidence given to show that it is probably a thermal chain reaction similar to the autoxidation of sodium sulfite and of benzaldehyde, investigated by Bäckström (2) and Alyea and Bäckström (3). In order to secure further proof of the chain mechanism of the autoxidation of stannous chloride, the effect of visible and ultra violet radiation on the reaction was investigated.

APPARATUS

The apparatus used was similar to that used in the studies of the thermal reaction. A reaction flask was made from a quartz tube of 1½ inches inside diameter, and 7 inches long. Indentations were made in the bottom, as was done with the glass flasks, to insure a better agitation. It was found impracticable to use a flask exactly like those of glass (1) with a bulb in the lower part. The quartz flask did not give a high enough area of gas-liquid interface to keep the solution saturated with oxygen and thus give the same reaction velocity as determined in the glass flasks, but it gave reproducible results, and thus allows a comparison of the results with positive catalysts and inhibitors.

The light source used was a capillary mercury vapor lamp of the type described by Daniels and Heidt (4). This lamp gives a high intensity in the ultra-violet region, and allows more accurate measurements than a low intensity lamp.

Some absorption measurements were made on the quartz monochromator described by Heidt and Daniels (5). Spectrograph work was done by means of a Krüss quartz spectrograph equipped with a single 60° prism.

ABSORPTION SPECTRUM OF STANNOUS CHLORIDE

Preliminary experiments having shown that ultra-violet radiation was effective in speeding up the autoxidation of stannous chloride, it was neces-

---

[1] This research was financed by a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman.

sary to determine what wave lengths were active in causing this result. The absorption spectrum for the stock solutions of stannous chloride (32 grams per liter of $SnCl_2$; 0.8 *N* in HCl) was determined on the spectrograph, and it was found that the region of complete absorption extends up to 3000 Å. Decreasing the concentration of stannous chloride shifts the limit of complete absorption toward the lower wave lengths.

CORRECTION FACTOR FOR POLYCHROMATIC LIGHT

The monochromator was not suitable for the full set of experiments on quantum yield, using a shaken cell, and no filter could be arranged which would give a high transmission of the mercury line at 3020 Å. and still shut out all lines at 3130 Å. and higher, so that it was necessary to use polychromatic light in these experiments. The light intensity in the quantum yield experiments was determined by the use of the uranyl oxalate actinometer described by Leighton and Forbes (6). A weighted average quantum yield of 0.553 was calculated for the range of wave lengths used, from the data given in their article on quantum yields for monochromatic light. In the determination, the uranyl oxalate actinometer was shaken at the same speed in the same flask as was used for stannous chloride in order to give comparable results. Since the range of absorption of uranyl oxalate and stannous chloride is different it was necessary to determine a correction factor to be applied to the number of quanta obtained by the actinometer. This factor was obtained by the use of two similar quartz cells in series. The actinometer solution was placed in the second cell. The first cell was filled successively with distilled water and stannous chloride stock solution, and the decomposition of the actinometer solution measured in each case. The ratio of the number of quanta absorbed by the stannous chloride to the number absorbed by uranyl oxalate was found to be 0.62 ±0.01. This factor was applied to all the runs with different lamps, since Daniels and Heidt have shown (4) that the distribution of energy in the ultra-violet region varies only slightly with the voltage at a constant wattage.

TABLE 1

Effect of light intensity on quantum yield

I_0	ϕ
quanta per minute	
$7.7\ (10)^{17}$	33.
5.2	29.
3.2	14.
2.0	12.

VARIATION OF QUANTUM YIELD WITH THE LIGHT INTENSITY

It is known that for many photochemical reactions the quantum yield ϕ varies with the intensity of the light. The variation in intensity was produced by different lamps and by varying the wattage of the lamps. Table 1 shows the effect on the quantum yield of the photochemical autoxidation of stannous chloride.

These intensities are given as the actual intensities causing reaction in the stannous chloride, that is, they are the actinometer intensities multiplied by the correction factor. The quantum yields are not accurate in the last figure, but two figures are given for comparison purposes.

The following sample of the calculations is given for reference.

Run No. 517

$$\text{“Light” reaction} = \text{Total} - \text{“dark” reaction}$$

$$= 7.86 - 0.86$$

$$= 7.00 \text{ cc. of } O_2 \text{ used in 22 minutes}$$

$$\frac{7.00}{22{,}400} \cdot \frac{716}{760} \cdot \frac{273}{298} \cdot \frac{2(6.06)\,(10)^{23}}{22} = 1.48(10)^{19} \text{ molecules of stannous chloride reacting per minute}$$

The actinometer solution decreased 2.80 cc. of 0.0328 *N* potassium permanganate in titer, after one hour exposure to the light.

$$\frac{(2.80)\,(0.0328)}{(1000)\,(60)\,(2)} \cdot \frac{(6.06)\,(10)^{23}\,(0.62)}{0.553} = 5.18(10)^{17} \text{ quanta per minute}$$

$$\phi = \frac{(1.48)\,(10)^{19}}{(5.18)\,(10)^{17}} = 28.6 \text{ molecules per quanta}$$

EFFECT OF CATALYSTS ON QUANTUM YIELD

If the thermal and photochemical reactions are completely analogous, accelerators and inhibitors should have the same effect on the photochemical reaction as on the thermal reaction. This is true for the catalysts used in the experiments. A few of the substances found to have pronounced effects on the thermal reaction were used, and gave the expected results as shown in table 2. It is to be noticed that picric acid, a strong inhibitor for the thermal reaction, reduces the quantum yield to almost exactly 1. The accelerators for the thermal reaction also accelerate the photochemical reaction as shown by the results. The last column of table 2 shows the relative effect of the catalysts used. In determining these values, the values for the quantum yield of the uncatalyzed reaction were interpolated from the results of table 1, expressed as a straight line proportionality between ϕ and I_0.

TABLE 2

Effect of catalysis on quantum yield

CATALYST	I_a	MOLECULES REACTING PER MINUTE	ϕ	PER CENT OF UNCATALYSED ϕ
	quanta per minute			
0.00002 *M* Picric acid	7.2 $(10)^{17}$	6.2 $(10)^{17}$	1.	3.
0.1 *M* Amyl alcohol	6.8	262.	39.	120.
0.1 *M* Allyl alcohol	6.1	266.	44.	150.
0.1 *M* Propionic acid	4.1	187.	46.	230.
0.002 *M* Thiourea	3.2	83.	26.	160.
0.065 *M* Hydroquinone	3.2	115.	36.	220.
0.065 *M* Catechol	3.2	86.	27.	170.
0.065 *M* Resorcinol	3.2	125.	39.	240.
1.75 *M* Isopropyl alcohol	3.2	140.	45.	280.
0.1 *M* *tertiary* Butyl alcohol	2.0	42.	21.	210.

TABLE 3

Test of Beer's law for stannous chloride solutions

SOLUTION	CONCENTRATION OF STANNOUS CHLORIDE	CONCENTRATION OF HYDROCHLORIC ACID	PER CENT LIGHT TRANSMITTED	α
	grams per liter	*grams per liter*		
a	3.0	6.0	87.6	6.5
b	8.0	16.0	66.7	7.4
c	13.0	26.0	37.9	10.9
d	21.0	42.0	8.4	17.2
e	31.0	62.0	1.0	21.8

BEER'S LAW STUDIES FOR STANNOUS CHLORIDE

In general, light-absorbing media follow Beer's law, which gives the variation in absorption of a given wave length with varying concentration and thickness of the absorbing layer.

$$\frac{I}{I_0} = e^{-\alpha c d}$$

Where I = the intensity of the transmitted light,
I_0 = the intensity of the incident light,
α = the molecular absorption coefficient,
c = the concentration (in moles per liter), and
d = the thickness of the layer.
(d = 1.3 cm. for the cell used).

Table 3 shows the results of these experiments on stannous chloride solutions. Hydrochloric acid was used to keep the stannous chloride from hydrolyzing, a constant ratio of hydrochloric acid to stannous chloride being used in all solutions. The wave length used was the 3130 Å. line, isolated by the use of the quartz monochromator. It can be seen that the value of α changes about threefold for a tenfold change in concentration of stannous chloride, showing that Beer's law does not hold. It was thus assumed that stannous chloride is not the absorbing medium. To test this hypothesis further, runs were made using a constant amount of stannous chloride with varying amounts of hydrochloric acid. The results are shown in table 4. In this case the value of α changes twelvefold for a thirty-sixfold change in the hydrochloric acid concentration. Hydrochloric acid alone shows no appreciable absorption at this wave length, so that the great change in α must be due to the influence of the hydrochloric acid on the stannous chloride. Thus the medium which absorbs the light quantum and becomes activated is not stannous chloride, nor the Sn^{++} ion, but must be some substance whose concentration *increases* with addition of hydrochloric acid to the system. The absorbing medium is thus either the complex chloro acid $HSnCl_3$ or H_2SnCl_4, or the ions $SnCl_3^{-}$ and $SnCl_4^{=}$ of those acids. That these complex ions are present in an acid solution was shown by Prytz (7).

TABLE 4

Effect of varying amounts of hydrochloric acid on the Beer's law constant

SOLUTION	CONCENTRATION OF STANNOUS CHLORIDE	CONCENTRATION OF HYDROCHLORIC ACID	PER CENT LIGHT TRANSMITTED	α
	grams per liter	*grams per liter*		
g	13.0	4.4	69.7	4.1
c	13.0	26.0	37.9	10.9
f	13.0	156.0	1.1	50.3

TABLE 5

Molecular absorption coefficient

Solution No. 10; 32.7 grams of stannous chloride per liter; 0.811 *N* hydrochloric acid

WAVE LENGTH	PER CENT LIGHT TRANSMITTED	α
2850 Å.	0.0	∞
3020	4.9	13.4
3130	28.4	5.6
3340	97.9	0.095
3650	100.0	0.0

MOLECULAR ABSORPTION COEFFICIENT

The molecular absorption coefficient was determined for a stannous chloride solution containing 32.7 grams of stannous chloride per liter and

0.811 *N* in hydrochloric acid, by use of the monochromator. Table 5 gives the results. These values of α are not applicable to other concentrations, because of the non-validity of Beer's law, but are included to show the range of partial and complete absorption.

SUMMARY

1. The autoxidation of stannous chloride is shown to be a photochemical chain reaction by the quantum yields of more than unity.

2. The photochemical and thermal reactions are affected similarly by accelerators and inhibitors; thus the hypothesis of a chain mechanism is supported for the thermal reaction.

3. Stannous chloride shows complete absorption below a certain limit; the limit is about 3000 Å. for the stock solutions used in the research, containing about 32 grams of stannous chloride per liter and being 0.8 *N* in hydrochloric acid, and is lower for more dilute solutions.

4. Stannous chloride was shown not to obey Beer's law. This was explained by the assumption that the complexes $HSnCl_3$ and H_2SnCl_4 are the active agents in absorbing the light, since the concentrations of these substances are increased by addition of hydrochloric acid to the system.

5. The molecular absorption coefficients for one stock solution are given, showing complete absorption of light at 2850 Å. and below, partial absorption from 3020 Å. to 3340 Å., and complete transmission at 3650 Å. and above.

REFERENCES

(1) Haring, Robert C., and Walton, James H.: J. Phys. Chem. **37**, 133 (1933).
(2) Bäckström, H. L. J.: J. Am. Chem. Soc. **49**, 1460 (1927).
(3) Alyea, H. N., and Bäckström, H. L. J.: J. Am. Chem. Soc. **51**, 90 (1929).
(4) Daniels, F., and Heidt, L. J.: J. Am. Chem. Soc. **54**, 2381 (1932).
(5) Heidt, L. J., and Daniels, F.: J. Am. Chem. Soc. **54**, 2384 (1932).
(6) Leighton, W. G., and Forbes, G. S.: J. Am. Chem. Soc. **52**, 3139 (1930).
(7) Prytz, M.: Z. anorg. Chem. **172**, 147 (1928).

MEASUREMENT OF THE RATE OF ADSORPTION AT CONSTANT PRESSURE

PAUL V. McKINNEY

Department of Chemistry, Rutgers University, New Brunswick, New Jersey

Received October 24, 1932

In the simplified formula for the process of adsorption as suggested by Langmuir, the rate of the process is dependent upon the pressure of the gas being adsorbed. For the simple case of a single gas the rate of condensation may be given by (1)

$$+\frac{dx}{dt} = k_1 p(1-\sigma)$$

and the rate of evaporation by

$$-\frac{dx}{dt} = k_2\sigma$$

Because of the importance of the measurement of the rate of adsorption in the determination of the activation energy (2) of the adsorption process, it was of interest to determine actually the significance of this pressure factor in the measurement. Most recent workers have used apparatus similar to that described by Pease (3). A quantity of gas is admitted and the velocity of adsorption is determined by the rate of pressure change. In one case reported the pressure actually decreased from 624 mm. to 235 mm. in 71 minutes. In the measurement of adsorption isotherms for which the process was devised, this change in pressure is of no consequence, since the process continues to equilibrium.

APPARATUS

The apparatus was constructed of Pyrex glass throughout and is illustrated in figure 1. Tube A containing the adsorbent was connected through a special stopcock with the gas burette E and manometer G. The traps B were cooled with solid carbon dioxide and ether. Capillary tubing was used except in the pump system. The manometer was arranged to act as a constant volume instrument and tungsten wire contacts were connected with a small electric light to serve as the indicator. The leveling bulb for the burette was supported by a wire over a pulley to a set of reducing gears. Thus the level of the mercury in the burette could be changed rapidly and with precision. In order to measure the rate of adsorption at constant pressure the manometer was adjusted to the reading for the pressure desired and the gas burette opened to the catalyst. The volume change of the process, at constant pressure, could be read directly from the burette each minute. By closing the burette after admission of the gas to be adsorbed this apparatus was also used to determine the adsorption at constant volume.

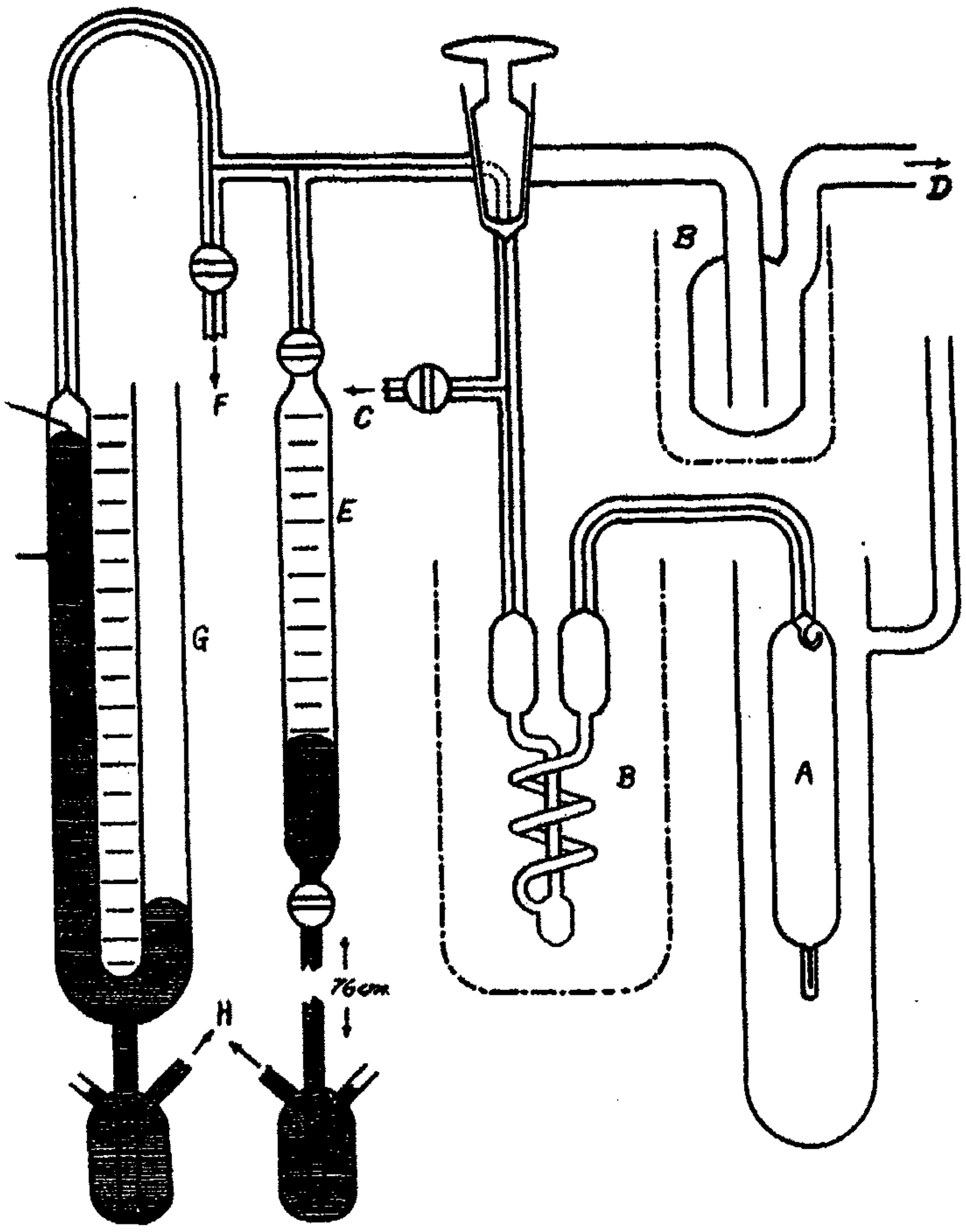


Fig. 1. Apparatus for the Measurement of the Rate of Adsorption

A, Adsorbent tube with boiler; B, traps cooled with carbon dioxide and ether; C, McLeod gage; D, mercury-vapor, Sprengle and oil pumps; E, gas burette; F, gas reservoirs and purification; G, constant volume manometer with electric contact; H, leveling bulbs.

VARIATION OF RATE WITH PRESSURE

A mixed oxide catalyst, MnO-Cr_2O_3, was selected to illustrate the effect of pressure on the rate of adsorption. For comparison the material was prepared as described by Taylor and Williamson (4). The data presented in table 1 and figure 2 was obtained on 24 grams of the mixed oxides. Be-

TABLE 1

Adsorption of hydrogen on a mixed oxide catalyst

24 grams of MnO-Cr_2O_3 at 132°C.

TIME	ADSORPTION NO. 3 VOLUME CONSTANT		ADSORPTION NO. 4. PRESSURE 480 MM.	TIME	ADSORPTION NO. 5 VOLUME CONSTANT	
	Pressure	Volume adsorbed	Volume adsorbed		Pressure	Volume adsorbed
	mm.	*cc.*	*cc.*		*mm.*	*cc.*
2	480	6.5	6.5		480	6.4
3	467	7.2	7.6		460	7.7
4	451	8.1	8.5		447.5	8.5
5	439	8.8	9.2		435	9.1
6	430	9.3	9.8		425	9.7
7	420	9.9	10.4		416	10.2
8	413	10.25	10.9		408	10.6
9	406	10.7	11.4		402	10.9
10	400	11.0	11.8		395	11.3
11	394	11.35	12.2		389	11.7
12	388	11.7	12.5		384	12.0
13	383	12.0	12.8		378.5	12.3
14	379	12.2	13.2		373	12.7
15	374	12.5	13.5		369	12.9
17	366	12.9	14.0		361	13.3
20	355.5	13.8	14.8		350	13.9
25	339.5	14.4	15.9		334	14.8
30	326	15.2	16.9		321	15.5
40	305	16.4	18.5		299.5	16.8
50	287.5	17.4	19.9		282	17.8
60	273	18.2	21.0		267.5	18.6
75	255	19.4	22.5		250.5	19.5
90	240	20.05	23.4	76	480	20.2
105	227.5	20.89	24.5	77		20.35
120	216.5	21.4	25.6	78		20.5
				79		20.7
				80		20.9
				82		21.1
				85		21.5
				90		22.0
				95		22.5
				100		23.0
				110		23.8
				120		24.6

fore the measurement of adsorption the sample was reduced at 350–370°C. for three days and evacuated twenty-four hours at 450–470°C. by means of mercury-vapor and oil pumps. After the determination of the inert space of the system with purified nitrogen, the material was again evacuated twenty-four hours at 450–470°C. A similar evacuation of twenty hours followed each adsorption measurement.

Adsorption No. 3 was carried out at constant volume by the method previously described to obtain the rate of adsorption. With all other conditions identical except that the pressure was maintained constant, curve 4 was obtained. It is quite evident that as the formula predicts, the adsorption at constant pressure continues at a higher rate than in those cases in which the pressure decreases. At the end of two hours in this case the difference is an increased adsorption of 4.2 cc. by the method advocated, amounting to 19 per cent of the total amount adsorbed by the former method in this length of time. A fifth adsorption was made in which the process was at constant volume during the first 75 minutes after which the pressure was increased immediately to 480 mm. and the adsorption measurements continued at that pressure. In this adsorption, curve 5, it was surprising to find the high rate at which after 75 minutes the adsorption increased toward the value previously obtained. After two additional adsorptions were made on the sample at 132°C. at constant pressure, which

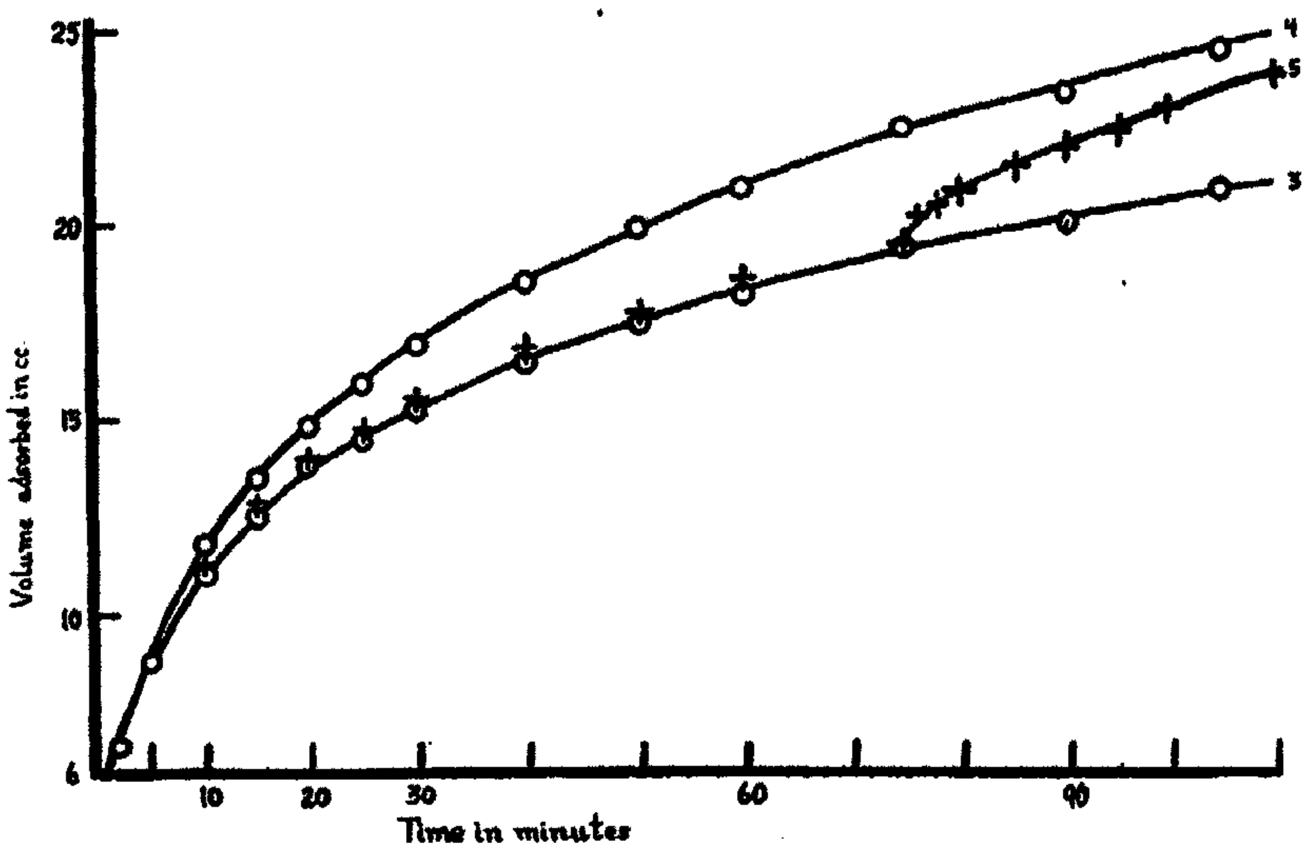


FIG. 2. RATE OF ADSORPTION

Curve 3 at constant volume; curve 4 at constant pressure in themselves agreed with number 4, similar results were obtained in adsorptions at 100°C. by the two methods.

STABILITY OF THE ADSORBENT SURFACE

Adsorbent surfaces are known to be highly complex. However the author has contended that by rigorously following a definite method of preparation and cleaning of the surface, reproducible results in a given sample should be obtainable. Two possible methods of determining whether a surface has been completely degassed are the use of the McLeod gage or the repetition of the evacuation and adsorption. The complete cleansing may of course result not in a surface of maximum activity but merely in one of constant activity. The McLeod gage was used previously (5) in the study of palladium to check the completeness of the degassing process. In the present study the amount of hydrogen adsorbed was less in the first two trials, table 2, than in the subsequent experiments. The method and time of each step of the process was identical throughout. Among the possible factors are the following. The extra evacuation after each adsorption may have finally removed all interfering materials, or the added period of heating during evacuation may have produced activating changes in the surface. The hydrogen adsorbed may have an activating effect upon the surface, cleansing it of other gases, or actually completing the reduction of the oxide. Burrage (6) has recently discussed the necessity of flushing the surface. Whatever the process, it is evident that in the present case the surface reaches a maximum activity and remains quite constant. This final surface has a larger capacity than that of Taylor and Williamson (see table 3), although the samples agree with each other more

TABLE 2

TIME	ADSORPTION 1	ADSORPTION 2
minutes	*cubic centimeters*	*cubic centimeters*
2	3.9	5.9
30	11.9	14.5
60	14.6	18.3
120	17.8	22.6

TABLE 3

Amount of adsorption

SAMPLE	TAYLOR AND WILLIAMSON	1ST ADSORPTION	3RD ADSORPTION	5TH ADSORPTION
minutes	*cc. per gram*	*cc. per gram*	*cc. per gram*	*cc. per gram*
10	0.39	0.34	0.46	0.47
30	0.45	0.50	0.63	0.65
60	0.53	0.61	0.76	0.77

closely than the first and last adsorption on the present sample. It is perhaps superfluous to remark that this increased adsorption is produced by the same method as is used in producing the most active catalytic surface, i.e., by repeated reduction.

ACTIVATION ENERGY

Although the purpose of this determination did not involve the calculation of activation energies, they may be obtained from the data at the two temperatures. Since the rates at each temperature are different depending upon the method used, it is not surprising to find some variation in the value of E resulting. This activation energy of adsorption varies with the fraction of the surface covered, the first gas adsorbed requiring less activation than the final amount. The data as presented in table 4 have been calculated so that they may be compared with the data of Taylor and Williamson. The present sample weighed 0.51 as much as that of the former authors and therefore the volume interval 15–20 cc. corresponds to that between 7.8–10.3 cc. for an equal fraction of the surface covered in the present sample, etc.

TABLE 4

Activation energy in adsorption

Hydrogen on $MnO–Cr_2O_3$ at 100–132°C.

VOLUME ADSORBED	E IN CALORIES PER MOLE ADSORBED	
	Pressure	Volume
cc.		
7.8–10.3	4,580	10,300
10.3–12.9	6,700	14,000
12.9–15.5	9,800	15,400
15.5–18.1	12,600	

CONCLUSION

The Langmuir theory of the adsorption process requires that the velocity of condensation be dependent upon the pressure. This has been proven to be experimentally true in the case of hydrogen adsorbed upon the mixed oxides of manganese and chromium. As a result, in the determination of the activation energy of the adsorption process from rate measurements it is necessary that the method used shall consider the effect of pressure. A method is here suggested for this measurement at constant pressure, previous work having been done at constant volume. Repeated adsorptions upon the same surface were found to increase in rates to a maximum on the third adsorption. After this amount of use the surface remained constant during five additional adsorptions. The conclusion is that the surface should first be shown to be stable before it may be used to obtain data at various temperatures for calculation and comparison. This apparatus and method is also ideally suited for the direct determination of the adsorption isobar.

REFERENCES

(1) See TAYLOR, H. S.: Treatise on Physical Chemistry, Volume II, p. 1072. D. Van Nostrand Co., New York (1931).
(2) TAYLOR: J. Am. Chem. Soc. 53, 578 (1931).
(3) PEASE: J. Am. Chem. Soc. 45, 1196 (1923).
(4) TAYLOR AND WILLIAMSON: J. Am. Chem. Soc. 53, 2168 (1931).
(5) TAYLOR AND McKINNEY: J. Am. Chem. Soc. 53, note 30, p. 3613 (1931).
(6) BURRAGE: Trans. Faraday Soc. 28, 192 (1932). The Adsorption of Gases.

HEATS OF WETTING OF CELLULOSE ACETATE BY ALIPHATIC ALCOHOLS AND AROMATIC HYDROCARBONS[1]

S. E. SHEPPARD AND P. T. NEWSOME

Research Laboratory of the Eastman Kodak Company, Rochester, New York

Received January 20, 1933

This paper is a further contribution to the study of the fine structure of cellulose ester plastics from the point of view of sorption (1). The energetics of sorption consist principally of heats of adsorption, wetting and swelling. In view of the polydisperse character of most of the cellulose colloids (2) it is quite possible that a swelling in a given liquid may consist of two acts, *viz.*, actual *solution* of a more disperse or lower molecular fraction, and wetting of a less disperse, higher molecular portion, which retains the gel structure. But at present we may regard heats of wetting and swelling as synonymous, with the proviso that later investigations may make necessary further differentiation.

Measurements have been made of the heat of wetting of an acetone-soluble cellulose acetate (40 per cent acetyl) in various non-solvent liquids at 25°C. The heat of wetting is defined as the calories of heat evolved per gram of dry acetate when the acetate is immersed in sufficient liquid to insure complete wetting.

Knoevenagel (3) measured the heat of swelling (wetting) of a cellulose acetate of 36.9 per cent acetyl in different mixtures of ethyl alcohol, benzene, and nitrobenzene. The heat of swelling in ethyl alcohol was about 650 calories per mole of cellulose acetate; in benzene, 1100 calories per mole; and in nitrobenzene, 1300 calories per mole.

The heats of wetting of various forms of cellulose (cotton, paper, wood) have been measured by Masson (4), Katz (5), Rosenbohm (6), Dunlap (7), and Barratt and Lewis (8).

EXPERIMENTAL

The heat of wetting was measured in a calorimeter consisting of a 1000-cc. Dewar flask fitted with a Beckmann thermometer, a stirrer, a heating coil, and a device for admitting the dry acetate similar to that used by Hedges (9) for measuring the heat of wetting of wool and silk. The calo-

---

[1] Communication No. 514 from the Kodak Research Laboratories. Presented at the Regional Meeting of the American Chemical Society held at Rochester, New York, February 6, 1932.

rimeter was packed in cotton in a cardboard box and the latter enclosed in an air thermostat at 25 ± 0.03°C. Five hundred cc. of liquid were used in each experiment and about 15 grams of dry cellulose acetate. The cellulose acetate was dried by heating twenty-four hours at 105°C. The acetate and liquid were kept in the thermostat for fifteen hours before mixing to insure equality of temperatures. In most cases the maximum temperature was attained within ten minutes. The cooling curve was followed for about twenty minutes. The heat capacity of the calorimeter was determined after each experiment by passing enough current through the calibrated heating coil to give about the same temperature rise as was observed in the wetting experiment. The required temperature corrections were made. The temperature rise varied from 0.15°C. to 1.00°C. The maximum deviation in check determinations was 5 per cent.

RESULTS

The results are shown in table 1. The first column gives the wetting liquids, the second column the molecular weight of the wetting liquid, and the third column the heats of wetting in calories per gram of dry acetate. The heat of wetting decreases with increase in molecular weight in a given homologous series. The time required for the maximum temperature rise (fourth column) may be taken as a measure of the rate of penetration of the liquid into the cellulose acetate. As would be expected, this time increases with increase in molecular weight in a given series.

TABLE 1

Heat of wetting of cellulose acetate

LIQUID	MOLECULAR WEIGHT	HEAT OF WETTING	TIME REQUIRED FOR MAXIMUM TEMPERATURE RISE	ADSORPTION BY SHEET FROM LIQUID AT 25°C.		ADSORPTION BY FIBERS FROM SATURATED VAPOR AT 25°C	
				Weight per cent	Millimoles per gram	Weight per cent	Millimoles per gram
		calories per gram	*minutes*				
Water	18	6.01	3	13.7	7.6	14.3	7.94
Methyl alcohol	32	7.52	3			51.5	16.1
Ethyl alcohol	46	5.65	3	21.4	4.6	34.8	7.56
n-Propyl alcohol	60	4.94	6	21.2	3.5	25.6	4.27
n-Butyl alcohol	74	4.25	13	16.8	2.3	28.0	3.78
Benzene	78	7.57	8	22.1	2.8	39.1	5.01
Toluene	92	5.78	15	16.9	1.8	23.0	2.50
m-Xylene	106	3.69	30	5.0	0.5	17.1	1.61
Cyclohexane	84	1.40	10	1.5	0.18	12.6	1.50

Our value for the heat of wetting of the acetate in ethyl alcohol is 5.65 calories per gram of acetate or 1509 calories per mole, assuming a molecular weight of 267. This is much higher than Knoevenagel's value of 600 to 700 calories per mole. Likewise, our value of 7.57 calories per gram or 2021 calories per mole for the heat of wetting in benzene is higher than Knoevenagel's value of 1100. The difference in the acetyl contents of the cellulose acetates is not sufficient to account for the discrepancy.

The heat of wetting of the precipitated cellulose acetate by water is 6.0 calories per gram. The heat of wetting of a similar cellulose acetate in the form of a sheet is approximately 7 calories per gram as obtained by extrapolation from the integral heat of adsorption curve.

Knoevenagel (3) regarded his results as supporting a conception of definite (stoichiometric) solvate formation for the sorption of liquids by cellulose esters. Thus, in a previous communication (10) he claimed that "regularities of a molar character were found for the liquids taken up in swelling equilibrium with cellulose acetate." Thus in the swollen cellulose acetate obtained with varying mixtures of nitrobenzene–alcohol, acetic acid–benzene, or acetic acid–water, a constant value was obtained for the quotients:

$$\frac{\text{Moles adsorbed alcohol (benzene, water)}}{\text{Moles cellulose acetate}}$$

He now concludes that "to these molar relations" an unexpected, far-reaching addition for nitrobenzene is made,—"The amount of heat developed per mole or weight unit of cellulose acetate divided by the sum of the sorbed moles of liquid is constant." The constant in question is, surprisingly, the same for experiments with nitrobenzene–alcohol, alcohol–benzene, and benzene–nitrobenzene. The actual values are given in table 2.

TABLE 2

Values of H/A

LIQUID	MOLECULAR WEIGHT	H HEAT OF WETTING (SWELLING) IN KILOGRAM-CALORIES PER MOLE OF CELLULOSE ACETATE	A ADSORPTION IN MOLES PER MOLE OF CELLULOSE ACETATE	H/A
Alcohol	46	0.6	6.8	0.11
		0.7	6.1	0.11
Benzene	78	1.1	9.9	0.11
		1.1	9.8	0.11
Nitrobenzene	123	1.3	11.8	0.11
		1.3	12.3	0.10

The "constancy" of the quotient H/A is good for these few substances. Our own values of heats of wetting do not bear out Knoevenagel's contention (see table 3).

TABLE 3

Values of H and A as found by the authors

LIQUID	HEAT OF WETTING	ADSORPTION	H/A
	calories per gram	*millimoles per gram*	
Water	6.01	7.9	0.76
Methyl alcohol	7.5	16.1	0.47
Ethyl alcohol	5.65	7.56	0.75
n-Propyl alcohol	4.94	4.27	1.16
n-Butyl alcohol	4.25	3.78	1.12
Benzene	7.57	5.01	1.51
Toluene	5.78	2.50	2.31
m-Xylene	3.69	1.61	2.29

Not only is the ratio of H/A quite inconstant, but our figures for the sorption, whether from liquid or saturated vapor, are of quite a different order from Knoevenagel's. This difference appears to be due chiefly to his experimental method, which involved measurement of liquid retained by precipitated cellulose acetate after centrifuging. This procedure does not appear to us likely to give correct values. In the case of complete solvents for cellulose esters, the existence of molecular compounds in certain cases (11) appears very probable, but in the case of sorption there does not appear to be any systematic evidence of stoichiometrical relations.

It was desired to obtain a relation between the heat of wetting and the corresponding amount of adsorption. It is not feasible to measure the adsorption by the precipitated material from the pure liquid but we can convert the precipitated acetate to a sheet, immerse it in the liquid, and weigh the amount sorbed after removing the excess from the surface. This sorption from the pure liquid by a sheet 0.005 inch thick is shown in columns five and six of table 1. The sorption of methyl alcohol could not be accurately measured in this way because of the evaporation during the handling of the sheet.

The sorption by the sheet, however, is probably less in most cases than that by the fibers under the same conditions, because of the smaller external surface of the sheet (12). Theoretically, the sorption by the fibers from the pure liquid should be the same as that by the fibers from the saturated vapor. Data for the latter obtained with a silica spring balance was shown in columns seven and eight of table 1. It will be seen that, with the exception of water, the sorption by the fibers from the saturated vapor is considerably higher than the sorption by the sheet from the pure liquid.

The sorption from the saturated vapor is composed partly of true surface adsorption and partly of capillary condensation but only the former contributes to the heat of wetting. It is, therefore, necessary to know how much of the sorption is surface adsorption and how much capillary condensation.

THE PORE VOLUME OF PRECIPITATED CELLULOSE ACETATE

Figure 1 shows the graph of the heat of wetting against the corresponding total sorption—assumed to be the same as that from the saturated vapor at the same temperature. In a previous communication (12) it was shown that the adsorption of the alcohols decreased with increase in molecular weight and appeared to become approximately constant at *n*-butyl alcohol. It was assumed that beyond this point there was no further capillary condensation. The curves of figure 1 indicate that capillary condensation in the alcohol series ceases at *n-propyl* instead of *n-butyl*, and in the aromatic hydrocarbon series at *toluene*. The prolongations of the lines through the origin enable us to determine the surface adsorption which is necessary to account for the heats of wetting of benzene and of methyl and ethyl alcohols. The excess sorption is due to capillary condensation and gives a measure of the pore volume filled by the liquid.

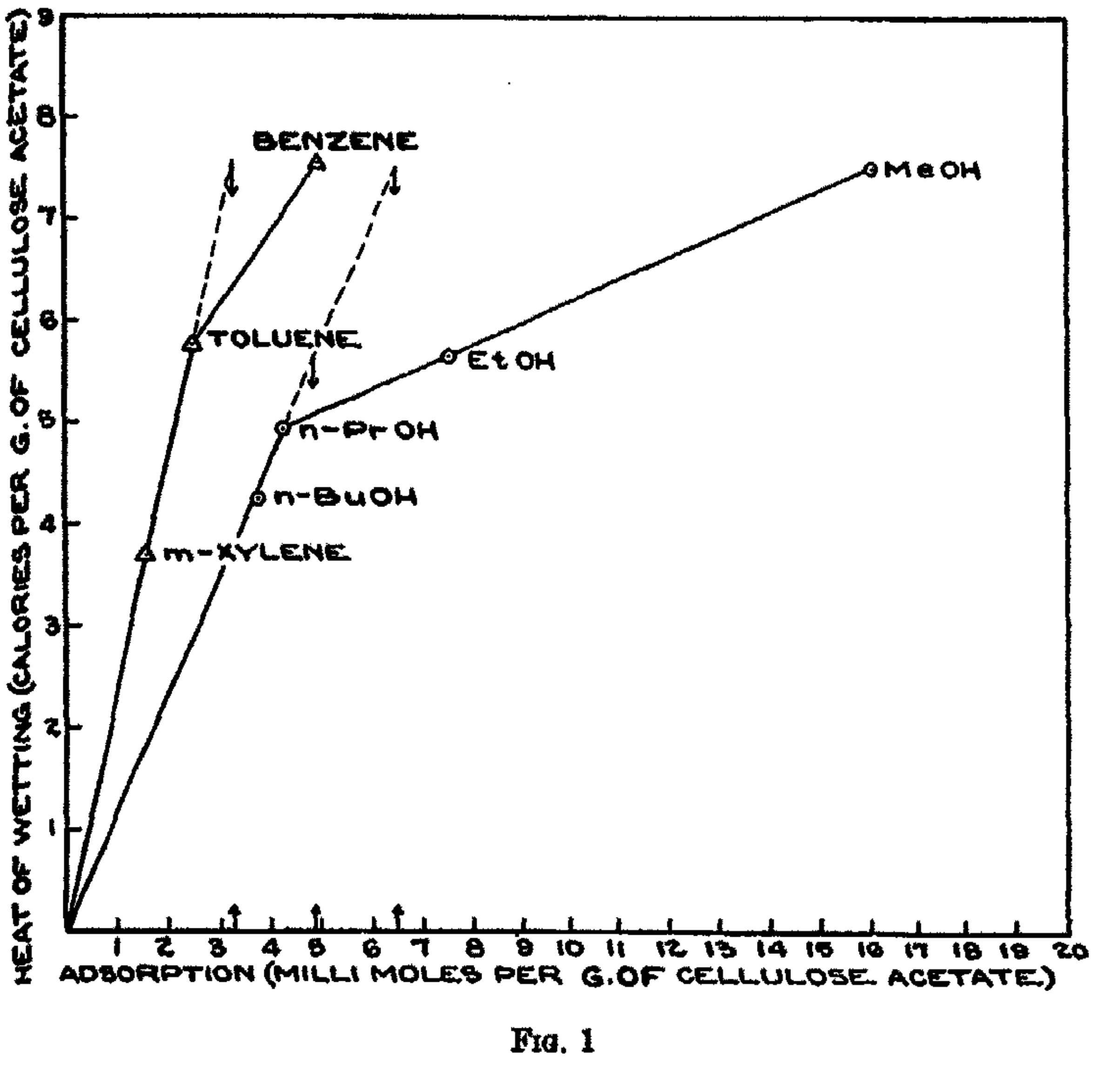


FIG. 1

Table 4 shows the surface adsorption and capillary condensation for the different liquids, together with the calculated pore volumes.

TABLE 4

LIQUID	SURFACE ADSORPTION	CAPILLARY CONDENSATION	DENSITY AT 25°C.	PORE VOLUME
	millimoles per gram	*millimoles per gram*		*cc. per gram*
Methyl alcohol	6.52	9.58	0.7866	0.389
Ethyl alcohol	4.87	2.69	0.7851	0.158
n-Propyl alcohol	4.27	0.0		0.0
Benzene	3.28	1.73	0.8734	0.155
Toluene	2.50	0.0		0.0

Methyl alcohol gives the largest amount of capillary condensation. The pore volume thus occupied is 0.389 cc. per gram of dry acetate.

The straight lines through the origin in figure 1 correspond to a constant net heat of adsorption of 2.30 calories per millimole of adsorbed liquid for the benzene series, and 1.15 calories for the alcohol series.

SPECIFIC SURFACE AREA

Bartell and Fu (13) have described a method for the determination of the specific area of adsorbents based on the heat of wetting and adhesion tension. They have derived the equation

$$a = \frac{-Q}{A - KT\dfrac{dS}{dT}}$$

where a is the specific area, $-Q$ is the heat of wetting, A is the adhesion tension, S is the surface tension of the liquid, T is the absolute temperature, and $K = \dfrac{A}{S} = \cos\varphi$ where φ is the contact angle between solid and liquid. The contact angle betewen cellulose acetate sheet and water was found by Nietz (14) to be 25°. $S = 71.97$ dynes per centimeter and $\dfrac{dS}{dT} = -0.1474$.

Substituting in the above equation, $a = 2.4 \times 10^6$ sq. cm. We have previously obtained the value 5.9×10^6 sq. cm. from alcohol vapor adsorption data (12). This figure was obtained from the total molar adsorption at the saturation pressure and is possibly too high because of some capillary condensation of the higher alcohols.

SUMMARY

1. The heat of wetting of an acetone-soluble cellulose acetate by various non-solvent liquids has been measured at 25°C.

2. The respective amounts of surface adsorption and capillary condensation have been deduced from a comparison of the heats of wetting with adsorption data.

3. Calculations of pore volume and specific surface have been made.

REFERENCES

(1) Compare SHEPPARD, S. E., AND NEWSOME, P. T.: J. Phys. Chem. **36**, 930 (1932).
(2) Compare McNALLY, J. G., AND GODBOUT, A. P.: J. Am. Chem. Soc. **51**, 3095 (1929).
(3) KNOEVENAGEL, E.: Kolloidchem. Beihefte **17**, 51 (1923).
(4) MASSON, O.: Proc. Roy. Soc. London **74**, 230 (1904).
(5) KATZ, J. R.: Proc. Acad. Sci. Amsterdam **13**, 958 (1911); **26**, 549 (1923).
(6) ROSENBOHM, E.: Kolloidchem. Beihefte **6**, 177 (1914).
(7) DUNLAP, M. E.: Forest Products Laboratory, Madison, Wisconsin, Proj. L-169.
(8) BARRATT, T., AND LEWIS, J. W.: J. Textile Inst. **13**, T113 (1922).
(9) HEDGES, J. J.: Trans. Faraday Soc. **22**, 178 (1926).
(10) KNOEVENAGEL, E.: Kolloidchem. Beihefte **16**, 180 (1922).
(11) McNALLY, J. G., AND SHEPPARD, S. E.: J. Phys. Chem. **35**, 2498 (1931).
TROGUS, C., TOMONARI, T., AND HESS, K.: Z. physik. Chem. **B16**, 351 (1932).
(12) SHEPPARD, S. E., AND NEWSOME, P. T.: J. Phys. Chem. **36**, 2306 (1932).
(13) BARTELL, F. E., AND FU, Y.: Colloid Symposium Monograph **7**, 135 (1929).
(14) NIETZ, A. H.: J. Phys. Chem. **32**, 255 (1928).

COMMUNICATIONS TO THE EDITOR

AN ATTEMPT TO SEPARATE ISOTOPES BY REVERSIBLE FRACTIONAL DISTILLATION[1]

This paper shows experimentally that the boiling points of the isotopic modifications of methylene chloride (CH_2Cl_2) differ by 0.005°C. or less. S. A. Peoples and L. Newsome (see Evans, Cornish, Lepkovsky, Archibald and Feskov: Ind. Eng. Chem., Anal. Ed., **2**, 342 (1930)) found no separation of the isotopes of chlorine by reversible fractional distillation of chlorobenzene, but their technique was improved for the present attempt, for which their 6.09 meter column was available.

Twenty liters of methylene chloride (Roessler and Hasslacher Co.) were carefully purified in the 6.09 meter column. Eighteen liters boiled within 0.1°C. or less, and this was returned to the cleaned still. The column was then operated at total reflux, and all traces of water very carefully removed from the condenser (in which any water collects). A calcium chloride tube was placed on the condenser vent. Water is sufficiently soluble in methylene chloride to reduce appreciably the specific gravity. Thirty cc. samples were now withdrawn at intervals for specific gravity tests, using a 25 cc. Leroy Weld type pycnometer (Central Scientific Co.), which made it possible to check individual weights of samples to less than 0.5 mg. The results, each being the mean of two determinations of $d^{25.10}_{25.10}$, are 1.32043 after 22 hours, 1.32039 after 64 hours, and 1.32046 after 117 hours (all at total reflux). The entire charge was then distilled off (all boiling within 0.1°C. or less), mixed, and found to have $d^{25.10}_{25.10}$ 1.32040. Values are not corrected for buoyancy of air.

Assuming Raoult's law, we write for the final limiting steady state at total reflux (Fenske: Ind. Eng. Chem. **24**, 483 (1932)):

$$X_{pA}/X_{pB} = \alpha^n X_A/X_B$$

where X_{pA}/X_{pB} is the ratio of the mole fractions of components A and B in the product, X_A/X_B is the same ratio in kettle, α is ratio of vapor pressure

---

[1] Aided by grants from the Committee for Research in Problems of Sex of the National Research Council, and from the Rockefeller Foundation. These funds have been generously augmented by the Board of Research and the College of Agriculture of the University of California.

of pure A to that of pure B, and n is the number of theoretical plates. The 6.09 meter column used, packed with 4 mm. × 4 mm. cylindrical glass beads, should give a separation equal to that of at least forty theoretical plates, so that $n = 40$. (Evans, Cornish, Lepkovsky, Archibald, and Feskov: Ind. Eng. Chem., Anal. Ed. **2**, 342 (1930) and Peters: Ind. Eng. Chem. **14**, 476 (1922).) For methylene chloride at 39.7°C., its boiling point (Carlisle and Levine: Ind. Eng. Chem. **24**, 146 (1932)), dP/dT is 0.035 atmospheres per degree. (Morrison and Duus: Chem. & Met. Eng. **39**, 230 (1932).) If both pair of *successive* isotopic forms of methylene chloride boil $y°$ apart; $\alpha = 1 + 0.035y$ *for* either pair. The composition of chlorine, Cl_2, is 57.6 per cent $Cl_2{}^{35-35}$, 36.6 per cent $Cl_2{}^{35-37}$ and 5.8 per cent $Cl_2{}^{37-37}$. (Giauque and Overstreet: J. Am. Chem. Soc. **54**, 1737 (1932).) Assuming the same ratios for the three isotopic forms of methylene chloride, and assuming their molal volumes in the liquid state to be identical, one calculates $1.32040–0.016y$ for limiting specific gravity of distillate. Comparing this with experimental values above given, it is seen that y must be 0.005°C. or less. This result is apparently at variance with the claim (Keesom and van Dijk: Proc. Acad. Sci. Amsterdam **34**, 42 (1931)) of a recognizable separation of the isotopes of neon in a reversible distilling column of nineteen actual plates.

The 6.09 meter column will separate in better than 95 per cent purity (with a single distillation), liquids boiling as little as 5°C. apart. The time for maximum enrichment at total reflux is then about twenty-four hours (one day). Hence even with a difference of 0.005°C. (the maximum possible for methylene chloride isotopes), to get about 95 per cent purity of isotopes, such a column must be 6 × 1000 or 6000 meters high, and the time for maximum enrichment would be increased to 1000^2 or 10^6 days. However, the right set of conditions for such a fractionation may have occurred in some places during the formation of the earth.

SUMMARY

The boiling points of successive isotopic forms of methylene chloride (due to the chlorine 35 and 37) are shown experimentally to differ by 0.005°C. or less. Hence in a liquid-vapor equilibrium type of fractionating column, the necessary height and particularly the necessary time of distillation, eliminate this method of separation. However this kind of fractionation may have occurred naturally in suitable geological formations.

H. J. HENRIQUES.
R. E. CORNISH.

The Institute of Experimental Biology
The University of California
Berkeley, California

CORRECTIONS

The following corrections should be made in the article "Application of the Double Layer Theory of Otto Stern. I.", appearing in This Journal **36**, 3157 (1932):

In equations 6 and 7, read a + sign instead of the − sign.
In equation 8, read "$\mathfrak{z} = 4 \times 1.67 \times 10^{-2}$.........."
In equation 9, read "295" in the exponent of e, instead of "2.95."
In equation 15, the exponent of e should read:

$$\frac{9.65 \times 10^4 \times 3 \times 10^9 \times 0.124}{3 \times 10^3 \times 2 \times 1.99 \times 4.183 \times 10^7 \times 295}$$

In equation 17, read "2.27×10^{-19}," instead of "2.27×10^{-17}."

Frank Urban.
H. L. White.

NEW BOOKS

Our Mineral Civilization. By THOMAS T. READ. Century of Progress Series. 5 x 7 in.; 165 pp. Baltimore: The Williams & Wilkins Co., 1933. Price: $1.00.

The author is a well-known writer in the field of mining engineering. The treatise on this subject is exceptionally well written and should be especially interesting to people who have not been trained as scientists and engineers.

The development and uses of the commercial minerals, important chemical elements, metals, and their alloys as applied by mankind is presented by the author in an interesting, clear, accurate, and concise manner. There are statistics, but not enough to bore the reader, and the general philosophy, economy, and comparisons remind one, to some extent, of the book *Creative Chemistry* by the late Dr. E. E. Slosson.

R. L. DOWDELL.

Säure-Basen-Indicatoren. Ihre Anwendung bei der colorimetrischen Bestimmung der Wasserstoffionenkonzentration. VON I. M. KOLTHOFF unter Mitwirkung von HARRY FISCHGOLD. 13.5 x 20.5 cm.; xi + 416 pp.; 26 figures. Berlin: Julius Springer, 1932. Price: 19.8 RM (geb.).

This volume, issued under a different title, is a much expanded fourth edition of *Der Gebrauch von Farbindicatoren.* The work is divided into three parts. The first two sections, i.e., "The dissociation of strong and weak electrolytes" and "The properties of acid-base indicators" contain an excellent discussion of the theory and modern viewpoint of these subjects. The third section dealing with "The colorimetric estimation of hydrogen ion concentration" contains the applications of the theories which have been developed to problems of practical application.

Probably no one is better qualified to write a handbook such as this than is Dr. Kolthoff, for it represents a field to which he has given major attention for a number of years, both as a research worker and as a teacher. The theoretical discussions go beyond most books which are designed to cover this field and include lucid discussions of the recent trends in the "activity" concept, including a thorough discussion of Brönsted's ideas on acid-base function. Brönsted has rightly pointed out that the hydrogen-ion, being a naked proton and accordingly an α particle, cannot exist as such except for an infinitesimally small length of time, that it will penetrate into the electron shell of the first molecule it comes in contact with and, thus associating itself with a neutral molecule, will form a molecule possessing a positive charge. Thus instead of speaking of "hydrogen-ions" we should more properly speak of the "hydronium ion concentration," (H_3O^+), which represents the concentration of the solvated protons. The Brönsted definition of acids and bases differs considerably from the older conceptions, but appears to possess real merit. Thus "an acid is a substance which is able to split off a proton, simultaneously forming a base, and a base is a substance capable of uniting with a proton, thus forming an acid." Thus the dissociation of an acid in water may be written

$$\underset{\text{acid}}{A} + \underset{\text{base}}{H_2O} \rightleftarrows \underset{\text{base}}{B^-} + \underset{\text{acid}}{H_3O^+}$$

This concept lays primary emphasis on the sign and magnitude of the charge of the central atom of a molecular configuration as determining acidic or basic properties rather than the criterion of "salt formation" which is regarded as an incidental phenomenon.

The present volume is especially valuable since it discusses acid-base dissociation in such solvents as ethyl alcohol. On the basis of Brönsted's definition both ethyl alcohol and water are bases, but water is four hundred times as strong a base as is ethyl alcohol; this accounts for the difference in behavior between aqueous and alcoholic systems. This section of the book especially appealed to the reviewer.

In the section devoted to the properties of indicators we find an excellent theoretical discussion, followed by a description of the various indicators, including formulas, melting point, and other physical properties, methods of purification, solubility and pH range and their suitability for use under various conditions and with various solvents. A new definition of an indicator is proposed, i.e. "Indicators are (apparently) weak acids or bases, whose inogene or aci- (or baso-) form possesses a different color and structure than the pseudo or normal form."

The third section of the book, dealing with the colorimetric estimation of hydrogen-ion concentrations, deals with the preparation and properties of buffer solutions, the technic of the colorimetric determination of hydrogen-ion concentration, the sources of error in the colorimetric methods, including an extended discussion of the effect of salts, proteins, and other colloids, temperature, etc., with the last chapter devoted to indicator papers. The book closes with an appendix of six tables showing the ion product of water at various temperatures, the ion activity product of water, the activity coefficient for various concentrations of electrolyte solutions, an extensive table of the dissociation constants of approximately one hundred and twenty acids and bases, including such compounds as the alkaloids, phenols, etc. (The reviewer wonders why the amino acids were omitted from such an imposing list, for they certainly are more commonly worked with than are many compounds included in the table), and an interpolation table for converting fractions of pH into C_H values. Excellent author and subject indices close the volume.

It is a book filled with valuable discussion and tabular data. The fact that other volumes on the determination of hydrogen-ion concentration are available should not deter one from purchasing this book, for it contains much material not otherwise readily accessible. It should be in every chemical library and in the hands of everyone interested in the control and measurement of hydrogen-ion concentration.

Ross Aiken Gortner.

Die Struktur der Atomkerne. By Dr. Siegmund Stransky. 22 x 15 cm.; 50 pp. Leipzig u. Wien: F. Deuticke, 1932. Price, 4*s.* 9*d.*

Dr. Stransky's monograph on the structure of the nucleus is entirely original and entirely speculative. There is evidence in favor of the conclusions he draws but it is of a numerical kind, in which the numbers are confined rigorously to integers. He does not consider other theories of the subject he is writing about, and it is at once patent to a reader that little reconciliation is possible between Dr. Stransky's views and the main *corpus* of knowledge that has been ground out of the research of the past twenty years. They lie, indeed, so far outside of the main stream of theory and experiment that I fear atomic physicists may fail to give them the patient consideration the author would like them to get.

Dr. Stransky is a modern Prout, a Prout, moreover, who has had in his time the discouragement of a Newlands. He tells us that for forty-five years he has occupied himself at invervals in arranging units of mass (protons, they would now be called) in such patterns that the most likely of them sum to the masses of the common elements, and that he has not always been able to get his work published. Like Prout he has started from the assumption that protons are the stuff from which all matter is built. The new points are that the protons are probably arranged in the nucleus in hexagons or fused hexagons like the CH groups in benzene, naphthalene, phenanthrene, and so forth, and secondly that the masses of the atoms of the elements of one particular group are based on one another. (For this purpose the subdivisions A and B of the groups of the Periodic Classification are ignored.) The atomic weights of copper and silver, for example, are based on those of lithium and the alkali metals. Just as naphthalene may be regarded as two benzenes less four carbon atoms, and picene as five benzenes less eight carbon atoms, so are heavy elements of a group so many times the masses of simple elements of the group less so many hydrogens. Thus Na, 23, is 4Li − 5, the atomic weight of lithium being taken exactly as 7, and Cs, 133, is 6Na − 5; the reason for subtracting 5 in these cases is that when four or six "benzene-rings" of protons are joined together most compactly there are five points held in common, and consequently no protons there. Occasionally some latitude is allowed in deciding what arrangements are most compact, and the various alternative masses arrived at serve as the various isotopes of the element under consideration. Thus nine "bricks" of twenty-three protons can be simply arranged so as to have either eight or ten points of contact with the possibility that the element so built up can have two alternative masses differing by two units. Much of the book is occupied with diagrams showing the patterns in which the nuclei of the atoms of the different elements are arranged by Dr. Stransky. The simpler ones look like the diagrams of carbocyclic chemistry; the more complex resemble snow crystals viewed through a microscope.

Dr. Stransky's general theory may have been plausible in days when atomic weights were thought to be whole numbers, or even in the early days of nuclear theory when the nucleus was regarded as built up of hydrogen protons, but the experimental work of F. W. Aston completely disposes of Prout's hypothesis in any form. It is the helium nucleus which is the chiefest brick in the nucleus, with the proton and possibly the neutron and the "demi-helion" as subsidiaries. None of these is any sort of arrangement such as Dr. Stransky postulates. The great importance of these ultimate units and the nuclei which are built from them at the present time is not that their masses are 4, 1, 2, 133, etc., but that their masses are in excess or defect of integers to an amount which is a function of their closeness of arrangement in the nucleus. Further, Aston has shown that there is little evidence of what might be called a periodic arrangement of the nucleus akin to that of the planetary electrons in an atom; if there were, one might deduce from the masses of the isotopes of tin those of the isotopes of lead by adding a constant amount, such as 88, to the masses of tin. To some degree this works, but it is not so universally applicable as to be regarded as an arrangement.

If further considerations were needed to be quoted against Dr. Stransky's theory, the experimental work on the discription of the nucleus which has been going on at Cambridge since 1919 would suffice. What is known of the nucleus from these experiments (and it is almost everything that is known) has no resemblance to Dr. Stransky's speculations.

Nevertheless Dr. Stransky has shown great ingenuity in his work. It is quite the best exposition of 'Proutism' that has appeared, and if it encourages others to begin a study of how the nucleus is built up from the real ultimate units, his labor will not have been altogether in vain.

A. S. Russell.

Chemische Technologie der Neuzeit. By O. Dammer. Second and larger edition, 5th volume. 19.5 x 27.5 cm.; xvi + 876 pp. Stuttgart: Ferdinand Enke, 1932. Price, bound RM.79, unbound RM.5.

This work deals with metals and alloys, and is one of those typical monuments of German industry and scholarship which not only demand but compel admiration. It begins with a good account of the technical methods of the preparation of alloys, and a comprehensive account of a formal phase rule treatment.

The book is full of excellent photographs; the colored ones are especially noteworthy.

From the point of view of the practical man the book is of the greatest interest. There are excellent photographs, for example, in the section on brass, of the serious technical defects which arise through the use of wrong temperatures. The references to the literature are numerous, and the reviewer, who has checked about twenty, has found them all correct.

It is difficult to see how anybody interested in non-ferrous alloys can afford to be without this book.

F. A. Freeth.

Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikatforschung in Berlin-Dahlem. Edited by Wilhelm Eitel. 29 x 21 cm.; 212 pp. Brunswick: Friedr. Vieweg und Sohn, 1932. Price RM.28.

The proceedings of this active Institute again cover a wide range. Working as it does in close coöperation with the silicate industries, it has been found necessary to widen the scope to include the study of the heat balance in technical processes, such as the manufacture of Portland cement. In this connection a description is given of the new 'Lepol' kiln, which although of German design has so far been erected only in Spain and in Luxembourg. By the use of a preliminary roasting chamber utilizing the waste heat, the actual kiln is greatly shortened, and a very considerable economy of fuel is effected. Other work on cement includes a study of the setting time of mixtures of Portland and aluminous cement, from which it appears that the properties of the mixtures are not additive.

Glass problems fill the greater part of the volume. With the help of the German glass manufacturers, a set of tables of the properties of glass, taking into account some 2500 publications, is in course of preparation. These tables will include the chemical as well as the physical properties. Several communications deal with the removal of color from glass, especially by means of cerium. Cerium dioxide is superior for this purpose to manganese dioxide, but it will cause darkening by ultraviolet light if arsenic or bismuth be present. This effect is corrected by the addition of small quantities of sodium sulfate, and the mutual influence of these additions is worked out. In opal glass, the crystals producing turbidity are identified as cristobalite, whatever the composition of the glass, although in fluoride glasses the presence of minute crystals of sodium fluoride has also been proved. The hydrothermal synthesis of calcium silicates and the action of carbonic acid under high pressure on the silicates have been studied, one result being the preparation of definite carbonate-silicate glasses, containing as much as 20 per cent of sodium carbonate. This memoir includes an interesting series of quantitative experiments on the equilibrium between carbon dioxide and glasses. The flow of molten glass in the Owens machine is considered theoretically, this paper to be followed by one in which the theoretical deductions are to be tested by an examination of the flow lines as shown by Schlieren.

As in previous years, there are several descriptions of improved apparatus and experimental methods, and a few communications having only an indirect bearing on the silicate industries are included, such as a study of vanadium oxide sols and another in which the dehydration and rehydration of brucite is examined, it being shown that a new phase is formed, and not simply a pseudo-structure. The editor is to be congratulated on the quality of the work done under his direction, and on the excellent presentation of it in this handsome volume.

C. H. Desch.

THE SOLUBILITY OF SILVER IN MERCURY. II

ROBERT E. DeRIGHT

Chemical Laboratory, The University of Rochester, Rochester, New York

Received October 29, 1932

Determinations of the solubility of silver in mercury at various isolated temperatures have been reported by several investigators (5, 8, 17, 14, 12, 15, 24), but Joyner (9) was the first to study the problem systematically. Several years ago Sunier and Hess (22) published some precise work on the solubility of silver in mercury over the range 80°C. to 200°C. Their results agreed remarkably well with those obtained by Joyner, who used a rather crude method. Since that time Murphy (13) has published a complete phase diagram for the system silver–mercury. He was interested, however, in the composition of the solid phase and cites the data of Sunier and Hess (22) for his liquidus curve at low temperatures.

Since Joyner (9) is the only person offering systematic data below 80°C., (four determinations) and his data in this range of temperature pointed to a marked flattening out of the solubility curve below 50°C., it was thought advisable to extend the precise work of Sunier and Hess (22) below 80°C.

MATERIALS

The mercury used was first purified by dropping it through a five-foot Meyer column containing 6 N nitric acid and was then washed with distilled water. The dried mercury was distilled in an all glass apparatus according to the method of Hulett and Minchin (7). Samples of this mercury yielded no weighable residue when evaporated according to the method of analysis of the amalgams in a stream of hydrogen.

The silver used was "1000 fine" foil, kindly supplied by the Philadelphia Mint. This foil was used as the solid phase either directly or after treatment by methods described later in this paper

APPARATUS

The solubility tube used, a modification of the one used by Sunier and Hess (22) and similar to the tube used by Sunier and Gramkee (21), was made of Pyrex glass. It differed in size from that of the latter, as the smaller solubility necessitated the employment of larger volumes of mercury.

The shaking mechanism differs little from that used by Sunier and White (23) with the exception that in one run a set of sixteen rather than eight tubes were run at the same time. The apparatus brought about complete transfer of the contents of the tube from one end to the other by rotating it through an angle of sixty degrees.

The tubes were immersed in a heavily lagged thermostat similar to the one described by Sunier and White (23). The bath was heated by electricity and steam, and was provided with a copper cooling coil. In the early runs, manual control of the temperature was resorted to, but in later runs a mercury thermoregulator of the type described by Clark (1) was used. When manual control was used the constancy approached ±0.02°C., while with the thermoregulator the temperature was held within the range of ±0.01°C.

Temperatures were read from mercury thermometers of the double diamond label manufactured by Hiergesell Brothers, and graduated in tenths of a degree. These thermometers were compared with thermometers standardized by the Bureau of Standards. The ice points were taken frequently but showed no change. Temperatures could be read to 0.02°C. with ease. Changes of temperature during the run were noted from a Beckmann thermometer inserted in the bath.

The weights used were calibrated according to the method of Richards as described by Fales (4) and compared with a weight checked by the Bureau of Standards.

EXPERIMENTAL PROCEDURE

After the solubility tube had been washed with 6 *N* nitric acid and distilled water, it was dried in an oven at 160°C. overnight or flamed with a Bunsen burner in a stream of air. The tube was then charged with 135 to 155 g. of mercury in the manner described by Sunier and Gramkee (2) and two to three hundred per cent excess of the silver required at that temperature, using Joyner's (9) data as a guide. The tubes were flamed and evacuated with a Cenco Hyvac pump to a pressure of 0.01 to 0.1 mm. of mercury read on a MacLeod gauge.

To determine the solubility at a certain temperature a total of eight tubes was made up (16 tubes in Run N). The run was made in the manner described by Sunier and White (23), four tubes being rotated at 5°C. above the solubility temperature preliminary to the insertion of the remaining tubes.

Later in the research it became evident that equilibrium had not been attained in the time allowed, so that all of the tubes were inserted at the same temperature and rotated for periods of from eight to two hundred and fifty-six hours.

Sampling was carried out in the manner described by Sunier and White (23).

The method of analysis was that used by Sunier and Gramkee (21) in the analysis of gold amalgams. A large Pyrex tube with a ground glass stopper, as shown in figure 1, was supported in an electric furnace. A mercury trap was provided to catch the condensed mercury swept through by the gas admitted at the opposite end. The capsules were supported on Sillimanite slabs, hence there was no possible contamination of evaporated mercury.

In order to test the applicability of this procedure to silver amalgams, various experiments were carried out. It was found that the mercury used left no weighable residue when evaporated by this procedure. Weighed pieces of silver foil lost no weight when heated for periods of twenty hours at 550°C. in a stream of hydrogen. Mercury was placed on this foil and then driven off by heating at 270°C. to 300°C.; the residues were then heated to 550°C. for several hours. When air was used the residues were consistently several tenths of a milligram heavier than their original weight. This could not be due to silver oxide formed, for it would be unstable at the temperatures employed, according to the free energy relationships cited by Lewis and Randall (11). Owing to the finely divided condition of the crystallized silver, occlusion suggests itself as a possibility. Steachie (20) refers to the occlusion of gases on finely divided metallic surfaces. When hydrogen, purified by bubbling through saturated solutions of potassium permanganate, sodium hydroxide, and 95 per cent sulfuric acid was used the residues came down to their original weight.

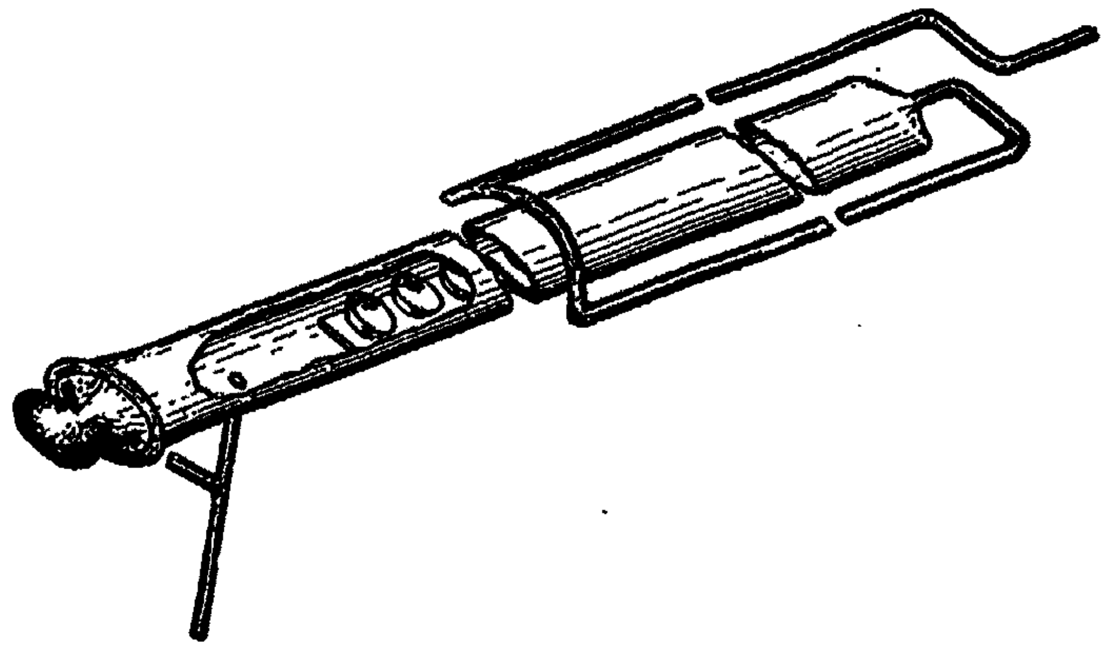


FIG. 1. EVAPORATION TUBE

To test the entire experimental procedure, eight tubes containing weighed quantities of silver and mercury were made up and carried through the entire procedure. The results of this experiment are tabulated in table 1. It is to be noted that the solubility of silver is much less than that of gold, so that, of necessity, much smaller residues must be weighed, and the amounts of mercury used must be much larger. Despite these disadvantages, from the composition found, the average deviation was less than one part per thousand.

TABLE 1

TUBE	SILVER TAKEN	MERCURY TAKEN	ATOMIC PER CENT TAKEN	ATOMIC PER CENT FOUND	DEVIATION
	grams	*grams*			*parts per thousand*
1	0.0912	143.928	0.1177	0.1182	4.2
2	0.0986	147.909	0.1238	0.1228	8.1
3	0.0877	145.417	0.1120	0.1124	3.5
4	0.0859	143.349	0.1113	0.1122	8.1
5	0.0949	144.816	0.1217	0.1218	0.8
6	0.0899	145.311	0.1148	0.1142	5.3
7	0.0940	137.088	0.1273	0.1267	3.9
8	0.0930	145.897	0.1184	0.1179	4.2
Average =			0.1184	0.1183	4.8

Deviation of average composition = 0.85 per 1000

TABLE 2

Run A

Time of run 6 hours (low side-4 hours); temperature 40.11°C. (high side-45.3°C.); silver—foil (mint); mercury—triple distilled.

TUBE NUMBER	SILVER AT START	WEIGHT OF AMALGAM	WEIGHT OF SILVER	ATOMIC PER PER CENT OF SILVER	DEVIATION FROM MEAN	REMARKS
		grams	*grams*		*p.p.t.*	
A-1	0.5	142.991	0.0880	0.1144	5	
A-2	0.5	144.533	0.0886	0.1139	0	
A-3	0.5	143.692	0.0872	0.1128	11	
A-4	0.5	142.416	0.0932	0.1216	x	Exclude
A-5*	0.5	146.070	0.0896	0.1140	1	
A-6*	0.5	142.993	0.0880	0.1150	11	
A-7*	0.5	143.285	0.0879	0.1140	1	
A-8*	0.5	142.772	0.0867	0.1129	10	
		Average =	Low side, 0.1137 High side, 0.1140	(3) 0.1139	5 per 1000	

Number of determinations, 7.

* High side.

EXPERIMENTAL RESULTS

In table 2 will be found a sample table of data for one run.

In table 3 will be found the table of data for Run N in which sixteen tubes were used and the solid phase varied as described later in this article.

TABLE 3

Run N

Time of run 256 hours; temperature 25.28°C.; silver as noted; mercury—triple distilled.*

TUBE NUMBER	SOLID PHASE	WEIGHT OF SOLID PHASE	WEIGHT OF AMALGAM	WEIGHT OF SILVER	ATOMIC PER CENT OF SILVER	DEVIATION FROM MEAN	REMARKS
		grams	*grams*	*grams*		*p.p.t.*	
A-1	Reed	1.7	144.951	0.0606	0.0777	11	
A-2	Reed	1.6	143.811	0.0620	0.0801	35	
A-3	Reed	1.6	146.676	0.0685	0.0868	102	Exclude
Ex.	Foil	1.0	155.377	0.4891	0.5841	x	No glass wool
E-1	Ag_3Hg_4	2.0	140.474	0.0631	0.0835	69	Exclude
E-4	Ag	1.0	138.439	0.3189	0.4275	x	Filtered through chamois
E-2	Ag_3Hg_4	2.0	141.603	0.0570	0.0748	18	Exclude
E-3	Ag	1.0	134.842	0.0673	0.0928	162	Exclude
C-1	Ag_3Hg_4	2.0	143.694	0.0695	0.0899	133	
C-2	Ag_3Hg_4	2.0	141.549	0.0570	0.0749	17	No glass wool Poor vacuum
C-3	Ag_3Hg_4	2.0	85.435	0.0346	0.0748	18	
C-4	Ag_3Hg_4	2.0	148.444	0.0602	0.0754	13	
H-1	Ag	1.0	143.853	0.0703	0.0908	142	Exclude
H-2	Ag	1.0	143.467	0.0617	0.0799	33	
H-3	Ag	1.0	144.120	0.0593	0.0765	1	
H-4	Ag	1.0	144.399	0.0588	0.0757	9	
Average =					0.0766	21.1 per 1000	

Number of determinations, 9.

* With the exception of the tube marked Ex., column 1.

TABLE 4

RUN	TEMPERATURE	SOLUBILITY	DEVIATION	NUMBER OF TUBES	TIME
	degrees C.		*parts per thousand*		*hours*
A	40.11	0.1139	5	7	6
B	50.02	0.1450	4	6	7
C	60.26	0.1901	27	8	7
D	70.54	0.2404	32	8	7
E	30.15	0.0965	91	8	7 Definite trend
F	80.94	0.2892	4	6	7
H	19.01*	0.0636	6	8	8
I	29.93*	0.0881	13	5	9
J	8.92*	0.0641	64	6	9
K	25.60*	0.0792	14	6	78
L	18.17*	0.0643	10	5	75
N	25.28*	0.0766	21	9	256

* All tubes approached saturation from the same side.

In table 4 will be found the summary of all runs.

Figure 2 is a plot of the log of the solubility versus the reciprocal of the absolute temperature. The slope of the line was determined from a large scale plot and the line corresponds to the equation

$$\log N = \frac{-1105.8}{T} + 0.5894$$

Of a total of one hundred and twenty-eight determinations made, thirty-eight have been rejected. Of this apparently large number of rejected tubes, sixteen are accounted for by Runs G and M, where equilibrium was not attained. Of the remaining twenty-two excluded, four tubes were broken, three amalgams bumped during evaporation, and difficulty was experienced in the filtration of four tubes. Therefore only eleven tubes were excluded, merely because their deviation was greater than four times the average deviation.

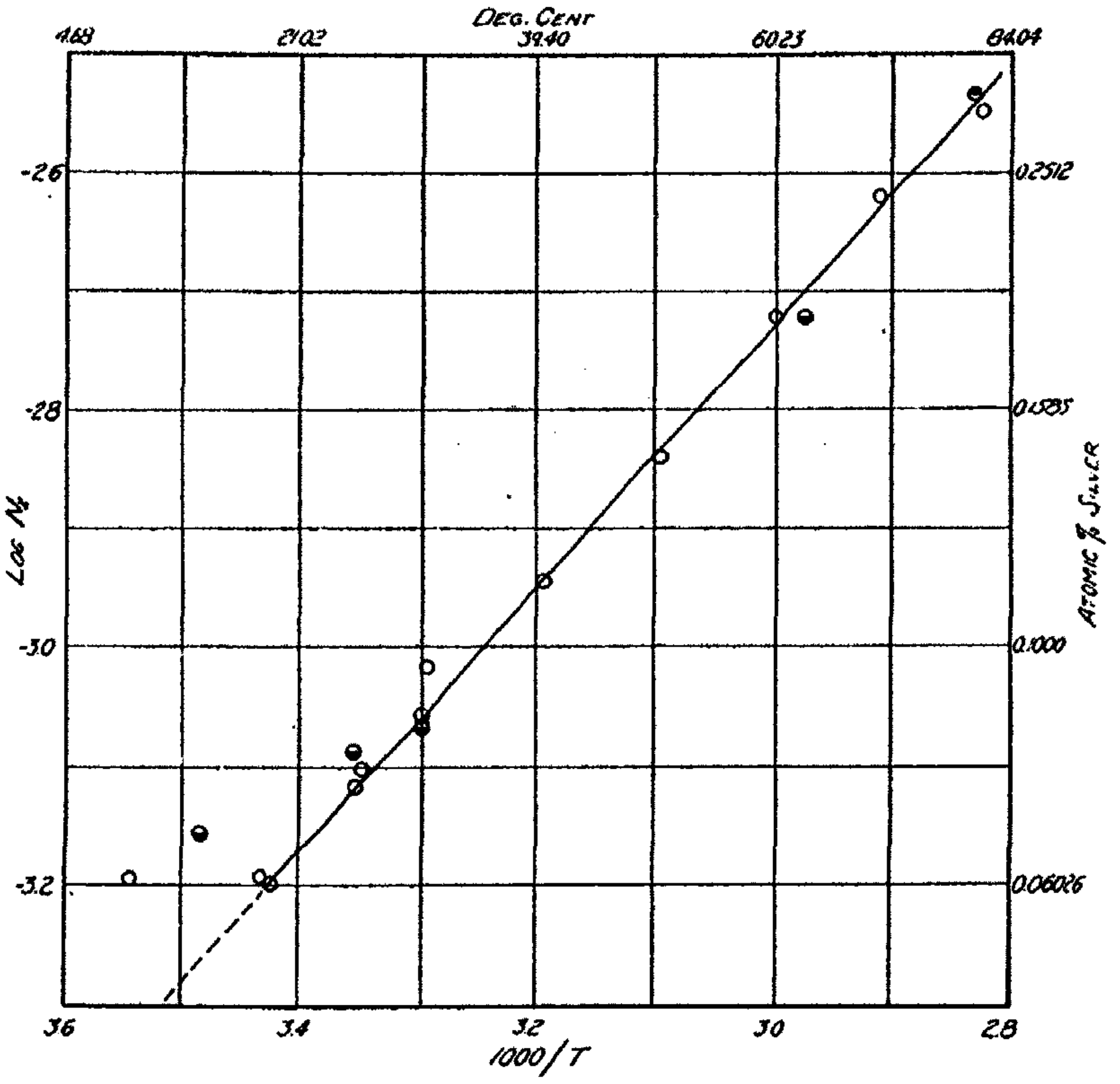


Fig. 2. The Solubility of Silver in Mercury

◒ Joyner; ◓ Sunier and Hess; ○ DeRight.

DISCUSSION OF RESULTS

It was realized at the inception of this investigation that, owing to the slight solubility of silver, it would be necessary to employ large tubes and to weigh the residues extremely accurately. After the completion of the blank run and the satisfactory results obtained, it was felt that little further difficulty would be experienced.

The solubilities at temperatures above 40°C. were first determined. Although in some cases rather large average deviations were found, the determinations seemed to be in fair agreement, and when plotted fell on a straight line. The slope of this curve was somewhat less than that determined by Sunier and Hess (22). This change in slope is not unusual at lower temperatures. The determination at 80°C., which was the lowest temperature at which Sunier and Hess (22) made measurements, was in good agreement with their result. Furthermore, in the range of temperature above 40°C., the data was in agreement with that of Joyner (9).

A hint of the difficulty present in the behavior of amalgams below 40°C. was given by Joyner's data. There was a marked break in the slope of his curve at 40°C. The slope of the curve at the lower temperatures approached zero.

In Run E at 30.12°C. there was a marked discrepancy between the four tubes of the high side and those of the low side. This seemed to be a criterion that equilibrium had not been attained. A very marked discrepancy existed between the two sides in Run G at 19.85°C. This disagreement was so marked that this run was omitted from table 4.

It was decided to make a second run near the temperature of Run G, rotating all eight tubes, from the low side, for eight hours (Run H) at a temperature of 19.01°C. This run yielded very satisfactory results, since all eight tubes gave an average deviation of only 6 p.p.t., a very low figure for such a small solubility. Furthermore the point, when plotted, showed no deviation from the straight line drawn in figure 2.

Run E was repeated in the same manner in Run I. Unfortunately, two of the tubes were broken and a third excluded. The remaining five were in good agreement.

Run J yielded a curious result. It was carried out in the same manner as Runs H and I. Although the six determinations retained were not in good agreement, their average deviation of 64 per thousand pointed to some regularity. The apparent solubility was greater than that obtained at 20°C. and showed some agreement with Joyner's results.

The impression gained from a first reading of Joyner's paper was that he had rotated his tubes in a constant temperature bath for periods of a fortnight. Upon closer inspection of his paper it was found that he had rotated his amalgams containing *both* silver and tin for the time indicated, but he made no specific statement of the time of rotation in the silver-mercury system. Furthermore, he claims the solubility he obtained was the equilibrium of Ag_3Hg_4 in contact with mercury, rather than of silver in contact with mercury. Murphy (13) states that silver amalgams attain equilibrium several times faster at 100°C. than at room temperature. Data is also available as to the rate of penetration of mercury into a silver surface at different temperatures (8). Therefore it seemed advisable to continue the runs at lower temperatures for longer periods of time.

Run K was to continue for seventy-five hours to note any difference in the solubility obtained at 25°C. Likewise new mercury was used in two tubes to see if any error could creep in, owing to the use of mercury evaporated from previous runs. The results of this run were in fair agreement among themselves and the mean result fell very close to the straight line obtained at higher temperatures.

Run L was a determination of the same type, at 18°C. Unfortunately, the contents of one capsule bumped, silver being transferred to two other capsules, so that it was necessary to exclude three values. The mean solubility obtained in this run was not in disagreement with previous runs, and fell on the straight line. This proved that the runs at 20°C. and 30°C. for a shorter period of time had practically reached equilibrium.

Run M was to continue for one week in the hope that equilibrium at 10°C. might be attained. This temperature was made possible through the use of a thermoregulator, cooling being brought about by pumping water from an auxiliary thermostat containing ice, through the copper cooling coil. In four of the tubes the solid phase consisted of silver which had been completely dissolved in mercury at a high temperature and then allowed to cool. The results of this run were very disappointing. There was too little agreement among the tubes to accord any credence to this determination. The four tubes, containing the solid phase mentioned above, filtered with great difficulty, the solid caking at the mouth of the capillary. Furthermore, the results showed a higher solubility than the other four, supporting the conviction that solid passed through with the liquid phase. Owing to the disagreement among the tubes this run was omitted from table 4.

At this point in the research a critical survey was made of the fourteen previous runs, with a view toward detecting any errors in procedure and introducing any helpful innovation. The following changes in procedure suggested themselves: (1) variation of the form of the solid phase, (2) variation of the liquid phase, (3) design of the tubes, i.e., the method of filtering, (4) the time of shaking, (5) the number of tubes.

Murphy (13), in his paper, states that equilibrium is much more readily reached when finely divided silver is used. Furthermore, it is to be noted that in the runs of Sunier and Hess (22) in which they obtained their smallest average deviation, silver filings rather than foil was used. Joyner claims his data to be that of Ag_3Hg_4 in equilibrium with mercury, and Murphy postulates the formation of this compound from the liquid phase at a higher temperature. It was decided to make use of this solid phase to explain the behavior of the amalgams.

The design of the tube would be rather dependent on the type of solid phase used. The use of glass wool above the capillary filter, or filtration through sintered glass, suggested themselves. A method of double filtration or decantation was considered, but did not appear to be applicable as finely divided silver, when wet with mercury, seemed to be dispersed quite uniformly throughout the liquid phase. The use of glass wool above a very fine capillary was deemed the most logical procedure.

An identical tube support was made so that sixteen tubes might be run at the same time.

The supplementary Run N was then made. A temperature of 25°C. was chosen because it could be easily attained and would establish the validity of the data to 20°C. The tubes used were identical with those previously used, with the addition of glass wool above the capillary. Although no objection to the use of the evaporated mercury could be found, it was decided to use new mercury. The time of shaking was increased to two hundred and fifty hours and sixteen tubes were used. Three distinct solid phases were used.

(1) Mr. G. H. Reed,[1] working in this laboratory several years ago on the solubility of silver in mercury at higher temperatures, made up several tubes containing silver and mercury. One of these tubes had been carefully preserved, but for some reason had not been analyzed. The silver had been in contact with the mercury for several years at room temperature. When opened, the solid phase was granular and brittle and retained none of the characteristics of the original foil. When all of the excess mercury was squeezed from the solid through a chamois, and a portion analyzed, it was found to have a composition approximating Ag_3Hg_4.

(2) Since Murphy cites the formation of Ag_3Hg_4, it was decided to attempt to prepare this compound. Weighed amounts of silver and mercury in the proportion of Ag_3Hg_4 were sealed in a tube and evacuated; the tube was so constructed that, by inversion, the contents could be transferred from one end to the other through a capillary. This acted as a criterion when the contents were entirely liquid. This tube was heated at 250°C. for forty hours, then raised to 500°C. and the contents filtered three times at intervals of one hour, thus insuring homogeneity of the contents. The tube was then cooled to 300°C. and held for twenty-four hours, cooled to 250°C. and held for fifty hours, and kept in an oven at 100°C. until introduced into the tubes. The contents of the tube were entirely solid, and had a bright crystalline appearance.

---

[1] See footnote (a), Sunier and Hess (22).

(3) Finely divided silver was prepared in a manner similar to that described by Tartar and Turinsky (25), who refer to Lewis (10). Some modifications were made. The silver employed was the "1000 fine" foil, and c. p. chemicals were used. The silver carbonate was heated in a stream of hydrogen at 250°C. to 300°C. for six hours, and then raised to 500°C. until there was no further loss in weight.

The temperature throughout the run was very constant, the thermoregulator being used. Two tubes were broken at the inception of the run. The contents of one was transferred to a tube with no glass wool, but yielded a very high result. The contents of one tube refused to filter, so they were removed and quickly squeezed through a chamois skin. The very high silver content obtained in this case is of significance.

The average solubility obtained from this run agreed very well with the straight line plot, hence establishing the straight line function to 25°C. or lower. Furthermore, the different variables used seemed to clear up any question of variable phases employed.

A consideration of available data leads one to some interesting speculations. First of all, the term "solubility" must be defined. Richardson (18) states, "a solution is a body of homogeneous character, the composition of which may be varied continuously within certain limits." Lewis and Randall (11a) give a more fundamental definition. Definitions may vary but the idea of homogeneity is always retained. Next the criterion of homogeneity must be defined. In ordinary aqueous or organic systems, this idea is overlooked, for the appearance of the solution is an immediate criterion. A cloudy or translucent appearance postulates a colloid sol, while a clear appearance is evidence of a real solution. The effect of light, then, is the means of classification in these systems. In the mercury system, the opacity prevents determination of the clearness, so that the amount of material that passes through the filter in the liquid phase has been a criterion of solubility. Too little attention has been paid to the size of the filter or conditions of filtration, i.e., pressure.

It is this fact that may account for the many discrepancies in data reported. Russell (19), working on amalgams other than silver and gold, reports some interesting findings. His method of analysis relies on the preferential oxidation of metals less noble than mercury, by shaking the amalgam with a solution of potassium permanganate. In one study he filtered identical amalgams through a Jena glass sintered filter and through chamois skin. He found the use of the chamois skin very unreliable, the apparent solubility inconstant and several times larger than when filtered through the sintered glass filter. This is in agreement with the result obtained when a chamois skin was used in Run N. A large majority of the excluded determinations in this paper have been "high."

Until there is some method of determining a homogeneous phase, other than filtration, the term "solubility" in a metallic system has a limited meaning, for particles may vary in size from atomic proportions to large aggregates. If this is true, and there is not a sharp gradation, solubility will be dependent on the conditions of filtration. Apparently, in the silver–mercury system, there is a distinct difference in size of silver particles above 40°C., while below that temperature there seems to be a gradual gradation. It seems, therefore, that the greatest credence should be accorded to the lowest results, provided that enough time has elapsed for equilibrium to be reached.

There is a possibility that a measurement of the light reflected from an amalgam, or some other optical means may be used by which homogeneity may be determined.

SUMMARY

1. Amalgams as dilute as 0.06 atomic per cent have been prepared, and analyzed with a precision approaching one part per thousand.

2. One hundred and twenty-eight determinations of the solubility of silver in mercury in the range 20°C. to 80°C. have been made.

3. Several forms of silver and intermetallic compounds have been used as the solid phase.

4. In the range of temperature from 20°C. to 80°C. the solubility changes according to the equation

$$\log N = \frac{-1105.8}{T} + 0.5894$$

5. The relation of the term "solubility" to particle size has been briefly discussed.

In conclusion the writer wishes to express his sincere appreciation to Professor Arthur A. Sunier who has so inspiringly and unselfishly directed this research.

REFERENCES

(1) Clark: Determination of Hydrogen Ions. The Williams & Wilkins Company, Baltimore (1917).
(2) de Souza: Ber. **8**, 1616 (1875); **9**, 1050 (1876).
(3) Eastman and Hildebrand: J. Am. Chem. Soc. **36**, 2020 (1914).
(4) Fales: Inorganic Quantitative Analysis, paragraph 82, p. 103. The Century Co., New York (1925).
(5) Gouy: J. Physics **4**, 320 (1895).
(6) Harteck: Z. physik. Chem. **134**, 1 (1928).
(7) Hulett and Minchin: Phys. Rev. **21**, 388 (1905).
(8) Humphreys: J. Chem. Soc. **69**, 243 (1896).
(9) Joyner: J. Chem. Soc. **99**, 195 (1911).
(10) Lewis: J. Am. Chem. Soc. **28**, 158 (1906).

(11) Lewis and Randall: Thermodynamics, p. 480. McGraw-Hill Book Company, New York (1923).
(11a) Ibid. p. 10.
(12) Mayer: Z. Physik **50**, 209 (1905).
(13) Murphy: J. Inst. Metals, March, 1931.
(14) Ogg: Z. physik. Chem. **27**, 285 (1898).
(15) Parravano and Jovanovich: Gazz. chim. ital. **49**, 6 (1919).
(16) Piersal: Phys. Rev. **23**, 785 (1925).
(17) Reinders: Z. physik. Chem. **54**, 609 (1906).
(18) Richardson: General Chemistry. Henry Holt and Company, New York (1928).
(19) Russell: J. Chem. Soc. **32**, 835 (1932); **32**, 891 (1932).
(20) Steachie: J. Phys. Chem. **35**, 2113 (1931).
(21) Sunier and Gramkee: J. Am. Chem. Soc. **51**, 1703 (1929).
(22) Sunier and Hess: J. Am. Chem. Soc. **50**, 662 (1928).
(23) Sunier and White: J. Am. Chem. Soc. **52**, 1842 (1930).
(24) Tammann and Strassfurth: Z. anorg. Chem. **143**, 357 (1925).
(25) Tartar and Turinsky: J. Am. Chem. Soc. **54**, 580 (1932).
(26) Van Hetteren: Z. anorg. Chem. **42**, 128 (1904).

THE DETERMINATION OF THE ISOELECTRIC POINT

LYLE VERNON ANDREWS AND D. J. BROWN

The Chemical Laboratory, University of Nebraska, Lincoln, Nebraska

Received January 18, 1933

The isoelectric point may be calculated as outlined by Kuhn (1) and Simms (2) from the basic and acidic ionization constants of the oxide. These constants are often unreliable. This electrometric method is suggested as a means of measuring the isoelectric point of an amphoteric oxide.

MATERIALS AND APPARATUS

A. Mercuric oxide. One of the best grades of commercial oxides, red variety, was used. Half-cells containing this commercial form of mercuric oxide gave potentials which agreed to within 0.0001 volt with half-cells containing red mercuric oxide prepared by decomposing purified mercuric nitrate.

B. Lead oxide, red variety, was precipitated from a hot 12 normal solution of potassium hydroxide, as described by Smith and Woods (3) by adding powdered lead acetate to the hot alkali. The oxide was washed by decantation with hot 10 normal potassium hydroxide, then washed thoroughly and repeatedly with hot distilled water, and dried over sulfuric acid in a vacuum desiccator. Analysis for lead, according to the gravimetric method of Brown, Moss, and Williams (4) gave 99.7 per cent of PbO. A small amount of water was evolved when the oxide was heated strongly.

C. Lead oxide, hydrated, was precipitated from a dilute lead acetate solution by the addition of a dilute solution of potassium hydroxide at room temperature. The precipitate was washed by decantation with warm distilled water and dried over sulfuric acid in a vacuum desiccator. Analysis gave the ratio of hydroxyl to lead as being very close to 2:1, showing the absence of a basic salt. The per cent of lead was 89.77, which agrees well with Mueller (5) who found 89.75 per cent and represented the composition of the oxide by the formula $(PbO)_3H_2O$, which requires 90.40 per cent of lead.

D. Potassium hydroxide solution was prepared as described by Ming Chow (6). A 50 per cent solution of one of the best grades of potassium hydroxide was electrolyzed in a tall form beaker, using a large sheet of platinum foil (8 × 10 cm.) for the anode and about 2 kilograms of redistilled mercury for the cathode. The beaker was covered and the mercury was stirred during electrolysis. A current of 10 to 15 amperes was passed through until the amalgam had become so crystalline it could no longer be stirred. It was washed several times with distilled water, then transferred to a 3-liter flask, and washed a few more times in the absence of carbon dioxide. The flask was then filled with distilled water and connected with a filtering tube and another flask. After about two weeks the amalgam had decomposed and the solution was filtered through an asbestos filter. The filtering tube was removed and a carbon dioxide trap, which permitted filling of a weight buret, was attached. The solution at no time gave a test for carbonate. The molality of the solution was determined by titrating with hydrochloric acid, standardized against sodium carbonate, and also by titrating against benzoic acid. Weight burets were used in these titrations. Solutions containing 0.1 mole of potassium hydroxide per thousand grams of water, were made up gravimetrically and the more dilute solutions made by diluting these, using calibrated pipets and volumetric flasks.

E. Doubly distilled water, distilled in an all Pyrex still, first from alkaline permanganate and then redistilled from the clean still, was used. It was kept in 5-gallon bottles and was protected from the carbon dioxide of the air.

Saturated solutions of the oxides were made in 200-ml. round bottomed, long necked flasks, fitted with ground glass stoppers and provided with rubber caps to prevent carbon dioxide from working past the ground glass stoppers. These flasks were almost filled with solvent, an excess of the solid oxide added, and then shaken in a constant temperature air bath at 25.0 ± 0.2°C.

Electrode vessels were kept in a thermostat bath at 25.00 ± 0.05°C.

Each half-cell consisted of a Pyrex test tube with a side arm, and a tube sealed on at the bottom and bent upward, carrying a smaller tube with a platinum wire sealed in at the lower end. It was stoppered with a rubber stopper coated with stopcock grease in order to prevent carbon dioxide from entering.

The side arms of the cells were dipped in a beaker containing the same solution that was in the cells, and covered with a layer of paraffin to prevent evaporation.

The only electrode vessel which presents enough novelty to warrant showing in a diagram, is the vessel shown in figure 1. This cell makes possible the measurement of potentials in very dilute solutions, even less than 0.0001 molal. The rate of diffusion in this vessel was tested with a dilute potassium permanganate solution. A number of days were required for the permanganate to diffuse from the right half into the left half of the cell.

All potentials were measured with a Leeds and Northrup type K potentiometer. The standard cell was checked frequently against a new cell, checked by the Bureau of Standards.

EXPERIMENTAL PART

The rate of solubility and nature of a solution of lead oxide, as given in the literature, is so uncertain that a few investigations were carried out in connection with this problem.

Randall and Spencer (7) determined the solubility of three lead oxides in alkaline solutions, ranging in concentration from about 0.05 to 0.3 molal. They claimed that in order to obtain saturated solutions of lead oxide, red variety, it was necessary to shake mixtures containing an excess of solid oxide for from twenty to fifty days. They shook the hydrated oxide, $(PbO)_3H_2O$, for from five to thirty days.

TABLE 1

Rate of solubility of $(PbO)_3H_2O$ *in water*

TIME OF STIRRING	MOLES OF Pb IN 1000 GRAMS OF SOLUTION
5 minutes	5.50×10^{-4}
15 minutes	5.75×10^{-4}
50 minutes	5.78×10^{-4}
4 hours	5.76×10^{-4}
24 hours	5.72×10^{-4}

TABLE 2

Rate of solubility of PbO (*red*) *in approximately 0.1 molal* KOH *solution*

TIME OF STIRRING	MOLES OF Pb IN 1000 GRAMS OF SOLUTION
20 minutes	3.897×10^{-3}
3 hours	4.193×10^{-3}
7 hours	4.356×10^{-3}
25 hours	4.417×10^{-3}
48 hours	4.429×10^{-3}
122 hours	4.425×10^{-3}

We determined the rate of solubility of hydrated oxide in pure water, and the rate of solubility of red oxide in approximately 0.1 molal potassium hydroxide solution, by adding about 3 g. of the solid oxide to about 2 liters of the solvent contained in a 3-liter conical flask, fitted with a stirrer equipped with a vaseline seal to exclude carbon dioxide, a filter tube containing an asbestos filter, which permitted withdrawal of samples while the solution was being stirred, and an inlet tube connected with a source of carbon dioxide-free air. Stirring was just vigorous enough to keep the major portion of the solid oxide suspended in the solvent. Samples were withdrawn through the asbestos filter at various intervals from the time stirring was started and were analyzed for lead. The results of the measurements are given in tables 1 and 2.

From the above measurements it would appear that saturated solutions of the hydrated oxide can be obtained in a few hours, and saturated solutions of the red oxide in a few days. The hydrated oxide was shaken for at least twelve hours and the red oxide for from seven to ten days.

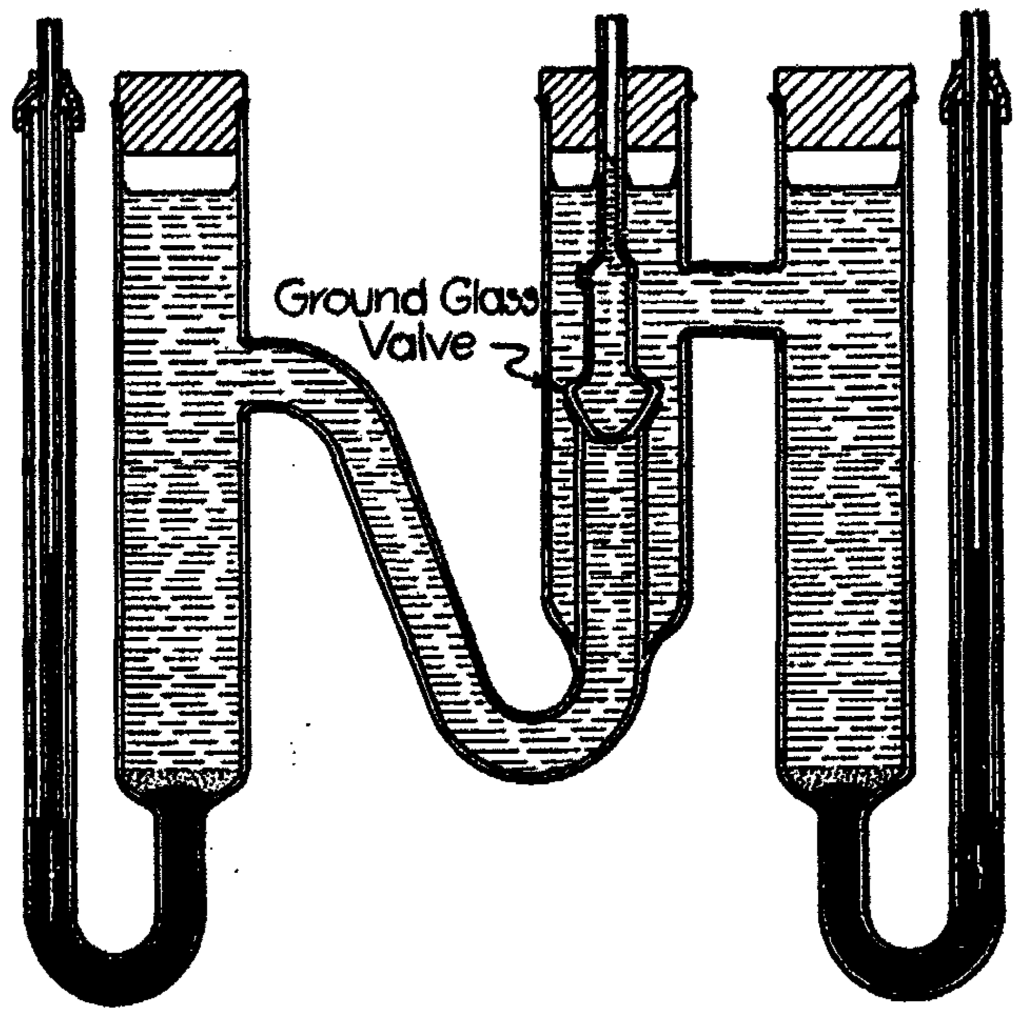


FIG. 1

In order to determine the basic characteristics of lead oxide and perhaps give a better idea of the nature of the solution, concentration cells of the type

$$Hg - HgO_{(s)} - KOH \parallel H_2O - PbO_{(s)} - HgO_{(s)} - Hg$$

were set up and measured in electrode vessels of the type shown in figure 1. The electrolyte in the right half-cell consisted of a saturated solution of lead oxide in water, while the electrolyte in the left half-cell consisted of potassium hydroxide solution.

The reaction in such a cell, when an electron current flows through the cell from right to left is

$$Hg + 2OH^- \rightarrow HgO + H_2O$$

in the left half-cell and

$$HgO + 2H_2O \rightarrow Hg + 2OH^-$$

in the right half-cell. The total change is the formation of OH^- in the right half-cell and consumption of OH^- in the left half-cell. The *E* of this cell must then depend upon the activity of the hydroxide ion in the two half-cells. The molality of the potassium hydroxide was varied and the *E* of the cell measured. When *E* is zero, the activity of the hydroxide ion in the two half-cells must be equal. This must be almost the same as the molality of the potassium hydroxide when the measured *E* is zero. Under these conditions the liquid junction potential will be very small.

TABLE 3

E.M.F. of cells $Hg - HgO_{(s)} - KOH \parallel H_2O - PbO_{(s)} - HgO_{(s)} - Hg$

MOLALITY OF POTASSIUM HYDROXIDE	E_a	E_b	AVERAGE *E* OF CELL
0.0010	0.0450	0.0435	0.0443
0.0004	0.0260	0.0255	0.0257
0.0002	0.0003	0.0004	0.0004
0.0001	−0.0135	−0.0165	−0.0150

TABLE 4

E.M.F. of cells $Hg - HgO_{(s)} - KOH \parallel H_2O - (PbO)_3H_2O_{(s)} - HgO_{(s)} - Hg$

MOLALITY OF POTASSIUM HYDROXIDE	E_a	E_b	AVERAGE *E* OF CELL
0.0010	0.0280	0.0190	0.0235
0.0004	0.0088	0.0090	0.0089
0.0003	0.0007	0.0009	0.0008
0.0002	−0.0068	−0.0075	−0.0072

That mercuric oxide is such a weak base as to have no effect on the alkalinity was demonstrated by measuring the *E* of the cell.

$$Hg - HgO_{(s)} - KOH\ (0.001\ M) \parallel H_2O - HgO_{(s)} - Hg$$

This cell gave a value of about 0.24 volt, which proves that the mercuric oxide in the right half-cell was not basic enough to interfere with the basic properties of lead oxide. By plotting the measured *E* of the cell against the logarithm of the molality of potassium hydroxide, a straight line is obtained which cuts the zero line when the activity of OH^- is the same throughout the cell.

In all measurements, a cell will be called positive when there is a tendency for an electron current to flow through the cell from right to left.

The data for this series of cells are given in table 3. By interpolation E is zero when log of molality of potassium hydroxide is -3.735. This gives the molality of potassium hydroxide as 1.84×10^{-4} and therefore the activity of the hydroxide ion in the lead oxide is 1.84×10^{-4}.

A similar series of measurements, table 4, was made with the hydrated oxide, $(PbO)_3H_2O$.

By interpolation the activity of the hydroxide ion in the hydrated lead oxide solution is 2.82×10^{-4}. If this comes from the primary basic ionization of the oxide, it is possible to combine this data with the solubility data in table 1 and calculate the primary basic ionization constant of lead oxide. The activity of the lead ion in such a solution can be estimated from the value -0.122 volt for the $Pb—Pb^{++}$ ($\alpha = 1$) electrode as given in Gerke's (8) compilation of electrode potentials, and the value -0.508 volt for the $Pb—PbO_{(s)} - OH^-$ ($\alpha = 1$) electrode as measured by Smith and Woods (3). By substituting these values in the equation

$$E = E_0 + \frac{0.0592}{2} \log \frac{\alpha Pb^{++}}{1}$$

we get

$$\log \alpha Pb^{++} = \frac{-2}{0.0592} (0.580 - 0.122)$$

$$\alpha Pb^{++} = 3.2 \times 10^{-16}$$

when αOH^- is unity, and the solution is saturated with lead monoxide (red). The solubility of the hydrated oxide is of the same order as the solubility of the red oxide, and we can assume that the product $\alpha Pb^{++} \times \alpha OH^-$ in a $(PbO)_3H_2O$ solution is a number of the order of 3.2×10^{-16}. When αOH^- is 2.82×10^{-4} as given above, αPb^{++} must be about 10^{-8}, which is so small that the secondary ionization of the oxide need not be considered. The ionization constant for the primary ionization $PbO \cdot x\, H_2O \rightleftarrows PbOH^+ + OH^-$ is

$$K = \frac{\alpha PbOH^+ \times \alpha OH^-}{\alpha PbO \cdot x\, H_2O}$$

$$\alpha PbOH^+ = \alpha OH^- = 2.82 \times 10^{-4}$$

$$\alpha PbO \cdot x\, H_2O = 5.75 \times 10^{-4} - 2.82 \times 10^{-4} = 2.93 \times 10^{-4}$$

$$K = \frac{2.82 \times 10^{-4} \cdot 2.82 \times 10^{-4}}{2.93 \times 10^{-4}} = 2.7 \times 10^{-4}$$

The above measurements and calculations indicate that a solution of lead oxide is a true solution, having an ionization constant characteristic of a moderately weak base.

In order to investigate the amphoteric properties of lead oxide and to determine its effect upon the reference electrode, a number of cells of the type

$$Hg - HgO_{(s)} - KOH \parallel KOH - PbO_{(s)} - HgO_{(s)} - Hg$$

were measured. The molality of the potassium hydroxide was the same in each half-cell. These are concentration cells similar to the cells in the previous series and the *E* of the cells will be zero whenever the lead oxide acts equally as an acidic and basic oxide. The data are given in table 5 and the graph in figure 2.

TABLE 5

E.M.F. of cells $Hg - HgO_{(s)} - KOH \parallel KOH - PbO_{(s)} - HgO_{(s)} - Hg$

MOLALITY OF POTASSIUM HYDROXIDE	E_a	E_b	AVERAGE E OF CELL
0.0200	0.0035	0.0036	0.0036
0.0100	0.0017	0.0018	0.0018
0.0075	0.0016	0.0016	0.0016
0.0060	0.0014	0.0015	0.0015
0.0055	−0.0006	−0.0005	−0.0006
0.0050	−0.0027	−0.0021	−0.0024
0.0010	−0.0070	−0.0065	−0.0068

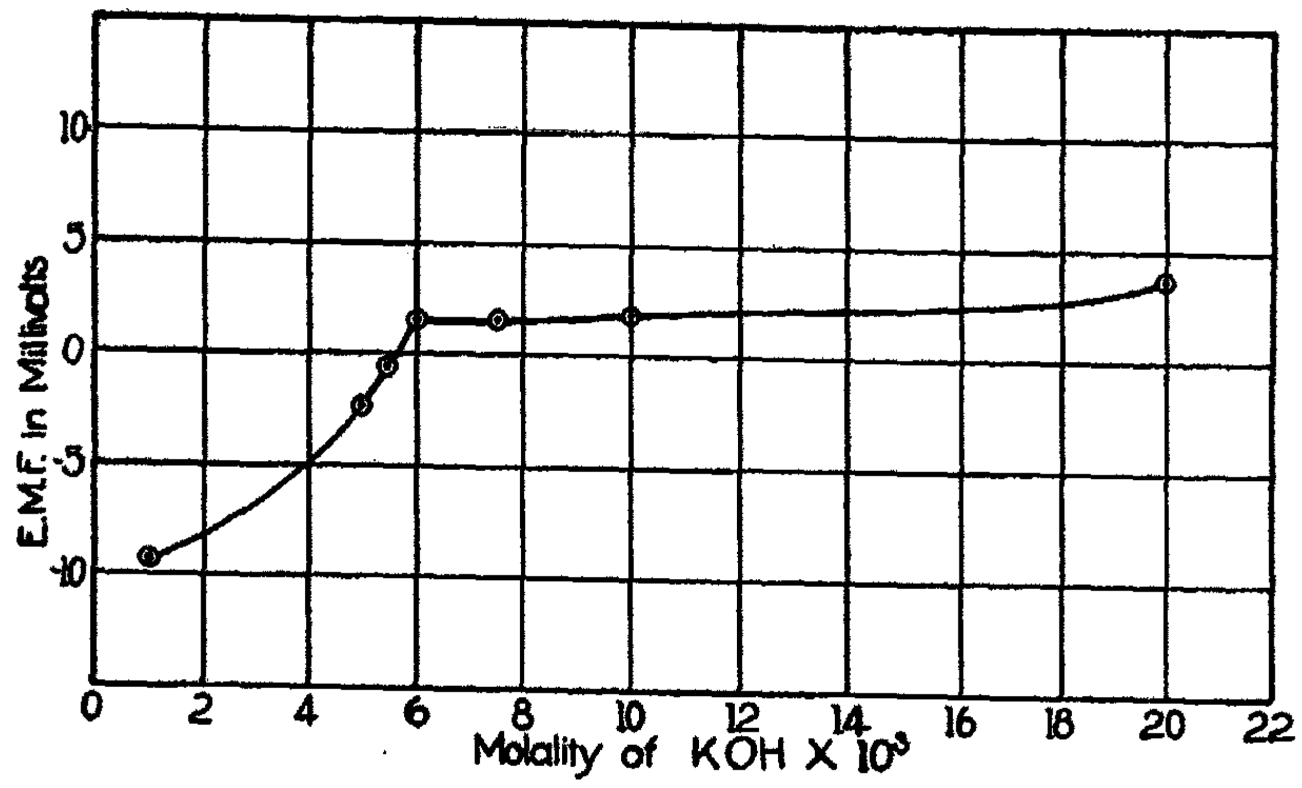


Fig. 2

The data in table 5 prove that in this range of alkalinity, the addition of red lead oxide does not destroy the reproducibility of the electrode. At concentrations of potassium hydroxide greater than 0.02 molal, the potentials showed a greater variation. The molality of potassium hydroxide at which the E curve cuts the zero line, read from figure 2 as 5.6×10^{-3} is called the isoelectric point of the oxide.

SUMMARY

The rate of solubility and the amphoteric properties of lead oxide have been studied, and a general method for measuring the isoelectric point of an amphoteric oxide has been suggested.

REFERENCES

(1) Kuhn: Z. physik. Chem. **114**, 44 (1924).
(2) Simms: J. Am. Chem. Soc. **48**, 1239 (1926).
(3) Smith and Woods: J. Am. Chem. Soc. **45**, 2632 (1923).
(4) Brown, Moss, and Williams: Ind. Eng. Chem., Anal. Ed., **3**, 134 (1931).
(5) Mueller: Z. physik. Chem. **114**, 129 (1928).
(6) Ming Chow: J. Am. Chem. Soc. **42**, 488 (1920).
(7) Randall and Spencer: J. Am. Chem. Soc. **50**, 1572 (1928).
(8) Gerke: Chem. Rev. **1**, 377 (1925).

CERTAIN PHYSICAL PROPERTIES OF DIVINYL ETHER

FRANCIS T. MILES AND ALAN W. C. MENZIES

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Received February 16, 1933

Divinyl ether has recently (1) been proposed as an anesthetic. A knowledge of some of its physical properties, and especially of its vapor pressures, was obviously desirable, and a study of certain of these properties is here recorded.

THE MATERIAL USED

A method of preparation of this substance has recently been worked out by Ruigh and Major (2) in the Laboratory for Pure Research of Merck and Company, Inc. They suggested the present work, and we are indebted to them for a sample of their purest product, it being the middle fraction, boiling over a range of 0.02°C., of a freshly prepared and purified batch of over a liter. These investigators show (2) that the product obtained by earlier workers has been of lower purity.

VAPOR PRESSURE MEASUREMENT

This was carried out by the static isoteniscope (3) method of Smith and Menzies. The pressure gauge consisted of a U-form Pyrex glass tube of 13-mm. bore, containing triple-distilled mercury, one limb of which was evacuated to a pressure of less than 0.01 mm. of mercury as measured by a McLeod gauge. The mercury levels were read off against a vertical mirror by means of a truly horizontal hair line ruled on a glass microscope slide fixed in a carrier which could slide the whole length of a graduated vertical steel bar 2½ meters long. The graduation of this bar is nowhere in error by over 0.01 mm. The reduction of the pressure readings to millimeters of mercury at 0°C. and g = 980.66 was carried out as described elsewhere (3). At Princeton, g = 980.18.

Temperature measurement above 0°C. was made by a mercurial thermometer graduated in tenths of a degree and certificated at the Reichsanstalt to the nearest ±0.02°C. at each 10°C. interval. The ice-point of this thermometer was of course redetermined. Below 0°C. another thermometer graduated to tenths was used, and its readings were corrected, through the courtesy of a colleague, by comparison with a platinum resistance thermometer whose readings are believed good to hundredths of a degree.

The temperature bath was a 4-liter beaker, containing either water or else carbon tetrachloride, adequately stirred by a rotating vertical shaft carrying three propellor-like agitators. By adding solid carbon dioxide the temperature could readily be lowered to −20°C.

In preparing the isoteniscope, we took due precaution to remove, by heating and exhausting, the moisture film from the surface of the glass.

TABLE 1

Vapor pressures of divinyl ether determined experimentally

OBSERVATION NUMBER	T (observed)	PRESSURE (observed)	T (calculated)	$T_{obs.} - T_{calc.}$
	degrees C.	*mm.*		
1	−19.70	85.7	−19.673	−.027
2	−19.69	86.0	−19.610	−.080
3	−16.55	101.5	−16.595	.045
4	−16.19	103.5	−16.235	.045
5	−10.02	143.7	−9.986	−.034
6	−9.18	150.0	−9.142	−.038
7	−0.39	230.0	−0.373	−.017
8	−0.04	233.4	−0.060	.020
9	4.06	282.4	4.089	−.029
10	13.58	426.6	13.608	−.028
11	14.01	433.9	14.017	−.007
12	14.39	440.5	14.382	.008
13	20.22	557.2	20.205	.015
14	20.22	557.5	20.218	.002
15	20.56	564.0	20.513	.047
16	20.65	566.7	20.635	.015
17	21.45	584.7	21.434	.016
18	21.79	592.8	21.787	.003
19	21.88	595.8	21.917	−.037
20	22.25	602.9	22.223	.027
21	23.66	636.5	23.636	.024
22	28.35	759.2	28.322	.028
23	28.64	767.0	28.600	.040
24	35.31	971.1	35.183	.127
25	35.64	985.2	35.597	.043
26	43.74	1294.2	43.693	.047
27	43.77	1296.2	43.741	.029
28	43.91	1311.5	44.101	−.191
29	49.33	1551.0	49.361	−.031
30	49.56	1565.7	49.664	−.104

EXPERIMENTAL RESULTS OF VAPOR PRESSURE MEASUREMENT

These are tabulated in table 1, in which the first three columns are self-explanatory.

In order to obtain a smooth curve through our experimental points, we chose a three-constant equation of the Rankine-Kirchoff-Dupré-Hertz type, and evaluated the constants as follows:

$$\log_{10} p_{\mathrm{mm.}} = 21.73592 - \frac{2085.11}{T_{\mathrm{abs.}}} - 4.81530 \log_{10} T_{\mathrm{abs.}} \qquad \text{(M)}$$

The fourth column in table 1 shows the temperatures calculated for the observed pressures by means of this equation. The fifth column serves to show (1) the closeness of fit, since the algebraic sum of the differences between calculated and observed temperatures is 0.042°C., and (2) the degree of consistence of the observations, for the sum of all the differences, each taken as positive, divided by the number of observations is 0.040°C., which may be considered as the average error of a single observation.

TABLE 2

Vapor pressure of divinyl ether calculated from equation M

	0	2	4	6	8
−30	*46.8*^{9}				
−20	*84.1*^{5}	*75.1*^{7}	*67.0*^{0}	*59.5*^{4}	*52.8*^{9}
−10	143.6	129.5	116.6	104.8	94.0^{1}
−0	234.1	213.0	193.5	177.5	158.9
0	234.1	256.8	281.3	307.6	335.9
10	366.3	398.8	433.6	470.8	510.5
20	552.7	597.7	645.4	696.4	750.2
30	807.3	867.8	931.6	999.1	1070.
40	1145.	1224.	1307.	1395.	1486.
50	*1582.*	*1683.*	*1788.*	*1898.*	*2014.*
60	*2134.*				

Extrapolated values are in italics.

Table 2 shows the vapor pressures of divinyl ether as calculated by equation M for each 2°C. interval from −30°C. to +60°C. We have extrapolated values for 10°C. beyond each end of our experimental range, and show these extrapolated values in italics. We publish these pressure values for such small steps of temperature so that interpolation, using p and t as variables, can be made directly without exceeding the experimental error of the observations.

The normal boiling point of divinyl ether, according to equation M, is 28.35°C. ±0.04°. This is in concordance with the normal boiling point, 28.3°C. ±0.2°, reported by Ruigh and Major.

DÜHRING'S, AND RAMSAY AND YOUNG'S RULE WITH ETHYL ETHER AS COMPARISON SUBSTANCE

Before the present measurements were made, Ruigh had obtained approximate values for the vapor pressures of divinyl ether by comparison with diethyl ether. For very closely analogous substances, the ratio T_V/T_E of the absolute temperatures at which two substances, V and E, have the same vapor pressure should remain approximately constant. At the normal boiling point, this ratio for vinyl and ethyl ethers is 301.45/307.54 or 0.9802. If this ratio is used, employing the values for ethyl ether found in International Critical Tables, the temperature discrepancy from our values for divinyl ether for the pressure 112.3 mm. is −0.50°C. and for the pressure 1277 mm. is +0.12°C. Therefore, not the Dühring but rather the Ramsay and Young equation

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} + c\,(T'_B - T_B)$$

is to be preferred, where $c = 0.00003$.

DENSITY AND SPECIFIC VOLUME

It is well-known that for ranges of temperature sufficiently removed from the critical temperature, the change of specific volume of a liquid with temperature may be represented satisfactorily by a quadratic equation in t, measured from a convenient point. For ethyl ether, such an equation is said in I. C. T. to represent the facts in the range 0°C. to 70°C. to one part in ten thousand. For our purposes, therefore, it was sufficient to measure the density of divinyl ether at three known temperatures near 0°, +13°, and +25°C. This we did by means of a dilatometer. From the values so obtained, we determined the three constants in the following equation:

$$d_t = [d_s + 10^{-3}\,\alpha\cdot(t - t_s) + 10^{-6}\cdot\beta\cdot(t - t_s)^2] \pm 10^{-4}\cdot\Delta \qquad \text{(D)}$$

in which $t_s = 0°\text{C}.$
$d_s = 0.79601$
$\alpha = -1.14582$
$\beta = -2.5706$
$\Delta = 2.$

LATENT HEAT OF VAPORIZATION

True values for this can be obtained from the Clapeyron equation, provided dp/dt and the specific volumes of both vapor and liquid are known. Although equation M above is an empirical equation, it nevertheless represents accurately the experimental facts, and we can, therefore, obtain true values of dp/dt by its use. We had already measured the densities of the liquid. It was, therefore, necessary to measure experimentally only the specific volume of the vapor. It is frequently forgotten that values obtained upon the assumption that a saturated vapor follows the simple gas laws may be in error by several per cent. Because the instability of divinyl ether makes it a difficult subject for precise vapor density work, we have contented ourselves with reporting its orthobaric density only at one temperature, the normal boiling point. The measurements were made in a 100-cc. bulb sealed to a graduated capillary in which the condensed liquid portion could be measured with an accuracy of ±0.03 per cent. The total content of divinyl ether in the apparatus was obtained by direct weighing. The orthobaric density of the vapor thus found was 0.00299_4 ±0.5 per cent, a mean of two observations. This value is $5._7$ per cent higher than the value computed by the simple gas laws.

Substituting in the rigid Clapeyron equation the experimental values thus found, we obtain 6260 and 89.4 calories as the latent heat of vaporization of divinyl ether at 28.35°C., per mole and per gram respectively, with an accuracy of ±0.5 per cent.

TROUTON'S CONSTANT

The value just reported yields 20.8 for this constant, as compared with 20.8 for diethyl ether using Mathews' (4) value for the latent heat of vaporization.

HILDEBRAND'S CONSTANT

It will be recalled that Hildebrand (5) found steadier constants than those given by Trouton's rule when he considered entropies of vaporization for series of liquids at temperatures chosen to yield vapors of the same concentration rather than the same vapor pressure. Using the concentration where $\log T - \log p = 0.5$, as in an example studied by Hildebrand, we find that, for divinyl ether, the appropriate temperature is near −21°C. and the constant is 14.2 instead of Hildebrand's standard or average value 13.7. Using Taylor and Smith's (6) values for the vapor pressure of diethyl ether, we find a value of 14.0 for Hildebrand's constant, calculated likewise for the above concentration, which is reached near −17°C.

SUMMARY

The vapor pressures of divinyl ether are reported in the range −30°C. to 60°C.

An equation is given relating experimental values of the density of the liquid to temperature.

The latent heat of vaporization at the normal boiling point is evaluated from the vapor pressure curve with the help of an experimental determination of the orthobaric volume of the vapor.

The constants of Trouton and Hildebrand are evaluated under standard conditions.

REFERENCES

(1) LEAKE AND CHEN: Proc. Soc. Exptl. Biol. Med. **28**, 151 (1930).
(2) RUIGH AND MAJOR: J. Am. Chem. Soc. **53**, 3663 (1931).
(3) SMITH AND MENZIES: J. Am. Chem. Soc. **32**, 1419 (1910).
(4) MATHEWS: J. Am. Chem. Soc. **48**, 562 (1926).
(5) HILDEBRAND: J. Am. Chem. Soc. **37**, 970 (1915).
(6) TAYLOR AND SMITH: J. Am. Chem. Soc. **44**, 3450 (1922).

ARE LIQUID SODIUM AMALGAMS COLLOIDAL?

A Discussion of the Paper of Paranype and Joshi

HENRY E. BENT

Division of Chemistry, Harvard University, Cambridge, Massachusetts

Received February 6, 1933

A recent issue of This Journal (1) contains an article by Paranype and Joshi which presents arguments purporting to show that sodium amalgams are colloidal in nature and that as such their properties depend on the method of preparation and treatment as well as on the concentration. If the conclusions of these authors are correct, most of the experimental data on sodium amalgams, and by implication the data on all of the alkali metal amalgams, become of doubtful value since in most cases the physical method of handling the amalgams has not been considered a significant factor. It would seem, therefore, worth while to analyze carefully the arguments of Paranype and Joshi and to present further evidence as to the nature of these solutions.

Two questions have been raised by Paranype and Joshi. First, does the method of preparing an amalgam affect the physical properties or is it sufficient to know the concentration, temperature, and pressure? Second, are sodium amalgams colloidal solutions? The answer to the first question does not necessarily answer the second, since it is possible that a reversible colloid might exist. The data and arguments presented by Paranype and Joshi will first be discussed and finally additional data which permit rather definite conclusions will be presented.

THE REPRODUCIBILITY OF AMALGAMS

Paranype and Joshi enumerate five different types of experimental data in which the results do not seem to be reproducible. They conclude that the different methods used in preparing the amalgams resulted in different colloidal solutions and account in this way for the experimental data. Let us consider these cases in detail. The data on the conductivity of amalgams obtained by Hine (2), Vanstone (3), Bohariwalla (4), and Davies and Evans (5) are described as follows: "Hine finds that the conductance of sodium amalgam passes through a minimum; Vanstone states that the conductivity concentration curve exhibits a maximum corresponding with $NaHg_2$; Bohariwalla and others obtain two discontinuities, one at 0.079

per cent Na and one at 0.272 per cent Na; while Davies and Evans report only one at 0.272 per cent Na." This treatment does not seem to give a correct picture of the facts. As a matter of fact the first, third, and fourth of these papers agree within the limits of experimental error. The agreement is far from perfect, but seemed to the original investigators satisfactory. Thus, to quote Davies and Evans, "It is difficult to decide with certainty whether these discontinuities in the curves are real, owing to the experimental difficulties;" and again, referring to their work and that of Hine, "It is seen that on the whole the results are in fairly good agreement." Bohariwalla states, "These breaks in the conductivity concentration curves in the case of sodium and potassium amalgams occur at the same composition as have been found by Hine." These data refer to amalgams of from 0 to 5 atom per cent sodium. Vanstone, on the other hand, was working with amalgams containing from 50–100 atom per cent sodium, and therefore his paper is quite irrelevant to the point in question.

The second instance of marked variation in properties has to do with the reactivity of amalgams prepared by Willstätter, Seitz, and Bumm (6) in iron, porcelain, or hessian crucibles. Since Willstätter considered the impurities present sufficient to account for the difference in the behavior of these amalgams, this does not seem to be evidence that pure amalgams have properties which depend on the method of preparation.

The next data to be discussed are those obtained by Vanstone for the phase diagram of sodium amalgams. Paranype and Joshi state, "At all concentrations he observed persistent superfusion and supercooling, which indicates that the freezing point of an amalgam is not definite but extends over a small range of temperature." This conclusion seems to be based on the rather unusual use of the word, "superfusion." The following quotation from Vanstone indicates that the phenomenon observed is nothing more than ordinary supercooling. To quote Vanstone, "The alloy was heated until entirely liquid, then allowed to cool slowly, meanwhile being vigorously stirred. The temperature was read every minute or half minute. In nearly all cases superfusion was observed and the points determined are the maximum temperature reached after overcooling." Nothing is said by Vanstone about heating curves, and we must therefore conclude that he is using the term "superfusion" as synonymous with supercooling. Supercooling is so commonly found for true solutions and pure compounds that it can not be taken to mean that there is any uncertainty regarding the melting point or transition temperature.

The fourth argument has to do with the uncertainty in the composition of the solid phase deduced from the phase diagram. This uncertainty arises chiefly from the fact that the curve is very steep in certain parts and there are many breaks in the curve. For example, in dilute solution Kurnakow states that it is uncertain whether the compound is $NaHg_5$ or

$NaHg_6$, while Schüller and Vanstone state that the compound is probably $NaHg_4$. It must be emphasized, however, that the disagreement is in the interpretation of the data and not in the data itself. These authors found the break in the temperature concentration curve at 17.95, 18.1, and 17.9 per cent sodium which is quite good agreement. The fact that the experimental data is of such a nature as to make the *authors* of these papers uncertain as to the composition of the solid phase does not indicate that the *solid phase* is of uncertain composition.

The last argument has to do with the change of viscosity of sodium amalgams with the time. The experimental work was carried out in the laboratory of Paranype and Joshi in 1928 but has never been published. In the absence of information regarding the methods of obtaining the data it is difficult to draw conclusions as to its significance. A possible explanation would be that the concentration of the amalgam was changing, owing either to surface oxidation or perhaps to incomplete solution of the solid amalgam, which melts at nearly 360°C. Since Paranype and Joshi state in another connection that their amalgams exhibit a scum on the surface when left in contact with their purest nitrogen perhaps the first of these explanations is the more probable. At any rate Paranype and Joshi come to the conclusion, in discussing other properties of amalgams, that they are lyophilic colloids. That the viscosity should increase with shaking is certainly not characteristic of lyophilic colloids and would indicate again that some other explanation must be sought for the viscosity data.

The above discussion leads to the conclusion that experiments cited by Paranype and Joshi do not indicate that the method of preparing pure sodium amalgams is of significance.

COLLOIDAL SOLUTION

The second proposition to be discussed is the question whether amalgams are colloidal or true solutions. Even though the method of preparing amalgams is of no significance, these solutions might be colloidal or partly colloidal. If such a solution were in mobile equilibrium it might be colloidal and still give properties determined by only the concentration temperature and pressure. This question cannot be answered with certainty, but one can scrutinize the arguments for and against the colloidal nature of the solution.

The argument of Paranype and Joshi in so far as it is based on the irreproducibility of the properties of amalgams has been discussed in the first part of this paper. They also give as evidence the fact that the transfer of sodium with the electric current is toward the cathode in concentrated amalgams and toward the anode in dilute solutions, thus resembling the behavior of certain colloidal solutions. If the colloid explanation were the only one possible this would have to be considered an argument. As stated by Paranype and Joshi, however, there are several other possible explanations, so that one cannot consider this by itself as proof.

Several experimental facts are cited (the effect of ultra-violet light on amalgams, the viscosity and surface tension) to prove that the solution cannot be a lyophobic colloid. These are of course of interest after one has concluded that the solutions are colloidal, but do not either prove or disprove this point.

Paranype and Joshi also say that they would expect the solid phase to be crystalline, the heat of solution to be very large, and the vapor pressure of mercury to be less than would be calculated for true solution. These are certainly not attributes of ordinary lyophilic colloids and to say the least do not suggest the colloidal state.

The fact that direct and alternating current measurements give the same value for the conductivity seems to be of no significance, inasmuch as practically all of the conductivity is electronic. Thus it has been shown (7) that the transference number of sodium in these amalgams is less than 10^{-5}. Conductance data would have to be precise to one part in one hundred thousand in order to give much information regarding the behavior of sodium. The data at hand do not begin to approach this degree of precision. If for no other reason than this, the conductance data are not significant in this connection.

In commenting on the work of Richards and Conant (8), Paranype and Joshi state that the deviations from the laws of ideal solution are to be attributed to either colloidal solution or experimental error. Were this true, practically all solutions would have to be considered colloidal, particularly aqueous solutions of strong electrolytes. The object of the experiments of Richards and Conant was to study a solution which gave large deviations from the laws of ideal solution, but they certainly had not the slightest thought that these deviations were due to "experimental error," or that they were due to the colloidal nature of the amalgams.

Finally the suggestion that the formation of scum on the surface of an amalgam is not always due to the formation of oxide but may be due to the disperse phase separating out on the surface, seems to be an argument based on faulty experimental data. Amalgams have frequently been kept for years by the writer in flasks which have been highly evacuated and baked to remove adsorbed water and during such intervals of time showed not the slightest tract of scum.

We may conclude, therefore, that no evidence has been presented which would justify one in concluding that these amalgams are colloidal. This, however, does not prove that amalgams are true solutions. There is some evidence, however, pointing toward true solutions. Perhaps the most convincing is to be found in vapor pressure data. It has been shown (9) that the vapor pressure curve in dilute solutions is that calculated from Raoult's law, thus indicating that we are dealing with single atoms of sodium as the solute. These atoms of course may be solvated, but this would not constitute a colloidal solution as suggested by Paranype and Joshi. To quote them, ". . . . Lewis, Adams, and Lanman formulated a theory and explained the initial decrease in conductivity . . . . as due to large aggregates of mercury atoms gathering around a sodium atom . . . . This conception of Lewis and coworkers appears to be very similar to the formation of a solutoidal colloid." One might infer from this statement that the hydration of ions in water solution is proof that aqueous solutions of strong electrolytes are colloidal.

The freezing point lowering in dilute amalgams is that calculated from Raoult's law. The calculated value is 1.9°C. per atom per cent and the experimental value is 1.9 (3), increasing in more concentrated solutions. A colloidal solution would give a smaller depression of the freezing point.

The excellent microphotographs of Vanstone, which show several types of crystals corresponding to the compounds indicated by the phase diagram, indicate that the solid phase is not colloidal.

The large heat of solution indicates that we cannot be dealing with a lyophobic colloid in which the disperse phase is sodium. Such a colloid would have a greater amount of energy in the form of surface energy instead of much less energy than the original components.

This leaves the possibility of a lyophilic reversible colloid in rather concentrated liquid amalgams. This is only a possibility, however, and until there is positive evidence one is bound to consider it as only a possibility.

SUMMARY

1. Contrary to the conclusion of Paranype and Joshi, there is no proof that the properties of pure sodium amalgams are determined by the method of preparation.

2. The hypothesis that sodium amalgams are colloidal rests upon certain properties which are common to the amalgams and to certain colloidal solutions. Since these properties can be accounted for in other ways, there is no proof at present that sodium amalgams are colloidal.

3. The following facts either prove or constitute strong evidence that sodium amalgams are true solutions.

(a) The freezing point depression of mercury in dilute amalgams is that calculated for an ideal solution.

(b) The vapor pressure lowering is that calculated for an ideal solution. In more concentrated amalgams the lowering is greater than is calculated for an ideal solution. A colloidal solution should show a smaller lowering of the vapor pressure.

(c) The microphotographs of Vanstone of the solid phases indicated by the phase diagram show definite crystalline structure.

(d) The large amount of heat liberated during the formation of an amalgam proves that it cannot be a lyophobic colloid in which the disperse phase is sodium.

REFERENCES

(1) Paranype and Joshi: J. Phys. Chem. **36**, 2474 (1932).
(2) Hine: J. Am. Chem. Soc. **39**, 882 (1917).
(3) Vanstone: Trans. Faraday Soc. **9**, 291 (1914).
(4) Bohariwalla: Indian J. Physics **4**, 147 (1929).
(5) Davies and Evans: Phil. Mag. [7] **10**, 569 (1930).
(6) Willstätter, Seitz, and Bumm: Ber. **61B**, 871 (1928).
(7) Lewis, Adams, and Lanman: J. Am. Chem. Soc. **37**, 2656 (1915).
(8) Richards and Conant: J. Am. Chem. Soc. **44**, 601 (1922).
(9) Bent and Hildebrand: J. Am. Chem. Soc. **49**, 3011 (1927).

PRIMARY SALT EFFECTS IN REACTIONS IN WHICH THE SUBSTRATE IS NEUTRAL

NICHOLAS N. T. SAMARAS

Department of Chemistry, Yale University, New Haven, Connecticut

Received September 30, 1932

It has been suggested by some authors (1) that the primary salt effects in reactions between an ion and an uncharged molecule are governed solely by the changes in the activity coefficient of the catalyzed molecule produced by salt addition. However, as already pointed out by Harned and Åkerlöf (2), experimentally determined values of f_B, the activity coefficient of the neutral substrate, account for neither the order nor the magnitude of the velocity constant variations in salt solutions. In this brief communication a new method of approach will be discussed.

Harned (3), in calculating the activity coefficients of hydrochloric acid in HCl–MCl solutions, has employed the equation

$$\log f = \frac{-.354\sqrt{2C_T}}{1 + A\sqrt{2C_T}} + 2B_a \cdot c_a + 2B' \cdot c_s \qquad (1)$$

B′ is an empirical constant characteristic of the salt. Butler (4), by considering the mutual salting-out of ions obtained an expression which may be used in the interpretation of the B constants. Carrying this idea further we may look upon the B' constant as determining the displacement, or salting-out, of the acid by the salt—inasmuch as in an HCl–MCl solution we have the displacement of hydrochloric acid not only by its own ions but also by the ions of the added salt—and use the Debye and MacAulay (5) expression to represent this part of the activity coefficient. A comparison of the proposed expressions for B and B' leads immediately to the relation

$$B' = B_a \frac{a_{\text{acid}}}{a_{\text{salt}}} \qquad (2)$$

a, the mean ionic radius, is defined by

$$\frac{1}{a} = \frac{1}{\Sigma \nu_i z_i^2}\left[\frac{\nu_+ z_+^2}{a_+} + \frac{\nu_- z_-^2}{a_-}\right] \qquad (3)$$

As the values of B' have been computed by Harned from thermodynamic measurements by means of equation 1, it is possible to test equation 2;

the agreement is quite satisfactory. Although it is doubtful whether B and B' as determined empirically from equation 1, are independently correct, and whether the Butler, and the Debye and MacAulay equations separately express completely these constants, equation 2 may be taken to be valid, as any other factors that may enter will be common to both B and B'; the recently published thermodynamic data of Hawkins (6) also support this equation, in spite of the fact that the B and B' values given differ somewhat from those of Harned. It is also interesting to note that B', being a partial, must be related to the B constants of both the salt and the acid; this relation for HCl–MCl solutions, using the data of Harned (7), is found empirically to be a very simple one.

$$B' = \frac{B_a + B_s}{2}$$

The introduction of the B' constants, as calculated from equations 2 and 3—the ionic radii values are those calculated from crystallographic data (8)—in the interpretation of primary salt effects, for the type of reaction considered, has led to interesting results, it being possible to account for the salt effects in all but one of the reactions examined. Because of the complexity of the problem, no strict theoretical justification can be given for this linking. We may, perhaps, regard the salting-out of a strong, highly soluble electrolyte as its displacement from the neighborhood of the ions of the added salt and therefore as its increased ability to collide with the substrate molecules to form the complex capable of decomposition. Further, it can be shown, from the empirical relation for a uni-univalent electrolyte

$$B' = \frac{B_a + B_s}{2}$$

together with the expressions for B and B', that the displacement coefficient may be also regarded as the change in the dielectric constant, provided that the mean of the $\bar{\delta}$'s ($\bar{\delta}$ is the molal lowering in the dielectric constant) as well as of the a's (defined by equation 3) for the catalyst and the salt is employed; this explanation would be in accord with the suggestion of Harned and Samaras (9).

It is known from experimental data that for reactions between an ion and an uncharged molecule the interionic-force term of the Debye and Hückel expression does not appear, the logarithm of the rate constant varying linearly with the salt concentration (the concentration of the catalyst being fixed) up to very high concentrations (6 or 7N); if, of course, both the ions of the catalyst exert a catalytic effect, this term does enter. The results of the present investigation are summarized in table 1.

That the characteristic factors by which the displacement coefficients

TABLE 1

Expressions for the primary salt effects

REACTION	CATALYST	SALT EFFECT
Cane sugar hydrolysis (i)...........	H^+	$\log k = 3B'\cdot n_s + R$
Acetylchloroaminobenzene transformation (ii)........................	H^+ and Cl^-	$\log k =$ (interionic-force effect) $+ 3B'\cdot n_s + R^{I}$
Cyanamide hydrolysis (iii)..........	H^+	$\log k = 2B'\cdot n_s + R^{II}$
Hydrogen peroxide decomposition (iv)..............................	I^-	$\log k = 2B_s\cdot n_s + R^{III} \approx 4B'\cdot n_s + R^{III}$
Diacetone alcohol decomposition (v)...............................	OH^-; cation also?	$\log k =$ (interionic-force effect) $- 2B'\cdot n_s + R^{IV}$
Ethyl acetate hydrolysis (vi).......	H^+	$\log k = \frac{1}{2}\log f_e + R^{V}$

R is a constant independent of the salt but characteristic of the reaction. The term involving B' is in each case the displacement coefficient of the catalyst. The salt concentrations are from about $0.4N$ to the highest concentration for which data are available. The salt effects are represented very satisfactorily by the expressions given.

(i) The salt data for this reaction are those of Kautz and Robinson (10), and for the medium effect in pure hydrochloric acid (i.e., for the slope of the $\log \frac{k}{n_{HCl}}$ vs. n_{HCl} line) those of Worley (11).

(ii) The empirical equation used by Åkerlöf (12) has been simply rewritten.

(iii) The values of the slopes of the $\log \frac{k}{k_0}$ vs. n_{salt} lines as given by Grube and Schmid (13) have been used. As neither the *B* constant for nitric acid nor the ionic radius of the nitrate ion is known, equation 2 cannot be employed, and the assumption has been made that the displacement coefficients of nitric acid in HNO_3–MNO_3 solutions are the same as those for hydrochloric acid in HCl–MCl solutions, which is perhaps justifiable as in the hydrolysis of sucrose it is found from the data of Worley that the medium effect for nitric acid is exactly the same as that for hydrochloric acid.

(iv) Harned and Samaras (9) have shown that for the hydrogen peroxide decomposition the salt effects can be interpreted by the *B* constants of the added salts; although B_{KI} is not known, by using the empirical relation $B' = \frac{B_{catal.} + B_{salt}}{2}$ together with equation 2, its value may be calculated to be nearly zero (which seems to be borne out also by activity coefficient curves), so that the partial B', which includes both the *B* for the catalyzing electrolyte and the *B* for the salt, will in this case involve B_s alone.

(v) The B''s employed are those of Harned and Åkerlöf (7a), as the calculation from equation 2 cannot be carried out, since the radii of the hydroxides are not known. The catalytic data are those of Åkerlöf (14) and the agreement obtained by using the equation given in the above table is remarkably good up to $6N$ salt concentrations.

(vi) Robinson (15) showed that the *square root* of the activity coefficient of the ethyl acetate accounted for the salt effects; it is possible, although highly doubtful as the order for the various salts is different, that $\log f_e$ is related to the B' constant. As this is the only one of the reactions examined for which the salt effects are given by $f_e^{\frac{1}{2}}$, we must regard it for the present as complicated by an unknown factor or factors.

are multiplied appear to be whole integers, as seen from table 1, must not be regarded as significant, in view of the uncertainty of the values of many of the fundamental quantities involved; all that may be claimed is that the B' constants account quite well for the greatest part of the salt effect. If we agree with Brönsted (16) and Bjerrum (17) that some kind of a complex is formed, we should expect to deal with a ratio of two displacement coefficients, so that for a reaction between an ion and an uncharged molecule and for uni-univalent salts we shall have,

$$\log \frac{k}{k_0} = 2[B_i' - B_s'] \cdot n_s \tag{4}$$

It may be shown that if the susceptibility, α, of the complex is greater than that of water, then the slope of equation 4 is positive and greater than $2B_i'$; similarly, the negative sign in the diacetone alcohol reaction may be accounted for on the assumption that $\alpha_s < \alpha_{OH} < \alpha_{H_2O}$. This scheme is by no means new, as the Brönsted (16) expression, assuming that A in equation 1, which involves the so-called mean distance of approach of the ions, is the same for the catalyst as for the complex, would lead to

$$\log \frac{k}{k_0} = [\beta_i - \beta_s + \beta_B] \cdot n_s \tag{5}$$

Equation 5 differs from equation 4 in that it involves the activity coefficient of the uncharged molecule; it should be pointed out, however, that the values of β_B, as determined from solubility measurements, are not of the same order as the B' constants, and it consequently appears that the kinetic factor F, given by the well-known expression,

$$v = k \cdot c_i c_B \cdot F$$

does not involve the activity coefficient of the neutral substrate.

A comprehensive and detailed examination of this field leads one to the realization that an exact theoretical treatment is impossible at present, not only because of the inherent complexity and obscurity of the problems of chemical reactivity and highly concentrated solutions, but also owing to the paucity, if not complete absence, of reliable data on such fundamental quantities as the dielectric constants of salt solutions. Nevertheless, it is hoped that the viewpoint presented here, supported as it is by experimental data, may be of some value in the final analysis of the problem.

The writer is indebted to Professor H. S. Harned for valuable assistance and information.

REFERENCES

(1) Scatchard: Chem. Rev. **10**, 237 (1932).
Gross: Monatsh. **53–54**, 445 (1929).
(2) Harned and Åkerlöf: Trans. Faraday Soc. **24**, 666 (1928).
(3) Harned: J. Am. Chem. Soc. **48**, 326 (1926).
(4) Butler: J. Phys. Chem. **33**, 1015 (1929).
(5) Debye and MacAulay: Physik. Z. **26**, 22 (1925).
(6) Hawkins: J. Am. Chem. Soc. **54**, 4480 (1932).
(7) Harned and Åkerlöf: Physik. Z. **27**, 411 (1926).
Harned: J. Am. Chem. Soc. **51**, 416 (1929).
(8) Pauling: J. Am. Chem. Soc. **49**, 765 (1927); that for the H^+ is the one given by Bragg: Phil. Mag. [6] **40**, 169 (1920).
(9) Harned and Samaras: J. Am. Chem. Soc. **54**, 9 (1932).
(10) Kautz and Robinson: J. Am. Chem. Soc. **50**, 1022 (1928).
(11) Worley: J. Chem. Soc. **99**, 349 (1911).
(12) Åkerlöf: J. Am. Chem. Soc. **49**, 2955 (1927); the equation used by Åkerlöf as given in this paper contains two typographical errors.
(13) Grube and Schmid: Z. physik. Chem. **119**, 19 (1926).
(14) Åkerlöf: J. Am. Chem. Soc. **48**, 3046 (1926).
(15) Robinson: Trans. Faraday Soc. **26**, 217 (1930).
(16) Brönsted: Chem. Rev. **5**, 231 (1928).
(17) Bjerrum: Z. physik. Chem. **108**, 82 (1924); **118**, 251 (1925).

STUDIES IN COPRECIPITATION. IV

THE COPRECIPITATION OF ALKALI IONS WITH CALCIUM OXALATE AND THE ADSORBENT PROPERTIES OF THE LATTER[1]

I. M. KOLTHOFF AND E. B. SANDELL

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received June 6, 1932

In a previous general discussion (1) of the phenomena of coprecipitation, the presence of foreign ions in the interior of a precipitate was quite generally ascribed to an adsorption of these ions during the growth of the crystalline precipitate. Therefore it may be expected that the order of the amount of coprecipitation in a series of cations or anions, respectively, will be the same as the order of adsorption at the external surface of the precipitate after it has been formed. In order to prove this conclusion, the adsorption of various electrolytes by aged calcium oxalate crystals has been determined. This study is preliminary in character. Many difficulties, especially of analytical nature, have been encountered, which have not yet been completely overcome; therefore a more extensive investigation of the adsorbent properties of calcium oxalate is reserved for the future. The results obtained in the present study are conclusive insofar as the relation between adsorbability and coprecipitation of ions is concerned.

According to the Paneth-Fajans adsorption rule, the adsorbability of a salt having an ion in common with the crystalline adsorbent should increase with decreasing solubility of the salt. J. S. Beekley and H. S. Taylor (2) in a study of the adsorption of silver salts by silver iodide obtained results in fair harmony with this rule; the agreement would have been still better if they had considered the deformation of the adsorbed anions. It follows from the Paneth-Fajans rule that the adsorbability of any individual ion will be larger the smaller the solubility of the compound that it can form with the ion of opposite charge in the adsorbing lattice. This conclusion, however, is not confirmed by the work of Sven Odén (3) and Mlle. L. de Brouckère (4); a more exhaustive discussion must be postponed until more experimental data are available.

---

[1] The material covered in this and following papers has been taken from a thesis submitted by E. B. Sandell (Du Pont Fellow in Chemistry at the University of Minnesota, 1931–1932) to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ADSORPTION OF ELECTROLYTES BY CALCIUM OXALATE

Preparation of aged calcium oxalate suspensions

Preparation I. 0.515 mole of calcium chloride hexahydrate dissolved in 1 liter of hot water was added slowly over a period of twenty minutes to 0.50 mole of ammonium oxalate dissolved in 3 liters of solution at 90°C. The precipitate was washed by decantation until washings were entirely chloride-free. The precipitate contained traces of chloride that could not be washed out; the amount did not exceed 0.01 per cent. The preparation was allowed to stand under water for a week before use in the adsorption experiments. The average crystal diameter was estimated to be 0.5 micron or less.

Preparation II. Precipitation was made in the same way as described under Preparation I, with the sole difference that at the end of the precipitation ammonium oxalate was a few per cent in excess. The preparation was washed by decantation thirteen times and kept under water for two weeks before being used. The average crystal diameter was estimated to be 0.5 micron or slightly more.

Preparation III. 1.00 mole of calcium chloride in 1 liter of hot water was added in a slow stream to 1.02 moles of ammonium oxalate in 3 liters of boiling water containing 2 cc. of hydrochloric acid. The time of addition was fifteen minutes. The precipitate was washed by decantation twelve times. It was kept under water for two months before using. The crystal size was slightly larger than in the preceding preparations.

Procedure

The carefully washed precipitate was mixed with water to give a suspension containing approximately 3 g. of calcium oxalate in 50 cc. From this suspension, well shaken, 50 cc. were removed with a pipet and transferred to a dry glass-stoppered bottle. Then 50 cc. of the solution containing the substance to be adsorbed were mixed with the suspension, and the whole was agitated in a mechanical shaker. The time of shaking is recorded in table 1. The adsorption took place at room temperature, 25±2°C. Because of the uncertainty involved in determining the small amount of substance adsorbed, the use of a thermostat was considered superfluous. After shaking, the mixture was filtered through paper, and 50 cc. of the filtrate was removed with a pipet and titrated with the suitable standard solution. In the case of the oxalates, 0.02 *N* potassium permanganate was used. The end-point correction was obtained by adding potassium iodide to the cold titrated solution and titrating the liberated iodine with 0.005 *N* sodium thiosulfate in the usual manner. The original solution containing the substance to be adsorbed was standardized in exactly the same way by taking 25 cc. In the case of the adsorption of iodates, 0.02 or 0.002 N sodium thiosulfate served for titrating the iodine liberated by adding iodide to the acidified solution, starch being used as indicator. Bromate was titrated in the same way. For the titration of hydrochloric acid and oxalic acid, dilute carbonate-free sodium hydroxide was used. All salts used in the adsorption determinations were of the highest purity. The oxalate solutions were prepared immediately before use to preclude the formation of carbonate by photochemical decomposition. The results of these experiments will be found in table 1.

TABLE 1

Adsorption by calcium oxalate monohydrate

SOLUTION	TIME OF AGITATION	EQUILIBRIUM CONCENTRATION	MICROMOLES ADSORBED PER GRAM OF CALCIUM OXALATE MONOHYDRATE		
			Preparation I	Preparation II	Preparation III
	hours	*molarity*			
Ammonium oxalate	1	0.0100	5.5	3.7	1.3 (3 hours)
Potassium oxalate	1	0.0100		4.8	2.7 (3 hours)
Sodium oxalate	1	0.0100	9.3	7.5	3.9
Sodium oxalate	3	0.0100	9.8	7.2	3.9
Lithium oxalate	1	0.0100		3.5	
Magnesium oxalate	1	0.0014	6.5		
Oxalic acid	1	0.0100	6.0 ($\text{Ox}^{=}$)	7.9 ($\text{Ox}^{=}$)	
Oxalic acid	3	0.0100	6.2 ($\text{Ox}^{=}$)	8.0 (H^+)	3.6 ($\text{Ox}^{=}$)
Ammonium iodate	1	0.00100		0.73	
Potassium iodate	1	0.00100	0.58	0.95	
Potassium iodate	1	0.0100	5.2	4.3	
Sodium iodate	1	0.00100		0.86	
Lithium iodate	1	0.0100		4.6	
Calcium iodate	1	0.00100	1.7	1.7	
Calcium iodate	3	0.00100	1.7		
Iodic acid	1	0.00100		1.32 (IO_3^-)	
Iodic acid	2	0.00100		1.57 (IO_3^-)	
Iodic acid	2	0.00082		18.0 (H^+)	
Potassium bromate	1	0.0100		2.0	
Sodium oxalate + sodium iodate	1	0.00100 0.00100		0.14 (IO_3^-)	

The millimoles of substance adsorbed per gram of calcium oxalate monohydrate equals

$$\frac{NF}{W}\left[V_2 - V_1\,\frac{(V_w + 50.00)}{50.00}\right]$$

where N = the analytical normality of the solution used for titration,
F = conversion factor (NF = molarity of solution of adsorbed ion),
V_2 = cc. of standard solution required to titrate 50.00 cc. of solution containing substance to be adsorbed,

V_1 = cc. of standard solution required to titrate 50.00 cc. of filtrate after equilibrium,

V_s = cc. of water in 50.00 cc. of calcium oxalate suspension (determined by weighing 50.00 cc. of suspension and deducting from this value the weight of calcium oxalate monohydrate obtained by evaporating the suspension to dryness and heating the residue at 105°C.), and

W = grams of calcium oxalate monohydrate in 50.00 cc. of suspension.

DISCUSSION OF RESULTS

The adsorption of alkali oxalates by aged calcium oxalate is very small in amount. Even with the fine precipitates used in these determinations it is not easy to obtain reproducible results. The most strongly adsorbing preparation of calcium oxalate in equilibrium with 0.02 N sodium oxalate, the alkali oxalate most strongly adsorbed, contains less than 0.1 per cent of its weight of the foreign oxalate on the surface. It is evident that from the analytical point of view external adsorption cannot play any important rôle in the contamination of calcium oxalate, especially when it is remembered that even this small amount of adsorbed substance is partly removed on washing the precipitate. In analytical precipitations the crystals are much larger than those used in these experiments, so that in considering the causes of contamination, it is possible to leave out of sight entirely that due to external surface adsorption.

The order of adsorption of the oxalates at room temperature at the same equilibrium concentration appears to be as follows: lithium < ammonium < potassium < oxalic acid, sodium < magnesium. Evidently the solubility of the oxalates does not alone determine the adsorbability, for then the order would be: potassium < oxalic acid < lithium < ammonium < sodium < magnesium. (Solubilities of oxalates: potassium 1.65, lithium 0.61, ammonium 0.39, sodium 0.28, magnesium 0.0020, oxalic acid 0.81 moles per thousand grams of water at 25°C.) Ammonium oxalate especially seems to be out of place. In agreement with the order of adsorbability, the amount of coprecipitation increases in the order ammonium < potassium < sodium < magnesium, as will be shown later. The mechanism of the adsorption of oxalic acid probably is somewhat different from that of the salts, since there is a possibility that some of it may be held at the surface in the form of bioxalate ions. In addition, it should be mentioned that the amount of iodic acid adsorbed, as found from the acidimetric determination, is much larger than that found from the iodate analysis. The explanation is that the preparation of calcium oxalate used contained coprecipitated calcium hydroxide, which was neutralized by the hydrogen ions. It was experimentally proved that in the case of hydrochloric acid and of iodic acid, more calcium than oxalate went into solution when calcium oxalate was shaken with the acids, thus indicating that calcium hydroxide existed on the surface of the precipitate and that this reacted with the hydrogen ions. Therefore, the results of acidimetric analysis cannot be used here for obtaining the amount of acid adsorbed. It is possible that the inequality in the adsorption of the two ions is partly to be attributed to an exchange adsorption between hydrogen and calcium ions.

Calcium iodate is more strongly adsorbed than the alkali iodates, as would be expected from the precipitation rule. From 0.001 molar solutions the adsorption of the alkali iodates is of the same order of magnitude; more work should be done over a wider range of concentrations in order to learn whether sodium iodate is more strongly adsorbed than potassium iodate, and the latter more strongly than ammonium iodate. From the figures in table 1, it will be seen that the adsorption of the alkali iodates increases very strongly with the concentration up to an equilibrium concentration of at least 0.01 molar. Since calcium iodate is much less soluble than calcium bromate (0.0078 and 3 moles per thousand grams respectively at 25°C.) a stronger adsorption of the former ion was anticipated. In agreement herewith a much stronger adsorption of potassium iodate than of bromate was found (Preparation II). Again, it was found in the study of the coprecipitation of anions that iodate is carried down to a much greater extent than bromate, if the precipitations are made under identical conditions.

Very interesting is the result of the experiment in which calcium oxalate was shaken with a mixture of sodium oxalate and sodium iodate containing 0.001 moles of each per liter. Although the amount of iodate adsorbed is six times less than in the absence of oxalate, it is evident that the latter is not able to replace all adsorbed iodate at the surface of the calcium oxalate. There is competition between the oxalate and iodate ions and since calcium oxalate is less soluble than calcium iodate, the former ion will be more strongly adsorbed than the latter, although oxalate is not able to prevent entirely the adsorption of the anion which is foreign to the lattice. The adsorbability is not determined by the fact whether the ion is identical with, or of the same size as, that of the same sign in the lattice. The result found explains why a coprecipitation of iodate or some other anion is found if, during the precipitation of calcium oxalate, an excess of oxalate ions is present in the solution, and why cations can be coprecipitated even if there is an excess of calcium present during the precipitation. The presence of the lattice ion does not entirely prevent the adsorption of foreign ions of the same sign.

COPRECIPITATION OF THE ALKALIES WITH CALCIUM OXALATE

The contamination of calcium oxalate by the alkalies was studied under the following heads:

1. Coprecipitation of alkali—sodium, potassium or ammonium—when the corresponding oxalate was used as a precipitant for calcium chloride. The results are given in table 3.
2. Special investigation of sodium coprecipitation. Sodium was present here as the chloride, not the oxalate, and ammonium oxalate was used as the precipitant for calcium. The results are given in table 4.
3. Investigation of alkali coprecipitation under analytical conditions. Ammonium oxalate was used as precipitant; the alkalies were present as chlorides. The results are given in table 5.

Methods of determining the alkalies in the calcium oxalate precipitate

Sodium. This cation was determined by the simple method of Barber and Kolthoff (5). The presence of calcium as chloride does not interfere in the procedure given by these authors, so that their directions have been followed with minor changes to better accommodate the method to the present problem of determining sodium in calcium oxalate. The calcium oxalate precipitate was first dried and then ignited at incipient red heat to convert it to calcium carbonate. The latter was dissolved in dilute acetic acid; the excess acid was removed by heating at 100°C. until solid calcium acetate remained. To the residue was added 10 cc. of zinc uranyl acetate reagent prepared according to the directions of Barber and Kolthoff. The resulting mixture was shaken until all the calcium acetate had been dissolved and was then allowed to stand overnight to insure the complete separation of the small amounts of sodium present. The precipitate was collected in a sintered glass filtering crucible and washed successively with the reagent and a saturated alcoholic solution of sodium zinc uranyl acetate; after washing several times with ether, it was dried by passing a stream of air through the crucible for five minutes and then weighed. Blanks with calcium oxalate to which had been added known small amounts of sodium gave satisfactory results. Only one small source of difficulty was encountered; sometimes after the ignition of the calcium oxalate, the residue contained small amounts of carbon. However, this substance could be removed by repeatedly evaporating the residue with small amounts of concentrated nitric acid.

Potassium. It is not easy to determine the potassium content of contaminated calcium oxalate precipitates. Sodium cobaltinitrite, the most sensitive precipitant for potassium, was chosen as the reagent most likely to give results satisfactory for the present purpose. The method finally adopted consisted in weighing the air-dried precipitate of sodium potassium cobaltinitrite formed in alcoholic solution. The determination was made in the following manner.

The washed and dried calcium oxalate precipitate was ignited at dull redness to convert it entirely to the carbonate. The residue was dissolved in a slight excess of hydrochloric acid and the resulting solution was evaporated to dryness. The calcium chloride residue containing the traces of potassium sought was dissolved in 5 cc. of 95 per cent alcohol at room temperature. When complete solution had been effected, 2 cc. of sodium cobaltinitrite prepared according to the directions of de Koninck (6) was added. In order to insure complete precipitation the mixture was allowed to stand overnight. The precipitate of sodium potassium cobaltinitrite was collected in a glass filtering crucible and washed successively with small portions of 70 per cent alcohol, 95 per cent alcohol and ether, and finally dried at room temperature by drawing air through the crucible for a short time. In order to test the reliability of the method as well as to determine the amount of potassium in the precipitate, blanks containing small known amounts of potassium in the presence of the same amounts of pure potassium- and ammonium-free calcium chloride as were present in the actual determination were run in the way just described. The results will be found in table 2. It is to be noted that potassium in the blanks was present as the chloride. In the table, however, the amount of potassium added, and found, is expressed in terms of the oxalate, the form in which potassium occurs in the contaminated calcium oxalate. The second column of the table gives the value of the experimentally determined factor:

TABLE 2

POTASSIUM OXALATE TAKEN	VALUE OF THE FACTOR $\frac{K_2C_2O_4}{\text{Wt. of ppt.}}$	POTASSIUM OXALATE FOUND (Factor = 0.20)	ERROR
mg.		*mg.*	*mg.*
0.20	0.18	0.22	+0.02
0.40	0.18	0.44	+0.04
0.70	0.24	0.58	−0.12
1.2	0.23	1.04	−0.18
2.0	0.20	1.98	−0.02

$$\frac{K_2C_2O_4}{\text{Weight of precipitate}}$$

The values obtained are not constant, which is to be attributed in part, at least, to the experimental errors necessarily associated with the handling and weighing of such small quantities of precipitate as are being dealt with here. The value of the factor adopted for use in the calculations is 0.20. The third column of table 2 gives the amount of potassium oxalate found using the factor 0.20; the agreement between the amount taken and that found is quite satisfactory for our purpose.

Ammonium. The ammonium content of calcium oxalate was determined colorimetrically with Nessler's reagent.[3] The washed precipitate of calcium oxalate was dissolved by warming with 2 cc. of concentrated hydrochloric acid diluted with a small volume of water. When all the calcium oxalate had dissolved, the liquid was cooled and diluted with approximately 75 cc. of water. To this solution was added 5 cc. of 6 *N* sodium carbonate in small portions with agitation. Finally, the volume was made up to exactly 100 cc. and after mixing, the liquid was filtered through a glass crucible. Ten cc. of the filtrate was taken and treated in a small vial of 20 cc. capacity with 0.5 cc. of sodium tartrate (50 grams in 100 cc. of water) and 0.5 cc. of Nessler's reagent. The color comparison was made with a series of standards in identical vials made up fresh and treated with sodium carbonate and Nessler's reagent simultaneously with the unknown. The standards usually differed by 0.002 mg. of ammonia. The color comparison was made a few minutes after mixing with Nessler's reagent. On standing, the unknown solution slowly became turbid, but the color comparison could be made quite leisurely without interference from this cause. The presence of tartrate is indispensable; in its absence the unknown becomes turbid so rapidly that the colorimetric determination is rendered impossible. Blanks run with ammonium-free calcium oxalate in the manner described gave satisfactory results, e.g., 0.06, 0.10 and 0.16 mg. of ammonium, respectively, were taken, and 0.06–0.07, 0.10–0.11, and 0.16 mg. were found.

Explanation of tables 3, 4, and 5: coprecipitation of alkalies

The solutions of calcium chloride and alkali oxalate used in these precipitations were all 0.25 *N*. In the ordinary precipitations, the salt in excess was contained in the precipitating vessel and the other solution was added to it with hand shaking until the excess of the first solution was 20 per cent. The volume of water originally added was such that after the precipitation had been made the total volume amounted to 100 cc. in each case. Filtration was made immediately after precipitation; in those cases in which the precipitate was formed in the cold, the filtration and washing required several hours on account of the very finely divided condition of the precipitate. Precipitates obtained in the cold were washed ten times with small portions of cold water, and those formed in hot solution a like number of times with hot water. Precipitation according to Hahn has already been described (7). For the crystal size of the various precipitates see table 2

---

[3] Nessler's reagent: 3.5 grams of mercuric iodide, 25 grams of potassium iodide, and 15 grams of potassium hydroxide in 100 cc. of solution.

of a previous paper (7). The amount of alkali oxalate coprecipitated is expressed in two ways in table 3: (1) as milligrams of anhydrous alkali oxalate per gram of calcium oxalate monohydrate, and (2) as millimoles of alkali oxalate per gram of calcium oxalate monohydrate. The alkalies are actually coprecipitated as the oxalates, as is proved by the fact that calcium oxalate precipitated in the presence of much alkali chloride contains merest traces of chloride. In table 4 the results of a systematic study of the coprecipitation of sodium present in the solution as sodium chloride, using ammonium oxalate as precipitating reagent, are reported. In table 5 some results on the coprecipitation of alkalies under conditions similar to those of the ordinary analytical practice are given.

TABLE 3

Coprecipitation of alkali oxalates with calcium oxalate

PRECIPITATE NUMBER	CONDITIONS OF PRECIPITATION	EXCESS ION DURING PRECIPITATION	AMOUNT OF ALKALI OXALATE COPRECIPITATED PER GRAM OF CALCIUM OXALATE MONOHYDRATE					
			Sodium oxalate		Potassium oxalate		Ammonium oxalate	
			mg.	*millimoles*	*mg.*	*millimoles*	*mg.*	*millimoles*
1	20 Ox to 24 Ca*, 55 H_2O; R.T.; 1 minute	Ca	24	0.18	19	0.115	5.5	0.044
2	20 Ca to 24 Ox, 55 H_2O; R.T.; 1 minute	Ox	18	0.135	14	0.085	8.0	0.064
3	As in 1, but at 100°C.	Ca	5.0	0.037	0.8	0.0051	0.8	0.0064
4	As in 2, but at 100°C.	Ox	8.5	0.064	1.2	0.0072	1.05	0.0083
5	Hahn's procedure. 21 Ca and 20 Ox; R.T.; 10 minutes	Ca	5.5	0.041	1.0	0.006	0.55	0.0044
6	Hahn's procedure. 20 Ca and 21 Ox; R.T.; 10 minutes	Ox	9.5	0.071	1.4	0.0085	1.15	0.0091
7	As in 5, but at 100°C.	Ca	5.0	0.037	0.5	0.0030	0.1	0.0008
8	As in 6, but at 100°C.	Ox	7.5	0.056	0.55	0.0033	0.1	0.0008
9	As in 2, but digested at 90–100°C. for 18 hours	Ox	See table 4		0.4	0.0024	0.2	0.0016
10	As in 4, but in the presence of 1 g. of NaCl	Ox			0.45	0.0027		

* 20 Ox = 20 cc. of 0.25 *N* alkali oxalate; 20 Ca = 20 cc. of 0.25 *N* calcium chloride; R.T. = room temperature.

DISCUSSION OF RESULTS

1. The coprecipitation of sodium is much greater than that of potassium and ammonium no matter what the conditions of precipitation are; the difference is most marked in hot solution, especially if the precipitation is made according to Hahn. The coprecipitation of sodium is then still

TABLE 4

Coprecipitation of sodium present as chloride

PRECIPITATE NUMBER	AMMONIUM OXALATE	CALCIUM CHLORIDE	EXCESS ION DURING PRECIPITATION AND AFTER	WATER	SODIUM CHLORIDE ADDED	TEMPERATURE DURING PRECIPITATION	REMARKS	$Na_2C_2O_4$ COPRECIPITATED PER GRAM OF $CaC_2O_4 \cdot H_2O$
	cc.	*cc.*		*cc.*	*moles*	*degrees C.*		*mg.*
1	20	24	Ca	55	0.05	R.T.		31.4
2	24	20	Ox	55	0.05	R.T.		34.0
3	20	24	Ca	55	0.10	100		12.7
4	20	24	Ca	55	0.05	100		9.9
5	20	24	Ca	55	0.01	100		5.9
6	24	20	Ox	55	0.10	100		19.7
7	24	20	Ox	55	0.01	100		9.7
8	As 7; stood five days before filtration							8.2
9	50	20	Ox	30	0.01	100		8.8
10	As 5, but in ammoniacal medium (2 cc. of concd. NH_3)							5.5
11	As 7, but in ammoniacal medium (2 cc. of concd. NH_3)							9.95
12	20	24	Ca	55	0.01	R.T.	Acid*	8.1
13	24	20	Ox	55	0.01	R.T.	Acid*	9.6
14	20	24	Ca	55	0.01	100	Acid*	5.5
15	24	20	Ox	55	0.01	100	Acid*	5.5
16	20	21	Ca	55	0.01	R.T.	Hahn's procedure	11.5
17	21	20	Ox	55	0.01	R.T.	Hahn	18.0
18	20	21	Ca	55	0.01	100	Hahn	9.0
19	21	20	Ox	55	0.01	100	Hahn	9.2
20	As 5, but in presence of 5 cc. of glacial acetic acid							4.45
21	As 7, but in presence of 5 cc. of glacial acetic acid							11.5
22	As 21; digested at 100°C. for 18 hours							8.7
23	24	20	Ox	50	0.01	R.T.	5 cc. of glacial acetic acid	18.2
24	As 23; digested at 100°C. for 18 hours							4.75
25	20	24	Ca	55	0.01	R.T.	Digested 18 hours at 100°C.	0.7
26	20	24	Ca	55	0.01	100	Digested 18 hours at 100°C.	1.1
27	As in 26							1.5
28	24	20	Ox	55	0.01	R.T.	Digested 15 hours at 100°C.	0.77
29	As in 28							0.82
30	24	20	Ox	55	0.01	100	Digested 18 hours at 100°C.	4.6
31	50	20	Ox	55	0.01	100	Digested 18 hours at 100°C.	0.9
32	20	24	Ca	50	0.01	90	Acid†	3.0
33	24	20	Ox	50	0.01	90	Acid†	3.7

* 2 cc. of concentrated HCl was added to volume of 100 cc., neutralized at R.T. with dilute ammonia (2 minutes).

† 5 cc. of concentrated HCl was added to volume of 100 cc., heated with 3 to 4 grams of urea at 90°C. for 20 hours.

TABLE 5

Coprecipitation of alkalies under analytical conditions

20 cc. of 0.25 *N* calcium chloride used in all experiments

PRECIPITATE NUMBER	CONDITIONS	$Na_2C_2O_4$ PER GRAM OF $CaC_2O_4 \cdot H_2O$
	A. Sodium	
1	30 cc. of 1 molar sodium chloride present. Precipitation made at 100°C. by adding 1 g. of ammonium oxalate in 50 cc. of water to 250 cc. of solution containing 5 cc. of concentrated hydrochloric acid; then neutralized with 4 *N* ammonia added dropwise.	*mg.* 13.0
2	30 cc. of 1 molar sodium chloride present. One gram of ammonium oxalate in 50 cc. of water added to 250 cc. of calcium solution at 100°C., containing 1.0 cc. of concentrated ammonium hydroxide. Time, 1 minute.	8.2
3	30 cc. of 1 molar sodium chloride present. One gram of ammonium oxalate in 25 cc. of cold water added all at once to calcium solution having total volume of 250 cc. Precipitation made at room temperature. Then digested at 100°C. for two days.	2.0
	B. Potassium	
4	0.020 mole of potassium chloride present. Precipitation made at 100°C. by adding 1 g. of ammonium oxalate to 200 cc. of solution containing 2 cc. of concentrated hydrochloric acid and neutralizing with dilute ammonia added dropwise.	1.4
5	0.020 mole of potassium chloride present. Precipitation made at 100°C. by adding rapidly dropwise 1 g. of ammonium oxalate in 50 cc. of hot water to 200 cc. of solution containing 1 cc. of concentrated ammonia.	0.3
	C. Ammonium	
6	One gram of ammonium oxalate in 50 cc. of water added to boiling calcium solution having a volume of 200 cc. Two cc. of concentrated hydrochloric acid present. Then neutralized with dilute (2 *N*) ammonia added dropwise.	2.4
7	Precipitation made by adding 1 g. of ammonium oxalate in 50 cc. of water to 200 cc. of hot calcium solution containing 1 cc. of concentrated ammonium hydroxide.	2.4
8	Exactly as in 1 except that 1.0 g. of ammonium chloride was present.	3.5

strong (0.5–1 per cent), while that of the other alkalies has decreased to less than 0.1 per cent and sometimes to only 0.01 per cent.

At room temperature—ordinary precipitation—more potassium is coprecipitated than ammonium, but at 100°C. the respective amounts are nearly the same, with an apparent tendency for potassium to exceed ammonium. Precipitates obtained according to the method of F. L. Hahn are contaminated equally if they have been formed in cold solution, but in hot solution more potassium is coprecipitated. In general, potassium tends to be coprecipitated to a greater extent than ammonium. *The order of coprecipitation of alkalies is therefore the order of adsorbability.*

2. It is interesting to note that calcium oxalate formed according to Hahn's procedure in hot solution in the presence of sodium contains as much of this element as when the precipitation is made in the ordinary way in hot solution, so that this special method of precipitation possesses no advantages. Hahn's method gives better results with potassium, and especially with ammonium, but since those elements contaminate the oxalate precipitate formed in the cold only to the extent of 0.05–0.1 per cent of the weight of the precipitate, its application is unnecessary.

3. The order and amount of coprecipitation of sodium added as chloride under various conditions (table 4) correspond in general to the results obtained by precipitating sodium oxalate with calcium (table 3). The high sodium coprecipitation obtained here in Hahn's method is due to the special way in which this procedure has been carried out, i.e., calcium and oxalate were added simultaneously to a solution of sodium chloride. The ratio of sodium to calcium or oxalate present at any moment was therefore large and the amount of sodium coprecipitated was consequently large as expected.

Whether calcium oxalate is precipitated in neutral or ammoniacal solution makes no difference in the amount of sodium carried down. Neutralization of a hydrochloric acid solution of calcium oxalate with dilute ammonia at room temperature or at 100°C. gives a precipitate which still contains as much sodium as that obtained by direct precipitation in neutral or ammoniacal medium. The ion in excess—calcium or oxalate—makes hardly any difference if a strongly acid solution is slowly neutralized.

Crystals of calcium oxalate that are very large can be obtained by adding urea to a strongly acid solution of calcium and alkali oxalate and then digesting the mixture (procedure of H. H. Willard); the slow neutralization of the acid gives a slow precipitation of the oxalate with the consequent formation of large crystals. These, however, still contain fairly large amounts—analytically speaking—of sodium, although less than when the precipitation is made in the standard way.

Only one method under most conditions will give calcium oxalate sufficiently free from sodium to allow its use for precise analysis, and that is the method of recrystallization of a finely divided precipitate formed at room temperature. By precipitating calcium oxalate in a volume of 50 to 75 cc. at room temperature and digesting, the fine crystals first precipitated undergo an entire structural change due to transformation of the higher hydrates, and grow at the expense of the finest, with the result that at the end of a day or so the crystals are a few microns in diameter and then contain much less sodium than originally. It is true that such a precipitate filters considerably more slowly than one obtained under the usual conditions of analytical precipitation. However, by the use of glass filtering crucibles such a precipitate can be filtered and washed in approximately half an hour. It seems to us that this method of procedure is far superior to that of double precipitation of calcium oxalate, which would otherwise be necessary if any considerable amount of sodium is present. The application of the results to analytical work will be discussed in a forthcoming paper.

4. When calcium oxalate is precipitated with excess ammonium oxalate (table 4), no other alkali ion being present, under analytical conditions either by neutralizing a hot acid solution with dilute ammonia or by adding ammonium oxalate directly to a faintly ammoniacal solution, then the amount of ammonium oxalate coprecipitated is of the order of a few tenths of a per cent. In the presence of much ammonium chloride this value becomes larger. Thus, precipitation from acid solution by neutralizing with ammonia in the presence of one gram of ammonium chloride gave a contamination of 0.35 per cent. This amount will not be serious in ordinary analytical work, especially since this error will be compensated by a slight solubility loss in washing with water if the determination is to be made volumetrically with permanganate. If the determination is made according to the gravimetric procedure, a coprecipitation of ammonium is, of course, immaterial.

5. In the precipitation of calcium oxalate from cold solutions, a larger coprecipitation of alkalies is found in the presence of an excess of calcium than of oxalate (table 3, experiments 1 and 2), a result in opposition to the rules of coprecipitation. The explanation of this more or less abnormal behavior is relatively simple. In a study of the formation of higher hydrates of calcium oxalate (previous paper (7)) it has been shown that at room temperature fairly large amounts of the higher hydrates are formed. The latter are not stable when left in contact with the mother liquor and are transformed into the monohydrate, this process being completed within twenty-four hours. The higher hydrates are stabilized by an excess of calcium, whereas oxalate ions promote the transformation. This transformation is accompanied by an internal structural change and a recrystallization resulting in a purification of the primary precipitate; this purification takes place much more quickly in a presence of an excess of oxalate

(experiment 2, table 3) than of calcium (experiment 1). The filtration and washing of the precipitates obtained at room temperature is slow, more than two hours being required. The amount of coprecipitated alkali found is, therefore, more or less accidental (see, for example, experiments 1 and 2, table 4, where more sodium was coprecipitated if oxalate was in excess); it may be expected that the primary precipitate formed in the presence of an excess of oxalate will contain more sodium than that separated from a solution containing an excess of calcium. That the above interpretation is correct will be shown in a discussion of the coprecipitation of iodate with calcium oxalate (next paper); and further, in a paper dealing with the internal structural changes on the aging of freshly prepared calcium oxalate, it will be demonstrated that the fresh precipitate formed in the cold is porous and permits fairly rapid effusion of foreign constituents from, or diffusion into, its interior. If no higher hydrates are formed (precipitation according to Hahn; experiments 5 and 6, table 3; 16 and 17, table 4), the coprecipitation of the alkalies is in harmony with the general rules, i.e., more alkali in the precipitate if the oxalate is in excess.

6. In the precipitation of calcium oxalate at higher temperatures invariably more alkali is carried down in the presence of an excess of oxalate than of calcium, a result in harmony with the rules of coprecipitation. The coprecipitation of sodium increases with increasing excess of oxalate in the medium. Since no higher hydrates of calcium oxalate are formed at higher temperature, this normal behavior was anticipated.

7. The amount of coprecipitation of alkalies at 100°C. is much less than at room temperature. At the present time it is impossible to make any predictions regarding the influence of the temperature upon the amount of coprecipitation, since the conditions of crystal growth, the speed of adsorption, and the adsorbability of the ions at the two temperatures are quite different, and no quantitative information is available for a systematic analysis of these factors at different temperatures. It is interesting to note that in contrast to the alkalies, the coprecipitation of the anions is invariably higher at 100°C. than at room temperature (compare with next paper).

8. Coprecipitation of one alkali ion does not prevent the carrying down of another alkali in the same precipitate. Thus it is shown by experiment 10 (table 3) that sodium and potassium are simultaneously coprecipitated, whereas comparison of results of experiments in tables 3 and 5 indicates that ammonium and potassium are carried down at the same time. This result is not surprising, because during the growth of the precipitate competition between the various foreign ions to be adsorbed at the surface of the growing particles takes place and the coprecipitation of the ion with the highest adsorption potential will predominate. A coprecipitation of only one type of ion if other kinds of the same sign are present, as D.

Balarew (8) claims to be the case, is contrary to what we may expect from our knowledge of adsorption and coprecipitation phenomena and to experimental evidence.

9. The coprecipitation of sodium with calcium oxalate does not increase linearly with the concentration of the alkali ion in the solution, but seems to be an exponential function of the latter (compare experiments 3, 4, and 5, table 4). Thus with 0.01 mole of sodium chloride in the solution 5.9 mg. of sodium oxalate were coprecipitated; with 1.0 mole in the same volume, 12.7 mg. of sodium oxalate were coprecipitated. Such an exponential relation may be expected from our knowledge of the relation between amount adsorbed and equilibrium concentration in the solution. Therefore, a relatively large coprecipitation of an ion which is strongly adsorbed may be expected even if it is present in fairly small concentrations.

10. Digestion of a freshly formed precipitate results in a purification of the crystals. The most effective method of obtaining pure calcium oxalate is by precipitation from a weakly acid solution (pH 4 to 6; compare paper V of this series) at room temperature and digestion for eighteen hours or so thereafter.

11. The reproducibility of the coprecipitation experiments is fairly good, if the precipitations are repeated under identical conditions.

SUMMARY

1. The order of the adsorption of alkali ions by, and coprecipitation with, calcium oxalate is the same, sodium being more strongly adsorbed and coprecipitated than potassium and the latter more strongly than ammonium.

2. Ammonium oxalate is less adsorbed and coprecipitated than the potassium salt, a result contrary to the adsorption rule of Paneth-Fajans.

3. The presence of an excess of the lattice ion in the solution decreases, but does not necessarily prevent, the adsorption and coprecipitation of ions of the same sign, foreign to the lattice.

4. The coprecipitation of alkali ions with calcium oxalate is larger if there is an excess of oxalate instead of calcium in the solution during the precipitation. An apparent exception to the coprecipitation rule is found if precipitation takes place from relatively concentrated solutions at room temperature. This abnormal behavior is explained by the fairly rapid transformation of the higher hydrates accompanied by radical structural changes and recrystallization after the precipitation.

5. A study has been made of the coprecipitation of alkali ions under analytical conditions. Sodium, especially, can seriously contaminate the precipitates.

6. By far the purest calcium oxalate is obtained if the precipitation is made at room temperature from relatively concentrated solutions at a

pH of 4 to 6 and the mixture is digested for about twenty hours on the steam bath.

7. The coprecipitation of the alkalies at 100°C. is much smaller than at room temperature.

8. Coprecipitation of one alkali ion does not prevent the carrying down of another alkali in the same precipitate.

9. The amount of sodium and other alkalies coprecipitated is an exponential function of the alkali concentration in the solution. Relatively speaking, there is already a marked coprecipitation in dilute solutions.

REFERENCES

(1) Kolthoff, I. M.: J. Phys. Chem. **36**, 860 (1932).
(2) Beekley, J. S., and Taylor, H. S.: J. Phys. Chem. **29**, 942 (1925).
(3) Odén, Sven: Arkiv. Kemi. Mineral. Geol. 7, No. 26 (1920).
(4) Pinkus, A., and Brouckère, L. de.: J. chim. phys. **25**, 605 (1928).
de Brouckère: J. chim. phys. **26**, 250 (1929); **27**, 543 (1930).
(5) Barber, H. H., and Kolthoff, I. M.: J. Am. Chem. Soc. **50**, 1625 (1928).
(6) de Koninck: Z. anal. Chem. **49**, 53 (1910).
(7) Sandell, E. B., and Kolthoff, I. M.: J. Phys. Chem. **37**, 153 (1933).
(8) Compare Balarew, D.: Kolloidchem. Beihefte **30**, 249 (1930).

6.252

STUDIES IN COPRECIPITATION. V

THE COPRECIPITATION OF ANIONS WITH CALCIUM OXALATE

I. M. KOLTHOFF AND E. B. SANDELL[1]

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received February 3, 1933

In this paper the results of an extensive study of the coprecipitation of the iodate ion will be described, and some data will be reported on the carrying down of bromate, chromate, sulfate, and the halides by calcium oxalate. In addition a study has been made of the ratio of calcium to oxalate in precipitates obtained under various conditions. This ratio is found to be smaller than the theoretical one if the calcium oxalate contains occluded oxalate, whereas it is larger than unity if a coprecipitation of calcium salts predominates. This investigation of the calcium-oxalate ratio was made primarily for these two purposes: (a) for studying the coprecipitation of hydroxyl ions (as calcium hydroxide) with calcium oxalate; (b) for finding conditions under which the ratio approaches the theoretical value. The practical significance will be discussed with other data in a forthcoming analytical paper.

I. COPRECIPITATION OF IODATE

Calcium iodate is a sparingly soluble salt and for this reason it may be expected that calcium oxalate precipitated from solutions containing iodate will be contaminated by it appreciably. This is actually found to be the case. The amount of iodate coprecipitated is usually never very large, but since even small amounts can be determined very simply and accurately, the coprecipitation of this ion with calcium oxalate has been studied in a systematic way.

The iodate in the precipitate was determined by transferring the washed calcium oxalate to a flask containing 50 to 100 cc. of water. Pure potassium iodide containing no iodate was then added, and finally hydrochloric acid to dissolve the precipitate and to liberate iodine by reaction of the iodate with the iodide. Hydrochloric acid must not be added before the iodide, for then some of the iodate will react with the oxalate and an insufficient amount of iodine will be liberated upon the subsequent addition of iodide. The liberated iodine was titrated with dilute sodium thiosul-

---

[1] Du Pont Fellow in Chemistry at the University of Minnesota, 1931–1932.

fate, usually 0.01 *N*, with starch as indicator. Blanks with pure calcium oxalate and known amounts of iodate gave satisfactory results.

The results of a systematic series of coprecipitation experiments are given in table 1.

EXPLANATION OF TABLES 1 AND 2

Part A. The calcium chloride solution used was 0.25 *N*, the ammonium oxalate solution 0.50 *N*. Ten cc. of potassium iodate solution containing 0.200 g. of the anhydrous salt were mixed with 24 cc. of calcium chloride solution and 55–65 cc. of water (this particular volume of water was

TABLE 1

Coprecipitation of iodate

A. Ammonium oxalate added to excess calcium chloride

NO.	TEMPERATURE	TIME OF PRECIPITATION	CC. OF 0.0100 *N* THIOSULFATE			REMARKS
			0.01 *N* HCl	0.05 *N* HCl	Concentrated HCl	
	degrees C.	*minutes*				
1	25	1			2.85	12 cc. of ammonium oxalate used instead of 10 cc.
2	25	1			2.85	
3	25	1			1.80	Heated to boiling before filtration
4	25	1			4.3	10 cc. of ammonium oxalate
5	25	1	1.00	—	3.8	
6	25	20	0.20		3.8	
7	25	1		1.45	6.5	50 cc. of calcium chloride
8	25	1		0.55	3.15	Mechanically stirred
9	25	15		0.45	2.3	Mechanically stirred
10	100	1			9.5	
11	100	1	0.35		9.9	
12	100	1		0.6	9.1	Stood 18 hours before filtration
13	100	1		0.55	10.2	
14	25	1	1.05		18.2	25 cc. of alcohol present
15	25	1		0.45	4.80	Precipitated in presence of 25 cc. of alcohol; then boiled 30 minutes before filtration
16	25	1			4.5	0.1 gram of agar present
17	25	1		0.75	7.0	10 cc. of 6 *N* acetic acid present
18	25	1		0.3	17.2	50 cc. of 6 *N* acetic acid present
19	100	1		1.1	13.1	25 cc. of alcohol present
20	100	1			11.0	0.1 gram of agar
21	100	1			12.7	10 cc. of 6 *N* acetic acid present
22	25	1		0.3	4.4	0.40 gram of potassium iodate
23	25	1		0.45	3.1	0.10 gram of potassium iodate
24	25	1		0.15	1.8	0.02 gram of potassium iodate
25	100	1		0.3	7.6	0.10 gram of potassium iodate
26	100	1		0.15	3.4	0.02 gram of potassium iodate

TABLE 1—*Continued*

B. Calcium chloride added to excess ammonium oxalate

NO.	TEMPERATURE	TIME OF PRECIPITATION	cc. OF 0.0100 *N* THIOSULFATE		REMARKS
			0.05 *N* HCl	Concentrated HCl	
	degrees C.	*minutes*			
1	25	1		2.4	
2	25	1	0.7	3.0	Mechanically stirred
3	25	10		2.5	Mechanically stirred
4	25	10	0.2	0.8	Mechanically stirred; 20 cc. of ammonium oxalate
5	25	1		2.9	Hand-shaken; boiled 5 minutes after precipitation
6	25	1	0.10	1.10	Stood 18 hours before filtration
7	25	1	0.15	1.5	Stood 13 days before filtration
8	100	1		6.1	
9	100	1	0.4	5.2	Stood 18 hours before filtration
10	100	1	0.5	6.55	Mechanically stirred
11	25	1	0.45	3.9	25 cc. of alcohol present
12	100	1	0.65	7.3	25 cc. of alcohol present
13	25	5	0.45	2.95	Calcium sprayed into solution with atomizer
14	25	5	0.5	1.6	Calcium sprayed into solution with atomizer; 20 cc. of oxalate
15	100	5	0.4	5.45	Calcium sprayed into solution

C. Precipitation according to F. L. Hahn

NO.	TEMPERATURE	TIME OF PRECIPITATION	ION IN EXCESS	cc. OF 0.0100 *N* THIOSULFATE			REMARKS
				0.01 *N* HCl	0.05 *N* HCl	Concentrated HCl	
	degrees C.	*minutes*					
1	25	22	Ca	0.4		19.9	
2	25	10	Ca		1.7	25.6	Mechanically stirred
3	25	15	Ca	0.65		16.6	Iodate was dissolved in oxalate, not in water in beaker
4	25	10	Ca		2.1	19.7	Only 0.10 gram of potassium iodate present; stirred mechanically
5	25	20	Ox	0.4		13.5	
6	25	10	Ca		3.9	49.3	50 cc. of 6 *N* acetic acid present; mechanically stirred
7	25	10	Ca		1.9	15.9	20 cc. of alcohol
8	25	10	Ca		1.7	14.0	20 cc. of acetone
9	25	10	Ca		2.8	30.3	Volume 300 cc.; 0.6 gram of potassium iodate present
10	100	20	Ca	0.15		12.90	
11	100	20	Ox	0.10		3.70	
12	100	10	Ca		1.7	34.8	50 cc. of 6 *N* acetic acid; stirred mechanically

chosen in order that the total volume of the solution after precipitation would be practically 100 cc.). To the resulting solution, 10 cc. of ammonium oxalate solution were added over the period of time indicated in the table, usually one minute. The mixture was shaken by hand except where noted. Deviations from this procedure will be found noted in the table under the heading "Remarks." Filtration was begun immediately after precipitation; the precipitate was washed with small portions of hot water, usually five to six in number. It should be mentioned that filter paper was used in this series of experiments for collecting the precipitate. After washing, the precipitate together with the filter paper was transferred to a flask, covered with a little water containing potassium iodide and then enough dilute hydrochloric acid added to make the acid concentration approximately 0.01 *N*. This treatment resulted in the liberation of a little iodine from the iodate present at the surface of the precipitate, which was then titrated with sodium thiosulfate (0.01 *N*). The greater amount of the precipitate still remained undissolved. Concentrated hydrochloric acid was next added to dissolve all the precipitate, and the iodine liberated again titrated. The volume of thiosulfate recorded under "concentrated HCl" in the table is the sum of all thiosulfate required in the titration. The object of this particular mode of procedure was to prove that most of the iodate existed in the interior of the crystal and that it was not mainly adsorbed on the external surface. The preliminary shaking of the precipitate with 0.01 *N* hydrochloric acid and iodide removes whatever iodate may be adsorbed and also dissolves the outer portions of the crystal, thus releasing some of the truly coprecipitated iodate, but the bulk of the crystal remains intact. The length of time that the precipitate was allowed to remain in contact with the dilute acid was usually one or two minutes. In some cases 0.05 *N* hydrochloric acid was used instead of 0.01 *N*.

Part B. The same solutions were used as in Part A and the precipitations made as before except that here the addition of reagents was made in the reverse way, i.e., calcium chloride was added to excess ammonium oxalate containing 0.200 g. of potassium iodate. The final excess of ammonium oxalate was 20 per cent except where otherwise noted.

Part C (Precipitation from extremely dilute solutions—F. L. Hahn's procedure). The solutions of calcium chloride and ammonium oxalate used were both 0.25 *N*. These were added simultaneously from respective burets to 60 cc. of water in which was dissolved 0.200 g. of potassium iodate. Either the calcium or the oxalate solution was kept approximately 1 cc. in excess during the entire addition. At the end of the precipitation 20 cc. of one solution, and 21 cc. of the other had been added. The liquid was stirred by hand unless otherwise stated. In one case (experiment 3) the iodate was dissolved in the ammonium oxalate solution and not in the water to which calcium and oxalate were added.

In the experiments reported in table 2 the precipitations were made in the various ways already described, but after precipitation the calcium oxalate was digested at 90°C. in contact with the solution from which it had been precipitated.

TABLE 2

Effect of digestion upon amount of coprecipitated iodate

NO.	CONDITION OF PRECIPITATION	CONDITIONS OF DIGESTION	CRYSTAL SIZE AFTER DIGESTION	CC. OF 0.0100 *N* THIOSULFATE		
				0.01 *N* HCl	0.05 *N* HCl	Concentrated HCl
			microns			
1	R. T.; calcium and oxalate in equivalent amounts	3½ hours at 95°C.	ca. 2			2.2
2	R. T.; 4 cc. of 0.25 *N* calcium in excess	18 hours at 85°C.	ca. 2			1.6
3	Same as 2	40 hours at 85°C.	2			1.35
4	Calcium solution evaporated to dryness and then precipitated with oxalate containing iodate; calcium in excess	68 hours at 90°C.	0.5–2	0.00	0.10	0.70
5	Calcium solution evaporated to dryness; treated with 10 cc. of oxalate containing iodate	Diluted to 100 cc. and digested 18 hours at 85°C.		0.05		1.45
6	6 cc. of 1 *M* calcium chloride precipitated with 10 cc. of 0.50 *N* oxalate at 100°C.	Total volume of mixture 100 cc.; digested 17 hours at 85°C.	1–2			1.4
7	100°C.; calcium in excess (4 cc. of 0.25 *N*)	18 hours at 85°C.	1–2			3.0
8	R. T.; 4 cc. of 0.25 *N* oxalate in excess	66 hours at 90°C.	2			0.2
9	Same as 8	68 hours at 90°C.	2			0.15
10	8 repeated at 100°C.	66 hours at 90°C.	2			0.90
11	2.5 cc. of 1 *M* calcium precipitated at R. T. with 12 cc. of 0.25 *N* oxalate	Diluted to 100 cc. after precipitation; 120 hours at 90°C.	Varied from 0.5 to 5	0.0		0.10
12	According to Hahn; oxalate in excess; R. T.	44 hours at 90°C.		0.00	0.90	6.60
13	Ordinary precipitation cold in presence of 25 cc. of alcohol; excess calcium	18 hours at 90°C.	1–2	0.00		0.30

* R. T. = Room temperature.

The amount of contamination recorded in the tables is the amount found in the weight of precipitate actually worked with, namely, 0.365 g. of calcium oxalate monohydrate.

Table 3 gives in a concise form the amount of iodate coprecipitated under various conditions.

II. COPRECIPITATION OF BROMATE, CHROMATE, AND SULFATE

The results recorded in table 4 were obtained by precipitating under conditions the same as described under iodate. In the case of bromate and chromate 0.0025 mole of the potassium salt was present in the solution from which precipitation took place. The bromate content of the calcium oxalate was determined iodometrically (potassium iodide added first, then hydrochloric acid). Only a few experiments with chromate were made. Chromate in the washed precipitate was determined iodometrically.

TABLE 3

Coprecipitation of iodate

NO.	MANNER OF PRECIPITATION	MILLIMOLES OF IODATE COPRECIPITATED PER GRAM OF CALCIUM OXALATE MONOHYDRATE
1	Oxalate added to excess calcium; room temperature	0.017
2	Calcium added to excess oxalate; room temperature	0.011
3	Oxalate added to excess calcium; 100°C.	0.044
4	Calcium added to excess oxalate; 100°C.	0.028
5	Ordinary Hahn method; calcium in excess; room temperature	0.075
6	Modified Hahn method; calcium in excess; room temperature	0.09
7	Modified Hahn method; oxalate in excess; room temperature	0.06
8	Modified Hahn method; calcium in excess; hot solution	0.06
9	Modified Hahn method; oxalate in excess; hot solution	0.017
10	No. 1 digested	0.012
11	No. 2 digested	0.001
12	No. 4 digested	0.004
13	No. 7 digested	0.03

The precipitations in the presence of sulfate were made in the same manner as previously described for the other anions. When it was intended to have calcium in excess during the precipitation, 20 cc. of 0.25 *N* ammonium oxalate were added to 24 cc. of 0.25 *N* calcium chloride in a volume of 80 cc. in the presence of 0.00100 mole of ammonium sulfate. The volume of the liquid after precipitation was thus 100 cc. When ammonium oxalate was to be in excess, 20 cc. of calcium solution were added to 24 cc. of diluted ammonium oxalate. The particular volume 24 cc. was chosen in order to give an excess of 20 per cent.

The contaminated calcium oxalate, after washing, was dissolved in

TABLE 4

Coprecipitation of bromate, chromate, and sulfate

NO.	CONDITION OF PRECIPITATION	COPRECIPITATED BROMATE	COPRECIPITATED CHROMATE	COPRECIPITATED SULFATE
		Cc. of 0.0100 *N* thiosulfate	Cc. of 0.0100 *N* thiosulfate	Mg. of $CaSO_4$ per gram of $CaOx \cdot H_2O$
1a	Oxalate added to excess calcium; R. T.	0.40	0.80	5.1
1b	As 1a, in presence of 2 grams of ammonium sulfate	0.2		
2a	Oxalate to excess calcium; 100°C.	1.45*	2.0	13.0
2b	As 2a, in presence of 2 grams of ammonium sulfate	0.65		
3	As 1, in presence of 25 cc. of alcohol	1.2	5.7	
4	As 3, repeated at 100°C.	2.0		
5	Calcium added to excess oxalate; R. T.	0.25		2.7
6	As 5, in presence of 25 cc. of alcohol	0.45		
7	As 5, but at 100°C.	—	—	5.3
8	As 2a, stood 1 week at R. T. before filtration	—	—	6.6
9	As 7, stood 1 week at R. T. before filtration	—	—	1.6
10	Hahn's procedure; calcium in excess; R. T.	2.7	1.5	8.8
11	As 10, but at 100°C.	1.5	—	10.0
12	As 10, oxalate in excess	1.5	—	2.9
13	As 11, oxalate in excess	—	—	1.9
14	Hahn's method; calcium in excess; 50 cc. of 3 *N* acetic acid; R. T.; 10 minutes	5.6	—	—
15	As 14, stood 18 hours at R. T. before filtration	4.9	—	—
16	Calcium in excess; acid solution neutralized at R. T. with dilute ammonia	—	—	4.2
17	As 16, but oxalate in excess	—	—	1.9

* As 2a, but with 0.006 mole of $KBrO_3$; coprecipitated 2.7 (cc. of 0.01 *N* thiosulfate).

TABLE 5

Coprecipitation of halides

NO.	CONDITION OF PRECIPITATION	MG. OF HALIDE PER GRAM OF CALCIUM OXALATE MONOHYDRATE
1	Oxalate added to excess calcium chloride at 100°C. in presence of 5 grams of sodium chloride	0.12–0.18
2	Same as 1, except 5 grams of potassium bromide present	0.2
3	Same as 1, except 5 grams of potassium iodide present	0.3
4	Hahn's method; calcium chloride in excess; room temperature	0.02
5	4 repeated at 100°C.	0.02
6	Oxalate added to excess calcium chloride at room temperature in presence of 35 cc. of alcohol	0.05
7	Oxalate added to excess calcium chloride at 100°C.	0.1

dilute hydrochloric acid, diluted to 50 cc., heated to boiling, and reprecipitated by neutralizing the acid solution with dilute ammonia. The filtrate from this precipitate, together with the washings, was acidified with hydrochloric acid and one drop of the concentrated acid was added in excess. This solution, containing all the sulfate originally in the calcium oxalate, was treated with 1 cc. of 0.5 *N* barium chloride at 100°C. The barium sulfate was filtered off into a glass filtering crucible after standing overnight. The precipitate was dried at 125°C. and then weighed. Blanks run according to this procedure gave satisfactory results:—calcium sulfate taken, 2.1 and 4.3 mg.; found, 2.1 and 4.5 mg. respectively.

It will be seen that the coprecipitation of calcium sulfate is quite large, especially in hot solution. If calcium is determined gravimetrically by weighing as carbonate, or oxalate (after digestion), the error produced by the presence of sulfate will be small enough to neglect, if the precipitation has been made in the usual manner by neutralizing an acid solution with ammonia; of course, if calcium is weighed as sulfate there will be no error.

III. COPRECIPITATION OF CHLORIDE, BROMIDE, AND IODIDE

The coprecipitation of these ions is so slight that no effort has been made to determine the exact amount. The results in table 5 were obtained by dissolving the washed precipitate in nitric acid, adding silver nitrate, and comparing the turbidity obtained with that produced with known amounts of halides in presence of a like amount of oxalate, nitric acid, and silver nitrate. The chloride content of calcium oxalate is therefore astonishingly small. Even in the presence of large amounts of sodium chloride it does not exceed 0.1 per cent. Bromide and iodide are likewise not carried down in appreciable amounts.

DISCUSSION OF RESULTS

1. All the anions here studied are more strongly coprecipitated under all conditions in the presence of an excess of calcium than of oxalate, a result in agreement with the coprecipitation rule. The effect of the lattice ion in excess is especially striking in the case in which the precipitation is carried out at room temperature in a medium containing about 30 per cent alcohol. In presence of an excess of calcium the amount of iodate coprecipitated corresponds to 18.2 cc. of 0.01 *N* thiosulfate; in presence of an excess of oxalate, the amount corresponds to 3.9. Other anions show an analogous behavior.

Changing the medium by the addition of alcohol or much acetic acid increases the amount of coprecipitation much more at room temperature than at 100°C.

2. Experimentally it has been proved that the coprecipitated ions are in the interior of the crystals and that only a small fraction is externally adsorbed.

3. The amount of coprecipitated iodate increases with the excess of calcium in the solution during precipitation and decreases with the excess of oxalate, a result in agreement with the rules of coprecipitation. A reverse behavior was anticipated and found in the coprecipitation of sodium (preceding paper).

4. The amount of coprecipitated iodate seems to be an exponential function of the iodate content of the solution. With 0.2 g. of potassium iodate in the solution, an amount corresponding to 1.8 cc. of 0.01 *N* thiosulfate is found in the precipitate; with twenty times more iodate in the solution, the coprecipitated quantity increases only 2.5 times (precipitation at room temperature). A similar relation is found if the precipitation is carried out at 100°C.; although the iodate content of the solution was increased five times, the coprecipitated amount increased less than twofold (experiments 25 and 26, table 1, A).

5. The speed of addition of reagent seems to have little if any influence upon the amount of coprecipitated iodate. In experiment 15 (table 1, B) the calcium solution was sprayed into the boiling oxalate–iodate mixture with an atomizer, the solution being mechanically stirred. When the calcium solution was added from a buret, other conditions being the same, and the reacting mixture just shaken by hand, approximately the same amount of iodate was found in the precipitate. If the precipitation is carried out in the ordinary way at room temperature, the amount of coprecipitated iodate seems to decrease slightly with increasing time of precipitation. Here, however, we must remember that the primary precipitate consists of higher hydrates, which are transformed with time into the monohydrate, resulting probably in a release of the coprecipitated iodate. But even at room temperature it was immaterial whether the calcium solution was added in a fine spray from an atomizer or from an ordinary buret (experiments 2, 3, and 13, table 1, B).

6. The maximum amount of anion coprecipitation is found by precipitation at room temperature from extremely dilute solutions (modification of F. L. Hahn's procedure). In spite of smaller crystallization velocity, and consequently the separation of much larger crystals than in the ordinary method, the greatest anion coprecipitation is obtained here. The amount of contamination is particularly large if approximately 25–30 per cent acetic acid is present during the precipitation (experiment 6, table 1, C). In a general discussion of the phenomena of coprecipitation (1) it was predicted that the amount of coprecipitation will increase to a maximum with increasing crystal size, this maximum being reached at a relatively small crystallization velocity. Further decrease of the latter will lead to diminishing coprecipitation. This maximum will not be reached at the same crystallization velocity for various ions, for the speeds of adsorption, adsorbability, and replacement by lattice ions are different for the various ions. From the result of experiment 9 (table 1, C) it is seen that the

amount of coprecipitated iodate increases to a maximum with increasing crystallization velocity. If the latter is still further decreased by working at 100°C., according to Hahn's procedure, the iodate coprecipitation diminishes, although the adsorbability of the iodate ion on calcium oxalate seems to be of the same order at 100°C. as it is at room temperature.

7. In agreement with the results obtained in the study of the alkali coprecipitation, it is found that digestion of the precipitate in the mother liquor before filtration results in a purification of the crystals (see table 2). If the primary precipitate consists of relatively large crystals (2 microns or more), part of the coprecipitated ions are lost by effusion through the capillaries of the crystalline particles. However, no adsorption equilibrium is reached, since most of the contaminant in the interior is no longer in open communication with the outside of the crystals. Again, the most effective method of obtaining pure crystals is precipitation from relatively concentrated weakly acid solutions (pH 4 to 6) at room temperature followed by digestion overnight. The purification is extremely pronounced when about 25 per cent alcohol is present during the precipitation.. It was found that a precipitate thus formed at room temperature contained iodate corresponding to 18.2 cc. of 0.01 *N* thiosulfate, and after digestion (experiment 13, table 2) only 0.3 cc.

If the precipitates are allowed to stand in contact with the mother liquor at room temperature before filtration, a distinct purification is noticed if they have been formed at this low temperature from relatively concentrated solutions. This purification process is to be attributed to transformation of the higher hydrates into the monohydrate accompanied by an entire structural rearrangement (compare experiments 1 and 7, table 1, B). Precipitates formed at 100°C. and aged at room temperature undergo little change, these conditions not being favorable for a recrystallization; therefore, no distinct decrease in the amount of iodate coprecipitated is noticed with the time of standing (experiment 12, table 1, A).

8. The coprecipitation of anions decreases in the order: iodate > chromate, sulfate > bromate > chloride, bromide, and iodide. The coprecipitation of the halides is negligibly small under all conditions, but that of sulfate may be of practical significance.

9. The coprecipitation of bromate is decreased by the presence of sulfate (table 4, experiments 1b and 2b), showing again that a coprecipitation of two ions of the same electrical sign may take place simultaneously. A similar result was found in the study of coprecipitation of cations.

10. All the anions here studied show the same behavior of being more strongly coprecipitated from hot solutions than from cold. Exactly the opposite result was obtained in a study of the coprecipitation of alkali ions with calcium oxalate.

11. It is of interest to compare the results of the studies on the copre-

cipitation of cations and anions with calcium oxalate with the postulates of the coprecipitation rules derived theoretically (1).

(a) In agreement with the rules it is found that a greater amount of a foreign cation is carried down by the precipitate if an excess of lattice anion is present during the precipitation, the amount of coprecipitation increasing with the concentration of lattice anion in the solution and diminishing with decreasing concentration of the latter. In the coprecipitation of anions just the reverse behavior is found, entirely in harmony with the rule.

(b) The occlusion of foreign ions is to be attributed to an adsorption during the growth of the crystals; the order of adsorption and coprecipitation is identical.

(c) The amount of foreign material in a precipitate decreases with the time of digestion before filtration. If the primary precipitate consists of very finely divided particles a slow recrystallization takes place, during which adsorption equilibrium is established. In the case of calcium oxalate, the purification is favored by the transformation of higher hydrates into the monohydrate, at least if the primary precipitate was formed at room temperature from relatively concentrated solutions. If the original precipitate is of such size that its solubility approaches that of the macrocrystals, an effusion of part of the impurities through capillaries in the crystals takes place during digestion.

(d) The maximum amount of coprecipitated ions is found at a certain crystallization velocity. No general statements can be made with regard to the location of this maximum, as it may be different for each ion. Since there is no adsorption equilibrium during the growth of the crystals, the crystallization velocity alone, other factors being the same, will not determine the amount of coprecipitation, as the speed of adsorption and desorption, the influence of the temperature on these, the adsorbability of the ions, and the competition between the lattice ions and foreign ions of the same sign to be adsorbed at the surface of the growing particles may be different for each case.

Therefore no general predictions can be made at the present time regarding the influence of temperature upon the coprecipitation. It is striking that all cations studied are less, and the anions more, strongly coprecipitated at higher temperatures than at room temperature.

(e) It should finally be mentioned that the interpretation of the phenomena of coprecipitation with calcium oxalate, if the latter is formed at room temperature from relatively concentrated solutions, is complicated by the fact that higher hydrates are formed, which are more or less readily transformed into the monohydrate. It appears that calcium oxalate is not the most favorable precipitate for a systematic study of coprecipitation phenomena; the investigations will be continued with other substances.

TABLE 6

Oxalate content of calcium oxalate precipitate

NO.	METHOD OF PRECIPITATION	OXALATE CONTENT OF PRECIPITATE WITH RESPECT TO CALCIUM
		per cent
1	40 cc. of ammonium oxalate added to 48 cc. of calcium chloride in a total volume of 160 cc.; room temperature; filtration and washing required several hours	100.76
2	40 cc. of calcium added to 48 cc. of oxalate in a total volume of 160 cc.; R. T.	100.55
3	1 repeated at 100°C.	99.50
4	2 repeated at 100°C.	99.60
5	50 cc. of 0.25 *N* calcium added rapidly dropwise to 350 cc. of solution at 100°C. containing 50 cc. of 0.50 *N* oxalate	100.0
6	Precipitation according to Hahn; 50 cc. of calcium and 49 cc. of oxalate added simultaneously to 200 cc. of water at R. T.; calcium solution kept 1 cc. in excess; time of precipitation, 20 minutes	99.50
7	As in 6, except that oxalate was in excess, i.e., 50 cc. of oxalate and 49 cc. of calcium used	99.95
8	Precipitation according to Hahn in hot solution (100°C. at beginning); calcium solution kept about 2 cc. in excess; total of 51 cc. of calcium and 49 cc. of oxalate used; time, 15 to 20 minutes	99.30
9	8 repeated with oxalate in excess; other conditions precisely the same	99.52
10	Precipitation according to Hahn in acid solution; 49 cc. of calcium and 51 cc. of oxalate added simultaneously to 200 cc. of water at R. T., containing 2.0 cc. of concentrated hydrochloric acid; oxalate was kept 2 cc. in excess; no precipitate appeared until more than 10 cc. of oxalate had been added; time of precipitation, nearly 15 minutes	99.94
11a	Precipitated as in 1, then digested at 100°C. for 24 hours	99.86
11b	Same as 11a	99.71
12	Precipitated as in 8, then digested at 100°C. for 24 hours	99.54 99.73
13	Precipitated as in 3 and then digested at 100°C. for 24 hours	99.58
14	Precipitated as in 4 and then digested at 100°C. for 24 hours	99.73
15	Precipitated as in 1; 20 cc. of 0.10 *N* hydrochloric acid then added and the mixture digested at 100°C. for 24 hours	100.06
16	Precipitated as in 2; 20 cc. of 0.10 *N* hydrochloric acid then added and the mixture digested at 100°C. for 24 hours	100.31
17	Precipitation made as in 1; precipitate was then allowed to stand in solution from which precipitated for 9 weeks	99.66
18	40 cc. of oxalate added to 48 cc. of calcium in 160 cc. of solution containing 1 cc. of 4 *N* acetic acid, at R. T., then digested at 100°C. for 18 hours	100.20

THE OXALATE CONTENT OF CALCIUM OXALATE PRECIPITATES

The results of the investigation of the oxalate content of the calcium oxalate precipitate in which the effect of such factors as temperature, order of precipitation (calcium or oxalate in excess), speed of precipitation, and the like were considered in a systematic way, are given hereunder.

The calcium chloride and ammonium oxalate solutions used were both 0.25 *N*; they were prepared from the best reagents obtainable. Precipitations were made, in general, either by the ordinary method or by that of F. L. Hahn. In the ordinary precipitations, the salt in excess was always contained in the precipitating vessel and the other solution was added to it dropwise from a buret with efficient hand agitation. The excess of calcium or oxalate, as the case required, present finally was 20 per cent. The volume of water originally present was such as to make the final volume 20 cc. By the method of Hahn is meant that mode of precipitation in which calcium and oxalate solutions are slowly added simultaneously from respective burets to water (or some other solution) at such a rate that one of the precipitants is kept about 1 cc. in excess of the other during the whole precipitation. Glass or porcelain filtering crucibles were used exclusively for collecting the precipitate. The precipitate was washed with cold water if the precipitation had been made in the cold, and with hot water if the precipitate had been formed at higher temperatures. Each precipitate was usually washed with ten portions of water of a few cubic centimeters each. The precipitate was divided into two parts after drying: in one, oxalate was determined by titration with tenth-normal potassium permanganate; and in the other, the actual amount of calcium present was found by converting the oxalate to sulfate. Further particulars regarding the precipitations will be found in table 6 which summarizes the results of the systematic study.

DISCUSSION

The interpretation of the preceding results does not present any particular difficulties. Calcium oxalate formed in neutral solution is always contaminated with calcium hydroxide. The oxalate content of a precipitate formed in the cold is larger than 100 per cent, but this is accounted for by the strong coprecipitation of ammonium oxalate at this temperature, which is sufficient in amount to overbalance the deficiency caused by the simultaneous coprecipitation of calcium hydroxide. Such a precipitate on digestion easily loses the occluded ammonium oxalate (see previous paper on coprecipitation of alkalies) but not the calcium hydroxide, which appears to be tenaciously held by calcium oxalate, and therefore the oxalate content of the precipitate falls below the theoretical. A precipitate formed in hot solution shows a deficiency in oxalate before digestion because ammonium oxalate is not carried down to any extent at this temperature; the oxalate content after digestion is sensibly the same as before. The precipitates formed slowly according to the procedure of Hahn also contain hydroxide, but to quite different extents depending upon the manner of precipitation. The contamination is greatest at 100°C. in presence of excess calcium and slightly less with excess oxalate. At room temperature a large coprecipitation occurs in presence of excess calcium, but the composition of the precipitate is nearly the theoretical when oxalate preponderates, just as would be expected. Hahn's precipitate formed in dilute acid solution is found to have the theoretical oxalate content within the limits of experimental error. If a precipitate thrown down at room temperature is digested in the presence of dilute acid, it loses all the hydroxide and gives crystals containing a slight excess of oxalate, probably in the form of oxalic acid. Finally, a precipitate formed at room temperature and allowed to stand in the solution from which precipitated loses ammonium oxalate and shows the same deficiency in oxalate as the digested precipitate (transformation of higher hydrate into monohydrate).

It was found that calcium oxalate tends to be contaminated much more strongly by hydroxide, or basic oxalate, than by acid oxalates or oxalic acid (to be described in an analytical paper). This behavior is readily understandable when it is recollected that calcium hydroxide is sparingly soluble. Hydroxide is so strongly adsorbed by calcium oxalate that recrystallization is not of much avail in producing a pure crystal. The decreasing solubility of calcium hydroxide with rise in temperature may contribute to the failure of the recrystallization method. Digestion in presence of dilute acid, however, removes the hydroxide.

SUMMARY

1. The coprecipitation of anions with calcium oxalate decreases in the order: iodate > chromate, sulfate > bromate > chloride, bromide, iodide. The coprecipitation of the halides under all conditions is negligibly small; that of sulfate may be of practical importance analytically.
2. All anions studied are more strongly coprecipitated in the presence of an excess of calcium than of oxalate, the amounts increasing with the excess of calcium and decreasing with excess of oxalate in the solution.
3. All the anions are more strongly coprecipitated from hot solutions than from cold, a behavior just the reverse of that shown by the cations.
4. It has been shown that a coprecipitation of two anions may take place simultaneously.
5. The amount of coprecipitated iodate is an exponential function of the concentration in the solution during the precipitation.
6. The maximum amount of coprecipitation of iodate has been found at a relatively small crystallization velocity.

7. The speed of addition of reagent seems to be of little influence upon the amount of coprecipitated iodate.

8. Hydroxyl ions are strongly adsorbed by, and coprecipitated with, calcium oxalate. Even on mixing neutral solutions of calcium chloride and alkali oxalate a coprecipitation of calcium hydroxide, to be attributed to a hydrolytic adsorption of hydroxyl ions during the precipitation, is found. The amount of coprecipitated hydroxyl ions increases with increasing alkalinity of the solution and must be considered in the volumetric determination of calcium as oxalate.

9. Coprecipitated hydroxyl ions are not entirely removed by recrystallization, thus showing their strong adsorbability. By precipitation or recrystallization from weakly acid medium all calcium hydroxide is removed.

10. Again it was shown that the purest calcium oxalate is obtained if precipitation is made at room temperature from relatively concentrated, weakly acid (pH 4 to 6) solutions and digested for twenty hours thereafter. The calcium-oxalate ratio in such precipitates approaches within the experimental error the theoretical 100.0:100.0.

11. In a discussion of the results of the coprecipitation of cations and anions with calcium oxalate, it has been shown that good agreement exists between theory and experiment.

REFERENCE

(1) KOLTHOFF, I. M.: J. Phys. Chem. 36, 860 (1932).

MAGNETIC SUSCEPTIBILITIES OF HYDROCHLORIC ACID AND LITHIUM CHLORIDE SOLUTIONS

ARTHUR F. SCOTT AND CHARLES M. BLAIR, JR.

The Rice Institute, Houston, Texas

Received January 28, 1933

The present paper is a report on some measurements of the magnetic susceptibilities of solutions of hydrochloric acid and lithium chloride over a wide concentration range. It may be stated in advance that in the case of the hydrochloric acid solutions our measurements do not show the maxima and minima in the susceptibility-concentration plot found recently by Farquharson (1). However, with the lithium chloride solutions there appear to be two definite discontinuities in the variation of the susceptibility with concentration.

METHOD AND APPARATUS

The method employed in determining the susceptibility of the solutions was the so-called "cylinder" method of Gouy (2). In this method a small glass tube, half filled with the solution, is suspended vertically from the arm of an analytical balance so that the lower edge of the meniscus is located in the middle of the pole gap of an electromagnet. When the magnetic field is excited there is a change in weight of the tube and its contents, which depends on the difference between the susceptibility of the air in the upper portion of the tube and the susceptibility of the solution. In order to eliminate the action of the magnetic field on the uniform glass tube, the latter was of such a length that both extremities were in a field of negligible intensity.

The essential details of the apparatus used in the present measurements may be summarized briefly. The magnet was one giving a field of about 5000 gauss with a current of 5 amperes passing through the coils. The pole pieces were conically tapered and had faces 2.5 cm. in diameter. The pole gap was kept constant at 1.1 cm. The cylinder which held the solution was a soft glass tube, sealed at one end, 14 cm. long and 7.9 mm. in internal diameter. The balance was an assay balance sensitive to less than 0.02 mg. It was mounted on a platform above the magnet and was unaffected by the field. To the left pan of the balance was attached a silk thread which, passing through an opening in the floor of the balance case, served as a suspension for the cylinder. At the lower end of the thread was attached a small glass plug provided with a thin rubber collar, over which the cylinder could be slipped and held firmly.

The routine of the experimental procedure may be described at this point. To the clean and dry cylinder a measured sample of the solution was transferred by means of a calibrated pipette which delivered 3.428 cc. of water. After the cylinder was attached to the suspension, its position was adjusted so that the lower part of the meniscus was at the center of the pole gap. The weight of the cylinder and the solution was then found with no current passing through the coils. Following this weighing the current was switched on and brought up slowly to 5 amperes. After an interval of one minute, which was allowed for the current and field to become constant, the weight of the cylinder and contents was again determined. When the gain in weight of the tube had been found, the current was cut off and the entire procedure, outlined above, was repeated without changing the contents of the tube. In practically every case a duplicate set of measurements was made with a second filling of the tube, thus yielding altogether four determinations of the change in weight produced by the magnetic field. Both as a check on the apparatus and for use in calculating the susceptibilities of the solutions, the gain in weight of pure water under the conditions just described was determined at frequent intervals during the course of the experiment.

The specific susceptibilities of the solutions were calculated by means of the formula:

$$\chi = \kappa \cdot \frac{w_1}{w_2} \cdot \frac{1}{d}$$

The constant κ is the volume susceptibility of the reference substance, water; w_1 and w_2 are the gains in weight of solution and water, respectively; and d is the density of the solution. The standard of reference (3) for measurements of this type is the mass susceptibility of water at 20°C., -0.720×10^{-6}. Therefore, since all of the present experiments were carried out at a temperature within one-half degree of 29°C., the constant κ has the value -0.717×10^{-6}.

The density d was determined in two ways. With the hydrochloric acid solutions the weight of the "cylinder" was found before as well as after the transfer of the known volume from the carefully calibrated pipette. The densities calculated from these data were found to be sufficiently accurate. The densities of the lithium chloride solutions could not be measured by the foregoing procedure because of the failure of these rather viscous solutions to drain completely. Accordingly they were determined separately in a 10-cc. pycnometer bottle.

PREPARATION OF SOLUTIONS

Three different series (I, II, III) of hydrochloric acid solutions were measured. The solutions of series I were prepared from a stock solution which was the middle third portion of the distillate obtained from approximately 6 *M* acid. The stock solution II was the last quarter fraction of a similar distillation. The distillation apparatus in both cases consisted of a Pyrex, glass-stoppered distilling flask over the side arm of which was slipped a quartz condenser. The distillate was collected in a Pyrex bottle, and therefore came in contact only with Pyrex or quartz. Duplicate gravimetric analyses of each of these stock solutions checked to within at least one part in five thousand and showed them to be very close to the constant boiling acid in strength. The various dilute solutions prepared from these two stock solutions were made by adding to a weighed quantity of the latter best thrice-distilled water. The weight of the resulting solution was then found and from these data the percentage composition of the diluted solution was calculated. The more concentrated hydrochloric acid solutions (III) were prepared by slowly passing dried hydrogen chloride gas from an all Pyrex generator directly into a weighing flask containing a weighed amount of water. The flask and contents were cooled with ice water during the absorption. The amount of hydrogen chloride gas absorbed was found from the gain in weight.

Two different series of lithium chloride solutions were measured. The lithium chloride used in preparing stock solution I was purified as follows: C. P. lithium chloride was dissolved in best water, filtered, and precipitated with ammonium carbonate. The resulting lithium carbonate was washed by decantation ten times with distilled water and eight times with hot distilled water to remove ammonia ion and contaminating alkaline carbonates. After drying, this purified carbonate was almost completely dissolved in best distilled hydrochloric acid. The resulting chloride was filtered to remove the residual carbonate and then evaporated in a quartz dish until crystals of lithium chloride appeared. The minimum amount of water required to dissolve the crystals was added and the resulting solution stored in glass-stoppered Pyrex bottles. Analysis of this stock solution showed it to be practically saturated. The various solutions of series II were prepared by Mr. R. W. Wilson for another experiment and were generously placed at our disposal. The purification of the lithium chloride in this case differed from that described above in only one essential. The chloride obtained by conversion of the carbonate was carefully crystallized. The crystals were washed and separated from the mother liquor by an efficient centrifugal process.

RESULTS

In table 1 are tabulated the experimental data bearing on the hydrochloric acid solutions. The number in the first column indicates the stock

TABLE 1

Specific susceptibility of hydrochloric acid solutions

SOLUTION SERIES	HYDROCHLORIC ACID	$-\chi \times 10^6$
	per cent	
II	6.54	0.712
II	9.15	0.710
I	15.00	0.704
I	15.48	0.702
I	15.95	0.702
I	16.48	0.700
I	16.83	0.700
I	17.36	0.701
I	17.81	0.699
I	18.20	0.698
II	18.53	0.700
I	18.66	0.694
I	19.28	0.698
I	19.81	0.696
II	20.19	0.696
III	26.45	0.688
III	27.27	0.688

TABLE 2

Specific susceptibility of lithium chloride solutions

SOLUTION SERIES	LITHIUM CHLORIDE	$-\chi \times 10^6$
	per cent	
II	4.12	0.716
II	9.66	0.712
I	11.02	0.710
I	13.88	0.708
II	16.28	0.707
I	17.08	0.706
I	17.97	0.705
I	18.74	0.704
II	18.97	0.705
I	19.75	0.703
I	20.85	0.699
I	22.59	0.696
II	26.02	0.689
I	32.80	0.679
II	34.90	0.678
II	42.08	0.669
I	44.49	0.665

from which each solution was prepared. The second and third columns give respectively the percentage concentration of the solutions and the calculated specific susceptibility. Table 2 contains the corresponding data for lithium chloride. It may be noted that these tables include results for all the solutions which were prepared.

In practically every case the figure given for the specific susceptibility is the mean result of at least four measurements of the gain in weight of the cylinder and solution, two each being made with separate fillings of the cylinder. The average deviation of the individual remeasurements amounts to less than 0.5 per cent. The latter figure is slightly less than the estimated precision of the least precise measurement, which was the determination of the change in weight. Since the sensitivity of the balance was 0.02 mg. and since the gain in weight was about 4 mg., the precision of this measurement would be approximately 0.5 per cent.

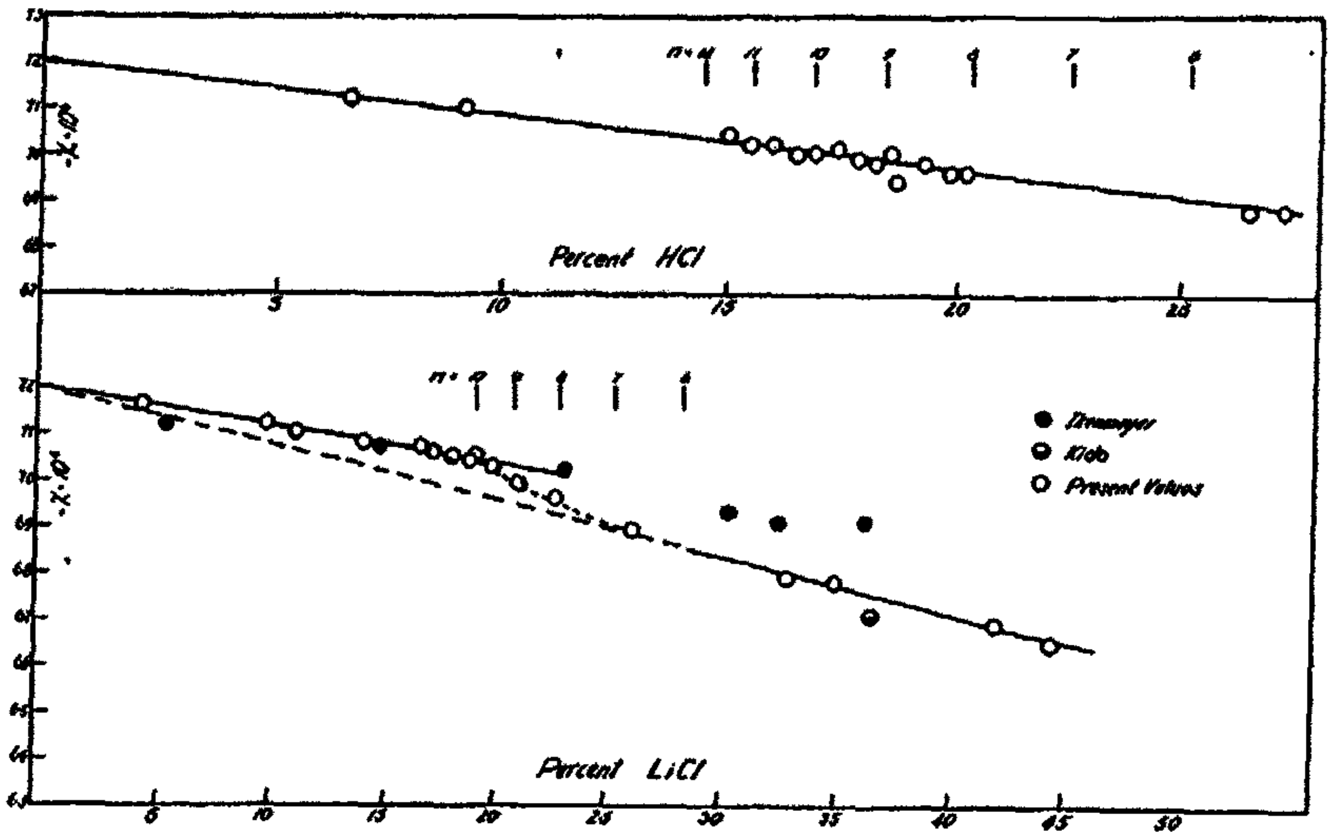


FIG. 1. THE SUSCEPTIBILITY-CONCENTRATION PLOTS FOR HYDROCHLORIC ACID AND LITHIUM CHLORIDE SOLUTIONS

DISCUSSION

The variation of the observed specific susceptibilities of the hydrochloric acid solutions with percentage concentration (figure 1) is linear within the limits of the experimental error, thus indicating that the susceptibilities of the solute and solvent are additive throughout the given range of concentration. If the drawn line is taken to represent the variation of the susceptibility with concentration, the specific and molar susceptibilities of hydrochloric acid are calculated to be -0.602×10^{-6} and -22.0×10^{-6}, respectively. These figures are identical with those obtained by Hocart (4) who, using the "ascension" method, claimed a precision of 0.1 per cent.

The present results are not in agreement with the recent measurements of Farquharson (1) by a different method. The susceptibility-concentration curve obtained by this investigator exhibits well-defined maxima and minima which occur in most cases at concentrations corresponding to stoichiometrical hydrates. A majority of the solutions measured in the present experiment fall within the concentration range ($HCl + 8H_2O$ to $HCl + 12H_2O$) where Farquharson found the greatest variation but, as can be seen in figure 1, there is no significant indication of the fluctuations to be expected. No explanation of the divergent results can be offered at this time.

The susceptibility-concentration data of the lithium chloride solutions (table 2) are also shown graphically in figure 1. It is at once evident that the variation of the susceptibility with concentration is not uniform over the entire concentration range. Before considering the possible significance of this irregularity it should be noted that Ikenmeyer (5), the only other investigator to have measured a series of lithium chloride solutions, found the variation to be quite normal. Since the two sets of measurements deviate[1] seriously only in the more concentrated solutions, it is of interest to observe that a recent single measurement by Kido (6) is in better agreement with present values than with those of Ikenmeyer.

A closer inspection of figure 1 shows that the variation of the susceptibilities of lithium chloride solutions with concentration is linear over two limited concentration ranges: 0 per cent to 19 per cent and from 28 per cent to the saturated state, 44.5 per cent. While the susceptibilities of the salt and water may therefore be treated as additive within the given limits, the susceptibility of the lithium chloride is clearly different in the two cases. Its two values, computed on the basis of the drawn lines, are:

	0 to 19 per cent lithium chloride	*28 to 44 per cent lithium chloride*
χ =	-0.637×10^{-6}	-0.598×10^{-6}
χ_m =	-27.0	-25.4

If this analysis of the data is correct, the non-linear variation of susceptibility with concentration in the intermediate concentrations range, 19 per cent to 28 per cent, must be attributed to the inconstancy of the susceptibility of the salt solute.

A clue to the cause of the assumed change in the susceptibility of the dissolved lithium chloride is to be found in the fact that the 19 per cent solution, which marks the upper concentration limit of one susceptibility value, has the composition $LiCl + 10H_2O$. The concentration limit of the

---

[1] In view of this disagreement it may be mentioned that Reicheneder (Ann. Physik. [5] 3, 58 (1929)), who subsequently employed Ikenmeyer's method to measure the susceptibilities of solutions of halogen acids, cricitized the method and concluded that it was definitely unsuited for precision measurements.

other susceptibility value is not so sharply defined but, from the variation of the susceptibility of the solute with the number of moles of water, it seems to be the solution (28.2 per cent) with the composition $LiCl + 6H_2O$. This connection between the changes in the susceptibility of the solute and the stoichiometrical composition of the solutions suggests immediately that the changes result from an alteration in the degree of hydration of one of the ions in solution. Although hydration is doubtless a factor, it is probably not the only one. For, according to theoretical considerations of Weiss (7), the loss of water of hydration should result in an increase rather than the observed decrease in the apparent magnetism of the solute. However, if as a consequence of the loss of water of hydration the non-hydrated ions become associated to form ion-pairs or clusters (8), the argument of Weiss would require a diminution of the diamagnetic susceptibility of the chloride ion. Since this last factor is conceivably greater than the hydration factor in its effect on the susceptibility, the observed alteration in the diamagnetic susceptibility of the lithium chloride may be the net result of two different changes occurring in the solution state.

Whatever the factors are that cause the susceptibility of lithium chloride to undergo a change with concentration, they may reasonably be expected to affect other physical properties of these solutions. Despite the fact that the evidence bearing on this conclusion is very fragmentary and in part conflicting, it does show that the concentrated solutions of lithium chloride are to be regarded as abnormal. A few cases of particular interest may be considered. Hüttig and Keller (9) measured the densities, refractive indices, and the absorption of solutions of the lithium halides at 20°C. The curves obtained by plotting the first two of these properties and coefficient of extinction against the number (n) of moles of water per mole of salt showed discontinuities when $n = 6$, near 30, and 75. Subsequent measurements (10) of the refractive indices of lithium chloride solutions at a number of different temperatures do not indicate, apparently, the discontinuities found by Hüttig and Keller. Further, from the variation with concentration of the apparent molal volume of lithium chloride in solution (11) it is clear that the variation of the density of these solutions with concentration undergoes an abrupt change at the same concentration observed in the susceptibility measurements, namely, $n = 10$. Moreover, since the densities of the more concentrated solutions are larger than those which would follow from the variation of this property in dilute solutions, it may be supposed that the change in the solution state above the critical concentration is not simply the breakdown of a "chemical" hydrate. Whether there is another discontinuity at $n = 6$ cannot be ascertained from the available data. While the apparent molal volume method gives a result different from that obtained by the less sensitive method of Hüttig and Keller, it does confirm their conclusion in the case of lithium bromide and possibly lithium iodide solutions that the density-concentration variation has a discontinuity at the concentration $n = 6$. Finally, in support of the supposition that in the concentrated solutions of lithium chloride the ions are in partial contact as ion-pairs an experiment by Blair and Schofield (12) may be mentioned. According to these investigators the flow-pressure curve of an almost saturated solution of lithium chloride is decidedly anomalous. Their results they interpret to mean that "small strains are not dissipated immediately during the flow, which may well be due to the persistent tendency of the ions to maintain a non-random distribution."

In conclusion the writers wish to acknowledge the generous advice and assistance which they have received from Professor Claude W. Heaps.

REFERENCES

(1) Farquharson: Phil. Mag. **12**, 283 (1931).
(2) Guoy: Compt. rend. **109**, 935 (1889).
(3) International Critical Tables, Volume VI, page 356.
(4) Hocart: Compt. rend. **188**, 1151 (1929).
(5) Ikenmeyer: Ann. Physik [5] **1**, 169 (1929).
(6) Kido: Science Repts. Tôhoku Imp. Univ. **21**, 149 (1932).
(7) Weiss: J. phys. radium **1**, 185 (1930).
(8) Fajans: Trans. Faraday Soc. **23**, 357 (1927).
(9) Hüttig and Keller: Z. Elektrochem. **31**, 390 (1925).
(10) Kohner: Z. physik. Chem. **B1**, 427 (1928).
Fontell: Soc. Sci. Fennica Commentationes Phys. Math. **4**, 8 (1927).
(11) Masson: Phil. Mag. [7] **8**, 218 (1929).
Scott: J. Phys. Chem. **35**, 2315, 3379 (1931).
Geffcken: Z. physik. Chem. **155**, 1 (1931).
(12) Blair and Schofield: Phil. Mag. [7] **11**, 890 (1931).

THE OXIDES AND HYDRATES OF ALUMINUM

JUNIUS D. EDWARDS AND MARTIN TOSTERUD

Aluminum Research Laboratories, New Kensington, Pennsylvania

Received February 17, 1933

The oxides and hydrates of aluminum have been the subject of many investigations because of their commercial importance and scientific interest. The apparent multiplicity of forms in which they occur, however, has led to much confusion in their identification. A recent contribution from Weiser and Milligan (1) is indicative of this situation. After reviewing part of the literature and describing their experimental work, they reach the conclusion that there is only one crystalline monohydrate of aluminum, namely, diaspore. The form which a number of other workers have characterized as monohydrate and an isomer of diaspore, they decide is either a new form of alumina, which they call delta-alumina, or perhaps a hemihydrate. This conclusion seems likely to be untenable, once all the facts are considered.

Probably Weiser and Milligan were unaware of the contribution on this subject published in "The Aluminum Industry—Aluminum and its Production" (2). The various forms of oxides and hydrates are there described with information regarding the monohydrates and methods of producing one of them. A brief review of these forms will be given before presenting additional evidence for the existence of the two forms of monohydrate.

ALUMINA

Corundum is the naturally occurring form of alumina,—Al_2O_3, or alpha-alumina, as it is commonly designated. Alpha-alumina is formed by heating any of the hydrates of aluminum to a sufficiently high temperature and is also the form commonly taken by fused alumina upon solidification.

Alumina may be produced in another form known as beta-alumina, by fusing alumina with small amounts of magnesia or sodium carbonate.

A third crystalline form of alumina, which is of considerable interest, is designated gamma-alumina. When aluminum monohydrate or trihydrate is dehydrated by heating, the product first formed is amorphous. With continued heating at higher temperatures of about 500°C., a new crystalline phase begins to appear, which has been identified by its x-ray pattern and named gamma-alumina. Continued heating at higher temperatures—above about 1200°C.—results in its conversion into alpha-alumina.

A fourth crystalline form of alumina has been reported by Barlett and designated as zeta-alumina (3).

ALUMINUM HYDRATES

There are two well-recognized and identifiable hydrates of aluminum, namely, the trihydrate and the monohydrate, and two crystal forms of each.

Aluminum trihydrate occurs in nature as the mineral gibbsite, which is found also in many types of bauxites. This hydrate, designated alpha-trihydrate (α-$Al_2O_3 \cdot 3H_2O$), is the product produced by auto-precipitation from sodium aluminate solutions, as in the Bayer process.

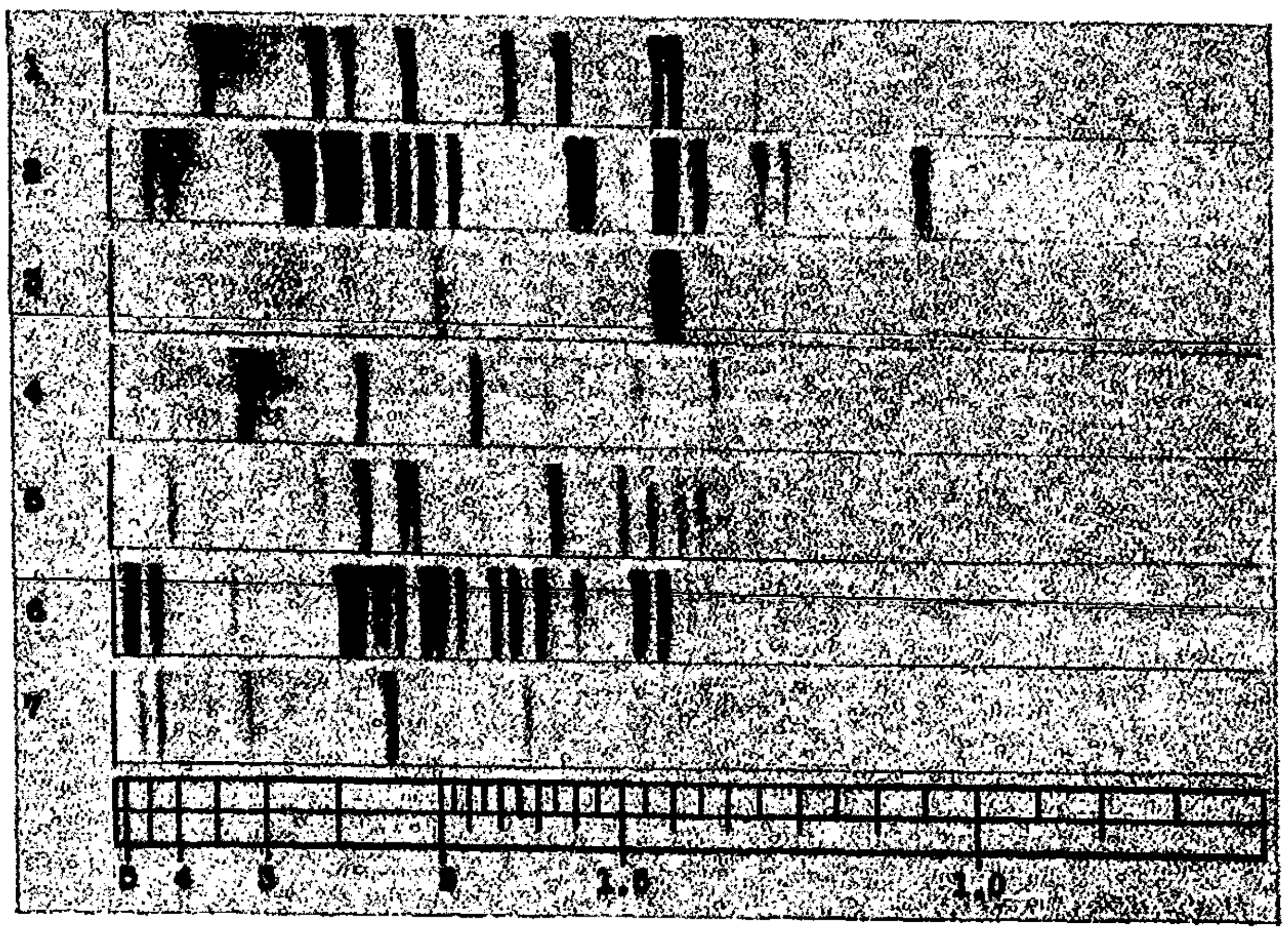


FIG. 1. X-RAY DIFFRACTION PATTERNS OF OXIDES AND HYDRATES OF ALUMINUM

1, α-Al_2O_3; 2, β-Al_2O_3; 3, γ-Al_2O_3; 4, α-$Al_2O_3 \cdot H_2O$; 5, β-$Al_2O_3 \cdot H_2O$; 6, α-$Al_2O_3 \cdot 3H_2O$; 7, β-$Al_2O_3 \cdot 3H_2O$.

Another crystalline trihydrate, designated as beta-trihydrate, can be produced by saturating sodium aluminate solutions with carbon dioxide under certain conditions, and by other precipitation methods. Beta-trihydrate shows a different x-ray pattern than the alpha-trihydrate and differs also from it in solubility. It appears to be a metastable phase, and goes over to the alpha form on continued shaking or long standing in contact with alkali.

Aluminum monohydrate, in the form known as alpha-monohydrate, is found in many bauxites, of which the French bauxites are typical. Alpha-monohydrate can be produced by heating alpha-trihydrate with alkali or water under pressure.

Another crystalline form of monohydrate is the mineral diaspore, and this form—carrying out the nomenclature previously employed—has been termed "beta-monohydrate." Beta-monohydrate has not yet been made synthetically, and we have not investigated it other than to make an x-ray pattern of a typical sample.

The x-ray patterns, according to the powder method, given by the various forms of alumina and the hydrates, are shown in figure 1.

THE MONOHYDRATES

Weiser and Milligan's conclusion that there is no monohydrate other than diaspore, is controverted by the fact that millions of tons of the alpha-monohydrate, described above, are found in nature (4), and by its synthetic production on a large scale. Its crystal pattern, as will be seen from the figure, corresponds to the so-called delta-alumina of Weiser and Milligan.

When the trihydrate is heated in water containing small amounts of sodium hydroxide, it is rapidly converted into alpha-monohydrate (5). For example, alpha-trihydrate, when heated for about twenty hours, more or less, in a solution of sodium hydroxide at a temperature of about 170°C., is converted substantially to monohydrate. The product, after washing and drying at 105°C., has a water content of about 16 per cent ($Al_2O_3 \cdot H_2O$ = 15 per cent H_2O). In this method the water content is reduced from the 34.6 per cent of the trihydrate to 16 per cent by heating in water. Apparently the product contains a small amount of adsorbed water. The monohydrate also may be approached from the other direction. The trihydrate was heated in air at 600°C. for one hour and the water content was reduced to 1.6 per cent; on x-ray examination this product showed the presence of some gamma-alumina but no other x-ray pattern. This dehydrated product was then digested in water plus sodium hydroxide at 150°C. for about fifteen hours, washed and dried at 105°C. This product had a water content of about 16 per cent and showed only the x-ray pattern we attribute to alpha-monohydrate. These experiments offer definite evidence of the existence of the alpha-monohydrate.

If a small amount of trihydrate is heated in air, most of it decomposes to an amorphous form, but if it is heated in sufficient bulk so that enough water vapor stays in contact with the material, some recrystallization to alpha-monohydrate may occur, but usually only a small percentage is so converted. The water content of the mixture can be reduced to 15 per cent or to 10 per cent, or to other values by changing the time and conditions of heating. Since an amorphous phase does not produce a diffraction pattern, the pattern of such a mixture is that of the monohydrate phase.

Very long aging in water at 100°C., as shown in Weiser and Milligan's experiment of aging for 1009 hours, will produce some alpha-monohydrate from amorphous alumina (their table 7 and figure 7). Weiser and Milligan's product, treated in this manner after drying at 50°C., had a water content of 19.35 per cent, and after heating for three hours in air at 160°C., it had a water content of 10.38 per cent. This product they considered to be either a new form of alumina with adsorbed water, or perhaps a hemihydrate. A mixture of about 70 per cent alpha-monohydrate with 30 per cent of amorphous alumina would have a water content of 19.50 per cent if the amorphous phase carried about 30 per cent adsorbed water. Upon drying such a mixture at 160°C., the adsorbed water would probably be substantially all removed without affecting the combined water of the very stable monohydrate, and the mixture would apparently have a combined water content of about 10.5 per cent. Here again, the amorphous phase does not produce a diffraction pattern, and the pattern of such a mixture is that of the monohydrate phase. Weiser and Milligan's conclusion that their "delta-alumina" is not a monohydrate seems to have come from the assumption that they had only one phase in their mixture dried at 160°C. (water content 10.38 per cent), since they got only one crystal pattern from such a mixture.

Confirmatory evidence for the existence of the alpha-monohydrate, as made by Tosterud's method, is presented by the thermal arrests observed on heating. If about 100 g. of the compound are placed in a crucible and heated in an electric furnace, an interesting series of observations is obtained from a sensitive thermocouple inserted in the mass. The time-temperature curve is smooth (see "C," figure 2) until a temperature of about 450°C. is reached, when an arrest showing heat absorption is recorded. This is the point where rapid decomposition of the monohydrate occurs. If trihydrate is heated, a similar decomposition point is observed at about 300°C. The decomposition point of the monohydrate is just as characteristic and reproducible as that for the trihydrate. Of course, the trihydrate and monohydrate will lose some water on heating at temperatures below these points, but the decomposition becomes quite rapid at the temperature range in question. The monohydrate is more stable at elevated temperatures than the trihydrate. The evidence for the existence of the alpha-monohydrate is just as complete, and parallels that for the alpha-trihydrate. Similar thermal arrests have been recorded by others in experiments of this character.

In figure 2 are also given heating curves for bauxites of two types. One, a trihydrate bauxite, gives a thermal arrest at about 250°C., and the other, a monohydrate bauxite, gives an arrest at about 425°C. The arrests observed with bauxites are usually somewhat lower than those observed with the pure hydrates. Other bauxites are known which contain both monohydrate and trihydrate, and the heating curves show both arrests. Furthermore, a heating curve made with trihydrate, if carried high enough and under proper conditions, sometimes shows a slight arrest at about 450°C., indicating the formation of some monohydrate from the trihydrate during the heating, but a curve made with pure monohydrate never shows the lower arrest.

The samples prepared by Weiser and Milligan according to Hüttig's procedure (K_1', K_1'', K_2, K_3, K_4 and L_3, figure 6) have an x-ray pattern which corresponds very closely to that of beta-trihydrate given in our figure 1. Additional discussion of beta-trihydrate is given in the article (2) previously referred to.

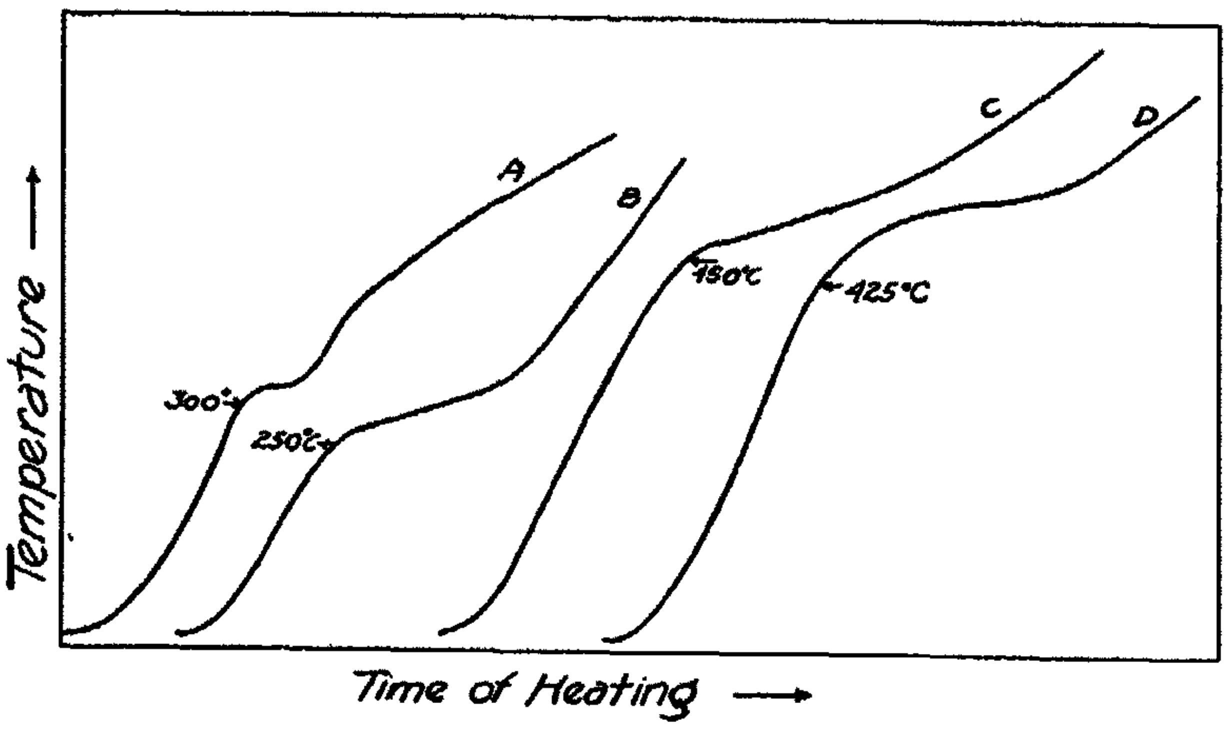


FIG. 2. HEATING CURVES

A, aluminum trihydrate; B, Arkansas bauxite; C, aluminum monohydrate; D, French bauxite.

While we have made no investigation of other forms of hydrate reported in the literature and reviewed by Weiser and Milligan, it seems quite likely, as they have concluded, that they are mixtures of other known hydrates, or incompletely crystallized products. Crystallization or recrystallization from a solid phase is attended with more difficulties than crystallization from a solution. In the conversion of precipitated amorphous alumina to a crystalline hydrate, there may be lines appearing in the x-ray diffraction pattern, or differences in the intensity of lines, which are caused by some incompletely crystallized product, and which can hardly be said to represent a new hydrate.

The x-ray data contributed in this paper are the work of W. L. Fink and K. R. Van Horn.

SUMMARY

There is a monohydrate of aluminum, $Al_2O_3 \cdot H_2O$, other than diaspore, and it is found widespread in nature and is being made commercially. Its existence can be demonstrated by chemical analysis, x-ray diffraction patterns, and thermal analysis.

Other forms of alumina and its hydrates are briefly reviewed.

REFERENCES

(1) Weiser, H. B., and Milligan, W. O.: J. Phys. Chem. **36**, 3010 (1932).
(2) Edwards, Frary, and Jeffries: The Aluminum Industry—Aluminum and its Production, p. 164. McGraw-Hill Book Company, New York (1929).
(3) Barlett: J. Am. Ceramic Soc. **15**, 361 (1932).
(4) Harder, E. C.: Ores of Aluminum, Chapter IV, p. 60, in The Aluminum Industry. McGraw-Hill Book Company, New York (1929).
(5) Tosterud, M.: Canadian patent 285,147; November 27, 1928.

THE STANDARD BATTERY

R. B. ELLIOTT AND G. A. HULETT

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Received January 3, 1933

A steady current is quite essential for precise potentiometric measurements (1). We observed that storage batteries gave a fairly constant current for certain portions of the discharge but were quite sensitive to temperature variations. This suggested the idea of using the combination due to E. Weston (U. S. patent 294824), Cd Am / $CdSO_4$ (saturated at 4°C.) / Hg_2SO_4 / Hg, which has practically no temperature coefficient of E.M.F. for ordinary temperature ranges. We made two of these batteries with cathode areas of 100 cm.^{2}, which when closed in series over a potentiometer current of 20,000 ohms gave us a current which was exceedingly constant for hours at a time, requiring no adjustment of the regulating resistance, and permitted measurements of E.M.F. to microvolts.

After a few months use the above batteries showed a markedly decreasing E.M.F., but on adding some sulfuric acid to the neutral electrolyte the E.M.F. soon returned to normal and remained quite constant, indicating that an acid electrolyte is essential to prevent the hydrolysis of the mercurous sulfate and resulting disturbances.

At that time we gave most attention to the area of the cathodes and concluded that 100 cm.^{2} cathode area would deliver satisfactorily one-tenth of a milliampere. Now we have obtained more experience and information about these batteries and find that attention should also be given to the polarization at the anodes of these batteries. Indeed the anode polarization appears to be the greater and we have sought for the most suitable ratio of anode and cathode areas for a desired current.

To this end we made standard batteries as follows. A 30-cm. (diameter) crystallizing dish was used and enough mercury added to cover the bottom of the dish. For the anode we used a 19-cm. "petri" dish that has a depth of only about 15 mm. and was partly filled with a 10 per cent cadmium amalgam. This anode was supported above the mercury cathode on a tripod made from glass rods. To further increase the anode area we stacked up several of these dishes, separating them by glass triangles made from 4-mm. glass rods. This battery was also provided with an independent small reference anode 1.5 cm. in diameter, so as to measure the polarization of anode or cathode independently when the battery was delivering a current.

Any current from these batteries will cause some polarization so that there is a drop in the E.M.F. if one is measuring to microvolts, but the drop occurs in less than one-half a minute and then the E.M.F. and current remain quite constant and satisfactory. When the current is interrupted these batteries soon regain their original E.M.F., even though they have been short-circuited and have delivered a much greater current than they were designed to give. Indeed, these batteries may serve as a quite satisfactory laboratory standard of E.M.F. which is independent of ordinary temperature changes, but they must be calibrated if one is concerned with the fourth decimal place in voltage.

To test the possibilities of these batteries we constructed two units as described below with cathode area of 666 cm.^{2} On a low glass tripod was placed a petri dish half-filled with 10 per cent cadmium amalgam with an anode area of 40.8 cm.^{2} A pilot anode served to determine separate polarizations. This battery showed a voltage of 1,018,100 microvolts and when closed over 20,000 ohms, promptly fell to 1,017,960 mmv. and was observed for 30 minutes with the results shown in table 1. All results are expressed in microvolts or 10^{-6} international volts.

TABLE 1

TIME	VOLTAGE	P_C	P_A
minutes	*mmv.*		
0	1,018,100	0	0
1	1,017,946	−4	−150
2.0	1,017,951	−7	−142
3.0	1,017,952	−7	−141
5.0	1,017,945	−7	−148
10	1,017,950	−6	−144
15	1,017,945	−9	−146
20	1,017,946	−7	−147
25	1,017,946	−8	−146
30	1,017,945	−8	−147

Table 1 gives some interesting and unexpected results. The polarization at the 40.8 cm. anode area was some 147 mmv. for a current of 0.0001 amp., while at the 666 cm.^{2} cathode the polarization was only 7 mmv. We had expected quite different results, so we replaced the 40.8 cm.^{2} anode petri dish with one with an area of 293 cm.^{2}, but the anode still showed markedly greater polarization than the cathode. So we proceeded to stack up four of the anode dishes, giving a total anode area of 1300 cm.^{2} to 666 cm.^{2} cathode area. The anodes were connected together and acted as a unit, while the 1.5 cm.^{2} pilot anode served to measure the polarization of both anode and cathode. The results are given in table 2. The polarization of the anode with about twice the area of the cathode is still somewhat greater than the cathode, but this battery with an anode area some twice as great as the cathode area seems to be a satisfactory one. We proceeded to get more detailed information on it. Measurements such as those in tables 1 and 2 were made when the above battery was closed over various resistances and the results are summarized in table 3.

TABLE 2

Cathode area 666 cm.^{2} Anode area 1300 cm.^{2} 5000 Ω. 0.0002 Ampere | Ω

TIME	P_A	P_C	P_{cell}	E.M.F. CELL
		mmv.	*mmv.*	*mmv.*
0	0	0.	0	1,017,687
1	−109	−81	−189	1,017,498
3	−110	−82	−192	1,017,495
5	−108	−82	−190	1,017,497
10	−108	−91	−199	1,017,488
15	−104	−95	−199	1,017,488
20	−106	−91	−197	1,017,490
25	−107	−94	201	1,017,486
30	−101	−101	202	1,017,485
	−105	−92		1,017,489 ± 3

TABLE 3

Battery No. 2. Anode 1300 cm.^{2} Cathode 666 cm.^{2}

INITIAL E.M.F.	RESISTANCE	CURRENT	AVERAGE E.M.F. FOR HALF-HOUR	VARIATION OF E.M.F. IN MMV. OVER ONE HALF-HOUR
mmv.	*ohms*	*milliamperes*	*mmv.*	*mmv.*
1,017,687	5000	0.2	1,017,490	±3.8
1,017,678	3000	0.33	1,017,371	±3.1
1,017,681	1000	1.0	1,016,806	±7.0
1,017,688	500	2.0	1,016,000	±5.0
1,017,667	250	4.0	1,014,371	±3.2
1,017,711	150	6.67	1,012,302	±1.5
1,017,698	100	10.0	1,009,786	±3.0
1,017,719	50	20.0	1,002,453	±10.0

The above results show a quite satisfactory performance. The polarization of course increases with the current drawn, but variation of the current, for the first half hour, decreases with increasing current; above 10 milliamperes it begins again to increase. With 150 ohms in circuit, or a current of 6.67 milliamperes, the variation of the current was only 1.5 parts in a million. This is a current of 1 milliampere for 100 cm.^{2} of cathode area and 200 cm.^{2} anode area, and represents the best performance. Even with a discharge of 20 milliamperes we had a constancy of one part in

100,000, a constancy that is quite unapproachable with any other battery or source of current.

Our experience and observations suggest the following specifications for these standard batteries. Owing to the size and structure of standard batteries they are not readily movable and so are best set up when they are to be used unless it is feasible to "wire" them to the point of use.

A satisfactory unit may be made in a 30-cm. diameter crystallizing dish, some 15 cm. deep, and with a flat bottom so that a minimum of mercury will continuously cover the bottom. Some 5 kilograms of mercury will be satisfactory. The best grade obtained from supply houses will suffice. The electrolyte should be acid by some 0.08 molar sulfuric acid and saturated with cadmium sulfate at approximately 4°C. Add 400 cc. of 1.84 density sulfuric acid to 4000 cc. of water and in this dissolve 5 kilograms of a good grade of $CdSO_4 \cdot 8/3\ H_2O$. The rate of solution of cadmium sulfate is remarkably slow, but overnight agitation with a motor-driven stirrer is effective. This gives some 5.4 liters of the electrolyte and covers the mercury in the 30-cm. dish to a depth of some 8 cm. From glass rods one may readily construct a low form of tripod that will support a 19-cm. petri dish a couple of centimeters above the mercury surface. The 19-cm. petri dishes are filled with enough 10 per cent cadmium amalgam to cover the bottom (some two kilograms of 10 per cent amalgam for 19-cm. petri dish). Four such dishes are stacked on the tripod, separated by triangles made from 5-mm. glass rods or tubes.

The amalgams are all connected to one binding post, while a wire protected by a glass tube connects the mercury cathode to the positive binding post. This mercury cathode is to be covered at all points with a thin layer of mercurous sulfate. The depolarizer requirements are not as exacting as for standard cells. The crystalline product (2) gives somewhat the best results, but the electrolytic product (3) is good, as is also the chemically prepared. One needs some 40 g. of mercurous sulfate for 100 cm.^{2} cathode area, so our unit in a 30-cm. dish requires some 300 g. of mercuric sulfate.

This may be made electrolytically (3), or satisfactorily as follows. To a liter of water in a suitable Erlenmeyer flask add 100 cc. of sulfuric acid (density 1.84), and in this dissolve 360 g. of mercuric sulfate ($HgSO_4$). From a tank of the liquid, bubble sulfur dioxide into this solution, reducing the mercuric sulfate, which at once begins to precipitate as a white product. When the mercuric sulfate is all reduced the sulfur dioxide begins to reduce mercurous mercury in fine globules. This finely divided mercury becomes entangled in the precipitate and gives it a gray color. When the product is a good slate gray the flow of sulfur dioxide is stopped, and the flask placed on a water bath with a motor driven stirrer. About 50 cc. of mercury was added to the system, which may be stirred at water bath temperature overnight. This permits the very fine globules of mercury, which have a greater solution tension than mercury (owing to surface tension) to go into solution and separate out on larger globules. Also there is a considerable recrystallization of the mercurous sulfate, owing to surface tension effects (4). This gives some 300 g. of mercurous sulfate, which is brought on to a Büchner filtering funnel, and the acid removed from it by suction. The cake of mercurous sulfate is just covered with a minimum of the electrolyte in which it is to be used, and this is drawn through with good suction, repeating two or three times. The cake is readily removed, freed from the filter paper and brought into the battery, where it disintegrates and tends to spread on the mercury cathode so that a satisfactory layer of the depolarizer is readily attained. When the anodes are put in place the battery is ready for use. The 30-cm. dish should have a good rim so that it may be tightly covered with a glass plate to prevent evaporation from the electrolyte. The electrolyte is nearly saturated with cadmium sulfate and a little evaporation would soon cause the crystallization of $CdSO_4 \cdot 8/3\ H_2O$, while the favorable temperature coefficient depends on the definite concentration of the $CdSO_4 \cdot 8/3\ H_2O$. With a little vaseline one may make sure that there will be no evaporation. On a high resistance circuit, i.e., over 20,000 ohms, two of these batteries have given excellent service for years. Some mercurous sulfate has been used up and the electrolyte has become slightly more concentrated. If one keeps a rough account of the current drawn, one may at any time by a simple calculation arrive at the amount of mercurous sulfate to add and the amount of water needed to dilute the electrolyte so as to restore the original condition. The E.M.F. of one of these batteries on open circuit, after it has rested for several hours, is a good criterion of the state of the electrolyte.

REFERENCES

(1) Hulett, G. A.: Phys. Rev. **27**, 34 (1908).
(2) Elliott, R. B., and Hulett, G. A.: J. Phys. Chem. **36**, 2083 (1932).
(3) Hulett, G. A.: Phys. Rev. **32**, 262 (1911).
(4) Hulett, G. A.: Z. physik. Chem. **37**, 385 (1901).

A SIMPLE METHOD FOR ACCURATE DETERMINATIONS OF VAPOR PRESSURES OF SOLUTIONS

D. A. SINCLAIR

University College, Auckland, New Zealand

Received January 12, 1933

INTRODUCTION

The importance of vapor pressure in the study of solutions warrants a far more extensive exploitation of this property than has yet been made. Many attempts have been made to evolve practical and accurate means of determination, but the amount of reliable data so far accumulated is very scanty indeed. Hitherto facility and accuracy appear to have been incompatible.

Undoubtedly the most accurate determinations of vapor pressure lowering, to date, are those of Lovelace, Fraser and coworkers (1), who by rigorous care in the removal of air and using a reliable sensitive manometer seem to have attained an accuracy to the order of less than 0.001 mm. The method is too elaborate for general application, but for standard determinations it has, as yet, no equal.

Reviews of the older methods are available in the literature. Recent determinations may be mentioned briefly.

Bousfield and Bousfield (2) used an apparatus which was very neat and compact, but these authors appear not to have appreciated fully the errors arising from residual air, and errors to the extent of nearly 10 per cent of the lowering are evident in the region of lower concentration. The pressure of residual air may be much greater than that indicated by the volume of the bubble of air remaining when the solutions have been brought to atmospheric pressure.

The most advanced development of the dynamical method has been made by Pearce and Snow (3). The accuracy attainable is of the order of 0.01 mm., but by taking a mean of several observations, values reliable to within a few thousandths of a millimeter may be obtained.

The dew-point method used recently by Hepburn (4) seems to be capable of useful application. An accuracy of 0.03 mm. is estimated. A method described by Hill (5), depending on the principle of the wet and dry bulb thermometer, may prove useful for some purposes. With moderately concentrated solutions the estimated accuracy is 2 per cent.

The limited accuracy of the various methods may be gauged from the fact that at 25°C. the molecular lowering for solutions of such salts as potassium chloride is only about 0.75 mm.

BOUSFIELD'S ISOPIESTIC METHOD

In the paper referred to above, Bousfield makes mention of a method for comparing the vapor pressures of solutions, called the "isopiestic" method and described in earlier papers. This method is apparently so simple that the absence of further mention of its application would appear to indicate that it did not fulfil expectations. According to Bousfield, four open cylindrical glass vessels containing different solutions are placed in a desiccator vessel, which is evacuated and placed in a thermostat for two or three days. By this time the solutions will have come into equilibrium by distillation of water, so that each will have the same vapor pressure. The concentrations are determined by weight and hence, if accurate data are available for one solution, equally accurate values may be assigned to the others. Results, apparently confirmatory, are quoted.

In order to test Bousfield's method, the author placed two crystallizing dishes containing respectively approximately 1 *M* potassium chloride solution and water in a vessel which was evacuated to 15 mm. and left for several days. The amount of distillation occurring was barely noticeable even when the dishes were floated on mercury, to aid temperature equalization. Presumably, the rate of distillation between two solutions differing in concentration by only 1 per cent would be 100 times as slow!

As pointed out by Bousfield, the attainment of equilibrium is dependent on the equalization of temperatures. When the air is removed the vapor pressures of all surfaces in the vessel must be the same, but the temperatures are different. However, the order of the magnitudes involved was apparently not realized. From data in the International Critical Tables the following calculations were made.

At 25°C. $\frac{dp}{dt}$ for water is 1.4 mm. per degree. Hence a pressure difference of 0.001 mm. at the same temperature corresponds to a temperature difference of 0.0007°C. at the same pressure.

The latent heat of vaporization of water at 25°C. is 2436 joules per gram. Therefore, if we have two surfaces differing in temperature by 0.0007°C. and separated by a medium of thermal conductance equivalent to one centimeter cube of the undermentioned materials, the times required for 1 gram of water to distil, or 2436 joules to flow, from one to the other may be calculated from the thermal conductivities (without convection) to be for (a) glass—10 years, (b) water—17 years, (c) gases—500 years, (d) mercury—15 months, (e) copper—10 days.

Considering these astonishing figures, it is surprising that the results quoted by Bousfield are as good as they are. Earlier papers show, however, that these figures were taken from series of experiments extending over several months, in which solutions were built up by distillation of water from the trough of the desiccator, weighings being made every two or three days. Apparently, no experiment was made to see if two solutions of the same salt came to the same concentration after two or three days and assumptions were made which were not sustained by later trials.

APPLICATION OF THE ISOPIESTIC METHOD

From the above considerations it would appear that the method as described by Bousfield is too slow to be suitable for practical application. However, by incorporating the following principles in the design of apparatus, it seemed probable that the method could be rendered practicable.

By providing good metallic conduction between the solutions, the retardation due to thermal resistance between them may be reduced to quite a small value. The factors limiting the rate of attainment of equilibrium would then be diffusion of solute and conduction of heat through the solutions. These could be accelerated by stirring and by making the solutions shallow. Too violent agitation is to be avoided, however, since minute heating effects would cause appreciable errors. Quantities of solutions as small as compatible with accuracy in weighing are also desirable, to minimize the amounts which have to distil.

THE METHOD ADOPTED BY THE AUTHOR

Preliminary experiments

Solutions of potassium chloride placed in silver-plated copper dishes fitting neatly together and mounted on a copper base were found to approach identity of concentration at quite a feasible rate, when rocked in an evacuated desiccator vessel in a thermostat. It was discovered that the rate was greatly increased by placing some solution in the crevices between the dishes. Evidently the temperature gradient here was reduced appreciably by the substitution of solution for vapor in the gaps. Using about 2-cc. quantities of approximately 1 *M* potassium chloride, it was found that a 25 per cent difference could be reduced to 1 per cent in twenty-four hours. During a series of experiments in which potassium chloride and cane sugar solutions were compared the following procedure was evolved.

Apparatus

The dishes were 1⅓ inches square by ¾ inch deep, a set of four being placed in square formation on a silver-plated block 1 inch thick. The block acted as a steadying heat reservoir as well as a conducting medium. The thermostat was believed to keep constant to about 0.01°C. at 25°C.

The variations need not necessarily be reduced to a very small amount, as the temperature waves are damped down considerably by the thick walls of the desiccator, and the massive copper block ensures that any small disturbance is equitably distributed. The heating lamp was blackened since the radiation, which had an appreciable effect on the regulator, would also be liable to affect the dishes and possibly maintain a permanent temperature gradient therein. The period and angle of oscillation were about 1 second and 20° respectively.

Procedure

The solutions were weighed into the dishes by pipetting in 2 cc. and weighing quickly to the nearest milligram. In the case of concentrated solutions the amount of solid in 2 cc. was sufficient to be weighed in directly with accuracy. In all determinations made, potassium chloride solutions were used as standard. Duplicates of each solution were inserted, being placed in diagonal opposition in the set, so as not to be in direct contact, and therefore to provide a more reliable mean.

Caustic soda of about the same concentration as the potassium chloride in the dishes was used as intermediate conducting solution, being preferred since it spread more easily over greasy surfaces.

The evacuation was effected by means of a water pump, the pressures being reduced to 15–20 mm. Complete removal of air is not required—merely sufficient to remove the diffusion retardation.

The dishes, on being removed from the desiccator, were kept covered while they were cooled rapidly in a stream of cold water and dried on the outsides with filter paper. An approximate weight was estimated, while still covered, and final weighing completed in a few seconds after removing the cover. Errors due to evaporation may amount to several milligrams and this is the largest error with the more concentrated solutions. A better plan would be to provide the dishes with permanent lids, but this refinement was not introduced at this stage.

The same set of solutions may be used to make as many as five or six determinations over a range of concentrations varying by about 40 per cent. The most convenient method of varying the concentrations, and that which gave the best results, was by distillation of water from the bottom of the desiccator. This distillation is chiefly indirect. The thermal conduction between the block and the walls of the vessel being poor, the block is heated from room temperature to 25°C. by distillation of water onto the block, from the water in the bottom which is heated more quickly. This water then distils into the dishes. Finally the block attains a slightly higher temperature than the thermostat and further distillation takes place into the solutions, at a rate depending on the flow of heat from the block to the thermostat. This is negligibly slow with dilute solutions, but is appreciable with concentrated solutions.

The removal of water by pumping off was difficult to accomplish satisfactorily. The best method was found to be to use high concentrations of intermediate solution.

The times required for the solutions to come sufficiently close to equilibrium vary according to viscosities, but other things being equal, rates of distillation should be proportional to the temperature difference. For the same percentage difference in concentration this is proportional to the concentration. For any one concentration the difference should be reduced equal fractions in equal times. With 0.5 *M* potassium chloride solutions the rate is greater than one-tenth in one day and so, if the solutions do not differ originally by more than 2 or 3 per cent, one day should be sufficient for an accuracy of 0.3 per cent. In general, one day was allowed for all solutions above 0.5 *M* and below this the times were increased, until at 0.1 *M* three days were allowed. This time gave uniform results.

Calculation of results

The actual calculations are simple, the molality being inversely proportional to the weight of water in the dish.

Potassium chloride was always taken as standard, the values obtained by Lovelace, Fraser and Sease (6) being taken as correct and assuming that the relative lowering is the same at 25°C. as at 20°C. The International Critical Tables state that the variation with temperature is inappreciable for this salt. The vapor pressure of water at 20°C. was taken as 17.535 mm.

Results are expressed in terms of molecular relative lowering, in conformity with the practice in the tables. The clearest method of exhibiting the results is by means of a graph, plotting molecular relative lowering against molality. Tables of values taken from the author's curves are provided to enable the curves to be reconstructed.

RESULTS

Cane sugar solutions

The choice of cane sugar as a solute for preliminary experiments was perhaps not the best, on account of the high viscosity of the solutions. Nevertheless, the results obtained were gratifyingly good.

The materials used were A.R. potassium chloride and a specimen of sugar prepared some years ago for research work in this College.

Determinations were made over a range of concentration from 0.2 *M* to 1.5 *M*, corresponding to 0.1 to 0.9 *M* potassium chloride. The results are shown in figure 1 and table 1. A better uniformity is desirable in the higher concentration region, but below 0.8 *M* the deviations from the smooth curve are less than 0.3 per cent, or less than 0.0007 mm. expressed as pressure. With three obvious exceptions the deviations in the higher region are of the order of 0.2 per cent., which at 1.4 M corresponds to about 0.0014 mm. Errors of 0.2 per cent are quite possibly introduced by losses by evaporation before weighing, and a better uniformity was not to be expected.

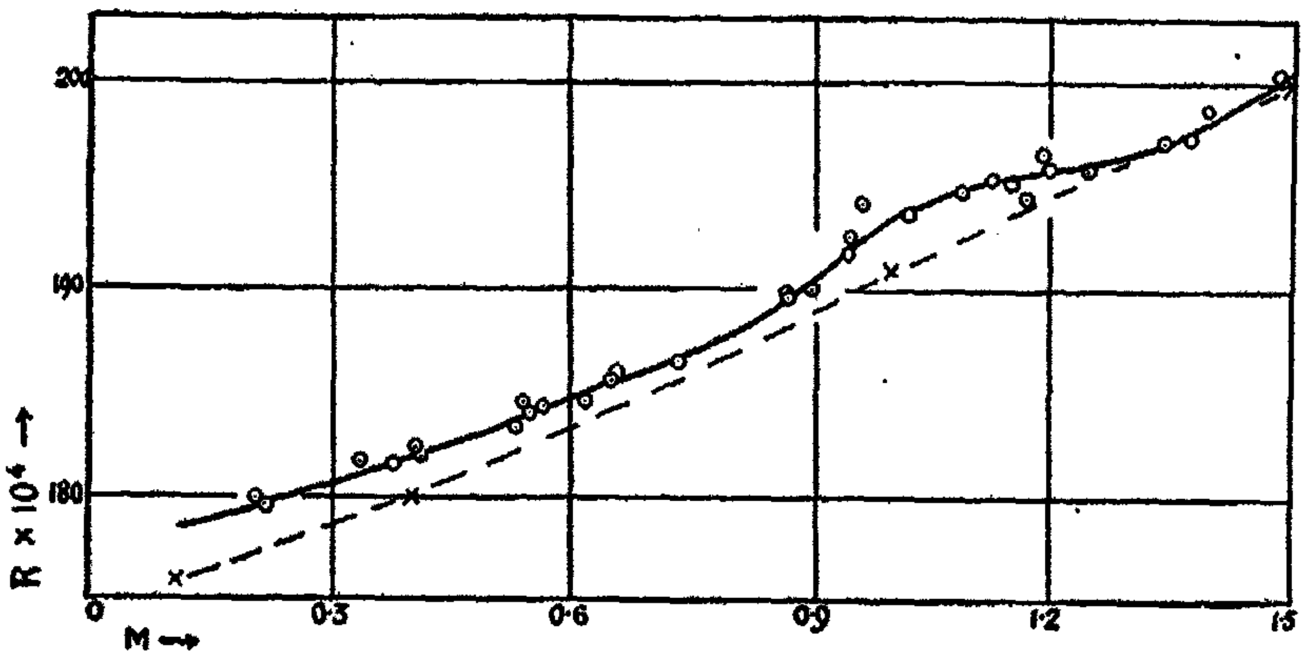


Fig. 1

TABLE 1

Values of $R = \frac{p_0 - p}{M p_0}$ *for sucrose solutions, at 25°C.*

M (moles per 1000 grams of water)	$R \times 10^5$
0.2	1796
0.4	1821
0.6	1848
0.8	1881
0.9	1906
1.0	1936
1.1	1951
1.2	1959
1.3	1967
1.4	1985

The curve obtained from the few points given in the International Critical Tables is also shown in figure 1. The original paper was not available to the author, but the determinations were probably made with the Lovelace and Fraser apparatus. The difference is not great and, except for the elevation between 0.8 and 1.3 M, is less than 0.002 mm. Although the difference in the molal lowering becomes greater in the dilute region, the actual difference in pressure becomes smaller and at 0.2 *M* is only about 0.001 mm.

The elevation between 0.8 *M* and 1.3 *M* corresponds to the elevation in the standard curve for potassium chloride (see figure 3). It may be eliminated by allowing deviations of 0.002 mm. in the measurements of Lovelace, Fraser and Sease, but this would be altogether too revolting to these authors. The real existence of this irregularity is supported by the independent measurements on lithium chloride solutions made by Lovelace, Bahlke and Fraser (1), which show a similar irregularity. It has also been observed recently by Burrage (7) that there is a parallelism in the curve for the solubility of lead chloride in potassium chloride solutions.

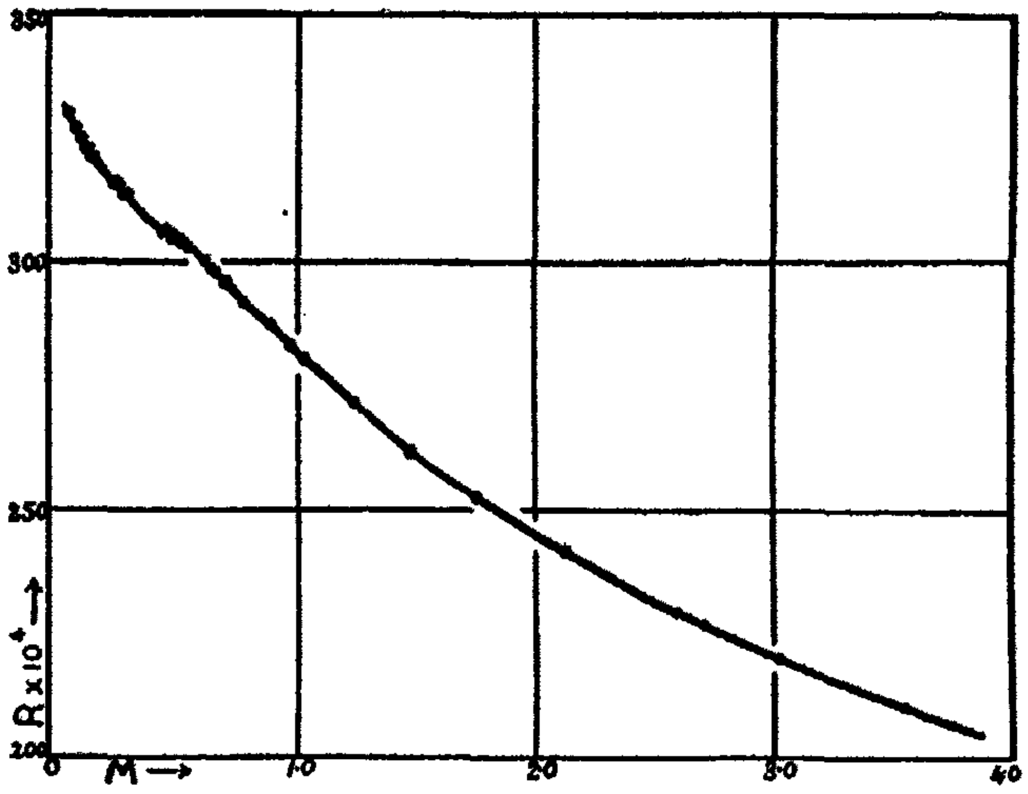


FIG. 2

The significance is uncertain, but it would appear that the irregularity is due to a property of water in this activity range which is independent of the type of solute. Further direct measurement in this region is highly desirable.

Sodium chloride solutions

A few determinations on sodium chloride solutions serve to show that the irregularity appears also in the curve for this salt. The author's determinations tend to confirm the values given in the International Critical Tables (original paper unavailable). Bousfield and Bousfield obtained values about 8 to 9 per cent higher.

The author's results are inserted as dots in figure 3.

Potassium toluene-p-sulfonate solutions

An extensive series of determinations was executed with solutions of this salt over a range of concentration from 0.1 *M* to saturation. The specimen used was some of a preparation used in previous research work in this College, and was taken as sufficiently pure without further test, other than that for water content. The salt crystallizes with one molecule of water of crystallization. This is, however, easily driven off. A sample of a batch dried at 130°C. in an air-oven for two hours did not lose weight further on being subjected to two hours' treatment with a stream of air under 20 mm. pressure at 130°C., dried over phosphorus pentoxide.

The results are exhibited in figure 2 and table 2. Satisfactory general uniformity was obtained. The distribution of points in the region of the irregularity unfortunately does not allow the exact shape of the curve to be determined here. The small irregularity, although quite evident, seems to be masked by a longer irregularity extending to 1.3 *M*, which may or may not be due to experimental error, since the five points from 0.79 *M* to 1.3 *M* were all obtained from one set only. Circumstances did not allow confirmation to be made.

TABLE 2

Values of R for potassium toluenesulfonate solutions, at 25°C.

M	$R \times 10^5$	*M*	$R \times 10^5$
0.1	3274	1.0	2820
0.2	3192	1.2	2727
0.3	3128	1.4	2641
0.4	3072	1.6	2572
0.5	3040	1.8	2508
0.6	3005	2.0	2450
0.7	2960	2.5	2316
0.8	2907	3.0	2210
0.9	2864	3.5	2118

The solubility of the salt does not appear to have been determined previously. From the vapor pressure of the saturated solution it was estimated by the author, by a short extrapolation, that the molality of the saturated solution was about 3.87.

COMPARISON OF MOLECULAR LOWERING CURVES

Figure 3 gives a comparison of the curves for five salts. The values for potassium nitrate and sodium chloride were taken from the International Critical Tables, while those for potassium and lithium chlorides are from the original papers previously referred to.

The comparison shows what wide variations exist among these simple salts with common anions and cations. A close parallelism between potassium nitrate and potassium toluenesulfonate is evident. Whether this is fortuitous or due directly to common properties of the sulfonic and nitrate ions must be decided by further investigations.

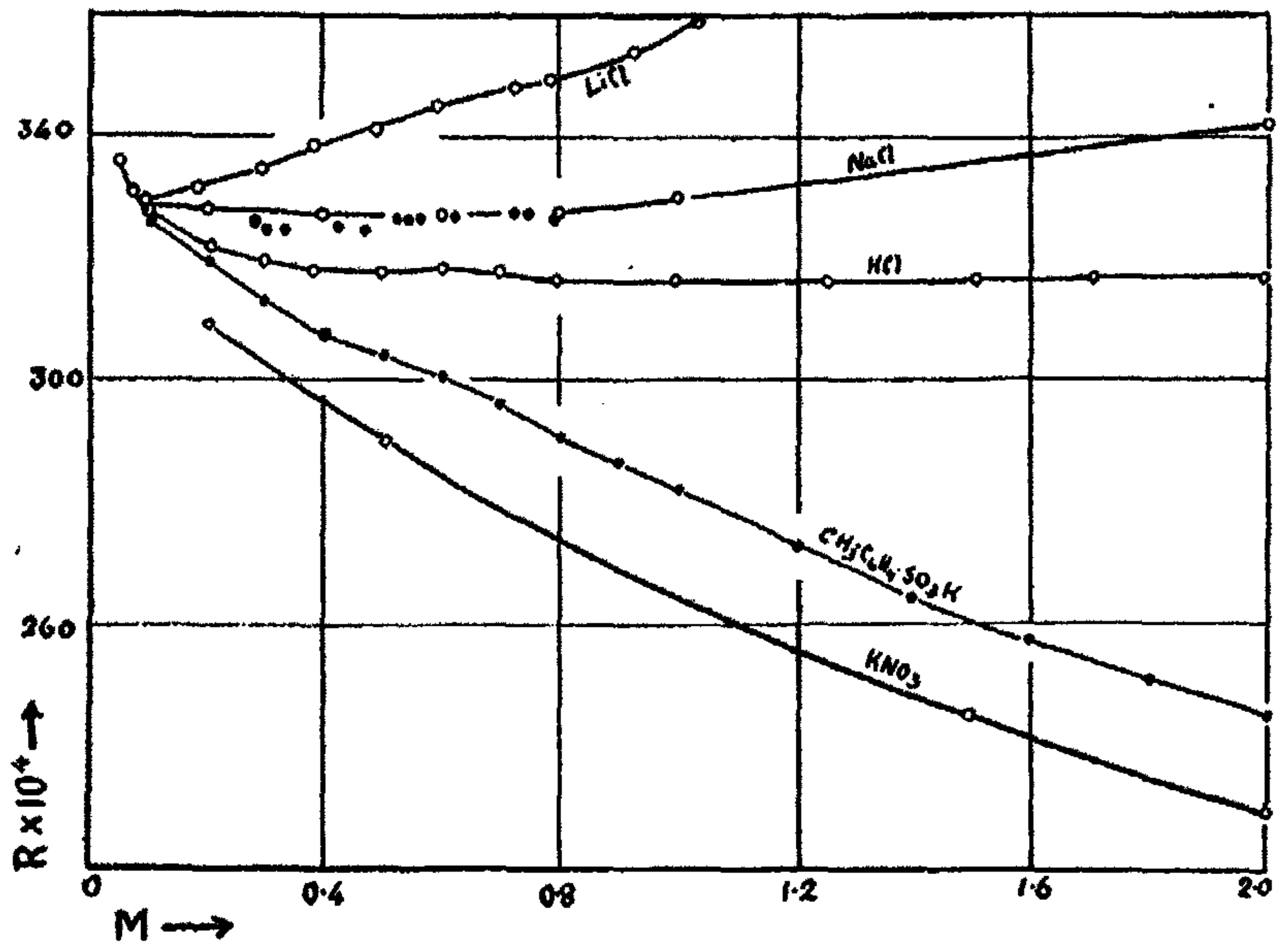


Fig. 3

CONCLUSION

The method described for determining vapor pressures of solutions appears to be capable of yielding results of a high degree of accuracy. The sensitivity is demonstrated by the clear discernment of irregularities, which are detected only by the most accurate direct measurements which have been made and are very close to the experimental error thereof. With greater refinement and care, even more accurate results should be obtainable, but for the present sufficiently good results are obtainable by the simple procedure described above.

The method should prove very useful in extending vapor pressure data, which are highly desirable and will become more and more important as the theory of solutions progresses into the more concentrated regions.

SUMMARY

Solutions may be brought rapidly into equilibrium as regards vapor pressure, and by taking one as a standard, values for the vapor pressure lowering may be obtained with an accuracy of 0.3 per cent or less for solutions of concentration above 0.1 *M*. Determinations have been made on solutions of sucrose, sodium chloride, and potassium toluene-*p*-sulfonate, using potassium chloride as standard.

The author desires to thank Professor F. P. Worley, under whose supervision this work was carried out, for his sustained interest, and for his assistance in preparing the paper for publication.

REFERENCES

(1) Lovelace, Bahlke, and Fraser: J. Am. Chem. Soc. **45**, 2930 (1923), and earlier papers.
(2) Bousfield and Bousfield: Proc. Roy. Soc. London **A103**, 429 (1923).
(3) Pearce and Snow: J. Phys. Chem. **31**, 231 (1927).
(4) Hepburn: J. Chem. Soc. **1932**, 550.
(5) Hill: Proc. Roy. Soc. London **A127**, 9 (1930).
(6) Lovelace, Fraser, and Sease: J. Am. Chem. Soc. **43**, 102 (1921).
(7) Burrage: Trans. Faraday Soc. **28**, 529 (1932).

THE INFLUENCE OF COMBINED OXYGEN ON THE ADSORPTION OF VAPORS BY POROUS SOLIDS. I

L. J. BURRAGE

King's College, London, England

Received October 14, 1932

I. INTRODUCTION

As a result of the development of the improved retentivity technique for the determination of isothermals (1), it has been found that the isothermals derived by this method consist of a series of sharply defined steps. The present investigation was undertaken to determine whether these rectangular steps could be obtained by the static technique. It has been stated previously (2) that carbon dioxide on the surface of the charcoal exerts a very disturbing influence on the breaks, and it seemed probable that the fact that the static isothermals heretofore had been found to consist of a series of curves might be due to this cause.

The difficulty of securing an oxygen-free surface has already been emphasized by the author (3), and in the present investigation the most elaborate care has been taken to obtain a charcoal surface as free from oxygen as possible. It has been found (4) that it is most difficult to remove the C_xO_y from an underactivated charcoal, and it was therefore decided to carry out the present investigation with a charcoal of this type, as, provided that the oxygen could be removed in this case leaving a charcoal yielding an isothermal of rectangular steps, then the same result might be expected with other charcoals. Charcoal D1 (5) was therefore chosen, since it fulfilled the necessary conditions.

EXPERIMENTAL

Since the experiment would probably involve the detection and measurement of small quantities of carbon dioxide, it was decided to effect this by means of the Pirani gauge technique. It was, therefore, necessary first of all to obtain the coefficient for carbon dioxide so that the $f(v)$ readings might be converted to pressures. In the cases of carbon tetrachloride (see Chaplin (6)) and carbon disulfide (determined by the author) the value of α has been found to be constant up to 0.2 mm. The Pirani measurements were carried out in the manner described by Chaplin (6) and the carbon dioxide pressures read off on a McLeod gauge of the type described by the same author (7). The results are given in table 1 and it is seen that the coefficient for carbon dioxide is constant up to a pressure of 0.06 mm., but at higher pressures the value steadily increases.

The experimental train employed in the main investigation was as follows:

A. Hyvac oil pump.
B. Leybold diffusion pump.
C. McLeod gauge.
Two-way tap

D. McLeod gauge.
E. Purifying charcoal and manometer tube.
F. Carbon tetrachloride supply bulb.
G. Freezing tube.
H. Pirani gauge.
I. Container in oven.

K. Freezing tube.
L. Pirani gauge.
M. Measuring apparatus in thermostat at 25°C.

TABLE 1

$f(v)$	p	a
	mm.	
9.70	0.377	0.039
6.218	0.218	0.035
4.707	0.160	0.034
3.057	0.094	0.031
2.309	0.065	0.028
1.427	0.038	0.027
0.724	0.021	0.028
0.705	0.019	0.027
0.357	0.0092	0.026
0.181	0.0048	0.027
0.065	0.0018	0.027

The technique employed in the filling and weighing of the charcoal container is the same as in the previous experiment (2). A to I comprise the complete apparatus used in removing oxygen and charging with carbon tetrachloride. The general technique employed was as follows. The charcoal was evacuated at room temperature to zero pressure and then for eighty hours at 800°C., till a pressure of 10^{-4} mm. was attained. Carbon tetrachloride was then liberated from the supply bulb F, which contained charcoal saturated with carbon tetrachloride and closed by a tap from the main apparatus. This vapor was separated from carbon dioxide by freezing out the carbon tetrachloride with melting methylcyclohexane at G. This carbon dioxide was adsorbed by the purifying charcoal E in the manner described by Chaplin (6). The evacuated charcoal was charged to saturation at 50 mm. pressure and the temperature of the oven raised to 50°C., the container tap being shut.

After standing at this temperature for some hours, the container tap was opened with liquid air on the freezer G. When equilibrium had been established the container tap was shut and the carbon monoxide pressure read. This was pumped away and the liquid air on the freezer replaced by melting methylcyclohexane. The pressure of the carbon dioxide was thus obtained. $CO = 4.5$ mm., and $CO_2 = 0.06$ mm.

The carbon dioxide was removed and the carbon tetrachloride allowed to stream back on the charcoal at room temperature. The container tap was again shut and the temperature raised to 100°C. and kept at this figure for five hours. The tap was then opened and the carbon monoxide and carbon dioxide measured as before. $CO = 5.0$ mm., $CO_2 = 3.5$ mm. These gases were pumped away and the carbon tetrachloride allowed to stream back on to the cooled charcoal. This process was repeated and the analysis gave 1 mm. CO and 0.03 mm. CO_2. This was pumped away as before, and the process again repeated, the analysis being $CO = 5 \times 10^{-3}$ mm. and $CO_2 = 1 \times 10^{-2}$ mm. Since this is the total removed, the actual pressure over the charcoal must be negligible. In order to see if all the oxygen had been removed from the charcoal, the container was heated for nine hours at 140°C., 1 mm. of CO and 2 mm. of CO_2 being obtained. Obviously after all this drastic treatment the charcoal is not oxygen-free. The isothermal should, however, be practically unaffected by the amount of oxygen which remains. The quantity of carbon tetrachloride adsorbed was 266.9 mg. per gram.

It has been pointed out before that carbon dioxide exerts a poisoning effect and therefore all charcoal isothermals which have been obtained heretofore are affected to a greater or lesser extent, the quantity figures being too small in all cases. The above results are at variance with the claims of previous workers that an oxygen-bare surface can be obtained by evacuation at 900°C. for twenty-four hours, since in the present instance, by flushing out with vapor, a total pressure of 14 mm. of combined oxygen has been generated after a preliminary evacuation of 800°C. for eighty hours.

The other arm of the two-way tap connects with a freezer K, a Pirani gauge L and an apparatus M, similar to that described in a previous publication (figure 1 in reference 2) from A to G, with the exception of the freezer C. A distinct improvement has been made in the apparatus, in that the whole is immersed in a glass-sided thermostat at 25°C. The calibration of the volume was carried out at this temperature and as a wide manometer was employed, a volume correction was applied for each reading. The volume of the bulb N was 53.3 cc. and the volume of the main apparatus 66.5 cc. at zero pressure. The quantities were calculated

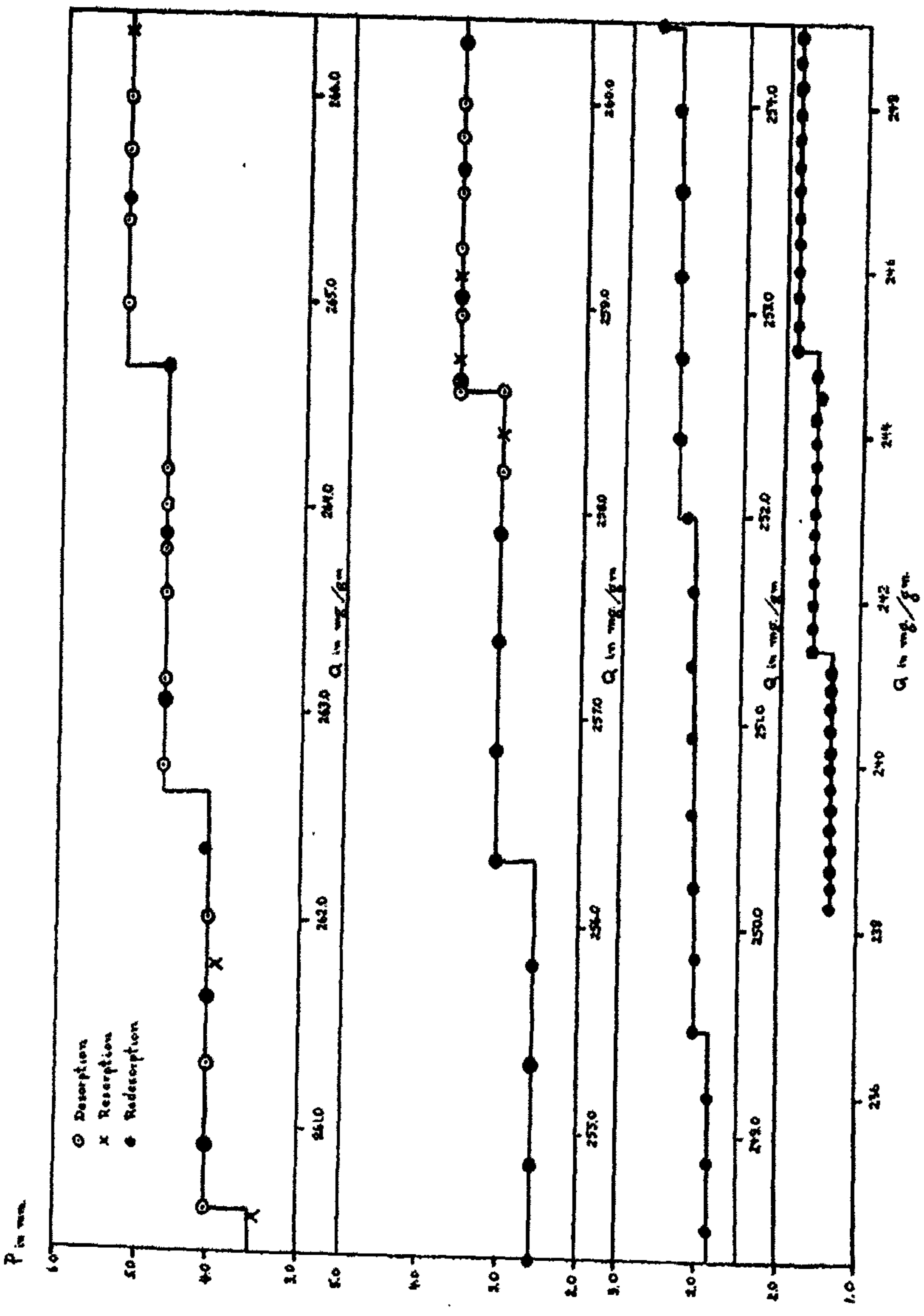

P in mm.
○ Desorption
× Resorption
● Redesorption
6.0
5.0
4.0
3.0
5.0
4.0
3.0
2.0
3.0
2.0
2.0
1.0
261.0
262.0
263.0
264.0
265.0
266.0
Q in mg./gm.
255.0
256.0
257.0
258.0
259.0
260.0
Q in mg./gm.
249.0
250.0
251.0
252.0
253.0
254.0
Q in mg./gm.
236
238
240
242
244
246
248
Q in mg./gm.

FIG. 1

by the pressure change method (2), and the pressures are considered to be correct to 0.01 mm. It has been found that over certain ranges of sorption values the dead space volume can be increased during desorption, or diminished during resorption, without alteration of pressure.

The complete results comprise a desorption curve, followed by resorption and further desorption, the resultant isothermal being shown in figure 1.

The figures obtained at the higher pressures are given in table 2 in the order in which they were obtained and show the degree of reversibility which has been attained.

TABLE 2

P	*Q*	*P*	*α*
mm.	*mg. per gram*	*mm.*	*mg. per gram*
5.24	265.98	3.01	258.19
5.23	265.72	3.03	258.38
5.24	265.37	3.59	258.74
5.23	264.98	3.59	259.15
4.70	264.17	3.54	260.57
4.71	264.00	4.00	261.78
4.70	263.79	4.70	263.83
4.70	263.58	5.22	266.30
4.70	263.15	5.22	265.48
4.70	262.73	4.71	264.67
4.12	262.01	4.71	263.86
4.12	261.30	4.71	263.05
4.12	260.60	4.18	262.33
3.56	259.99	4.12	261.62
3.57	259.82	4.12	260.91
3.58	259.55	3.56	260.29
3.58	259.28	3.56	259.67
3.57	258.96	3.56	259.05
3.38	258.59	3.56	258.63
3.02	258.59	3.07	257.90

At the close of the experiment a check weighing was carried out and a comparison made with the quantity calculated by the pressure change method.

	mg. per gram
By weight	238.5
By pressure change	238.28

In view of all the stages involved this is good agreement.

DISCUSSION

As will be seen from figure 1, a most important fact has resulted from this experiment, in that isothermals on charcoal obtained by the static technique consist of a series of rectangular steps. It has already been shown that this type of isothermal is obtained by the improved retentivity technique, instead of a series of curves as had been previously obtained by both static and retentivity techniques.

It is clear, therefore, that this true structure of the charcoal isothermal only results when the surface is free or almost free from foreign adsorbed matter. During the whole of the course of this experiment no trace of carbon dioxide was detected when the carbon tetrachloride had been frozen out. Another very interesting point was the rate of attainment of equilibrium, which was instantaneous during both sorption and desorption, no change being detected after standing for seventy-two hours. The isothermal was found to be absolutely reversible, which is again of interest, since previously (8) marked drift had been found with carbon tetrachloride isothermals on this charcoal.

A discussion of the pressure intervals of the breaks and the quantity values of the steps will be deferred until a later publication. For obvious reasons it is extremely difficult to get two points on the vertical section, but this has been achieved at a $Q = 258.59$ mg. per gram, thus justifying the drawing of vertical portions in other instances. In each case, however, the exact value lies between two adjacent points, the quantity taken being arbitrarily chosen.

It has been mentioned in a previous publication (5) that the reason why breaks had not been found by other workers was due to insufficient points being determined on the isothermal. The author improved on this by taking 350 points in a range of 81 mm. (2), and in the present paper 100 points have been obtained in a pressure range of approximately 4 mm. This fact, together with the reversibility which has been obtained, leave no doubt as to the true structure of the isothermal on charcoal.

SUMMARY

1. The coefficient for carbon dioxide has been determined by the Pirani gauge technique.

2. The charcoal was very thoroughly evacuated and freed from oxygen as completely as possible by flushing with vapor.

3. A carbon tetrachloride isothermal was obtained by the static technique at 25°C., comprising rectangular steps.

4. Reasons have been advanced for previous isothermals being found to consist of a series of curves.

REFERENCES

(1) Burrage: J. Phys. Chem. **37**, 33 (1933).
(2) Burrage: J. Phys. Chem. **36**, 2272 (1932).
(3) Burrage: Trans. Faraday Soc. **28**, 192 (1932).
(4) Burrage: Unpublished.
(5) Burrage: Proc. Roy. Soc. London **130**, 610 (1931).
(6) Chaplin: Proc. Roy. Soc. London **A121**, 344 (1928).
(7) Chaplin: Phil. Mag. **2**, 1198 (1926).
(8) Allmand and Chaplin: Proc. Roy. Soc. London **129**, 235 (1930).

THE TRANSITION POINTS OF SALT HYDRATES IN VARIOUS NON-AQUEOUS SOLVENTS

WALTER W. LUCASSE AND HAROLD J. ABRAHAMS

The John Harrison Laboratory of Chemistry, The University of Pennsylvania,
Philadelphia, Pa.

Received August 16, 1932

Many methods have been used to determine the transition points of polymorphous solids and of salt hydrates. For both types of systems conductance methods have been used in various forms, taking advantage, particularly, of the difference in conductance due to the different solubilities of the two forms. In an earlier paper (1) it has been shown that with a constant amount of solvent and solute a break occurs in the resistance-temperature curve at the transition point when the solution of a salt hydrate in a non-aqueous solvent is heated over a short range of temperature in this region. The break in the curve is presumably due to the change both in the salt at this point and the simultaneous change in the solvent medium. The earlier study was limited to solutions of various concentrations in ethyl alcohol and alcohol containing small amounts of water. In the present paper are given results obtained with a number of additional salts in methyl, ethyl, propyl, and isoamyl alcohols, pyridine, acetone, and ethylene glycol.

APPARATUS, MATERIALS, AND METHODS

The cell used was in the form of a U-tube with the electrodes sealed in one arm and the thermometer placed in the other. The design permitted the solution to be transferred from one arm to the other to insure uniformity and obviated any change in the cell constant due to slight differences in proximity of the thermometer to the electrodes. The similar placement of the bulb of the thermometer and the electrodes, together with the very slow rate at which the temperature of the bath was increased, made it possible to assume that the temperature in both parts of the cell was the same. The thermometer was graduated in tenths of a degree and had been checked against a standard thermometer. Connection was made through the stopper bearing the thermometer with a mercury trap which prevented any loss of the vaporized solvent from the system and minimized concentration changes due to the high vapor pressure of the solvents.

The ethyl alcohol was prepared by allowing ordinary commercial alcohol to stand over freshly broken lime for several days, after which it was distilled over a slow water bath, only the middle portion being retained. The acetone was purified with sodium bisulfite and dehydrated in the usual manner. The other solvents and the salts used were all high grade products and no attempt was made to purify them further.

In most of the determinations saturated solutions were used. A quantity of the solvent was shaken for some time in a dried, air-tight container with an excess of solute and after being allowed to settle the clear supernatant liquid was transferred to the cell. In some determinations the saturated solution was diluted with pure solvent before being introduced into the cell, and in others less solute than that required to make a saturated solution was used. In each case the bath was brought up to a temperature a few degrees below the transition point of the salt before introducing the cell, after which the temperature of the bath was raised at the rate of about eight degrees an hour. Frequent readings of the resistance were then taken simultaneously with those of the temperature within the cell.

TABLE 1

$LiNO_3 \cdot 3H_2O = LiNO_3 \cdot \frac{1}{2}H_2O + 2\frac{1}{2}H_2O$ *in pyridine* (*series 1*), *in acetone* (*series 2*), *in amyl alcohol* (*series 3*)

$CaCl_2 \cdot 6H_2O = CaCl_2 \cdot 4H_2O\beta + 2H_2O$ *in propyl alcohol* (*series 4*)

SERIES 1		SERIES 2		SERIES 3		SERIES 4	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
22	1193	24	46.96	24.2	505.0	25	319.5
24	1181	25	46.77	25.3	492.9	26	314.3
26	1169	26	46.21	26	486.9	27	309.9
28	1157	27	45.84	27	473.4	28	305.5
30	1146	28	45.47	28	463.9	29	301.8
32	1137	29	45.11	29	454.7	30.1	296.9
34	1125	30	44.93	30	448.4	31.1	293.4
36	1116	31	44.57	31	438.6	32.1	288.7
38	1107	32	44.21	32	428.2	33.0	285.2
40	1099	33.2	43.68	33	419.7	34	281.8
		34	43.51	34	411.4	35	277.8
		35	43.16	35	403.2		

RESULTS

In table 1 are given the results obtained with lithium nitrate in pyridine, acetone, and amyl alcohol. In the first column of each series are given the temperatures and in the second the corresponding resistances. Plots were made of the various determinations, using both the resistances and the logarithm of the resistances as ordinates against the temperatures as

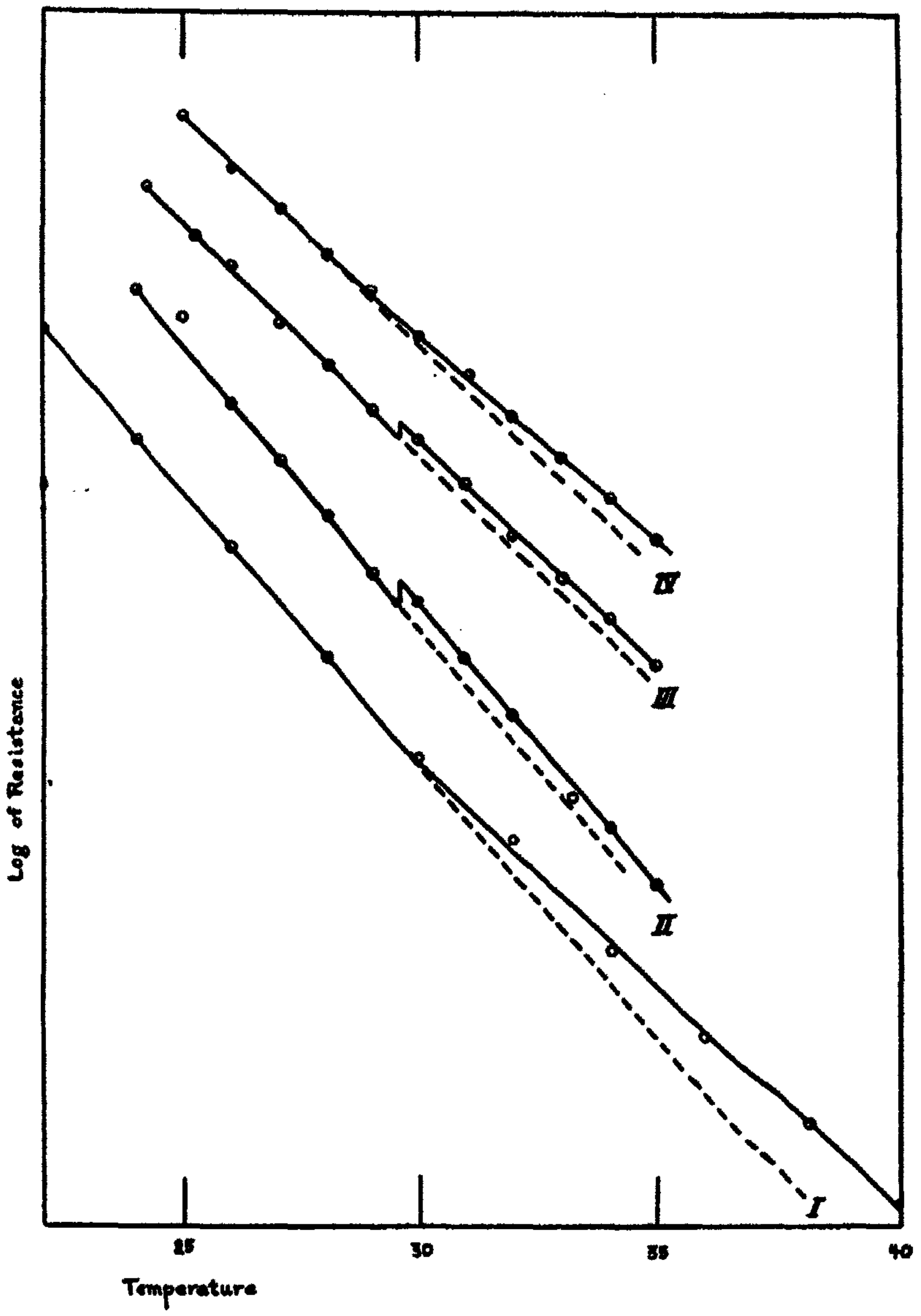


Fig. 1

abscissae. In both plots curves were obtained which approached straight lines in the neighborhood of the transition points. With the logarithmic plot the curves seemed to remain straight over a longer temperature range and so in the final plots and in the calculations the relationship between the temperature and the logarithm of the resistance was used. Such a plot of the data given in table 1 appears as figure 1, where the ordinates of the individual curves were adjusted in order to show several curves on a single plot. In each case smooth curves are drawn through the experimental points and the curve obtained below the transition point extended beyond this temperature as a broken line for emphasis. The value for the transition temperature calculated from the data obtained from solutions of lithium nitrate in pyridine agrees well with that found by Donnan and Butt (2) from solubility measurements, i.e., 29.6°C.

TABLE 2

$CdBr_2 \cdot 4H_2O = CdBr_2 \cdot H_2O + 3H_2O$ *in methyl alcohol (series 1), in ethyl alcohol (series 2)*
$Zn(NO_3)_2 \cdot 6H_2O = Zn(NO_3)_2 \cdot 3H_2O + 3H_2O$ *in methyl alcohol (series 3), in ethyl alcohol (series 4)*

SERIES 1		SERIES 2		SERIES 3		SERIES 4	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
26	62.87	28	556.2	28	113.2	28	196.5
28	61.61	30.5	546.2	30	112.3	30	192.6
30	60.50	32	538.6	32.2	111.4	32	188.8
32	59.41	34	530.0	34.2	110.5	34	185.5
34	58.22	36	522.6	36	110.1	36	182.1
36	57.29*	38	515.3	38	109.2	38.2	179.3
38	56.15	40	508.1	40	108.3	40	177.1
40	55.03*	42	501.1	42	107.5	42	174.7
42	54.16	44	495.1			44	172.2
44	53.19						
46	52.24						

The method of calculation as shown below depends upon the abrupt change in the slope of the resistance-temperature curve at the transition point, and the identity of the resistance at this temperature. The curves for lithium nitrate in acetone and in amyl alcohol (Curves II and III) are of interest even though they do not permit of the calculation of the transition point by the method here used. In both cases there is an abrupt change in the curve between 29°C. and 30°C., indicating the transition point between these temperatures, but the solvent medium and the number and nature of the conducting particles change in such a way as to make the temperature coefficient above and below the transition point almost identical. Thus in these two solvents parallel lines were obtained in each case in place of intersecting curves, making calculation of the exact transition point impossible. The last series in table 1 and Curve IV are based on the data obtained for solutions of calcium chloride in propyl alcohol. The value calculated for the transition point in this solvent is in fair agreement with that previously found for the salt in ethyl alcohol and with the value given by Bancroft (3) for the equilibrium temperature for the hexahydrate and the β-tetrahydrate.

TABLE 3

$ZnBr_2 \cdot 2H_2O = ZnBr_2 + 2H_2O$ *in pyridine* (*series 1*)

$CoCl_2 \cdot 6H_2O = CoCl_2 \cdot H_2O + 5H_2O$ *in glycol* (*series 2*), *in pyridine* (*series 3*), *in methyl alcohol at different concentrations* (*series 4, 5, and 6*)

SERIES 1		SERIES 2		SERIES 3	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
25	8982	25.1	788.2	20	22670
27.5	8766	26	762.6	22	22240
29	8660	27	738.1	24	21880
31	8487	28	714.4	26	21530
33	8334	29	691.5	28	21040
35	8184	30	666.8	30.5	20470
37.5	8021	31.1	648.3	32.5	20010
39	7925	32.1	627.7	34	19700
41	7768	33	610.3	36	19170
43	7675	34.1	591.1	38	18710
45	7553	35	574.7	40	18190
46	7493			42	17680

SERIES 4		SERIES 5		SERIES 6	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
24	336.3	24	78.19	24	32.54
25	334.3	25	77.54	25	32.22
26	330.9	26.1	77.06	26	31.96
27	329.6	27.1	76.58	27	31.70
28	327.6	28	75.95	28	31.51
29	325.6	29	75.48	29	31.32
30	323.6	30.1	74.86	30	31.07
31	321.7	31.1	74.40	31	30.82
32	319.1	32.1	74.10	32	30.58
33	317.8	33	73.79	33	30.44
34	315.9	34	73.49	34	30.27
35	314.0			35	30.08
				36	29.85

In table 2 are given the results obtained with cadmium bromide and with zinc nitrate, each in methyl and in ethyl alcohol. Solubility or other determinations leading to values of the transition point of an accuracy comparable to those used in the earlier paper for these and the remaining salts considered here do not seem to be available. In the previous work the average deviation from the established value of the transition found by this method using the above cell was about two-tenths of a degree. The emphasis in the present study, however, was placed upon extending the method to a larger number of solvents rather than establishing the exact values. The transition point of cadmium bromide according to Mellor (4) from consideration of the available data is 36°C. The value for zinc nitrate is given as about 35°C. Wasilieff (5) claims to have made a tetrahydrated salt and that it forms an eutectic with the hexahydrate at 35.4°C. Calculation of the data for this salt in ethyl alcohol gave 35.4°C. as the transition point; in methyl alcohol a curve was obtained similar to those for lithium nitrate in acetone and amyl alcohol.

In table 3 are given the data obtained from solutions of zinc bromide in pyridine and of cobalt chloride in ethylene glycol, in pyridine, and in methyl alcohol of various concentrations. The transition point of zinc bromide is given by Mellor (6) from consideration of solubility data as 35°C. According to a plot of the data compiled in Seidell (7), the transition point of cobalt chloride between the hexahydrate and monohydrate is at about 31°C. Landolt and Börnstein (8), on the other hand, indicate the transition point of the hexahydrate and dihydrate at about 50°C. and the possibility of a polymorphous transition of the hexahydrate between 30°C. and 35°C. Compilations of the solubility data for cobalt chloride in water show a curve which rises gradually as an almost straight line to about 30°C., at which point there is an abrupt curvature to about 50°C., where the line is cut by an almost straight line giving the solubility at higher temperatures. Corresponding with these points, the color of the solution changes from rose to violet and finally to blue. Numerous theories have been advanced to explain the changes in color and solubility, including equilibria of various salt hydrates, double salts, complex ions, and hydrated ions. The several viewpoints are summarized by Friend (9), who also mentions the change in color in aqueous salt solutions and in non-aqueous solvents.

In table 3 we have indicated the transformation as being that between the hexahydrate and the monohydrate, and calculation led to a transition temperature at about 31°C. The real change taking place at this temperature may be of quite a different nature and much more complicated. Whatever the cause, however, we found quite pronounced breaks in the resistance-temperature curves in all cases. The different solvents and concentrations gave different colored solutions, but in each case the break in the curve seemed to come at about the same point. The single exception was for the solution in glycol, where the calculated point was found to be 1.6°C. below that of the average in the four other solutions—in pyridine and in methyl alcohol. The deviation being so much greater than the average deviation would indicate an influence of the solvent rather than experimental error.

A single determination was made with this salt in the vicinity of 50°C., using ethylene glycol as solvent. A pronounced break was found in the curve at about 47°C. which again, owing to the solvent, may be lower than the true transition point for the change taking place at this higher temperature. In view of the findings given here it would appear that there is some abrupt change which takes place at about 31°C., and a further transformation at the higher temperature where the sharp change in the solubility curve is found.

TABLE 4

Calculation of transition points

SALT	SOLVENT	a	10^3b	a'	$10^3b'$	t	t'
Lithium nitrate	Pyridine	3.1255	−2.220	3.1145	−1.847	29.5	29.6
	Acetone					29–30	29.6
	Amyl alcohol					29–30	29.6
Calcium chloride	Propyl alcohol	2.6587	−6.190	2.6513	−5.932	28.7	29.2
Cadmium bromide	Methyl alcohol	1.9054	−4.120	1.8986	−3.927	35.2	ca. 36
	Ethyl alcohol	2.8415	−3.433	2.8246	−2.960	35.7	ca. 36
Zinc nitrate	Methyl alcohol					34.2–36	ca. 35
	Ethyl alcohol	2.4108	−4.200	2.3692	−3.026	35.4	ca. 35
Zinc bromide	Pyridine	4.0542	−4.038	4.0346	−3.483	35.3	35.0
Cobalt chloride	Glycol	3.2632	−14.62	3.2162	−13.04	29.7	ca. 31
	Pyridine	4.4394	−4.162	4.4873	−5.690	31.3	ca. 31
	Methyl alcohol	2.5916	−2.721	2.5849	−2.510	31.8	ca. 31
	Methyl alcohol	1.9666	−3.063	1.9295	−1.860	30.8	ca. 31
	Methyl alcohol	1.5896	−3.252	1.5712	−2.663	31.2	ca. 31

CALCULATION OF THE TRANSITION POINT

As indicated above, the curves giving the relationship between the temperature and the resistance of solutions of salt hydrates in non-aqueous solvents approach straight lines at the transition points which in most cases intersect at this temperature. Equations giving the resistance as a function of the temperature may be developed, and since the resistance becomes identical at this point, the temperature may be calculated. In the present study it was found more advantageous to use the logarithm of the resistance, and equations for the two parts of the curve over the range where they appeared to be straight lines were calculated by the method of least squares in the form

$$\log R = a + bt$$

The results of such calculations are given in table 4. In the first and second columns are given the various salts and solvents. The constants a and b, given in the third and fourth columns, refer to the equation below the transition point and the values a' and b', in the fifth and sixth columns, are for the corresponding curve above the transition point. Solution of the equations for t yields the values of the transition points given in the next to the last column. In the final column, under t', appear such comparative data as can be found in the literature. In the tables above, all points obtained in the temperature interval are given. In the determination of the equations of the curves by this method, however, a few points may legitimately be omitted if from the plot they seem to be in error. This should be done particularly when such a point lies at or near the end of the curve and would thus, owing to the small number of points, have a considerable effect upon the slope of the curve and wipe out the self-consistency of the earlier points. This was found necessary in the present study only in the case of cadmium bromide, and the points omitted in the calculations are indicated in the table by asterisks; the remaining points in this curve and all of the points in the other curves were given equal weight. If from the graph a point appeared to be at the intersection of the lines it was included in the calculation of both curves. Obviously in order to achieve a high degree of accuracy with this method of determining the transition point, a larger number of points should be obtained for each branch of the curve so as to make the method of least squares truly significant.

SUMMARY

In the above study the transition points of a number of salt hydrates have been determined by observing the abrupt change of the resistance-temperature curves of solutions of these substances in several non-aqueous solvents. In most cases the numerical value of the point can be calculated, since merely a change in slope occurs at the point. Examples are also given, however, where the slope remains nearly constant, but the magnitude of the resistance changes abruptly. In all cases except for solutions of cobalt chloride in ethylene glycol the transition point was found to be independent of the solvent and, within the accuracy of the experiment, comparable with that found by other methods.

REFERENCES

(1) LUCASSE AND HARRIS: J. Phys. Chem. **30**, 930 (1926).
(2) DONNAN AND BUTT: J. Chem. Soc. **83**, 335 (1903).
(3) BANCROFT: The Phase Rule, p. 71. The Journal of Physical Chemistry, Ithaca, New York (1897).
(4) MELLOR: Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume IV, p. 567. Longmans, Green and Company, New York (1923).

(5) Landolt-Börnstein Tabellen, Volume I, p. 687. J. Springer, Berlin (1923).
(6) Reference 4, p. 566.
(7) Seidell: Solubilities of Inorganic and Organic Substances, Volume I, p. 256. D. Van Nostrand Company, New York (1919).
(8) Reference 5, p. 648.
(9) Friend: A Textbook of Inorganic Chemistry, Volume IX, Part I, p. 39. J. B. Lippincott Company, Philadelphia (1920).

THE CHANGE IN THE TRANSFORMATION TEMPERATURE OF COPPER SULFATE AT 56°C. WITH THE SOLVENT MEDIUM

HAROLD J. ABRAHAMS AND WALTER W. LUCASSE

The John Harrison Laboratory of Chemistry, The University of Pennsylvania, Philadelphia, Pa.

Received August 16, 1932

Studies of the resistance of saturated solutions of copper sulfate in water have shown a break in the curve at about 56°C. (1). Electromotive force and solubility measurements have likewise indicated a change at about this point. In summarizing his data, Etard (2) gives two equations, one for the solubility at temperatures below 55°C. and another for that at higher temperatures. The change taking place at this temperature has been variously interpreted as a transition (3) from an α to a β pentahydrate and as the point of formation of $3CuSO_4 \cdot 4CuO \cdot 12H_2O$.

In the preceding paper, determinations of the transition points of salt hydrates have been given from a study of the resistance of solutions of constant concentration in several non-aqueous solvents. In all cases, except for solutions of cobalt chloride in ethylene glycol, the transition temperature was found to be the same within the experimental error as that given by other methods. In this system it was found that the break in the curve was about 1.6°C. below the transition point as indicated by other methods, or about four times the average deviation from the mean value found for this salt in other solvents. The transition temperature in general is lowered by the presence of foreign substances and different methods do not always yield the same value, but it was suggested that the effect in this case may have been due to the solvent. In the present paper are given results for the transformation of copper sulfate in glycerol-alcohol mixtures where the temperature is lowered several degrees.

The apparatus and method was entirely the same as in the previous paper. The results are given in table 1 where the resistances at various temperatures are given for solutions of copper sulfate in glycerol–alcohol mixtures of different proportions. The ethyl alcohol was purified and dehydrated as before. The copper sulfate and glycerol were of high quality and were not further purified. The solvent was made up by volume, seven parts of alcohol and three of glycerol, for example, being used for the 70 per cent alcohol solution. The solutions were prepared by shaking an excess of the pentahydrate with a quantity of the mixed solvent in an air-tight container. After settling, a portion of the supernatant liquid was transferred to the cell.

TABLE 1

The resistance of copper sulfate in glycerol-alcohol mixtures

SERIES 1		SERIES 2		SERIES 3		SERIES 4	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
42	4234	30	13500	42	2976	40	2226
44	3985	32	12180	44.2	2811	42	2120
46	3759	34	11130	46	2689	44	2012
48	3532	36	10150	48	2552	46	1913
50	3353	38	9256	50	2427	48	1816
52	3164	40	8408	52	2313	50	1734
54	3004	42	7698	54	2209*	52	1653
56	2845	44	7043	56	2097	54	1572
58	2700	46	6398	58	1998	56	1498
60	2561	48	5864	60	1908	58	1434
		50	5388			60	1374
		52	4975			62	1312
		54	4661				
		56	4314				
		58	4025				

SERIES 5		SERIES 6		SERIES 7		SERIES 8	
Temperature	Resistance	Temperature	Resistance	Temperature	Resistance	Temperature	Resistance
36	5756	40.2	2546	42.2	15590	40	9577
38	5302	42	2397	44	14380	42	9124
40	4899	44	2230	46	13170	44	8699
42	4638	46	2092	48	11930	46	8333
44	4180	48.2	1946	49	11410	48.4	7887
46	3874	50.4	1814	50	10960	50	7658
48	3605	52	1732	52.2	9908	52	7330
50	3333	54	1623	54	9182	54	7019
52	3117	56	1536	55	8822	56	6765
54	2920	58	1444	56	8476	58	6494
56	2734	60	1365	58	7807	60.2	6236
58	2579					62	6038
60	2405					64	5823

In all cases, plots of the data obtained showed breaks in the curves at temperatures below 56°C. Constants for the equation

$$\log R = a + bt$$

for the portion below and above the break were calculated and the values of the transformation temperature calculated as in the previous paper. In table 2 the results are listed according to the increasing alcoholic content of the solvent. The series number given in the first column refers to the data in table 1 and gives the order in which the determinations were made.

TABLE 2

The transformation temperature of copper sulfate

SERIES	PER CENT ALCOHOL	a	10^4b	a'	$10^4b'$	t
7	20	5.0385	−2.002	4.9587	−1.841	49.6
2	30	4.7283	−2.004	4.5172	−1.576	49.3
5	50	4.3700	−1.698	4.2248	−1.405	49.6
6	60	3.9936	−1.463	3.9094	−1.292	49.2
1	70	4.1621	−1.276	4.1066	−1.164	49.6
3	80	3.9381	−1.106	3.9087	−1.048	50.7
4	80	3.7850	−1.094	3.7342	−0.9949	51.3
8	90	4.3649	−0.9635	4.2855	−0.8140	53.1

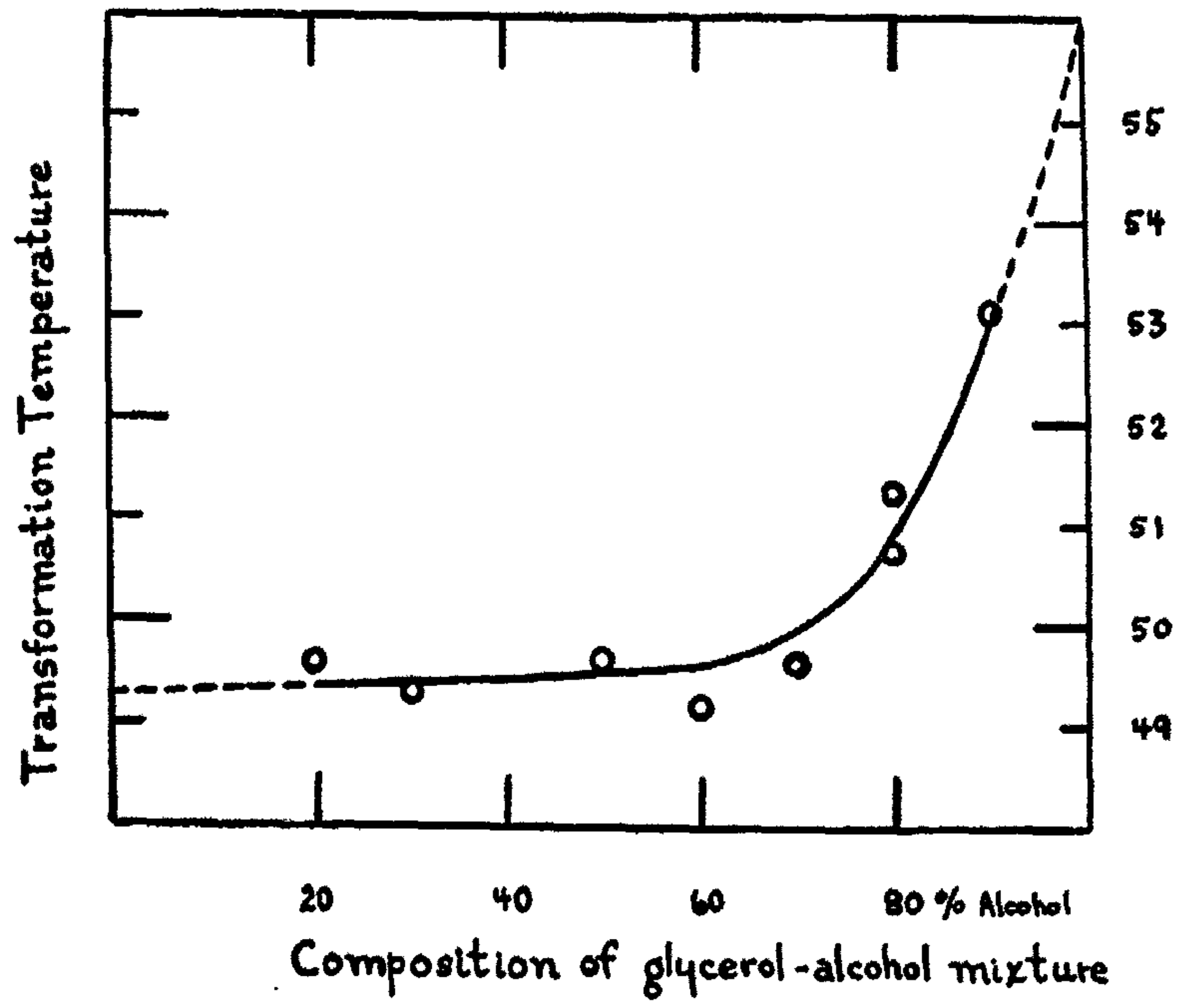


FIG. 1

The third and fourth columns give the values of the constants for the equation below the transformation temperature and the next two columns the corresponding values for the curve above this point. In the last column are listed the calculated transformation temperatures of the salt in the solvent of composition given in the second column.

A plot of these temperatures as a function of the alcoholic content of the solvent is given in figure 1, where the abscissae show the solvent composition and the ordinates the corresponding temperatures. Measurements in solutions of lower alcoholic content were difficult because of the high viscosity of the glycerol, and at higher concentrations because of the slight solubility of copper sulfate in alcohol. The smooth curve passing through the experimental points has been extended as a broken line in each direction to the pure components of the solvent.

The previous studies have shown that the transition points of the various salts used have been the same in solutions of ethyl alcohol as the values determined by other methods than the one used here, and the form of the curve with increasing alcoholic content makes it logical to extrapolate to 56°C. as the temperature at which the transformation would take place in this solvent, could sufficient amount be dissolved to determine the point. It is possible that at concentrations of glycerol greater than 80 per cent the curve again rises rapidly to 56°C. Should the curve be of that form, it would show the mutual lowering of the transition point by the added component of the solvent in each case. In the range measured, however, the curve shows no tendency to rise in the region of higher glycerol content. In view of the work with other solvents and with alcohol–water mixtures, it seems unlikely, also, that traces of water or other impurities in the glycerol would lead to a constant depression in the material used. Nor does it seem likely that the form of the curve shown in the figure is due to any reaction or dehydrating effect of the glycerol. The measurements for series 1, 3, 5, and 7 were carried out as soon as the solutions were made up; those for 2, 6, and 8 about five hours after making the solutions; and for series 4 about forty-eight hours after.

It appears from this study, therefore, that copper sulfate undergoes a definite transformation at about 56°C. and that this temperature may be lowered by the solvent medium (4). As in all of the cases studied, since the solutions were saturated only at room temperatures, the break in the curve is due to a change in the system as a whole and not to the different temperature-solubility relationships of the two forms. Conclusions as to whether this change is between two forms of the pentahydrate or of a more complicated nature cannot be drawn, although it would seem that the formation of the compound indicated above would cause a more pronounced break in the temperature-resistance curve.

REFERENCES

(1) COHEN: Z. physik. Chem. **31**, 164 (1899).

(2) ETARD: Compt. rend. **104**, 1615 (1887); Ann. chim. phys. [7] **2**, 503 (1894). See however, AGDE AND BARKHOLT: Z. angew. Chem. **39**, 851 (1926).

(3) Landolt-Börnstein Tabellen, Volume I, p. 651. J. Springer, Berlin (1923).

(4) MACLEOD-BROWN: Chem. News **109**, 123 (1914).

PHOTOSYNTHESIS IN TROPICAL SUNLIGHT. VI

THE PRESENCE OF FORMALDEHYDE IN RAIN WATER

N. R. DHAR AND ATMA RAM

Chemical Laboratories, University of Allahabad, Allahabad, India

Received September 17, 1938

Since 1864, when Baeyer gave out his formaldehyde hypothesis, numerous attempts have been made to obtain formaldehyde *in vitro* from carbon dioxide and water on exposure to light. Usher and Priestley (1), Baly, Heilbron, and Barker (2), Dhar and coworkers (3), Mezzadroli and collaborators (4) and others obtained evidence of formaldehyde formation from carbonic acid or bicarbonates in presence or absence of catalysts, when exposed to light. On the other hand, Spoehr (5), Baur and Rebman (6), Porter and Ramsperger (7), Bell (8), Emerson (9), Zschiele (10) and Mackinney (11) obtained negative results, although the latter worker made the following statement:—"The status of this problem is extraordinarily involved, though it can hardly be doubted that some workers have succeeded in obtaining formaldehyde *in vitro.*" Recently, Baly and coworkers (12) seem to contradict their earlier results.

It appears not only that the formation of formaldehyde is favored by radiations of short wavelengths, but also that a high light intensity is absolutely essential; some workers in this field could not obtain formaldehyde because of the low light intensity used.

In a recent communication, Dhar and Atma Ram (13) have been able to obtain larger yields of formaldehyde by the photoreduction of carbonic acid and bicarbonates by metals like magnesium, cerium etc.

It is well known that carbonic acid and water vapor exist in the atmosphere; under the influence of ultra-violet light from the sun, they should combine and form formaldehyde and oxygen. Hence, it seems probable that formaldehyde should be present in the atmosphere.

If appreciable amounts of formaldehyde were present in the atmosphere, formaldehyde should be partially washed down with rain water. In the last few months, in order to test whether formaldehyde occurs in rain water, we have analyzed numerous samples of freshly collected rain water obtained at Allahabad, Barlowganj (Mussoorie), altitude 5500 ft., and at a village 420 miles from Allahabad. In all cases we have got immediate and definite evidence of the existence of formaldehyde in both distilled and

TABLE 1

DATE	NUMBER OF HOURS AFTER WHICH THE SAMPLE WAS ANALYZED	AMOUNT OF FORMALDEHYDE PER LITER OF RAIN WATER	REMARKS
		grams	
July 15, 1932	12	0.00075	After bright sunshine.
July 20, 1932	7	0.00082	After bright sunshine for 5 days.
July 21, 1932	4	0.0005	After a cloudy day.
July 26, 1932	Immediately	0.001	After 5 days of bright sunshine and clear sky.
July 26, 1932	12	0.0004	It had already rained 3 hours before.
July 27, 1932	Immediately	(1) 0.00082 (2) 0.0006 (3) 0.00045	After a bright day. Three different samples were collected one after the other.
July 28, 1932	Immediately	0.00045	It had rained the previous evening.
July 29, 1932	9	0.00052	After 9 hours of clear sunshine.
July 30, 1932	Immediately	(1) 0.00045 (2) 0.0004 (3) 0.0003	After a cloudy day. Three samples were collected one after the other.
July 31, 1932	5	0.0003	It had rained in the night.
July 31, 1932	Immediately	0.0003	Very slow rainfall.
July 31, 1932	8	0.00015	After a cloudy day. Rainfall throughout the whole night.
August 1, 1932	Immediately	(1) 0.00015 (2) Extremely small	Heavy rainfall for 3 hours.
August 2, 1932	4	0.00015	Occasional sunshine for 1 hour on the previous day.
August 3, 1932	Immediately	0.00025	After 4 hours of sunshine on the previous day.
August 3, 1932	Immediately	0.00025	Cloudy day. Heavy rainfall.
August 3, 1932	Immediately	0.00015	It had rained 3 hours before.
August 4, 1932	5	0.00015	Rained in the night.
August 4, 1932	Immediately	0.00022	Rained after sunshine for 2 hours.
August 5, 1932	Immediately	0.00022	Rained the previous evening.
	Immediately	0.0005	Bright sunshine throughout the day and rained in the evening.
	Immediately	0.00045	
	7	0.0003	
August 6, 1932	Immediately	0.0003	Rainfall in the night.
August 7, 1932	6	Absent	Heavy rainfall throughout the day and night.
August 7, 1932	Immediately	Absent	Heavy rainfall throughout the day and night.
August 7, 1932	Immediately	Absent	Heavy rainfall throughout the day and night.

TABLE 1—*Concluded*

DATE	NUMBER OF HOURS AFTER WHICH THE SAMPLE WAS ANALYZED	AMOUNT OF FORMALDEHYDE PER LITER OF RAIN WATER	REMARKS
		grams	
August 8, 1932	9	Absent	Cloudy the whole day.
August 9, 1932	Immediately	0.00045	After 5 hours of bright sunshine, it rained.
August 9, 1932	Immediately	(1) 0.0003 (2) 0.00015 (3) Very small	Cloudy. One of the heaviest rainfalls.
August 10, 1932	Immediately	0.00015	Cloudy the whole day and a very heavy rainfall the previous day.
August 12, 1932	4	0.00015	Cloudy on all the previous days.
August 15, 1932	Immediately	0.0004	Bright sunshine on the previous day.
August 16, 1932	Immediately	0.0003	Rained in the night.
August 17, 1932	Immediately	0.0003	Occasional sunshine for 2 hours. A heavy rainfall.

undistilled rain water, as tested by Schiff's reagent and Schryver's reagent, and by the reduction of ammoniacal silver nitrate.

In a recent note to Nature, it has been reported by us that formaldehyde occurs in freshly collected rain water. We have now estimated quantitatively the amounts of formaldehyde in rain water, and we have observed that the amount of formaldehyde in rain water increases if the shower is preceded by sunshine. When there is no sunshine between two showers the amount of formaldehyde is small, as will be clear from the results recorded below. Moreover, when rain water is analyzed immediately after the shower, the amount of formaldehyde is greater than when the rain water is analyzed after some time, because a part of the formaldehyde is lost by vaporization and another part undergoes polymerization (cf. Norrish and Kirkbride (14)).

The following experimental procedure was adopted: The rain water was collected in large porcelain dishes, placed on a tall stool in a clear space. Definite volumes of rain water were distilled and the distillate was analyzed for formaldehyde. An excess of standard $N/10$ solution of iodine was added to the distillate and 10 per cent sodium hydroxide solution till a permanent yellow color was developed. The reaction was allowed to proceed for about fifteen minutes, and then the mixture was acidified with strong hydrochloric acid to liberate the excess of iodine, and the iodine liberated was titrated against $N/100$ sodium thiosulfate solution. 1 cc. of $N/10$ iodine = 0.0015 gram of formaldehyde. The experimental results are given in table 1.

DISCUSSION

It is well known that hardly any radiation from the sun shorter than 2900 Å. is available on the earth's surface. It is generally believed that a very thin layer of ozone (3 mm. when reduced to 760 mm. pressure) formed in the atmosphere at higher altitudes is capable of absorbing solar radiation shorter than 2900 Å. This ozone is supposed to be formed by the absorption of shorter radiations by the oxygen of the atmosphere. In a recent communication, R. Mecke (15) has assumed that the photodecomposition of ozone by ultra-violet light with wavelengths shorter than 2655 Å. is a primary reaction, whilst the formation of ozone requires excited oxygen molecules and the efficiency of the photo-ozonization process can be raised by resonance effects. Thus, according to Mecke, the two primary photochemical reactions leading to an equilibrium are:—

$$O_3 + h\nu\ (\lambda < 2655\ \text{Å.}) = O_2' + O' \qquad (1)$$
$$O_2 + O_2\ (\lambda < 2025\ \text{Å.}) = O_3 + O' \qquad (2)$$

In each of these reactions excited oxygen atoms are supposed to be formed. Mecke has assumed the existence of several secondary reactions and has shown that at low pressure and small ozone concentrations, which are undoubtedly met with at high altitudes of the atmosphere, the law of equilibrium concentration is obeyed:—

$$3O_2 \rightleftarrows 2O_3$$

$$[O_3]^2/[O_2]^3 = K\ \text{(constant)}$$

From absorption measurements by various physicists, it is concluded that the mean altitude of the ozone layer in the atmosphere is about 50 kilometers and at this height the atmospheric pressure is about 10^{-3} atmosphere. According to Fabry and Buisson (16), the total thickness of the ozone layer when reduced to normal pressure is 3 mm., i.e., 0.4 10^{-6}, taking the height of the homogeneous atmosphere as a unit (7.99 kilometers).

From our experimental results, it is quite clear that formaldehyde also exists in the upper layers of the atmosphere, formed by the combination of carbon dioxide and water vapor in presence of the ultra-violet light of the sun. It is well known that the reaction

$$CO_2 + H_2O + 112\ \text{Cal.} = HCHO + O_2$$

requires ultra-violet light of wavelength approximately 2550 Å.

In recent years, Henri and Schou (17) and Herzberg (18) have measured the absorption spectrum of formaldehyde. They have observed that the absorption spectrum extends from 3700 Å. to 2500 Å. The spectum shows rotational fine structure down to 2750 Å., but between 2750 Å. and 2670

Å. predissociation begins which continues up to 2500 Å. The predissociation limit is shifted by 70 Å. towards the visible region when the temperature is elevated to 220°C. There are about 35 to 40 bands between 3700 Å. and 2500 Å. in the formaldehyde absorption spectrum. The maximum is at 2935 Å., characteristic of aldehydes. It is apparent, therefore, that not only does ozone absorb the short wavelengths from the sun, but the formaldehyde present in the atmosphere also absorbs the short rays of the solar radiations. Hence the absorption of the solar radiations shorter than 2900 Å., which has been attributed so far to the presence of ozone, may be partially due to the presence of formaldehyde. The maximum absorption of formaldehyde is at 2935 Å., but the maximum absorption of ozone appears to be at 2655 Å. Hence it seems that the ultra-violet rays filtered through the ozone layer may be absorbed by formaldehyde present in the atmosphere.

Water vapor is present in an appreciable amount in the atmosphere even at a height of 100 kilometers, but the amount of carbon dioxide present at the height of 40 kilometers is exceedingly small, less than 0.01 per cent. It appears therefore that formaldehyde in very small quantities may be formed nearly at the same height where ozone is photochemically generated in the atmosphere.

The dissociation energy of water is 110 Cal., whilst that of the oxygen molecule is 118 Cal. Hence it appears that the wavelength of the ultraviolet light capable of breaking up the O—H link may be slightly greater than that required to break the O=O link. When the O—H link is broken up, the carbon dioxide present in the atmosphere may be reduced to formaldehyde by the hydrogen atoms formed by the dissociation of water molecules. It seems that the atmospheric height at which formaldehyde is formed may be less than that where ozone is formed.

Just like ozone, formaldehyde is also photochemically decomposed. According to the recent experiments of Norrish and Kirkbride, the main products of the photodecomposition of formaldehyde are carbon monoxide and hydrogen. It is evident therefore, that the following equilibrium may

$$HCHO \rightleftarrows CO + H_2$$

exist in the atmosphere. It is well known that the upper atmosphere is rich in hydrogen. Consequently, owing to the presence of hydrogen in the upper atmosphere, the photodecomposition of formaldehyde will be markedly hindered, and appreciable amounts of formaldehyde can exist at an altitude of 40 to 50 kilometers or at lower altitudes. As water vapor exists in small quantities even at a height of 100 kilometers, the atmospheric formaldehyde may be washed down by the rain water. That is why all samples of rain water contain more or less formaldehyde. At the end of a very heavy shower, the amount of formaldehyde in the rain water becomes exceedingly small. At Barlowganj (U. P., India) which is situated at the height of 5500 ft. above the sea level, 8 inches of rain fell in five hours on the 12th of July, 1932, and at the end of the shower, some rain water was collected; the amount of formaldehyde in the freshly collected rain water was exceedingly small as tested by Schryver's reagent or by the reduction of ammoniacal silver nitrate solution.

In order that an appreciable amount of formaldehyde may be detected in rain water, the rain should be collected after some sunny days and should be analyzed as quickly as possible after the collection.

That the formaldehyde in the atmosphere is not generated from the decomposition of substances of vegetable origin on exposure to light is clear from the fact that hardly any formaldehyde is detected in the air near the land where there is plenty of vegetable matter. We passed several liters of air from an open space through 50 cc. of water placed in a stoppered flask for six hours, and on distilling the water no trace of formaldehyde was detected. It rained the same evening, when the above mentioned experiment was performed and the rain water collected contained an appreciable amount of formaldehyde.

It will be interesting to note that in a recent communication (19), it has been shown that there is evidence that the formaldehyde band is present in the solar atmosphere. It appears from spectroscopic evidence that formaldehyde, like cyanogen gas, may be present in the absorbing atmosphere of the sun.

Formaldehyde present in the atmosphere and rain water, even in small quantities, serves as a ready made food for plants. According to Sir J. C. Bose (20), in small doses, it serves as stimulant to the growth of plants. It can act as an antiseptic, can purify the air, and can act as a disinfectant to the soil.

SUMMARY

1. It has been observed that freshly collected rain water contains formaldehyde to the extent of 0.001 to 0.00015 g. per liter.

2. The amount of formaldehyde in rain water increases if the rain is preceded by bright sunny days. When the days are cloudy and there are frequent showers, the amount of formaldehyde decreases and may be altogether absent immediately after a very heavy shower.

3. The rain water should be immediately analyzed when collected, because a part of the formaldehyde is lost by vaporization and another part by polymerization.

4. It is believed that the formaldehyde in rain water is formed by the combination of carbon dioxide and water vapor present in the atmosphere by the absorption of ultra-violet light from the sun.

5. Formaldehyde in rain water cannot be due to the photodecomposition of substances of vegetable origin.

6. Formaldehyde vapor shows light absorption between 3700 and 2500 Å., the maximum absorption being at 2935 Å., characteristic of aldehydes. It appears that not only does ozone absorb radiations of short wavelengths from the sun, but also the formaldehyde present in the atmosphere absorbs solar ultra-violet radiations.

7. It appears that the water molecules are decomposed by absorption of short wave radiations and the hydrogen atoms set free reduce carbon dioxide to formaldehyde, which may be formed in the atmosphere at heights less than those where ozone is generated.

REFERENCES

(1) Usher and Priestley: Proc. Roy. Soc. London **B84**, 101 (1911).
(2) Baly, Heilbron, and Barker: J. Chem. Soc. **119**, 1025 (1921).
(3) Dhar and coworkers: J. Phys. Chem. **29**, 926 (1925); **35**, 1418 (1931); **36**, 567 (1932).
(4) Mezzadroli and collaborators: Atti accad. Lincei **6**, 160 (1927); Gazz. chim. ital. **59**, 305 (1929).
(5) Spoehr: J. Am. Chem. Soc. **45**, 1184 (1923).
(6) Baur and Rebman: Helv. Chim. Acta **5**, 928 (1922).
(7) Porter and Ramsperger: J. Am. Chem. Soc. **47**, 79 (1925).
(8) Bell: Trans. Faraday Soc. **27**, 771 (1931).
(9) Emerson: J. Gen. Physiol. **13**, 163 (1929).
(10) Zscheile: J. Am. Chem. Soc. **54**, 973 (1932).
(11) Mackinney: J. Am. Chem. Soc. **54**, 1688 (1932).
(12) Baly and coworkers: Proc. Roy. Soc. London **A116**, 212 (1927).
(13) Dhar and Ram: Nature **129**, 205 (1932); Z. anorg. allgem. Chem. **206**, 171 (1932).
(14) Norrish and Kirkbride: J. Chem. Soc. **1932**, 1518.
(15) Mecke, R.: Trans. Faraday Soc. **27**, 375 (1931), Discussion on photochemical processes.
(16) Fabry and Buisson: J. phys. **3**, 163 (1913).
(17) Henri and Schou: Z. Physik **49**, 744 (1928).
(18) Herzberg: Trans. Faraday Soc. **27**, 378 (1931).
(19) Dhar: Z. anorg. allgem. Chem. **206**, 270 (1932).
(20) Bose: Physiology of Photosynthesis, p. 71. Longmans, Green and Company, New York (1924).

COMMUNICATIONS TO THE EDITOR

THE DECOMPOSITION OF OZONE BY ALPHA PARTICLES AND BY THERMAL MEANS[1]

I should like to report the results of experiments carried out one and a half years ago with W. Feitknecht in this laboratory on the decomposition of pure ozone by alpha particles from radon at room temperatures. The M/N ratio, the number of molecules decomposed per ion pair, was found to be high, varying from about 4,500 at 50 mm. ozone to about 15,000 at 300 mm. ozone. The rate of decomposition followed the equation

$$-\frac{d\,[O_3]}{dt} = \frac{dp}{dt} = K[O_3]^n$$

where for a series of runs n was found to be 1.5. Very good constants were obtained throughout a given run and the constant was the same for different pressures. The rate was independent of the presence of oxygen. The M/N ratio was found to be proportional to $[O_3]^{2/3}$. Since ionization by alpha particles is practically proportional to the pressure in the range investigated, this makes the rate of decomposition proportional to $[O_3]^{1.67}$, in substantial agreement with the rate found. It is thus seen that rather long chains are possible in ozone decomposing at room temperatures. These facts provide evidence in favor of the viewpoint of Riesenfeld and Wassmuth (Z. physik. Chem. 8B, 314 (1930)), but not that of Schumacher and Sprenger (Z. physik. Chem. 6B, 446 (1930)). These experiments are to be extended and will be reported on later.

More recently, during a study of the kinetics of the explosion of ozone induced by hydrogen, a rather complete series of experiments on the thermal decomposition of pure ozone was made at 85°C. between initial ozone pressures of 40 to 200 mm. and in different glass and quartz vessels. The rate of decomposition is represented by the equation

$$-\frac{d\,[O_3]}{dt} = \frac{dp}{dt} = K\,[O_3]^{1.5}$$

K remains constant down to 80 per cent decomposition, which is as far as the reaction was carried usually. K seems to depend on the initial concentration, for it increases somewhat as the latter is raised. In a

---

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

given run the rate is independent of the oxygen concentration, but K is higher for an initial mixture containing ozone plus oxygen than for a similar amount of ozone alone.

On investigating the published results on this subject of Schumacher and Sprenger (loc. cit.), who employed a 5-liter cylindrical vessel, Riesenfeld and Wassmuth (Z. physik. Chem. **143**, 408 (1929)), and Riesenfeld and Bonholtzer (Z. physik. Chem. **130**, 255 (1927)), it is found that their experiments also are represented very well by the same relationship. When corrections are made for the temperature, using the known temperature coefficient, and when allowance is made for the initial pressure, the rate constants of their experiments derived from the above relationship agree quite well with the present ones. These authors have explained their rates by supposing that a monomolecular and bimolecular reaction are occurring simultaneously despite the fact that their corrected "true" monomolecular and bimolecular constants change with initial pressure (particularly the monomolecular constants, see Z. Physik. Chem. **143**, 408 (1929)).

All the experiments are now in agreement and may be assumed to be correct. The interpretation yet remains. It seems more natural for the reaction to be represented by a simple formula rather than to introduce unnecessary complications of simultaneously occurring monomolecular and bimolecular reactions. The 1.5 power indicates that the reaction is to be explained by a chain mechanism, just as in the alpha ray experiments. What this mechanism is will be left for a future publication.

Bernard Lewis.

U. S. Bureau of Mines
Pittsburgh Experiment Station,
Pittsburgh, Pa.

THE ADSORPTION OF RADON BY SILICA GEL

In view of the work of Francis (Kolloid-Z. **59**, 292 (1932)) on the adsorption of radon by silica gel, certain measurements of ours, made under widely different conditions, should be of interest. Our measurements were made by a static method, using comparatively large amounts of radon; the pressure of the other gases present was very low, not more than four or five times that of the radon itself. The silica gel used in these experiments was a clear glassy gel which had been purified by treatment with concentrated nitric acid. It was then dried in a stream of air at about 300°C., and finally electrodialyzed for a long period of time. Before use it was dried once more at 300°C. The gel contained about 5 per cent of water.

In one experiment, 34 millicuries of radon were left in a glass tube, which contained 1 g. of silica gel, for twenty-four hours. The portion of the tube containing the silica gel was then sealed off from the rest, and the radon contents of both tubes were determined by means of a gamma ray electroscope. Allowing for the free space in the tube which contained the gel, the distribution coefficient (radon per gram of gel divided by the radon per cubic centimeter of free space) was found to be 144. This lies between the highest value (44) observed by Francis for an aged gel, and the highest value (335) for a freshly prepared gel. In his experiments a flow system was used and equilibrium was reached between the gel and a very small amount of radon mixed with air at atmospheric pressure.

In a second experiment about 100 millicuries of radon was allowed to distribute itself between 1 g. of silica gel at room temperature and a tube (of about 5 cc. capacity) which was immersed in liquid air. At equilibrium 43 per cent of the radon was found to be adsorbed on the gel. This indicates a surprisingly large difference in the adsorptive capacity of silica gel and (Pyrex) glass for an inert gas.

ROBERT LIVINGSTON.
L. H. REYERSON.

School of Chemistry,
University of Minnesota,
Minneapolis, Minnesota

NEW BOOKS

Report on Band-Spectra of Diatomic Molecules. By W. JEVONS, D.Sc. 26 x 18 cm.; viii + 308 pp. London: The Physical Society, 1932. Price: (paper covers) 17s. 6d. net; (in cloth) 20s. 6d.

It is difficult to rate this book too highly. The author has devoted some three years to its preparation, and remarkable clarity of exposition and care for detail are maintained throughout, betraying no signs of any desire to hasten a conclusion. This is praiseworthy in view of the rapid development of the mechanical significance of band-spectra, and it is indicative that such a lengthy report can be written from the "observational, rather than the purely theoretical, aspect of the subject." We may take this as signifying that the fundamental principles are so firmly established that the "theoretical results necessary for the interpretation of the analyses of bands and band-systems" may be "briefly stated, with no indication of the quantum-mechanical methods used in their derivation." This is now possible, whilst only a few years ago textbooks on spectroscopy essentially dismissed the whole of band-spectra with a casual reference to their probable association with molecules.

The report, in the words of the author, is "mainly addressed to the physicist who has not hitherto taken up band-spectra as a subject for special reading or laboratory work;" in the opinion of the reviewer the author should have made wider claims, since the larger proportion of chemists are unfamiliar with the modern interpretations of the fundamental principles of their science by mathematical physicists. Here is an opportunity for the chemist to see how the spatial and thermal properties of molecules are rigorously defined by spectroscopy, how conceptions of valency are being altered and extended, and how the excitation of individual molecules as a necessary preliminary to chemical reaction is bound up with alterations in their detailed electronic structure, the conditions and consequences of such alterations being well on the way to spectroscopic determination. In short, we may be nearing the time predicted by Mulliken when the advance of mathematical technique is such that it may be easier to calculate the properties of polyatomic molecules than to determine them experimentally.

It is to be emphasized that however clear, logical, and fluent the presentation of the results and conclusions in spectroscopic work may be—and the present report is a model in that respect—no benefit is likely to be derived from casual reading. This is due partly to the complexity and all-embracing nature of the subject, and partly to the extensive notation required, and the author does well to insist upon frequent reference to the valuable glossary offered in Appendix I. Mulliken's notation as used, although it has produced order out of chaos, has rendered more complicated some of the simpler expressions familiar to spectroscopists, and may need further revision when our knowledge of the band-spectra of polyatomic molecules approaches a similar finality.

Certain matter, generally of a descriptive nature, has been relegated to small type, with the suggestion that it might be omitted by the "more casual reader," but if this process is applied to Chapter V, dealing in a most able and concise way with line-spectra and the electronic states of atoms, this reader will find the remaining half of the book largely unintelligible. Nothing but praise is to be found for the typography of the Cambridge Press, and for the sixty-four diagrams, all of which seem to have been specially prepared by the author for the report.

It is hardly possible to select any portion of the book for individual praise, but the chapter on the isotope effect is well done, and represents the first reasonably complete account of the phenomenon. As an indication of how far the references are up-to-date, one may cite the identification of H^2 (page 211), and the isotopes of germanium (page 227). The most valuable feature from the point of view of those already working in the field of band-spectra lies in the table of constants for electronic states and band-systems given in Appendix II. The foreword to the Appendix should be consulted for an appreciation of the possibilities offered by the data provided, and although any approach to completeness is disclaimed, it is difficult to see what purpose would be served by any further search of the literature by those interested.

The time is scarcely ripe for a similar report dealing with the theoretical significance of the observed results, and the author has probably done wisely in attempting no discussion of such problems as valency. The stress on the observational aspect leads to the dismissal of the phenomenon of predissociation in two pages, and one can but wait with great interest for the eventual appearance of a companion volume. The work as it stands is a magnificent achievement, and the highest praise is due to the successful collaboration of the author, printers, and publishers.

C. R. BAILEY.

The Method of Dimensions. By PROF. A. W. PORTER, F.R.S. 17 x 11 cm.; v + 80 pp. London: Methuen and Company, 1933. Price: 2/6.

In this volume, one of the recent additions to Methuen's series of short monographs on physical subjects, Professor Porter has collected together important applications of the method of dimensions. The more fundamental and still controversial subject of units has up to the present time had the greater attention, and the author has done well to bring to our notice the existence of a very useful tool. It is important however that the student should realize the limitations of the method; it should be used only when other methods of approach have failed to give an understanding of the physics of the problem. A little greater emphasis on this aspect of the subject, together with a rather more extended introductory treatment of units, would perhaps have increased the value of the book, particularly for the physical chemist. A historical introduction stressing the fundamental work of Newton, and, later, of Fourier, leads the way to discussion of such problems as the time of swing of a simple pendulum, the flow of fluids, surface tension, and heat effects. A final section deals with electromagnetic and electrostatic units. Many references to original papers and summary articles are given and one or two blank pages at the end are available for notes. The present writer had hoped to see, from the point of view of historical interest, some reference to Einstein's early application of the method of dimensions to the determination of the frequency of vibration of atoms in a solid body. This is not, however, to detract from the large amount of useful information which Professor Porter has set before us, and the book will be of considerable value to all students of physics and physical chemistry.

J. T. RANDALL.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 30: Barium. 26 x 18 cm.; xviii + xvi + 390 pp. Berlin: Verlag Chemie G. m. b. H., 1932. Price: 64 M. (subscription price 56 M.).

This volume gives a very complete account of the chemistry of barium and its compounds and is complete in itself. There are thirty-one figures in the text. The literature references are thoroughly covered and no doubt practically all have been seen in the original, as in previous volumes of the work. The mineralogy and geology of barium and the physical properties of the element and its compounds are fully dealt with and the literature includes the year 1932. The book is indispensable both to chemists and physicists and maintains the high standard of previous volumes.

J. R. PARTINGTON.

Structure Symbols of Organic Compounds. By INGO W. D. HACKH. viii + 139 pp. Philadelphia, P. Blakiston's Son and Co. Price: $2.50.

The author has devised an ingenious set of shorthand symbols for organic compounds, which he advocates as a substitute for—or rather, improvement on—the ordinary structural or graphic formulas using the chemical symbols of the elements and the usual connecting bonds.

As a teaching device, the reviewer doubts very much if these symbols would have the value claimed for them, namely, that they make it possible to include a larger amount of organic chemistry in the usual courses; and it would appear that the new symbols might have the definite disadvantage of getting the student even further away from reality than the usual structural formulas do, since in the new symbols no symbols for carbon, hydrogen, nitrogen, or oxygen appear.

But as a tool for advanced students and research workers, these new symbols appear highly advantageous, for they amount to a shorthand way of representing the structural formulas and can be written in much less time than even the most abbreviated structural formulas. This, it seems to the reviewer, is the field in which these symbols have their greatest advantage, and this advantage is a considerable one.

The first thirty-five pages of the book are given over to a discussion of the formulas, and then follow twenty-nine plates showing the formulas for about a thousand typical organic compounds. There is an index.

LEE IRVIN SMITH.

Einführung in die Tonphotographie. Photographische Grundlagen der Lichttonaufzeichnung. By J. EGGERT AND R. SCHMIDT. 23 x 15.5 cm.; vi + 137 pp. Leipzig: S. Hirzel, 1932. Price RM. 7. Card covers.

The ear is far less tolerant in judging the reproduction of sound than the eye in judging the scale of intensities in a monochrome photograph. The difficulties encountered in reproducing sound free from distortion are therefore very considerable, and it is partly for this reason that so much experimental work has been carried out to investigate the photographic technique of sound recording. Few people could be found who are in better position to write an explanatory book on this difficult subject than Professor Eggert and Dr. Schmidt. They have been working in this field for some years and have now produced an excellent little book which should be welcomed by all interested in the general problems of photographic sensitometry as well as by those engaged more narrowly in the actual problems of sound-recording. The book is well printed on good paper; there are one hundred and twenty-two very good illustrations, together with literature and general indexes.

S. O. RAWLING.

Handbuch der Spectroscopie. Band VIII, Lieferung 1. By H. KAYSER and H. KONEN. 26 x 18 cm.; iv + 654 pp. Leipzig: S. Hirzel, 1932. Price RM.67.50.

It is now thirty-two years since the first volume of Kayser's Handbuch was published, and it is interesting to read today in the preface to that volume the scheme Professor Kayser had in mind for the complete work. The fourth volume was to contain the complete account of the emission spectra of each element, with a supplementary volume on experimental methods. He hoped to add a fifth volume to include astrophysical spectroscopy. We signal today the publication of the first part of an eighth volume, which is to be devoted entirely to the emission spectra of the elements. The phenomenal advance in knowledge of emission spectra, which has given rise to the continued expansion of this great treatise, occasions a reflective mood. Whilst one may legitimately wonder what may possibly be the state of knowledge of the spectra of the elements described in the final section of this volume, compared with that of those now dealt with, one cannot but hold up to admiration the devoted labors of Professor Kayser and Professor Konen and of their six collaborators, which have given to the scientific world a book so urgently needed.

The present volume deals with the spectra of the elements from silver to copper, arranged as previously in the alphabetical order of their symbols. In general, the series terms and individual lines have been expressed in the modern notation, but this has in some cases been impossible. Difficulties arose from the want of agreement amongst authors in the use of the modern system, and also from the want of consistency in its use by individual authors. A conversion to the modern notation was at times found to be impossible without a re-investigation of the whole spectrum, which would have involved much time and indeed does not lie within the purview of a book which aims at a faithful presentation of published work. In these cases the original notation used by the author has been given.

It must be remembered that the present volume is part of a supplementary volume to those already published. Thus in the tables of wave-lengths only those measurements are included which have been published since Volume VII was written. Furthermore, the literature references for each element are numbered consecutively to those given for that element in Volume VII. In general, therefore Volume VIII should be used in conjunction with Volumes V to VII.

Under each element the line and band spectra are dealt with, the latter also as measured in the absorption spectra of such compounds as have been examined. The emission spectra are extended into the very short wave-length region of the x-rays. The measurements of the Zeeman and Stark effects are included of all lines which have been examined, and the Raman effect is also added. As may be readily appreciated, the latter measurements are given only where they stand in immediate relation to the simpler spectra, the broader application to organic compounds being omitted. Lastly there are to be found the measurements of fluorescence and reasonance spectra so far as these have been studied.

In assessing the value of this new volume, an excerpt from the authors' preface may be quoted as a text. If, they say, there be found some want of uniformity as the result of the collaboration, we believe that this will be far outweighed by the advantage gained both from the more rapid continuation of the work and from the fact that the collaborators are experts in different sections, whilst in these days a single individual can scarcely gain an equal mastery of the whole. As specialization in spectroscopy becomes more narrow, so is one the more pleased to have at hand a well coördinated and admirably compiled account of the whole field of emission spectra. The literature of the subject is much enriched by its publication.

C. C. C. Baly.

Das Rhenium. By Dr. W. Schröter, with an introduction by Dr. W. Noddack. 25.5 cm. x 16.5 cm.; pp. 59. Stuttgart: Ferdinand Enke, 1932. Price: RM. 5.50.

Though we welcome this account of the earlier chemistry of rhenium it is, we feel, published at an unlucky moment. Since rhenium became available commercially a number of workers have so extended our knowledge of the element that some parts of the book, and those not unimportant, are already out of date and misleading. While much of the book is very useful and illuminating, the reader, unfortunately, cannot be quite sure, especially about the simple chemistry of rhenium, without checking it by the original publications of the last two years or so or by the excellent account given in the recently published volume of "Mellor."

The extraction of rhenium from various minerals, particularly molybdenite, and its subsequent purification are fully described, but the brief account of its technical production carefully refrains from any indication of the actual source of the element.

Much interesting information is given about metallic rhenium but the description of its compounds needs correction, even in a review. There is no sure evidence of hexavalent rhenium or of the rhenates indicated on pages 12 and 39. The existence of Re_2O_8, described at length on pages 32 and 33 has been disproved. No mention is made of the very characteristic and interesting pentoxide, Re_2O_5. Rhenium hepatachloride and hexachloride, which are described (page 39), do not exist; while the very characteristic volatile, black, crystalline tetrachloride, the main product of the action of chlorine on the metal, is not even mentioned (pages 40 to 42). Another serious omission is that of the equally characteristic and interesting volatile, stable oxychlorides, $ReOCl_4$ and ReO_3Cl.

The book concludes with a section on the occurrence of rhenium and tables which show very clearly how insignificant that occurrence is except in certain varieties of molybdenite from Norway and Japan. A bibliography of the literature of rhenium is given from its discovery in 1925 to 1931, but this, as has been indicated, omits recent work including some papers published in 1931.

Applied X-rays. By G. L. CLARK. Second edition (first edition, 1927). pp. 470. New York: McGraw-Hill Book Co., 1932. Price: $5.00.

The growth of the application of x-ray science to a study of material structures is remarkably demonstrated by a comparison of the two editions. The new volume is about 200 pages longer than the first. The first part of the later edition deals with the fundamental physics of x-rays, use of x-ray spectra in chemical analysis, and description of modern equipment. Chapter 3, dealing with x-ray tubes, is an excellent feature of the book. A variety of high grade tubes for the various uses, radiography, deep therapy, crystal analyses, and chemical analysis, is now available and these are clearly described. Anyone planning to select equipment will find this chapter very useful. The following chapter on high tension equipment also contains much useful information.

The second half of the book describes the standard methods of x-ray analysis of crystals, but does not list the line-extinctions corresponding to the different space groups. For this purpose, recourse must be made to tables by Wyckoff or other workers. Then follows an excellent summary of the results of crystal analyses of inorganic compounds, and of alloys, giving due attention to the excellent contributions to crystal chemistry by Goldschmidt and Westgren. One chapter is devoted to carbon compounds with descriptions of the work in laboratories of Sir William Bragg and of Trillat. A good deal of attention is given to the study of the condition of solids as regards grain-size, orientation, internal strain and mechanical deformation. This branch of x-ray science will undoubtedly be extended more and more in the near future. The effects of drawing wire and rolling sheet metal on crystal orientation and on physical properties are already a subject of much interest.

The last chapter is devoted to high polymers, such as rayon, cotton, rubber, and human muscle. Many studies of stretching fibers are reported and illustrated with excellent photographs. The new high-intensity x-ray tubes permitting very short exposures will prove useful in this field.

The book forms part of the International Series in Physics, edited by F. K. Richtmyer. It should prove a useful part of the working library of all investigators in x-ray science.

N. W. Taylor.

INTERNATIONAL TABLE OF THERMOCHEMICAL DATA

Authors who have published papers on thermochemistry within the last five years are requested to send two copies of their papers to Dr. L. J. P. Keffler, The University, Liverpool, England. The Committee on Thermochemistry of the Union Internationale de Chimie proposes to publish a Table of Thermochemical Data, and has submitted this request through the Federal Council for Chemistry.

543

ADHESION TENSION

Pressure of Displacement Method

F. E. BARTELL and H. J. OSTERHOF

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

Received March 23, 1933

Preliminary papers describing a pressure of displacement method for the measurement of adhesion tension were first published from this laboratory in 1927 (1). At that time the method used was new; it was time-consuming and required much patience and exactness of technique. Calculations were dependent upon the use of contact angle values, which values were of necessity obtained in the course of the investigation and by indirect methods. Certain fundamental assumptions were made which, though apparently justified, had not been subjected to rigorous experimental tests. Although there was no reason to believe that the results were seriously in error, publication of the major part of them was withheld until portions of the work had been rechecked and the soundness of each individual step of the method more definitely established.

As one step in the determination of contact angles, the pore radii of compressed powder membranes were determined by the pressure of displacement method. Comparison of results obtained with this method and with a method based upon application of Poiseuille's law showed close agreement (2). This fact tended to justify the use of the pressure of displacement method for the measurement of pore radii.

The angle of contact formed between certain liquids and a solid in the presence of air, and of certain liquid-liquid systems in contact with solid, were determined by different methods. Values obtained for liquid systems in transparent single capillary tubes (3) in which measurements were made directly by a photomicrographic method, were in good agreement with those obtained by the pressure of displacement method.

Adhesion tension, A_{12}, has been defined as the difference between the surface tension of solid, S_1, and the interfacial tension of this solid, S_{12}, in contact with a given liquid, i.e.,

$$A_{12} = S_1 - S_{12}$$

There has been some question as to whether the indirect pressure of displacement method will actually give a true measure of the value $S_1 - S_{12}$. In this method as developed it was necessary to measure interfacial contact angles, θ_{23}, of organic liquid and water in contact with each other against a solid. In some of the systems studied by us there must have been an appreciable mutual solubility of the organic liquid and water. It was not known to what extent this mutual solubility would invalidate the final results. The free surface energy values of the interfacial systems (solid-air and solid-liquid) should be numerically equal to the interfacial tension values of these systems and the symbols, S_1 and S_{12}, have been used also in referring to free surface energy values. When used to represent free surface energy values, the expression $S_1 - S_{12}$ should represent the energy of immersion, i.e., should represent the free surface energy change which occurs when the solid substance is immersed within the liquid.

To test this point an investigation was undertaken in which the energy of immersion of a solid (silica) was determined for a series of organic liquids (4). It was found that energies of immersion thus obtained show good agreement with those calculated from data obtained with the pressure of displacement method. It thus appears that the adhesion tension value of a given solid-liquid system (i.e., for the systems studied) as determined by the pressure of displacement method is numerically equal (or at least very nearly equal) to the free surface energy change which occurs when the solid is immersed in the liquid.

Every step of the pressure of displacement method has been checked by at least one different and independent method and in every case the results obtained have been found to be in agreement. It appears, therefore, that all assumptions which were made in connection with the pressure of displacement method were justified. Accordingly we feel that we can now release data which have been accumulated over a period of years. In the present paper will be presented the data obtained in the preliminary work (i.e., prior to 1927), and in later papers will be given data obtained in more recent researches. Much of the latter work has been done with materials of a high degree of purity and with such improvements in method as have developed as the work has progressed.

PRELIMINARY EXPERIMENTS

Some of our first experiments on relative wetting of solids by liquids were made by means of the method of Reinders (5) and of Hofman (6). Solids used were carbon black, ultramarine blue, and Prussian blue. Liquids used were water and different organic liquids. About equal quantities of water and of organic liquid were put into a test tube with a small amount of the finely divided solid and shaken. It was noted that carbon went exclusively to the organic liquid phase and ultramarine blue to the water phase, while Prussian blue failed to show a decided selective wetting tendency. If the Prussian blue powder were first wetted by water it tended to remain in the water phase; if first wetted by organic liquid it was then not readily wetted by water, but in either case a fairly large proportion of it tended to remain finally at the water-organic liquid interface. This method was useful in obtaining qualitative evidence on relative degrees of wetting of different solid-liquid systems, but no quantitative relationships could be obtained with it.

DISPLACEMENT OF ONE LIQUID BY ANOTHER FROM A SOLID

It occurred to us that instead of observing to which liquid phase the solid particles would go, it might be to advantage to reverse the procedure and by working with a comparatively large amount of solid, as a compact membrane, to determine in which direction the liquids would move. It was believed that data obtained should give information concerning the interfacial tension relationships of the system, and hence information concerning relative degrees of wetting.

If a diaphragm be prepared by firmly packing a finely powdered solid, it forms a membrane containing a large number of fine capillary pores; membranes of this type have previously been employed for the measurement of osmotic pressures (7, 8).

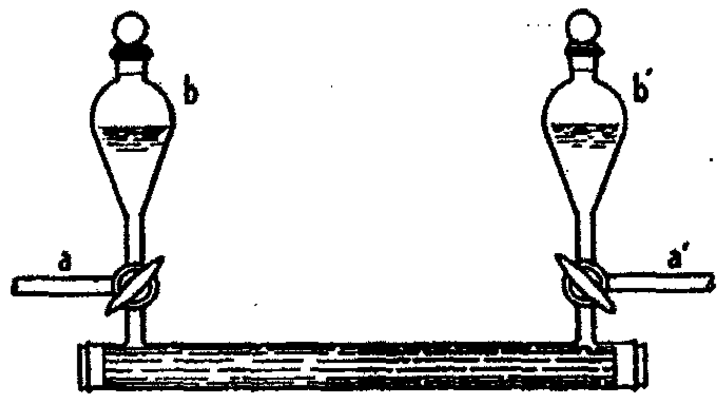


FIG. 1. APPARATUS FOR LIQUID DISPLACEMENT

From the theory of capillary action it may be concluded that a liquid will not pass through such fine capillary pores unless it first wets the pore walls, but that, if the liquid does wet the pore walls, it will travel through the pores and so-called capillary action will occur. In case two liquid columns are in contact within such pores, other factors being equal, that liquid giving the higher interfacial tension against the solid will be displaced by the other liquid.

The first apparatus used by us for liquid displacement is represented in figure 1.

It consisted of a glass tube 3 sq. cm. in cross-section and 20 cm. in length provided with three-way stopcocks, with outlet tubes, *a* and *a'*, and glass reservoirs, *b* and *b'*, mounted near the ends. Pigment wetted by one of the liquids was packed into the tube to the half-way mark, and pigment wetted with the other liquid was packed against this until the tube was filled, after which stoppers were inserted in the ends of the tube. In this way two thick membranes were obtained, each wetted by a liquid, the two liquids being immiscible and in contact. In case of liquid displacement the direction and the amount of displacement could be determined by noting the change in length of the liquid columns in the outlet tubes. Any loss of liquid by leakage or by evaporation could be detected by comparing the movement in one capillary tube with that in the other.

The initial results obtained are shown in table 1. Fairly good checks were obtained in a series of experiments with each of these systems. When Prussian blue was used as solid there was practically no movement of the liquid column in either direction. The results were all in good agreement with those obtained in the test tube experiments mentioned above. The apparatus can be easily constructed and is suitable for qualitative measurements.

Various types of apparatus were next tried, but for lack of space will not be described.

TABLE 1

NO.	SOLID PHASE	LIQUID A	DISPLACES LIQUID B	IN 5 HOURS
1	Powdered glass	Water	Benzene	100 cm.
2	Powdered glass	Water	Turpentine	8 cm.
3	Carbon black	Benzene	Water	60 cm.
4	Carbon black	Turpentine	Water	45 cm.
5	Ultramarine blue	Water	Turpentine	20 cm.
6	Ultramarine blue	Water	Benzene	70 cm.
7	Ultramarine blue	Water	Kerosene	36 cm.

DEVELOPMENT OF METHOD AND APPARATUS FOR DETERMINATION OF DISPLACEMENT PRESSURES

The displacement cell used in the main investigation herein described is shown in figure 2.

The cell consisted of a cylindrical tube of brass, into which the powdered solid could be firmly compressed. This was accomplished by means of tightly fitting perforated plungers.[1] A fine-mesh cloth disc was placed over the powder to prevent escape through the perforations. After compression of powder the plungers were firmly secured in place by means of steel yokes, bolts, and nuts. The apparatus was made leak-proof by employing rubber, leather, or lead gaskets, which were held tightly in place by screwing down a threaded nut and gasket. Glass capillary tubes were fastened securely into the outer ends of the plungers. One of these tubes

---

[1] In practice special packing plungers are used. In construction they are similar to the plungers herein described.

was fastened by means of a ground glass joint to a pressure gauge or manometer. The other tube served as a displacement indicator. Movement of liquid within the cell was detected by movement of the meniscus of the liquid in this (capillary) tube.

The solid to be studied was reduced to a fine powder. Best results were obtained by grading this powder to a uniform particle size (200 mesh to 300 mesh is highly satisfactory). This powder, dry or thoroughly wetted by liquid as the case might demand, was packed in about 1-g. increments in the manometer end of the cell by means of a laboratory hydraulic press. A packing pressure of approximately 150 atmospheres was used. After the cell was about three-fourths full, the solid material wetted by the displacing liquid was then added and compressed. While the cell was still in the press and under pressure, the plungers were secured in place by the steel yokes and bolts. The apparatus, when assembled, was found to withstand internal pressures as high as 100 atmospheres without exhibiting leaks.

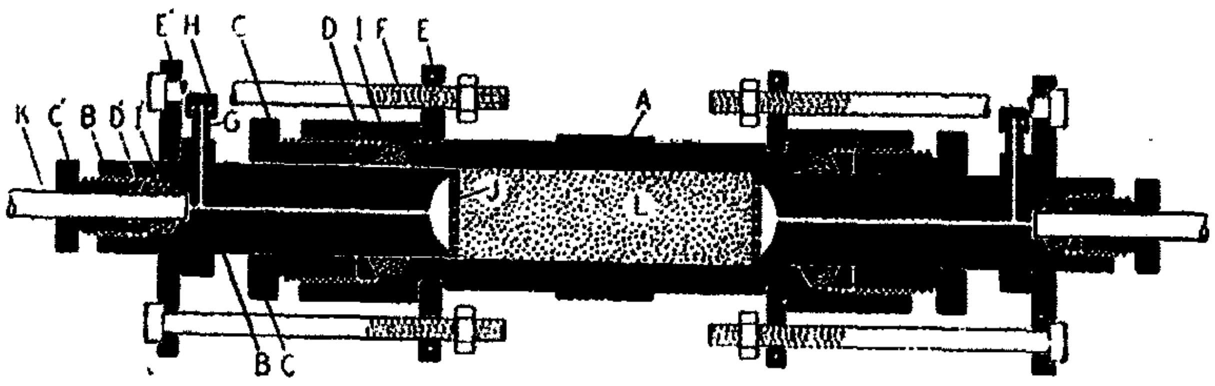


Fig. 2. Displacement Cell

A, cell casing; B, plungers; C, packing gland; D, packing ring; E and E', steel yoke; F, steel bolts; G, outlet tube; H, cap; I, packing material; J, perforated plate; K, glass capillary; L, powdered solid.

METHOD OF OBTAINING DISPLACEMENT PRESSURES

After the cell had been properly filled with wetted powder it was quickly attached to the indicator tube and manometer. Air pressures were set up of such magnitude as to prevent an appreciable movement of liquid within the cell. As the liquid tended to move, the opposing pressure was increased. In this way the pressure was built up to the maximum value necessary to prevent any advance of liquid. This operation usually required a number of hours. Sometimes twenty-four to thirty-six hours elapsed before it could be concluded that maximum or equilibrium pressure had been reached. Each of the pressure values recorded is an average of a number of independent runs. It often required a number of days to obtain one properly checked pressure of displacement value. Pressure values obtained by a series of runs for any given system usually checked to within less than 1 per cent.[2]

MATERIAL USED

The carbon used was a Germantown lampblack. It was treated with ether to remove greasy material, then dried and heated for a short time to approximately 1200°C. It was finally evacuated at less than 10^{-4} mm. pressure for sixty to seventy hours and wetted with the required liquid while still under vacuum. The silica was technical "Tripoli" which was treated with hydrochloric acid, thoroughly washed with water, dried and heated in a muffle furnace to approximately 1200°C. Analysis gave 99.15 per cent silica. It should be pointed out that all results recorded for a given solid were obtained from a single batch of solid material.. The liquids were of average C. P. grade and were not highly purified. It was thought that in this initial work an attempt to use highly purified materials was not justified.

RESULTS

The results obtained with silica and with carbon black are given in table 2.

The effective pore radius, r, was calculated from displacement pressures of benzene–air and was found to be 2.1×10^{-4} cm. for silica and 9.3×10^{-5} cm. for carbon.

The adhesion tension of α-bromonaphthalene against silica, A_{12}, was found to be 41.92, and of water against silica, A_{13}, 81.5 dynes per centimeter. The adhesion tension of water against carbon, A_{13}, was found to be 54.74 dynes per centimeter. With these adhesion tension values for water against the two solids, the adhesion tension values of the other liquids could be determined (provided the values of the interfacial contact angles θ_{23} were known) since the values of their interfacial tension, S_{23}, could be obtained from the literature. The following equation is applicable:

$$A_{12} = A_{13} + S_{23} \cos \theta_{23} \text{ (for silica)}$$

In their work on liquid absorption, Bartell and Hershberger (9) made the observation that "the order of decrease in the free surface energies which occur when a polar solid is wetted by each of a series of zero contact angle liquids is the same as the order of decrease in free surface energies

---

[2] In a recent article (Davis and Curtis: Ind. Eng. Chem. **24**, 1137 (1932)) describing the use of this method in another laboratory, it was pointed out that "results have been checked with the same briquettes within about 5 per cent and with different briquettes within about 8 per cent maximum variation for a given liquid." These results can mean only that the method as used in that laboratory was not under proper control for accurate work.

which occur when water is brought into contact with this same series of liquids."

In view of this generalization the liquids given in table 2 are placed in the order of progressive decrease in free surface energy exhibited when they are brought into contact with water. This order is likewise the order of decreasing interfacial tension values (column 3) of the organic liquid-water systems. It is interesting to note that this order is, with few exceptions, the order found for increasing adhesion tension values, A_{12}, for silica (column 7).

TABLE 2

Adhesion tension data

Organic liquids against carbon and against silica

	S_1	S_{12}	CARBON $r = 9.5 \times 10^{-4}$ cm. A_{12} (for water) = 54.74		SILICA $r = 2.1 \times 10^{-4}$ A_{12} (for water) = 81.5 A_{12} (for α-bromonaphthalene) = 41.92	
			θ_{12}	A_{12}	θ_{12}	A_{12}
Carbon disulfide	31.3	48.1	41°35′	90.77	37°10′	43.2
Carbon tetrachloride	26.1	44.5	44°45′	86.38	19°00′	39.5
α-Bromonaphthalene	44.0	41.6	35°03′	88.81	13°30′	41.1
Toluene	28.1	36.1	40°40′	82.10	38°50′	53.4
Benzene	28.3	34.6	40°30′	81.03	28°40′	51.2
Chloroform	26.5	31.6	37°25′	79.83	43°40′	58.7
"Decalin"	31.0	26.7	35°45′	76.38		
Nitrobenzene	43.3	25.3	11°00′	79.58	37°30′	61.4
"Tetralin"	32.8	22.4	11°35′	76.70		
Butyl acetate	24.1	13.2	33°00′	65.78	44°40′	72.1
Ethyl carbonate	25.8	12.4	29°25′	65.55		
Amyl acetate	24.4	10.9	34°40′	63.68	44°45′	73.7
Ether	16.5	10.7	61°30′	59.85		
Propyl acetate	23.8	9.6	29°15′	63.09	42°55′	74.4
Ethyl acetate	23.4	6.8	50°20′	59.07	37°10′	76.1
Aniline	42.5	5.7	15°45′	60.22	82°05′	73.8
Amyl alcohol	23.7	5.0	35°25′	58.77	37°45′	77.5
Benzyl alcohol	39.4	4.8	32°50′	58.73		
Isobutyl alcohol	22.4	1.8	0°00′	56.60	5°45′	80.7

It is also to be noted that the order of a series of liquids showing increasing adhesion tension values against silica is just the reverse of the order showing increasing adhesion values against carbon. Liquids giving the highest adhesion tension values against silica give the lowest adhesion tension values against carbon and vice versa.

It is further to be noted that for each one of this series of liquids the sum of the adhesion tension values of liquid against carbon and against silica is practically a constant. This is a striking fact, and will probably lead to an important generalization. It is felt, however, that further information should be obtained before an explanation is attempted. Data with other solid-liquid systems are now being obtained in the hope that an obvious and valid generalization may be deduced.

WORK OF ADHESION

When the liquids are arranged in groups representing similar chemical constitution, consideration of the different work of adhesion values brings out interesting relationships when the different work of adhesion values are considered (table 3). The work of adhesion values, expressed by the equation,

$$W_a = S_1 + S_2 - S_{12}, \text{ or } W_a = A_{12} + S_2$$

are, for the different members of a given group (liquids of similar constitution), of very nearly the same magnitude when considered for a given system, i.e., for either carbon, silica, or water.

TABLE 3

Work of adhesion of a series of liquids against carbon, silica and water

	CARBON W_a	SILICA W_a	WATER W_a
Benzene	109.3	79.4	65.7
Toluene	110.2	81.5	64.1
Nitrobenzene	122.8	104.7	90.1
Aniline	102.7	117.2	108.9
α-Bromonaphthalene	132.8	85.1	74.5
Tetralin	109.5		82.5
Decalin	107.4		76.4
Chloroform	106.2	85.2	67.0
Carbon tetrachloride	112.4	65.6	53.7
Carbon bisulfide	122.1	74.5	55.3
Ethyl acetate	82.5	99.5	88.7
Propyl acetate	86.8	98.1	86.3
Amyl acetate	88.1	98.0	85.6
Butyl acetate	89.8	96.2	84.0
Amyl alcohol	82.5	101.2	90.8
Isobutyl alcohol	79.0	103.1	92.7
Ethyl carbonate	91.4		85.5
Ethyl ether	76.4		77.9
Water	126.8	153.6	144.16 (= W_c)

The work of adhesion values of benzene and of toluene against carbon are practically the same. The values for these two liquids against silica are similar, and the values against water are likewise very nearly the same. The other aromatic compounds give high work of adhesion values against carbon. Aniline and nitrobenzene give relatively high values, both against silica and against water. This is probably due to the effect of the polar group. Chloroform, carbon tetrachloride, and carbon disulfide give high values against carbon, but considerably lower values against both silica and water. The alcohols give slightly higher values against silica than do the acetates. When the work of adhesion values are considered from the standpoint of molecular orientation the results are in approximately the order one would expect.

It has been pointed out earlier in the paper that no high degree of purity is claimed for the liquids used and that the characteristics of the solids cannot be accurately described. In later investigations it has been found that the adhesional properties of carbon can be altered, and that these properties are dependent upon the precise treatment to which the carbon has been subjected (10). But little was known of the structure of the silica used in this investigation since it was "purified" technical "Tripoli." In subsequent investigations carried out in our laboratories fused quartz, analyzed white sand, and other forms of comparatively pure silica have been used. With these latter materials the adhesion tension values have been somewhat lower (in some cases 6 dynes lower) than those obtained with the "Tripoli." The adhesion tension values for water against these pure silicas were found to range from 76 to 79.5, as compared with the value 81.5 found in this investigation. Inasmuch as all the other values determined are dependent upon the water–silica value, the values for the other liquids are correspondingly lower in the later work. At the time the work herein reported was carried out, only one liquid forming a contact angle against silica was used, namely, α-bromonaphthalene. In later work a number of other liquids have been used and have been found to give values which are in agreement. Recent work with α-bromonaphthalene has shown that contact angle values obtained with it are dependent largely upon the precise nature and manner of treatment of the silica surface (11). The data herein presented are reasonably accurate for the surfaces used, however, and since they may prove to be of considerable practical value, should be made available. Much time must elapse before the exact degree of accuracy of the values can be definitely determined, but when used in the light of relative values they are certainly significant.

SUMMARY

1. An account is given of the preliminary work carried out in the development of methods for the determination of adhesion tension data.

2. The pressure of displacement method for the measurement of adhesion tension is described in considerable detail.

3. Adhesion tension values and work of adhesion values obtained with a series of liquids against silica and against carbon are given.

REFERENCES

(1) BARTELL AND OSTERHOF: Ind. Eng. Chem. **19**, 1277 (1927). Fifth Colloid Symposium Monograph, p. 113. The Chemical Catalog Co., Inc., New York (1927).
(2) BARTELL AND OSTERHOF: J. Phys. Chem. **32**, 1553 (1929).
(3) BARTELL AND MERRILL: J. Phys. Chem. **36**, 1178 (1932).
(4) BARTELL AND ALMY: J. Phys. Chem. **34**, 985 (1932).
(5) REINDERS: Kolloid-Z. **13**, 235 (1913).
(6) HOFMAN: Z. physik. Chem. **83**, 385 (1913).
(7) BIGELOW AND ROBINSON: J. Phys. Chem. **22**, 99 (1918).
(8) BARTELL AND OSTERHOF: Fourth Colloid Symposium Monograph, p. 230. The Chemical Catalog Co., Inc., New York (1926).
(9) BARTELL AND HERSHBERGER: Ind. Eng. Chem. **22**, 1304 (1930).
(10) BARTELL AND SMITH: Ind. Eng. Chem. **21**, 1102 (1929).
(11) BARTELL AND WOOLEY: Unpublished observations.

MIGRATION STUDIES WITH COLLOIDS. I

THE EFFECT OF ELECTROLYTES AND OF COLLOIDS OF OPPOSITE SIGN ON THE STABILITY OF COLLOIDAL SYSTEMS

FRED HAZEL AND DAVID M. McQUEEN

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received July 20, 1932

A. THE EFFECT OF ELECTROLYTES ON THE STABILITY OF COLLOIDAL SYSTEMS

INTRODUCTION

It is well known that addition of electrolytes to lyophobic colloids, whose prime factor of stability is an electric potential originating in the Helmholtz double layer, results in a decrease in the stability of the dispersed particles. When sufficient electrolyte is added the decrease in stability is manifested by coagulation of the sol. Schulze (1) long ago found that electrolytes with polyvalent ions were the better coagulators. This generalization is modified (2), however, by the adsorbabilities of the ions.

Hardy (3), while studying the cataphoresis of denatured egg albumen, concluded that coagulation resulted only when there was no migration of the particles in an electric field. Powis (4), however, has shown in the case of hydrophobic colloids that it is not necessary to reduce the particles to an isoelectric condition in order to produce coagulation.

Since there thus appears to be a definite relationship between the rate of cataphoresis and colloidal stability, migration data may be used as a measure of the stability of sols, assuming that these measurements are proportional to the stabilizing potential. It is to be emphasized that velocity determinations offer a means of following changes in the stability of suspensoids before coagulation takes place. An ultramicroscopic technique was employed in the present investigation. This method affords a high degree of accuracy in measuring cataphoresis and in addition presents the unique opportunity of obtaining reliable velocity measurements after coagulation has taken place.

The data submitted in Part A are on a group of sols which were used in the mutual coagulation study reported in the following paper.

PREPARATION OF SOLS

The following sols were used: positive arsenic trisulfide, iron oxide, aluminum oxide, chromium oxide, and negative iron oxide, stannic oxide, manganese dioxide, arsenic trisulfide.

Attempts were made to prepare the positive arsenic trisulfide sol by recharging a negative sol with thorium nitrate solution. However, these efforts were unsatisfactory in that considerable precipitation of arsenic trisulfide always resulted regardless of the method of mixing. Subsequently it was found that if a solution of arsenious oxide was added to a dilute solution of thorium nitrate and hydrogen sulfide passed into this mixture, a stable positive sol was formed. The sol was then washed with hydrogen.

The positive iron oxide sol was prepared by hydrolysis of ferric chloride in boiling water and then purified by dialysis for a week at 70–90°C. The negative iron oxide sol was obtained by adding an equal volume of a dilute potassium ferrocyanide solution to a portion of the positive sol. It required only 0.025 millimol of the electrolyte per liter to produce a stable negative colloid.

The other colloids were made by standard methods. The sols were dialyzed in collodion sacks to reduce the presence of electrolytes to a minimum.

EXPERIMENTAL

The cataphoresis determinations were carried out by a method previously described (5).

Samples of sol for observation with the ultramicroscope were prepared by diluting the original stock colloids. The amount of dilution was determined by the "visibility" of the particles. It was desired to employ the maximum concentration of colloid that would permit the observation of a single particle with the means at hand. In this manner it was possible to obtain reliable coagulation data along with the velocity measurements. The systems on which data are given were made by mixing 25 cc. of electrolyte solution with an equal volume of sol. The samples were run approximately one-half hour after mixing. The time necessary for a particle to traverse 200 μ was recorded. Ten readings were taken in alternate directions using a potential of 91.5 volts between electrodes 11.5 cm. apart. The mean was selected for calculation of the velocity.

After the velocity determinations had been made the samples were set aside for twenty-four hours. Observations for coagulation were then made.[1]

---

[1] In the interests of space economy, migration and coagulation data are not presented in tabular form. Migration data are represented graphically. Coagulation data may also be interpolated from the graphs since, within close limits, the sols coagulated when the velocity of the particles had been reduced to $\pm 2.0\ \mu$ per second per volt per centimeter.

RESULTS

The order of anions in reducing the migration velocity of the aluminum oxide sol is $Fe(CN)_6 > PO_4 > CrO_4 > SO_4 > Cl$. The same order is maintained with positive iron oxide. Figures 1 and 2 show graphically the behavior of the two sols with electrolytes. The data with chromium oxide are plotted in figure 3. A different order of the anions is encountered with this sol, i.e., $CrO_4 > SO_4 > PO_4 > Cl$. The position of the ferrocyanide ion in the lyotropic series was not determined. For concentrations up to 0.016 millimol per liter the tetravalent ion had no more effect in discharging the chromium oxide particles than the phosphate ion. Increasing the concentration of potassium ferrocyanide past 0.016 millimol per liter led to the formation of a gelatinous precipitate which clogged the cataphoresis cell and made working conditions impossible.

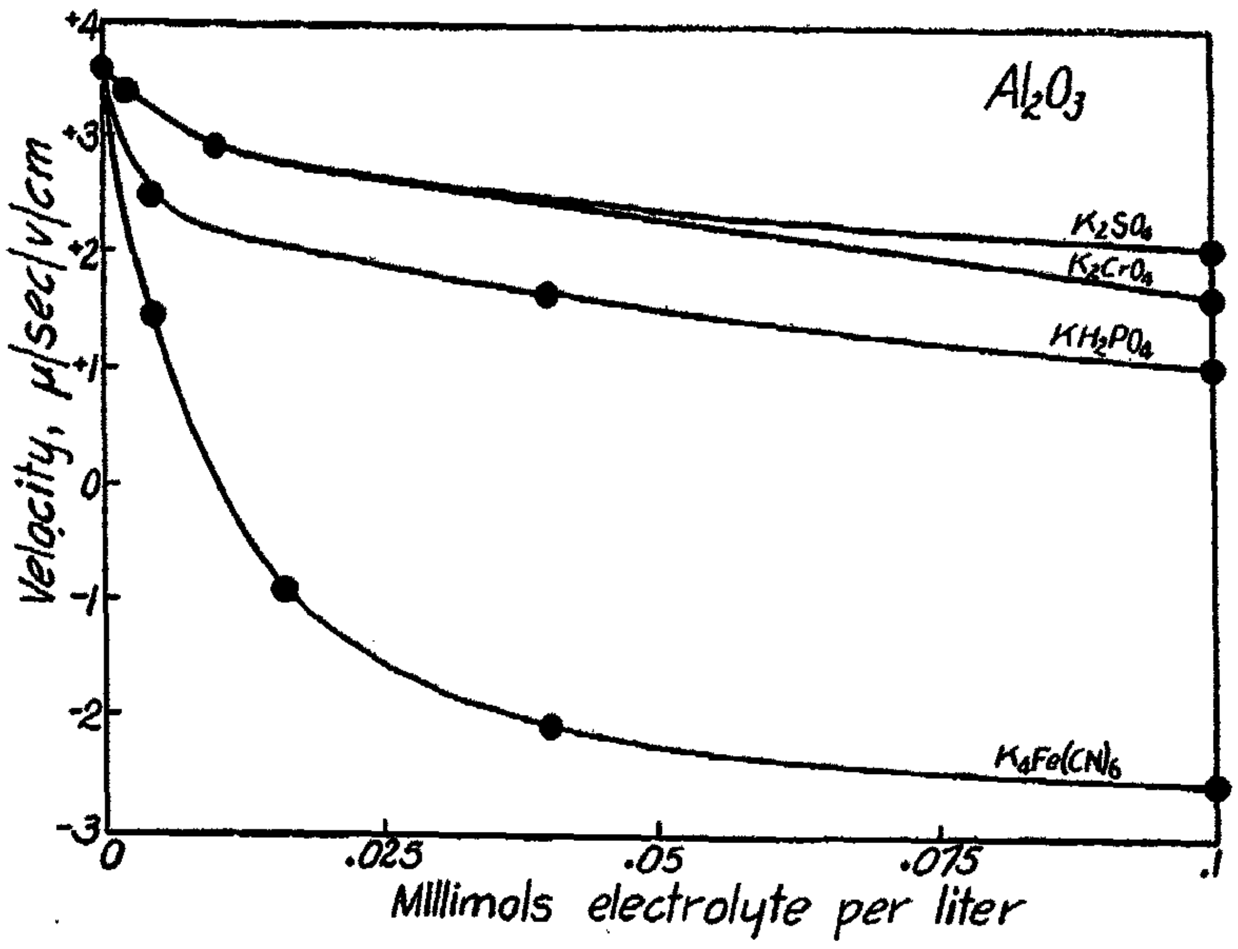


FIG. 1

Figure 4 brings out the following order of anions with positive arsenious sulfide: $Fe(CN)_6 > SO_4 > PO_4 > CrO_4 > Cl$. The position of the sulfate ion is questionable, since at low concentrations it is not as effective as phosphate. The striking thing about figure 4 is the potassium chromate curve. It does not seem probable that the potassium ion would charge the micelle in the presence of the bivalent chromate ion. A faint greenish opalescence had been noted in the samples containing potassium chromate. This suggested a reduction to chromic ion by the hydrogen sulfide incompletely removed when the sol was washed with hydrogen. To test this

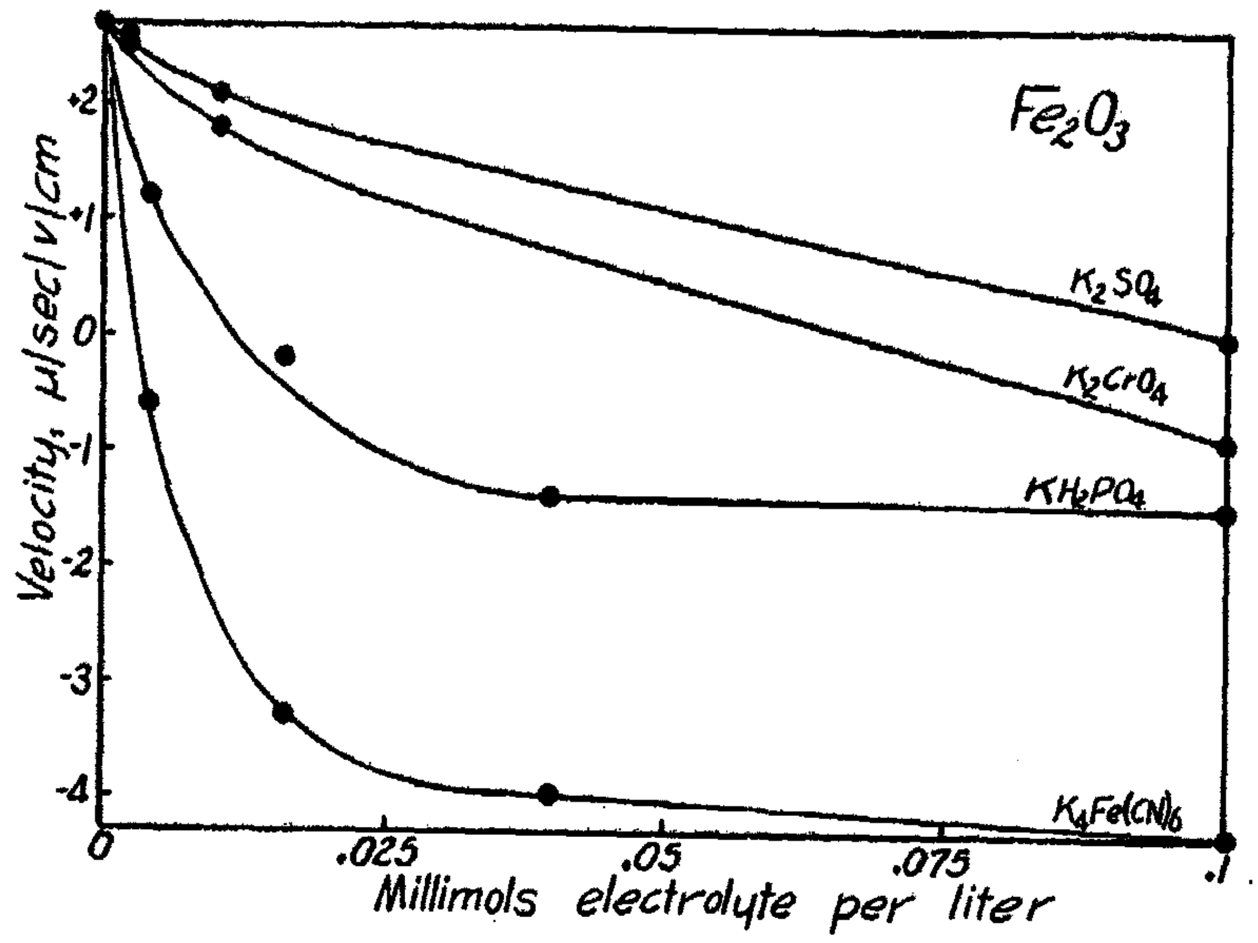

Fe$_2$O$_3$
K$_2$SO$_4$
K$_2$CrO$_4$
KH$_2$PO$_4$
K$_4$Fe(CN)$_6$
Velocity, μ/sec/v/cm
+2
+1
0
-1
-2
-3
-4
0
.025
.05
.075
.1
Millimols electrolyte per liter

Fig. 2

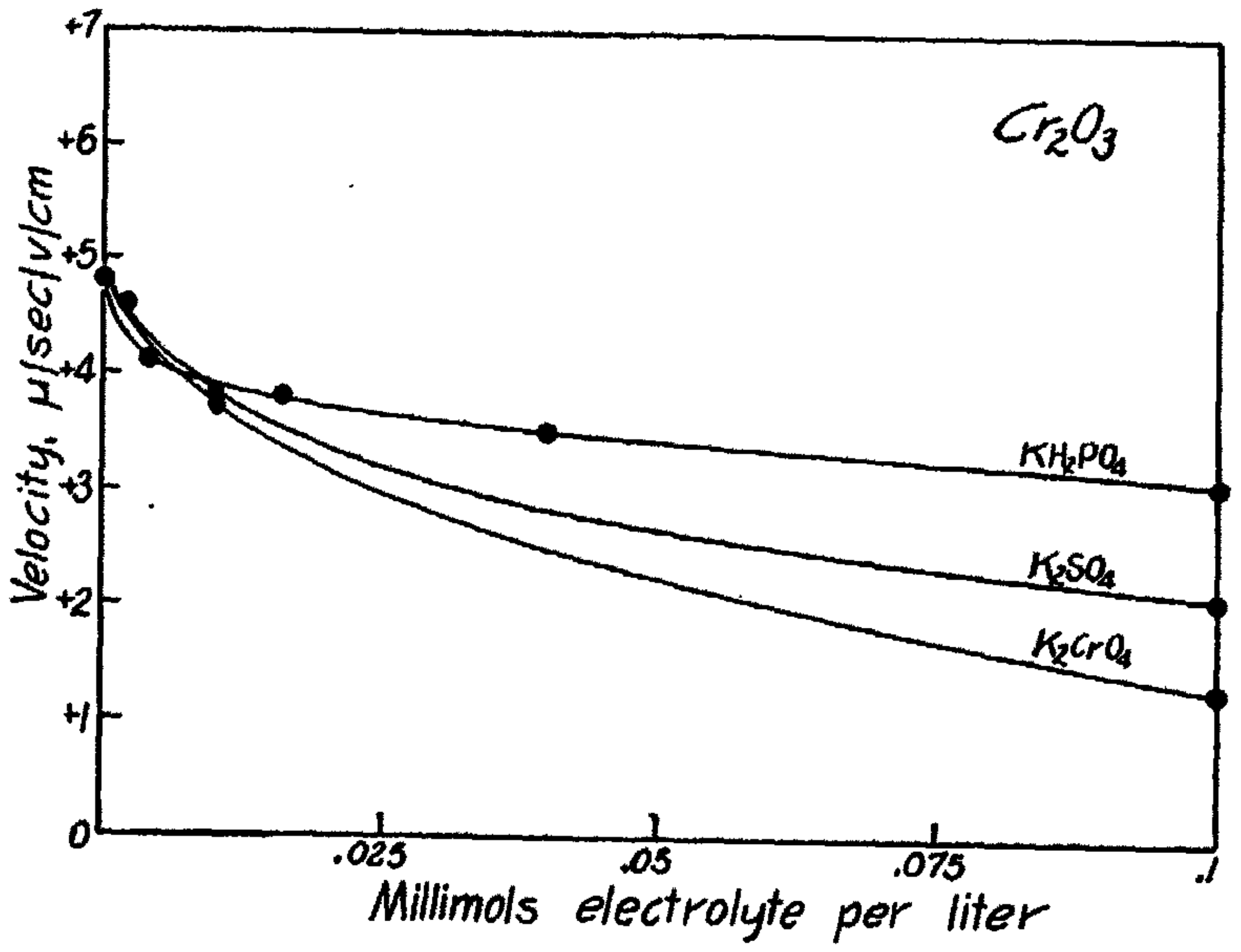

Cr$_2$O$_3$
KH$_2$PO$_4$
K$_2$SO$_4$
K$_2$CrO$_4$
Velocity, μ/sec/v/cm
+7
+6
+5
+4
+3
+2
+1
0
.025
.05
.075
.1
Millimols electrolyte per liter

Fig. 3

point potassium chromate was added to a negative arsenic trisulfide sol until the mixture contained 0.1 millimol of the electrolyte per liter. The migration velocity of the negative sol was reduced from −3.4 to −1.0 μ per second per volt per centimeter and the sol coagulated. This indicates strongly that the anomalous behavior of chromate with positive arsenic trisulfide can be explained by the reduction of the bivalent negative ion to chromic ion. The results with the negative arsenic trisulfide sol and potassium chromate were probably due to failure to remove all of the unadsorbed hydrogen sulfide during the process of washing with hydrogen. If it be assumed that adsorbed hydrogen sulfide is not free to act as a reducing agent, then the behavior of an arsenic trisulfide sol with chromate ion should give an indication of its purity. One is in a quandary when removing the hydrogen sulfide from an arsenic trisulfide sol, because if the washing is carried out too far the arsenic trisulfide hydrolyzes.

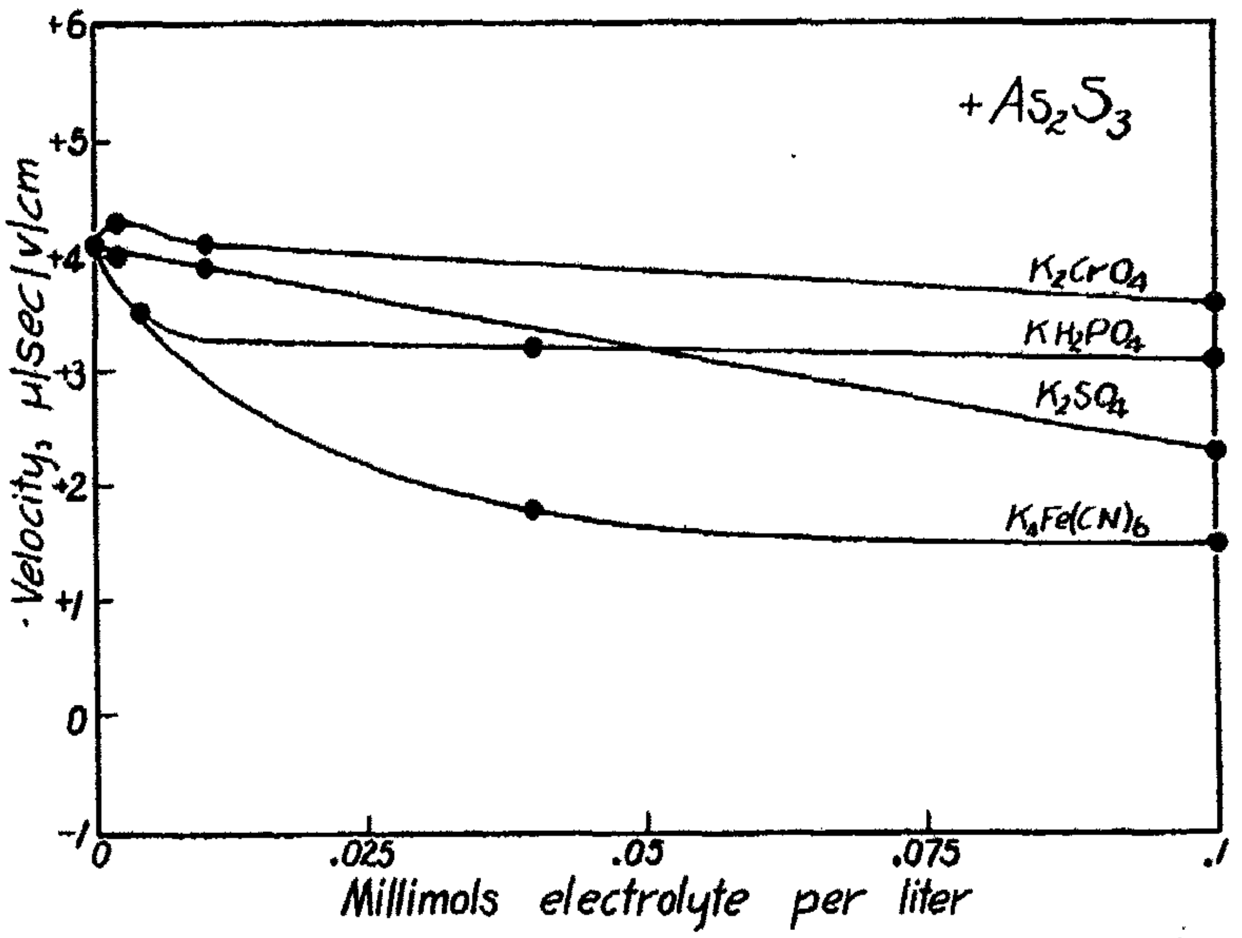


FIG. 4

The data with negative sols and electrolytes are plotted in figures 5 to 8. From figure 5 the order of cations with arsenious sulfide is Th > Cr > Al > Fe > Ba > K at low concentrations, with aluminum and iron exchanging places at higher concentrations. The stannic oxide curves in figure 6 give Th > Al > Cr > Fe > Ba > K for the order of ions at the lower concentrations, with the order changed to Al, Th > Ba > Cr > Fe > K at the highest concentration studied. The order of cations with man-

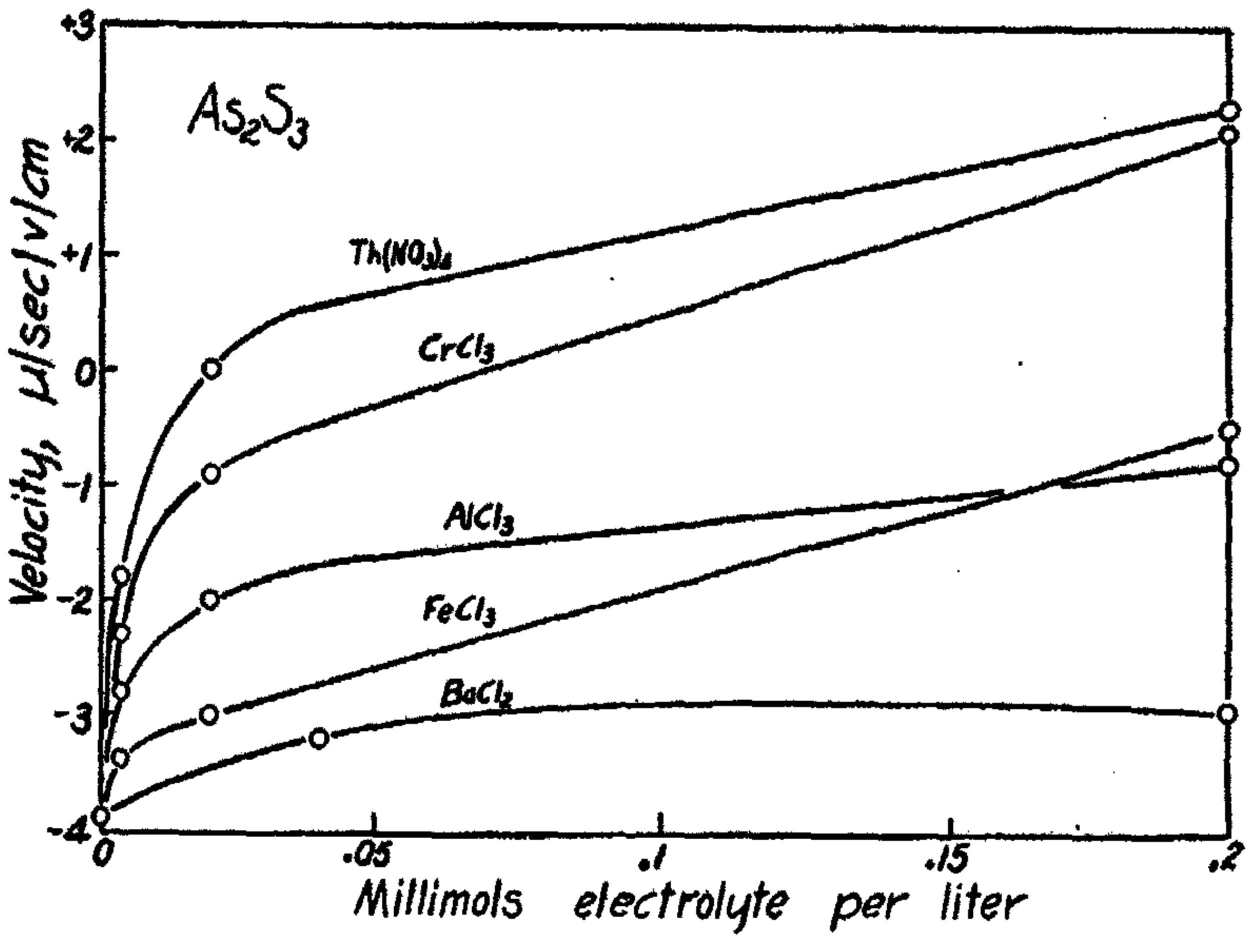

As_2S_3
$Th(NO_3)_4$
$CrCl_3$
$AlCl_3$
$FeCl_3$
$BaCl_2$
Velocity, μ/sec/v/cm
+3
+2
+1
0
-1
-2
-3
-4
0
.05
.1
.15
.2
Millimols electrolyte per liter

Fig. 5

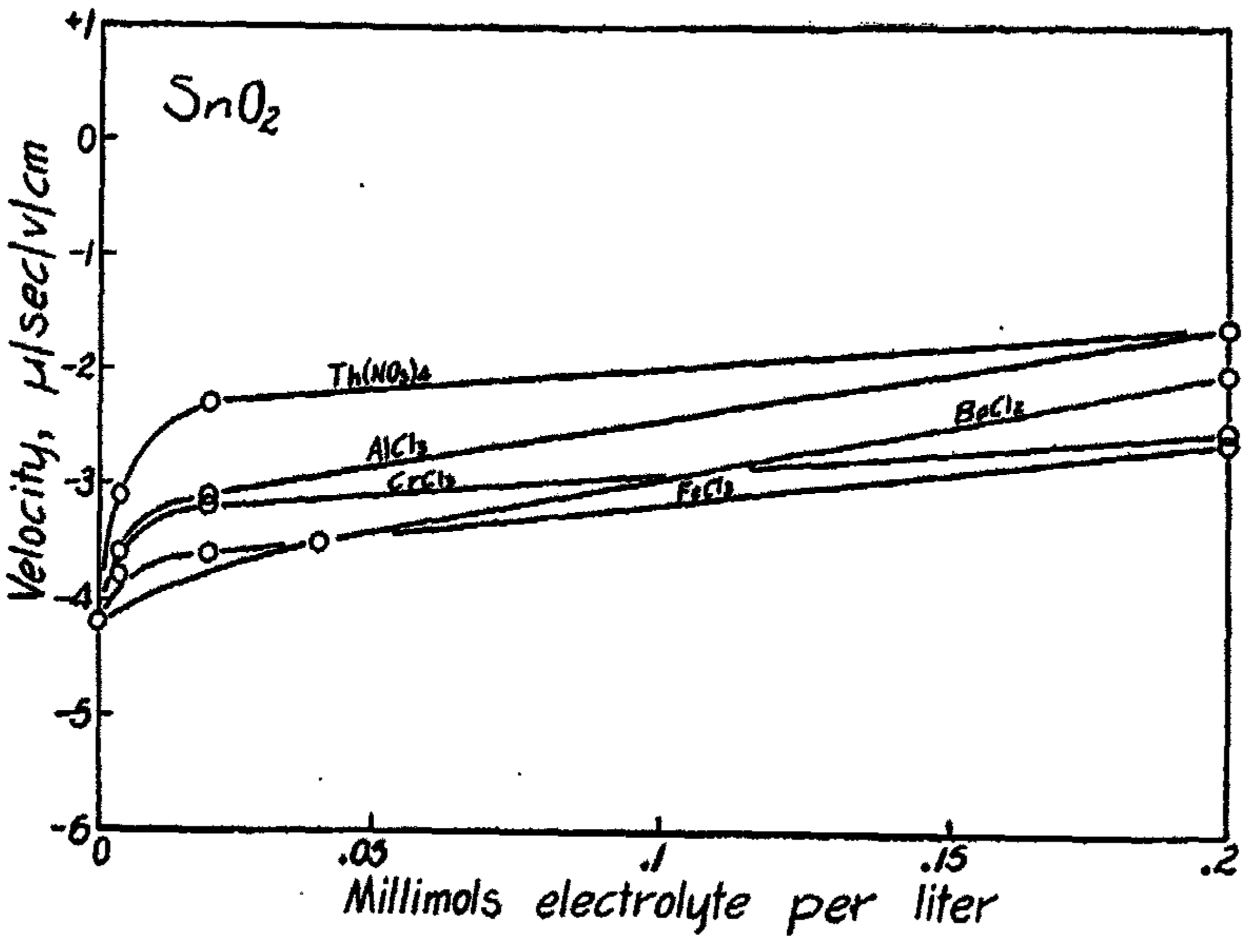

SnO_2
$Th(NO_3)_4$
$AlCl_3$
$CrCl_3$
$BaCl_2$
$FeCl_3$
Velocity, μ/sec/v/cm
+1
0
-1
-2
-3
-4
-5
-6
0
.05
.1
.15
.2
Millimols electrolyte per liter

Fig. 6

ganese dioxide is Th > Al > Cr, Fe > Ba > K but this is altered to Th > Cr, Fe > Al > Ba > K when 0.2 millimol per liter of the electrolytes is present. Figure 8 with negative iron oxide indicates that Th > Cr > Al > Fe > Ba > K is the order of effectiveness of cations in decreasing the mobility of the particles.

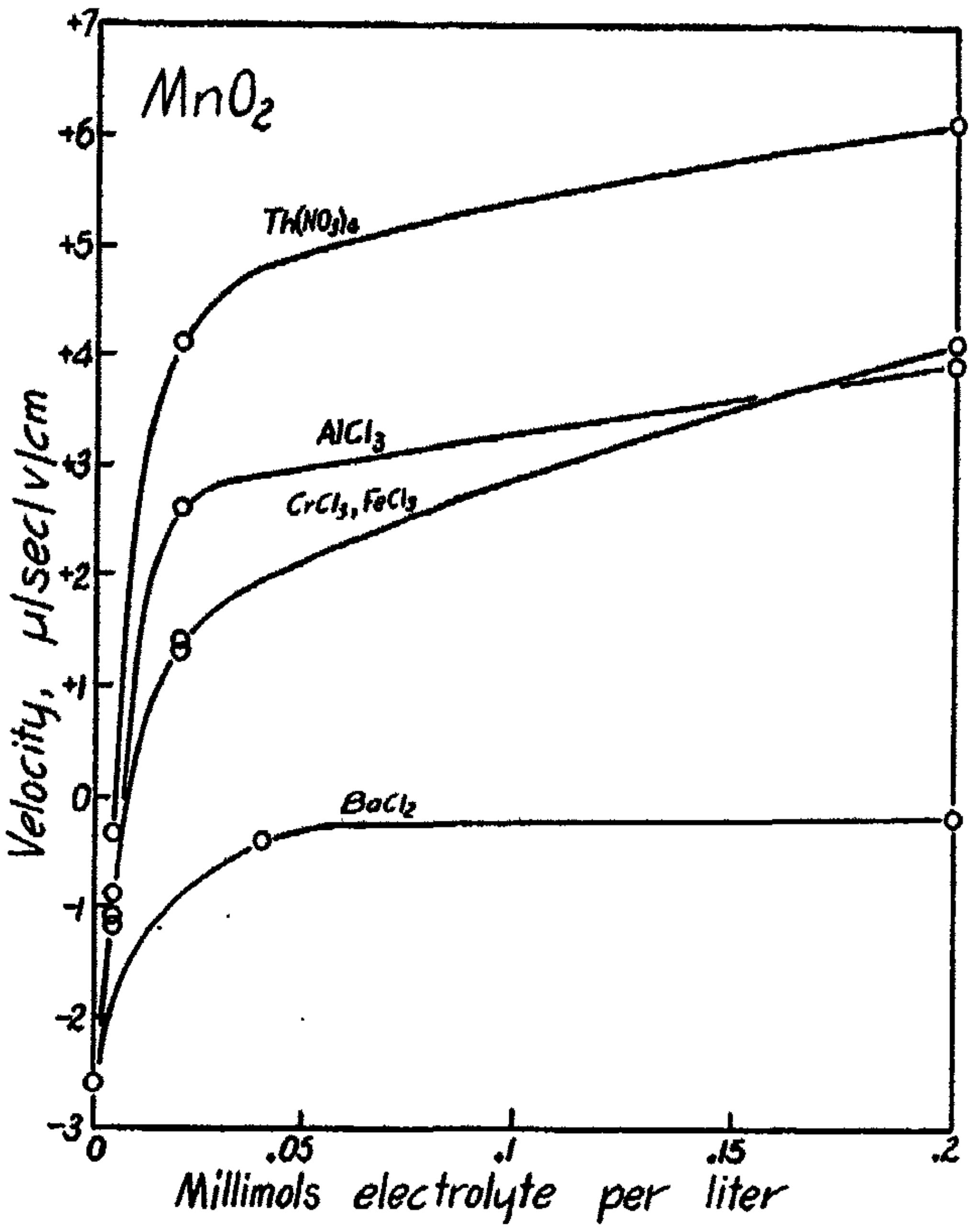


FIG. 7

If we are to assume that there is a relationship between migration velocity and stability, the above orders of ions might serve as lyotropic series.

Some of the salts used were considerably hydrolyzed, as evidenced by the following pH values determined with a glass electrode.[3] The data are for $M/1000$ solutions.

[3] The pH data were kindly supplied by Mr. Herbert Ellison.

Electrolyte	*pH*
$AlCl_3$	3.6
$CrCl_3$	2.8
$FeCl_3$	2.3
$Th(NO_3)_4$	2.7

It is evident that the amount of free acid varies with the electrolytes. Therefore it was thought of interest to investigate the effect of the hydrogen ion on the migration velocity of the sols. Figure 9 shows the behavior of negative sols with hydrochloric acid. Hydrochloric acid exhibits a strong, antagonistic, charging action with the arsenic trisulfide sol. At low concentrations the acid is quite inactive in discharging the tin oxide particles, but it is very effective at higher concentrations.

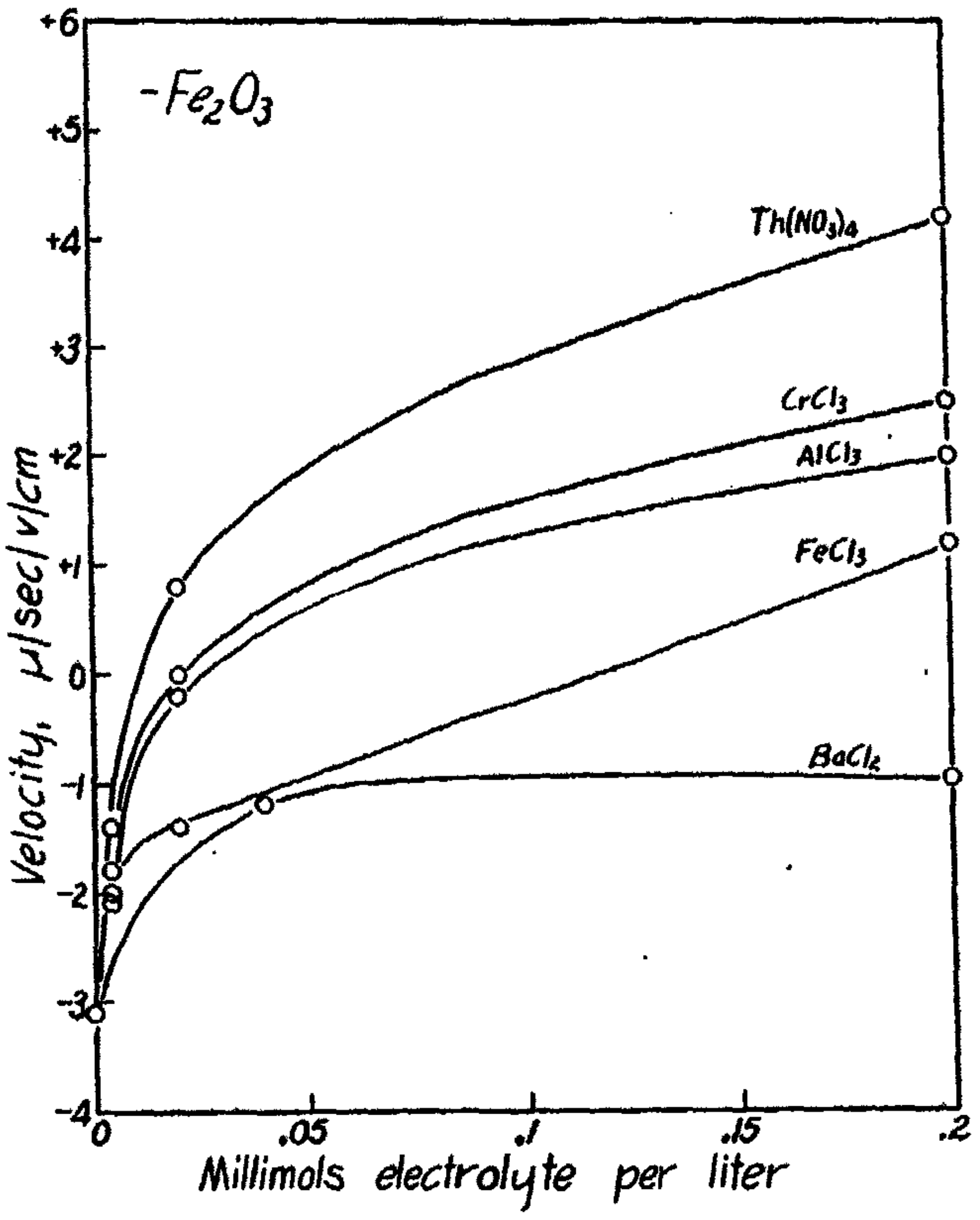


FIG. 8

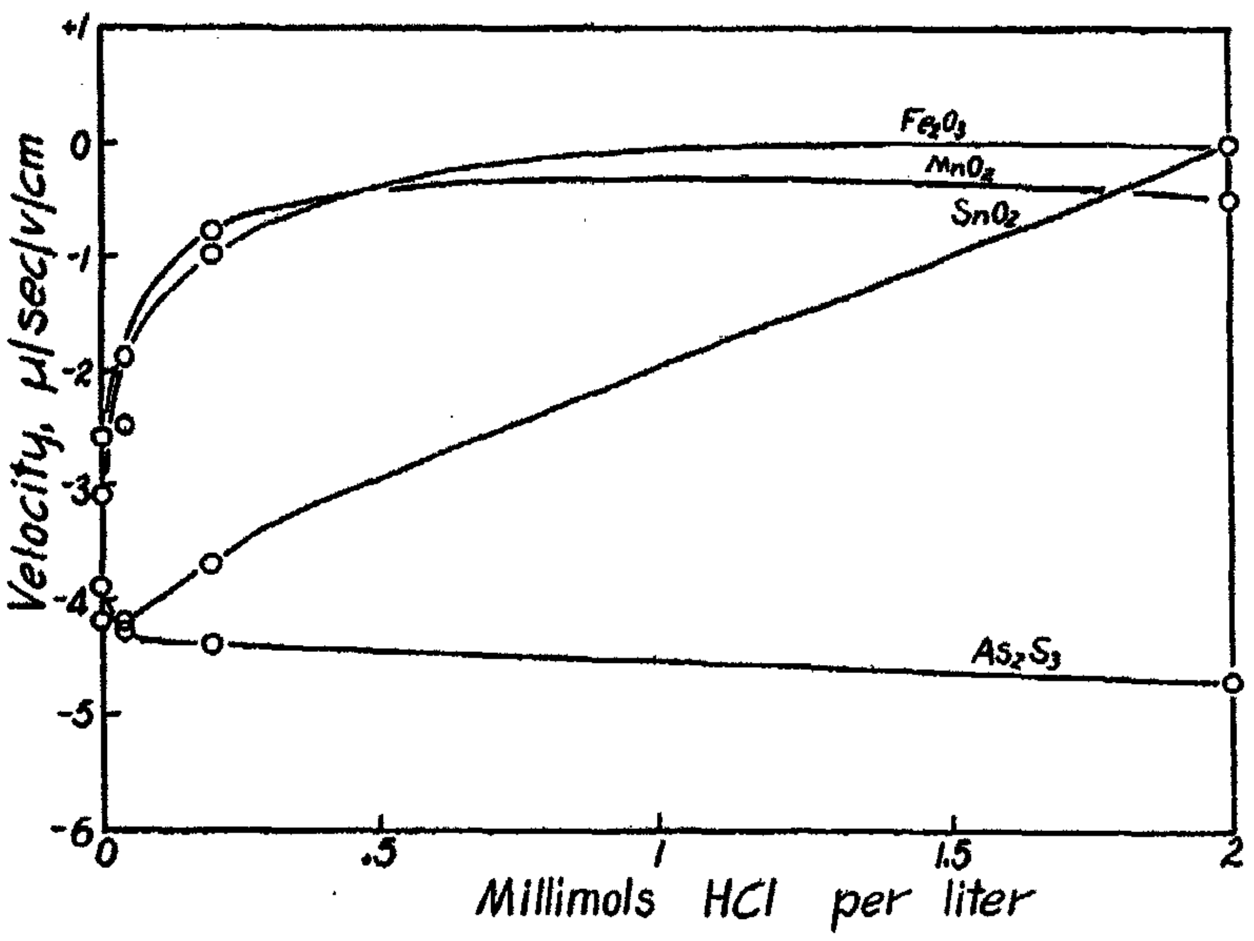


FIG. 9

DISCUSSION

At this point it is necessary to distinguish between lyotropic series associated with the coagulation of sols and the lyotropic series presented here. The former are obtained by determining coagulation values, i.e., by noting the minimum concentration of electrolyte which produces complete precipitation in a given length of time. When different ions are used it is found that different concentrations are required to produce coagulation. The ion which coagulates the sol in the lowest concentration is given first place in the lyotropic series. As a rule the higher the valence of the coagulating ion the more prominent is its position in the series. It has been shown by Powis (4) that coagulation occurs when the stabilizing potential is reduced to 30 millivolts. A critical potential with the above value corresponds to a migration velocity of about 2 μ per second per volt per centimeter in our experiments. Thus we can form an opinion concerning the attributes of an ion as a coagulator from the concentration needed to reduce the mobility of the colloid particles to the critical value.

In the present study the data necessary for deducing lyotropic series were obtained by adding the same concentration of different ions and noting the decrease in mobility of the sol particles. The ion which produced the greatest decrease in velocity was given the leading position in the series, the other ions being placed accordingly.

The electrolyte curves in figures 1 to 4 for positive sols are well defined at velocities greater than 2 μ. This fact makes it possible to deduce lyotropic series which would be identical with lyotropic series determined from flocculation values for the same sols.

Figure 7, for manganese dioxide, shows that there is no difference in the concentration of trivalent ions required to reduce the velocity of the particles to the critical value, i.e., to produce coagulation. On entering the unstable zone the curves spread out. This may be interpreted to mean that there is a difference in the degree to which ferric ions, aluminum ions, and chromic ions enter the double layer in the unstable zone. The same phenomenon is shown with negative iron oxide in figure 8. Thus, although flocculation data sometimes fail to indicate the existence of lyotropic effects, they may be present and well defined.

An inspection of the curves in figures 5 to 8 for negative sols shows that the order of coagulating ions can be deduced clearly only in the case of arsenic trisulfide. The lyotropic series is Th > Cr > Al > Fe > Ba > K. In figure 5 the ferric chloride and aluminum chloride curves cross. At a concentration of about 0.15 millimol per liter the two electrolytes are equally effective in decreasing the velocity of the colloid particles. The migration velocity at this concentration is about 0.9 μ per second per volt per centimeter. The low velocity indicates the presence of an excess of electrolyte over that needed for coagulation. At higher concentrations ferric chloride becomes more effective than aluminum chloride in decreasing the velocity. The hydrochloric acid data throw no light on this unexpected behavior. These data do show, however, that the lyotropy with ferric chloride, aluminum chloride, and chromium chloride is not determined by the degree of hydrolysis of the salts. The fact that the curves cross in an unstable region (between $-2.0\ \mu$ per second per volt per centimeter and the isoelectric point) where the probability of adhesion is high is of doubtful significance. Figure 7 shows that the same phenomenon is encountered in a stable region with recharged manganese dioxide. The electrolyte curves with stannic oxide, plotted in figure 6, are irregular before the first coagulation zone is reached.

Somewhat similar results to these have been obtained by P. Tuorila (6) while investigating the migration velocity of clay suspensions on the addition of electrolytes. For example, at concentrations below 7 millimols per liter silver ion was found to be more effective than potassium ion in reducing the mobility, whereas, at concentrations over 7 millimols per liter potassium ion was more effective than silver ion in this respect. The relation of concentration to the lyotropic series was even more pronounced in the case of sodium permutite suspensions. At concentrations of about 0.0025 *N* the series found by Tuorila is Ba > Sr > Ca > Mg; at about 0.005 *N* the series is Ca > Sr > Ba > Mg; while at 0.015 *N* the series becomes Mg > Ca > Sr > Ba. The same investigator also observed different lyotropic series for different sols, e.g., for a paraffin sol the order of cations is Li > Na > K > Cs > Ag > H, while for a clay suspension the series is Li > Na > Ag, K > Cs > H.

The pure positive sols of this study had markedly different mobilities, e.g., the particles of the chromic oxide sol migrated with a velocity of 4.8 μ per second per volt per centimeter when no added electrolyte was present. The ferric oxide particles had a velocity of 2.7 μ per second per volt per centimeter under the same conditions. A survey of figures 1 to 4 shows that the sulfate ion reduces the velocity of chromic oxide particles to the greatest extent; then follow arsenic trisulfide, iron oxide, and aluminum oxide. Phosphate ion reduces the mobility of the sols in the following order: $Fe_2O_3 > Al_2O_3 > Cr_2O_3 > As_2S_3$. If more were known about the electrical conditions at the interface and if the adsorbabilities of the neutral materials for these ions were known, an explanation for the inversions in order of the sols might be obtained.

B. EFFECT OF COLLOIDS OF OPPOSITE SIGN ON THE STABILITY OF COLLOIDAL SYSTEMS

The sols used in the mutual coagulation study, as well as the method of measuring migration velocities, were the same as in the sol-electrolyte investigation. In preparing the samples for observation the same method of mixing was followed in each case. That is, the sol which was to be present in the smaller amount was diluted to 50 cc. with distilled water and added to 50 cc. of the pure oppositely-charged sol. The mixture was shaken by hand during the addition and then set aside for one-half hour before making any observations.

The results are shown in figures 10 to 17. In all cases the mixtures had the appearance of homogeneous colloids, i.e., the particles all travel in the same direction with uniform velocity.

DISCUSSION

From an electrokinetic standpoint the behavior of colloids with colloids of opposite sign is strikingly similar to the behavior of colloids with electrolytes that contain a highly adsorbable ion of opposite sign. Thus when either of these substances is added in small amount to a sol, the latter experiences a decrease in mobility and a diminution in stability. When the added substance is a colloid of opposite sign precipitation occurs upon reaching the critical velocity.[3] When an excess of oppositely-charged colloid is mixed with a sol the latter is recharged. In all of these instances the behavior is well-known from electrolyte addition.

---

[3] The critical velocity, 2 μ per second per volt per centimeter, observed in these experiments corresponds to a critical potential of 30 millivolts (calculated from the Helmholtz-Perrin formula containing the factor 4).

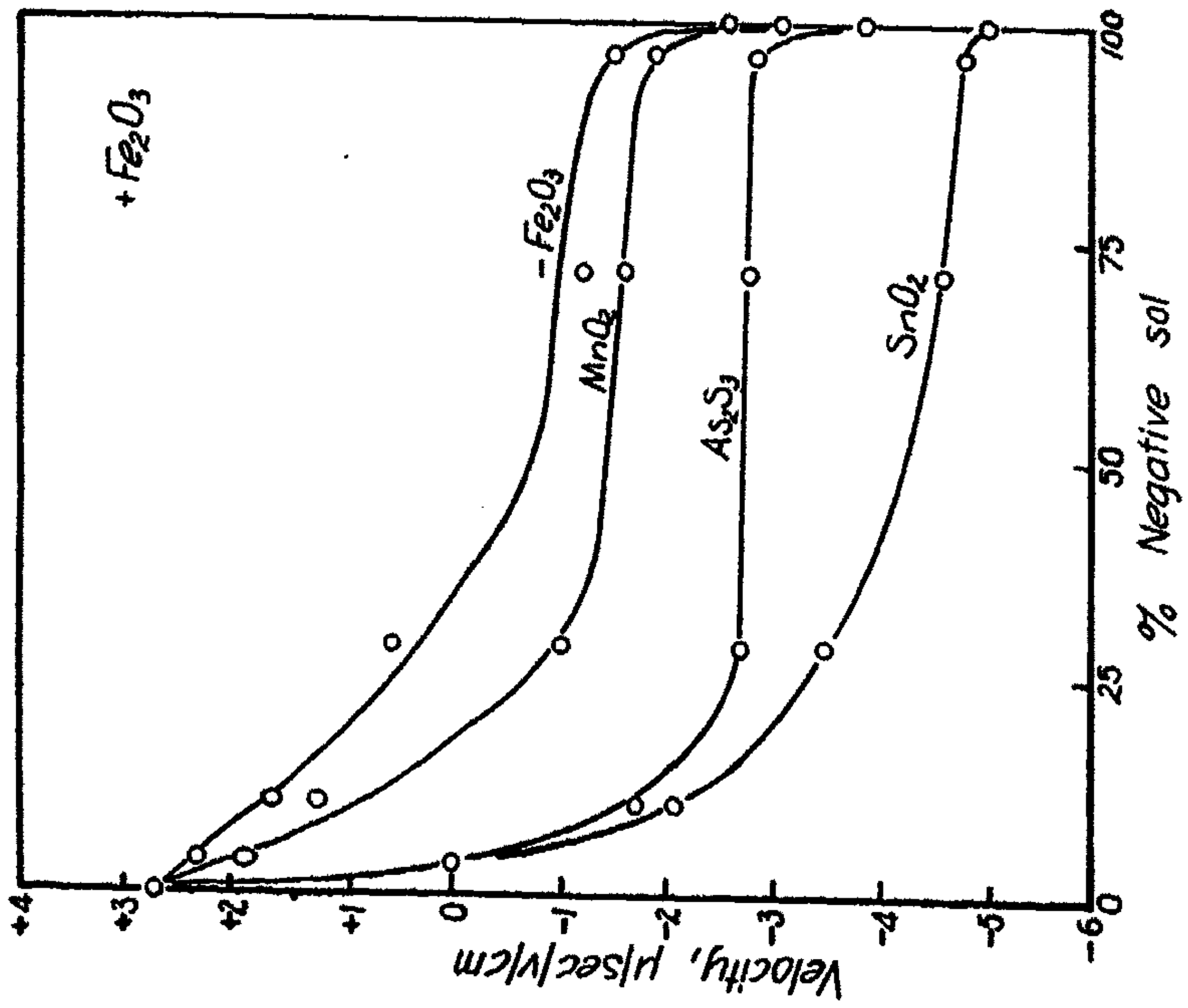

+Fe2O3
-Fe2O3
MnO2
As2S3
SnO2
Velocity, μ/sec/v/cm
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
-6
0
25
50
75
100
% Negative sol

Fig. 10

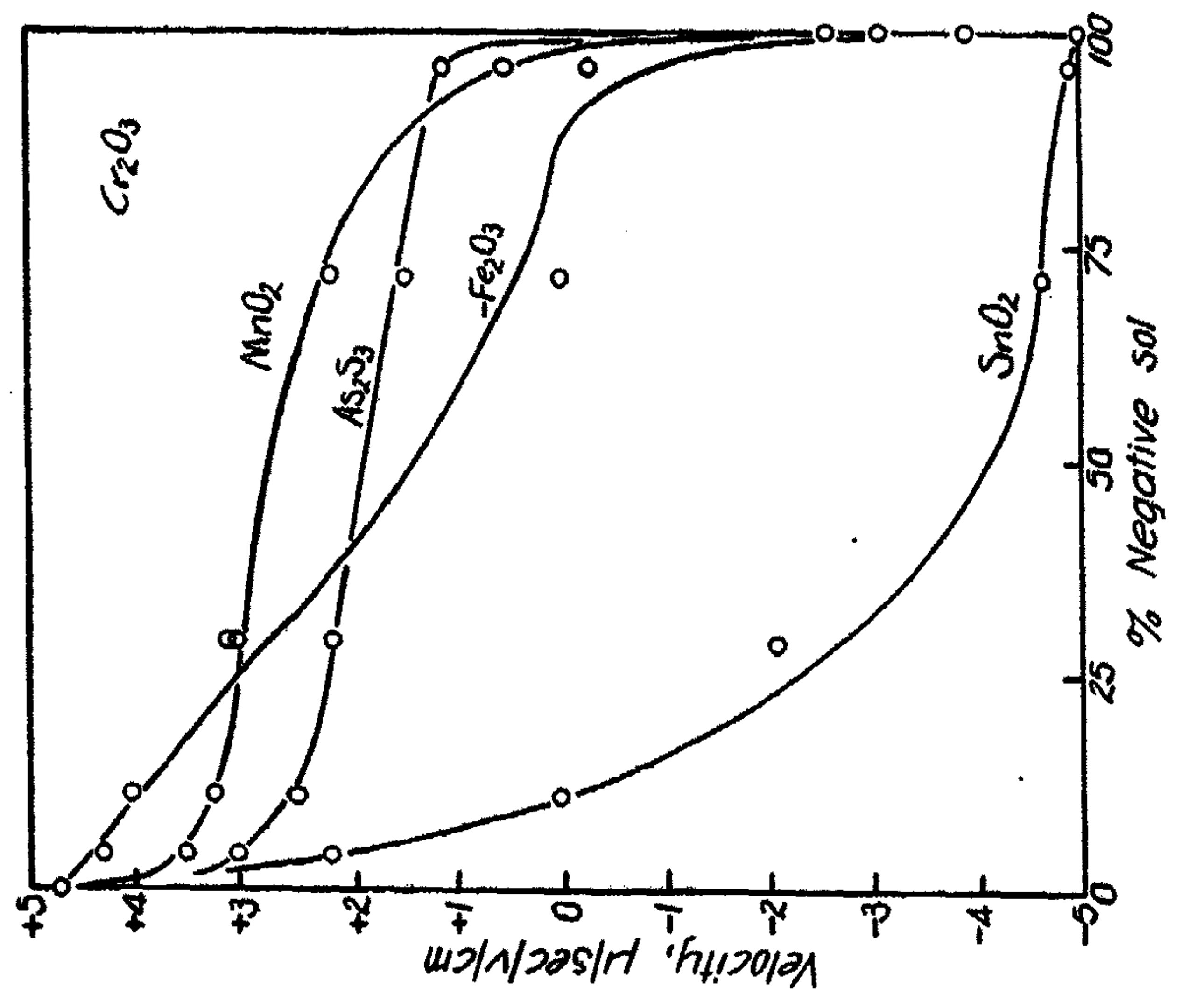

Cr2O3
MnO2
As2S3
-Fe2O3
SnO2
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
0
25
50
75
100
% Negative sol

Fig. 11

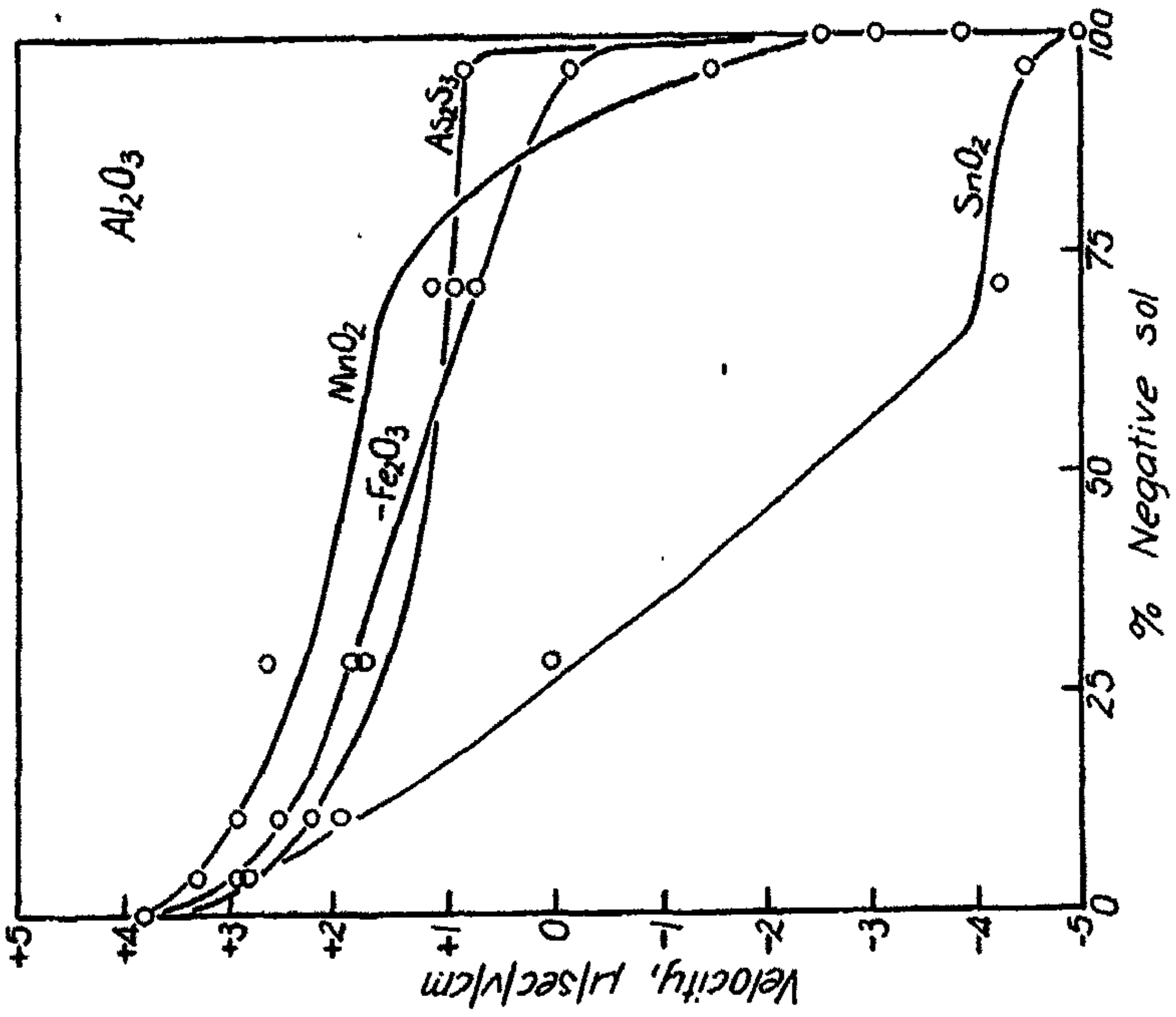

Al_2O_3
MnO_2
$-Fe_2O_3$
As_2S_3
SnO_2
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
% Negative sol
0
25
50
75
100

FIG. 12

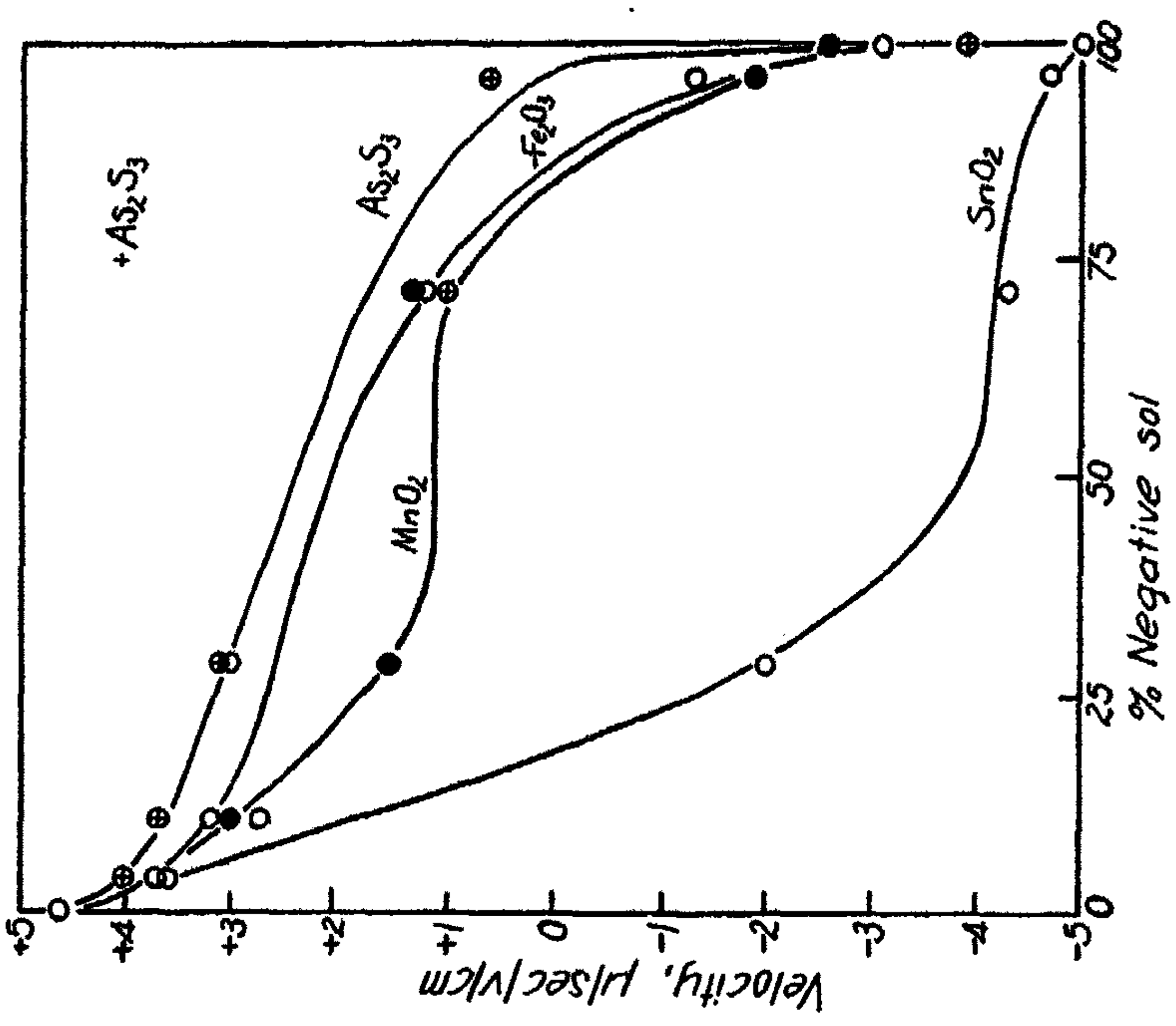

$+As_2S_3$
As_2S_3
Fe_2O_3
MnO_2
SnO_2
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
% Negative sol
0
25
50
75
100

FIG. 13

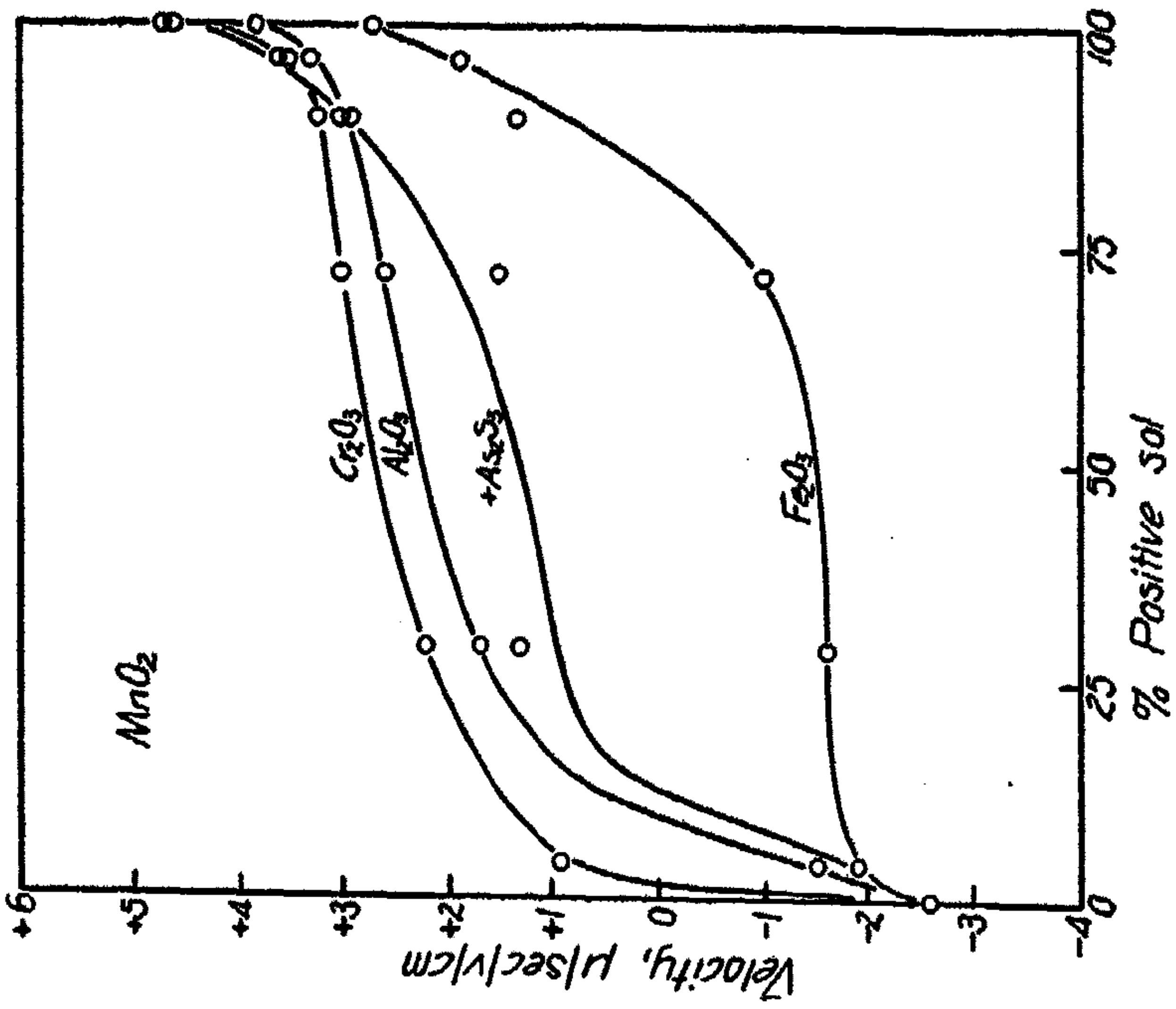

MnO_2
Cr_2O_3
Al_2O_3
$+As_2S_3$
Fe_2O_3
Velocity, μ/sec/V/cm
+6
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
0
25
50
75
100
% Positive sol

FIG. 15

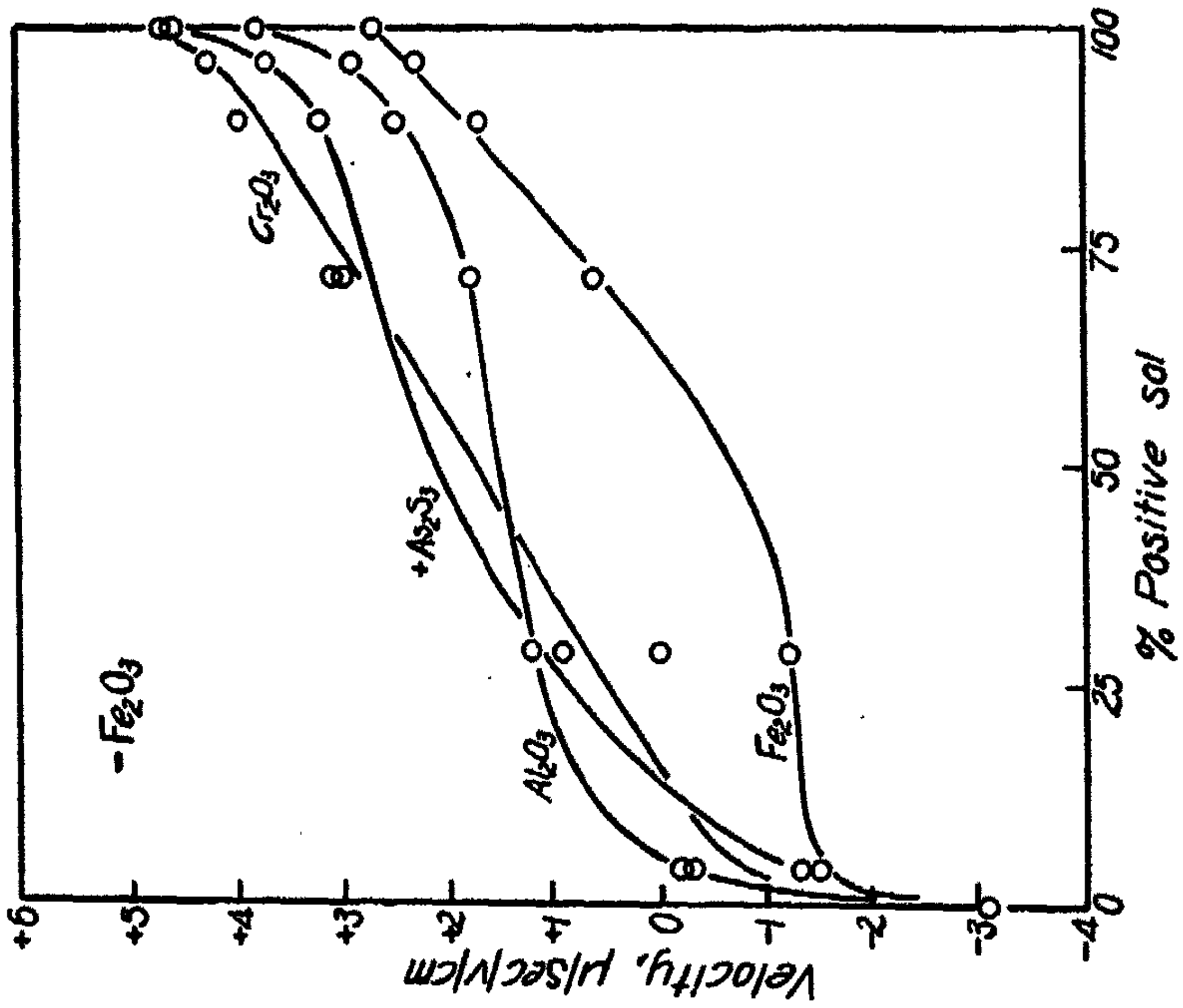

$-Fe_2O_3$
Cr_2O_3
$+As_2S_3$
Al_2O_3
Fe_2O_3
Velocity, μ/sec/V/cm
+6
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
0
25
50
75
100
% Positive sol

FIG. 14

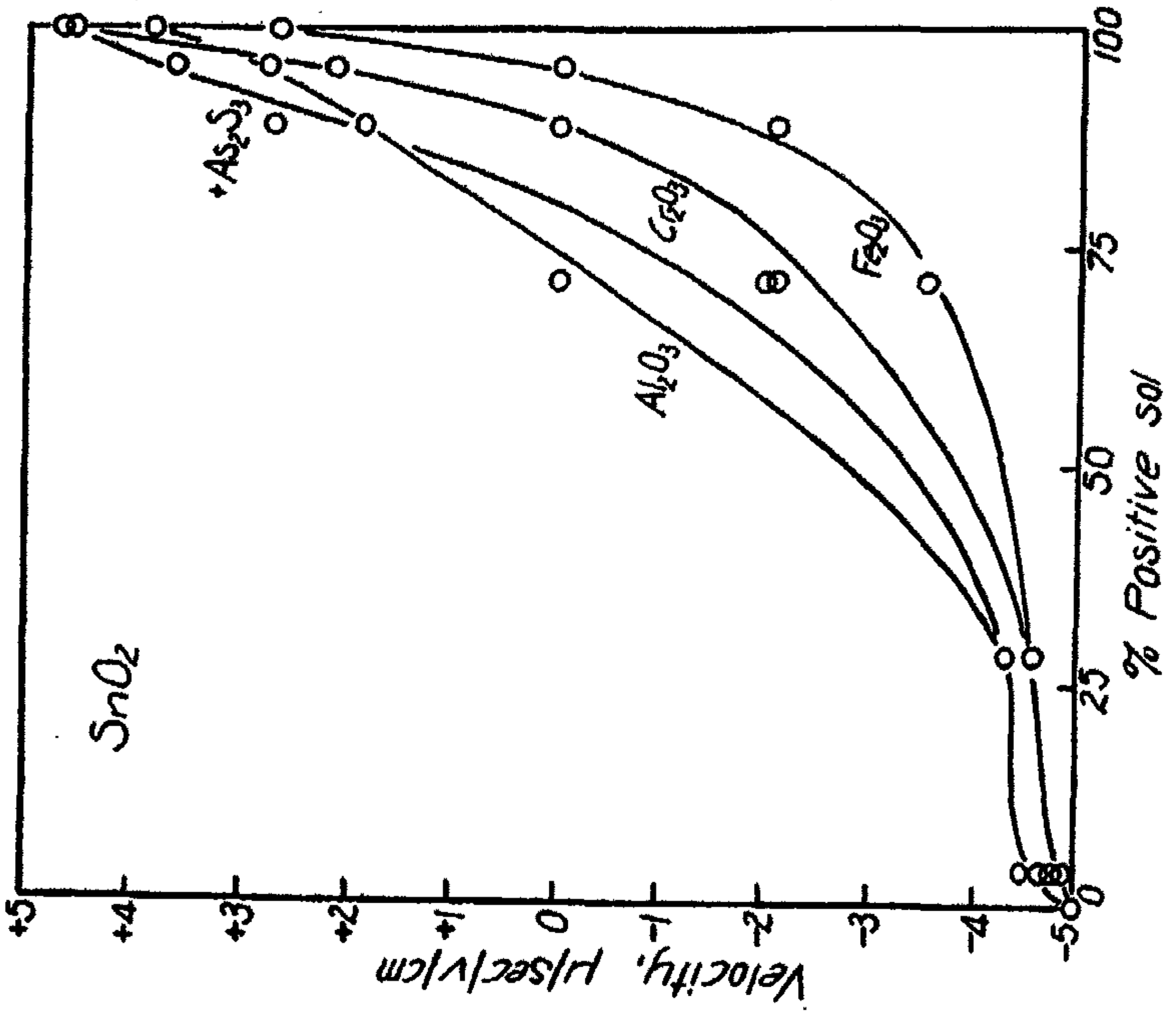

SnO$_2$
+As$_2$S$_3$
Cr$_2$O$_3$
Fe$_2$O$_3$
Al$_2$O$_3$
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
% Positive sol
0
25
50
75
100

FIG. 16

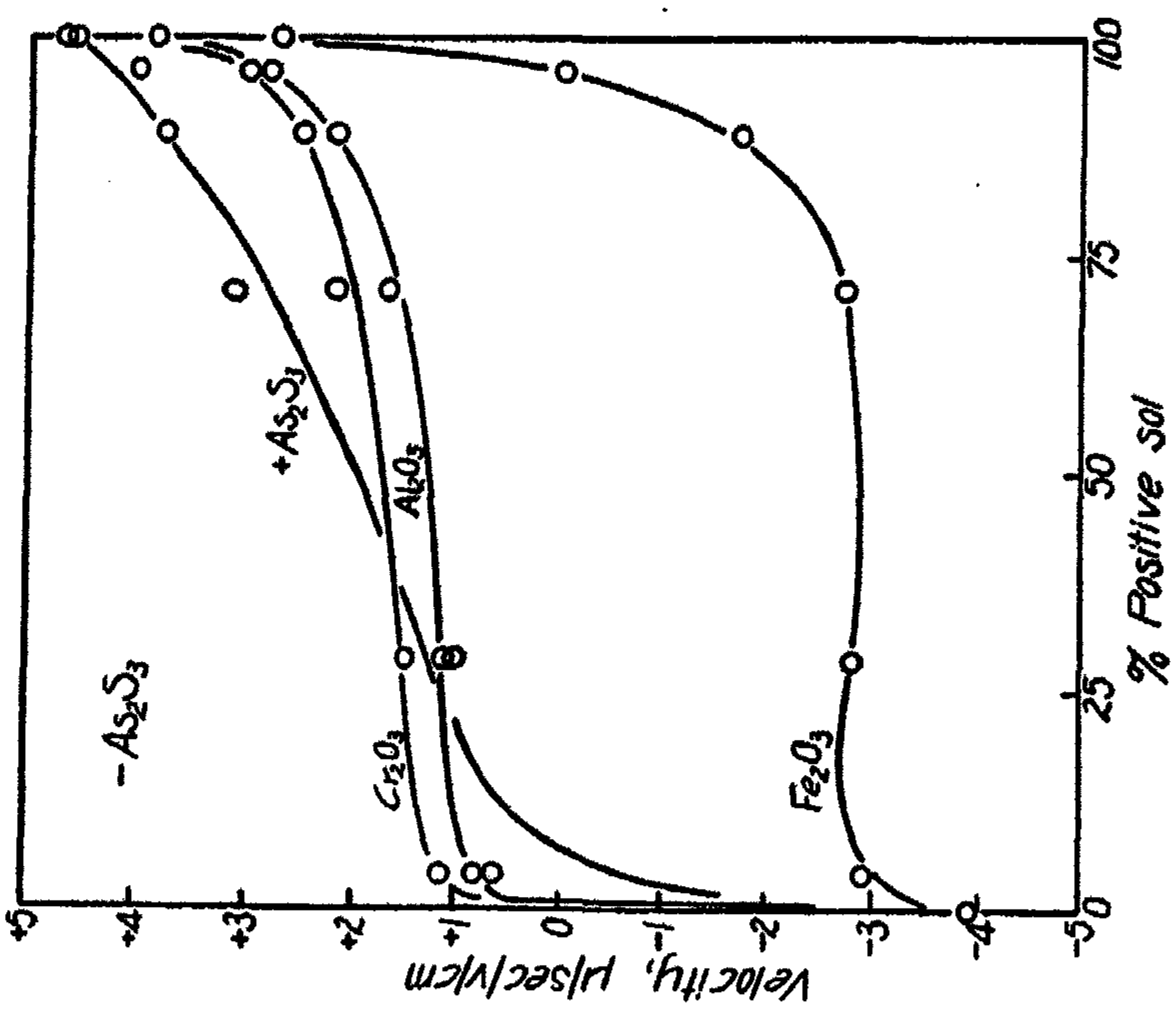

-As$_2$S$_3$
+As$_2$S$_3$
Al$_2$O$_3$
Cr$_2$O$_3$
Fe$_2$O$_3$
Velocity, μ/sec/v/cm
+5
+4
+3
+2
+1
0
-1
-2
-3
-4
-5
% Positive sol
0
25
50
75
100

FIG. 17

From an inspection of figures 10 to 17, it is at once apparent that effects analogous to the lyotropy of electrolytes exist. In reporting this lyotropy, however, there is some question as to the method of comparison. Either of two methods may be employed directly with plots between migration velocity and concentration of added substance. That is, any ordinate (concentration = constant) or any abscissa (velocity = constant) might be drawn and the order of the curves cutting these lines would serve as a "lyotropic" series. If flocculation methods are used to study mutual coagulation a third way appears plausible, i.e., assuming the midpoint of the concentration range in the flocculation zone represents the optimum of precipitation and observing the values of these points for the different systems. This method was used by Weiser and Chapman (7). As they observed, the zone of flocculation may be either narrow or broad. The fact that a wide zone exists shows at once that the discharge curve has flattened out, but the position of the curve (from flocculation data) must only be a matter of speculation. Thus the system iron oxide–manganese dioxide (figure 15) would give an optimum, by this method, which really represents a mixture possessing an appreciable negative mobility. Similarly, the systems chromium oxide–arsenic trisulfide, aluminum oxide–arsenic trisulfide (figure 17) give apparent optima which represent mixtures possessing appreciable positive mobilities. Where the coagulation zone is narrow, however, so that the discharge curves pass through as approximately straight lines, then the apparent optimum corresponds with the isoelectric point.

The lyotropy observed in this study may be presented in the following manner.

Velocity = constant = 0

Positive sol	*Order of negative sols*
As_2S_3	$SnO_2 > MnO_2 > Fe_2O_3 > As_2S_3$
Fe_2O_3	$SnO_2, As_2S_3 > MnO_2 > Fe_2O_3$
Al_2O_3	$SnO_2 > MnO_2 > Fe_2O_3 > As_2S_3$
Cr_2O_3	$SnO_2 > Fe_2O_3 > MnO_2 > As_2S_3$
Negative sol	*Order of positive sols*
As_2S_3	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
Fe_2O_3	$Al_2O_3 > Cr_2O_3 > As_2S_3 > Fe_2O_3$
MnO_2	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
SnO_2	$Al_2O_3 > As_2S_3 > Cr_2O_3 > Fe_2O_3$

Concentration = constant = 50 per cent

Positive sol	*Order of negative sols*
As_2S_3	$SnO_2 > MnO_2 > Fe_2O_3 > As_2S_3$
Fe_2O_3	$SnO_2 > As_2S_3 > MnO_2 > Fe_2O_3$
Al_2O_3	$SnO_2 > Fe_2O_3, As_2S_3 > MnO_2$
Cr_2O_3	$SnO_2 > Fe_2O_3 > As_2S_3 > MnO_2$

Negative sol	*Order of positive sols*
As_2S_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$
Fe_2O_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$
MnO_2	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
SnO_2	$Al_2O_3 > As_2S_3 > Cr_2O_3 > Fe_2O_3$

Since the percentage concentration calculated in all data is a volume percentage and does not refer to the number of particles, the significance of the lyotropy at 50 per cent is doubtful. The point of interest, however, is the fact that it is different from the lyotropy at the isoelectric point.

It will be observed that the lyotropic effects apparent in figures 10 to 13, at low concentration of added sol, are quite different from the lyotropy manifested in the presence of high concentration of added sol. This is analogous to the change in lyotropy with concentration of added electrolyte.

SUMMARY

1. An ultramicroscopic method has been used to follow the changes in stability of sol-electrolyte mixtures and of mixtures of oppositely-charged colloids with changes in concentration.

2. Lyotropic series for the coagulating ions were determined for each colloidal system.

3. In some cases for a given sol the position of ions in the lyotropic series was altered when going from a low concentration to a higher one. Thus the series are, at low and high concentrations, respectively,

For negative arsenic trisulfide: Th > Cr > Al > Fe > Ba > K
Th > Cr > Fe > Al > Ba > K

For stannic oxide: Th > Al > Cr > Fe > Ba > K
Al, Th > Ba > Cr > Fe > K

For manganese dioxide: Th > Al > Cr, Fe > Ba > K
Th > Cr, Fe > Al > Ba > K

4. It has been demonstrated that lyotropic effects, which may be obscure from flocculation data, are shown clearly by cataphoretic measurements.

5. The mobilities of mixtures of oppositely-charged colloids are somewhere between the mobilities of the pure colloids comprising the mixture.

6. The mixtures coagulate when the mobility is lowered to a critical value.

7. Lyotropic series, indicating the relative effectiveness of a number of oppositely-charged sols upon a given sol, have been given.

8. Evidence has been cited to show that the lyotropy encountered varies with the given sols as well as with the concentration of the added colloid.

The authors are indebted to Professors J. H. Walton and C. H. Sorum for their kind interest and helpful suggestions during the course of this study.

REFERENCES

(1) Schulze: J. prakt. Chem. **25**, 431 (1882); **27**, 320 (1883).
Linder and Picton: J. Chem. Soc. **67**, 63 (1895); **87**, 1906 (1905).
(2) Bancroft: J. Phys. Chem. **19**, 363 (1915).
(3) Hardy: J. Physiol. **24**, 288 (1899).
(4) Powis: Z. physik. Chem. **89**, 186 (1915).
(5) Hazel and Ayres: J. Phys. Chem. **35**, 2930 (1931).
(6) Tuorila, P.: Kolloidchem. Beihefte **27**, 44 (1928).
(7) Weiser and Chapman: J. Phys. Chem. **35**, 543 (1931).

MIGRATION STUDIES WITH COLLOIDS. II

The Mechanism of the Mutual Coagulation Process

FRED HAZEL and DAVID M. McQUEEN

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received July 20, 1938

INTRODUCTION

The phenomenon to which the term "mutual coagulation" has been applied may be defined as the precipitation occurring when two colloidal systems are mixed. Although noted by Graham (1) in 1862, the first survey of mutual coagulation was made by Linder and Picton (2), who observed that the mutually precipitating sols were of opposite charge. Further, they cited the fact that in mixtures of strongly-negative and weakly-positive sols the resultant migration in an electric field was toward the anode unless a large excess of the positive sol were used. That is, mixtures of oppositely-charged sols are unstable only within certain limits of concentration. These general results were confirmed by a number of investigators (3) but made especially clear by Biltz (4).

In 1910, Lottermoser (5), studying the behavior of mixtures of positive and negative silver iodide sols, attempted to explain the attendant coagulation as a consequence of a reaction between the stabilizing electrolytes—silver nitrate and potassium iodide. Making use of this idea and the well-known fact that certain combinations of negative sols, in which reactions between the peptizing ions might be assumed, are unstable (6), Thomas and Johnston (7) have deduced a general mechanism. Their view that the coagulation in the system ferric oxide–silicic acid is a result of the reaction $H^+ + OH^- = H_2O$ and, as such, should have an optimum where the concentrations of sodium hydroxide and hydrochloric acid are equivalent was upheld over a limited range.

On the other hand Wintgen and Löwenthal (8) were led to conclusions diametrically opposed to a chemical mechanism. In a study of the system chromium oxide–stannic oxide they found that the maximum precipitation corresponds to that calculated from the charge of the particles (determined from transference experiments (9)). The results of Biltz (4) have also been used to show that the electric charge is the dominant factor in mutual coagulation. From his data excerpts have been made to prove the assertion that the order of effectiveness of a series of positive sols does not change if different negative sols are used (10). This practice has not been in vogue since Bancroft (11) pointed out that the importance in Biltz' results lay in the deviations from the order in such series.

Weiser and Chapman (12), considering the widths of the flocculation zones in terms of the concentrations of the mutually precipitating sols, came to the conclusion that the mutual coagulation process may be determined by a number of factors, namely, electrical neutralization, mutual adsorption of the particles, interaction between stabilizing ions, and the presence of excess electrolyte in the sols. They again observed inversions in the precipitating powers of a series of negative sols with a number of positive sols.

It has been demonstrated that the ultramicroscopic technique used with sol-electrolyte systems can be satisfactorily employed in studying the velocities of mixtures of oppositely-charged colloids (13). Since such mixtures appear to behave as homogeneous colloidal systems in the important respect that the particles under the influence of an electric field all migrate in the same direction and with the same velocity, it was believed that some information as to the nature of the units of the systems might be afforded by an investigation of their behavior with electrolytes.

EXPERIMENTAL

In general the systems used in this study were prepared by mixing two of the oppositely-charged colloids used in the previous studies. However, so little of the aluminum oxide and manganese dioxide stock sols remained that these were diluted with an equal volume of water before mixing. Two stock mixtures were made from each pair of oppositely-charged sols—one having a net positive and the other a net negative charge.

The method of adding the electrolyte solutions and observing the migration velocities was the same as that reported for unmixed colloidal systems in the first paper of this series (13), with the exception that the total volume of each sample was 50 cc. rather than 100 cc.

RESULTS

The data for mixtures bearing a net positive charge are plotted in figures 1 to 3. Similar data for mixed sols bearing a net negative charge are plotted in figures 4 to 8.

In all cases it is apparent that the addition of an ion carrying a double charge or greater increases the stability of a mixture possessing a net charge of the same sign. It will also be observed that the phenomenon seems to be different from the usual type of charging of a colloid by a highly adsorbed ion of like charge. Table 1 and the plot of the data therein (figure 9) make this difference more obvious.

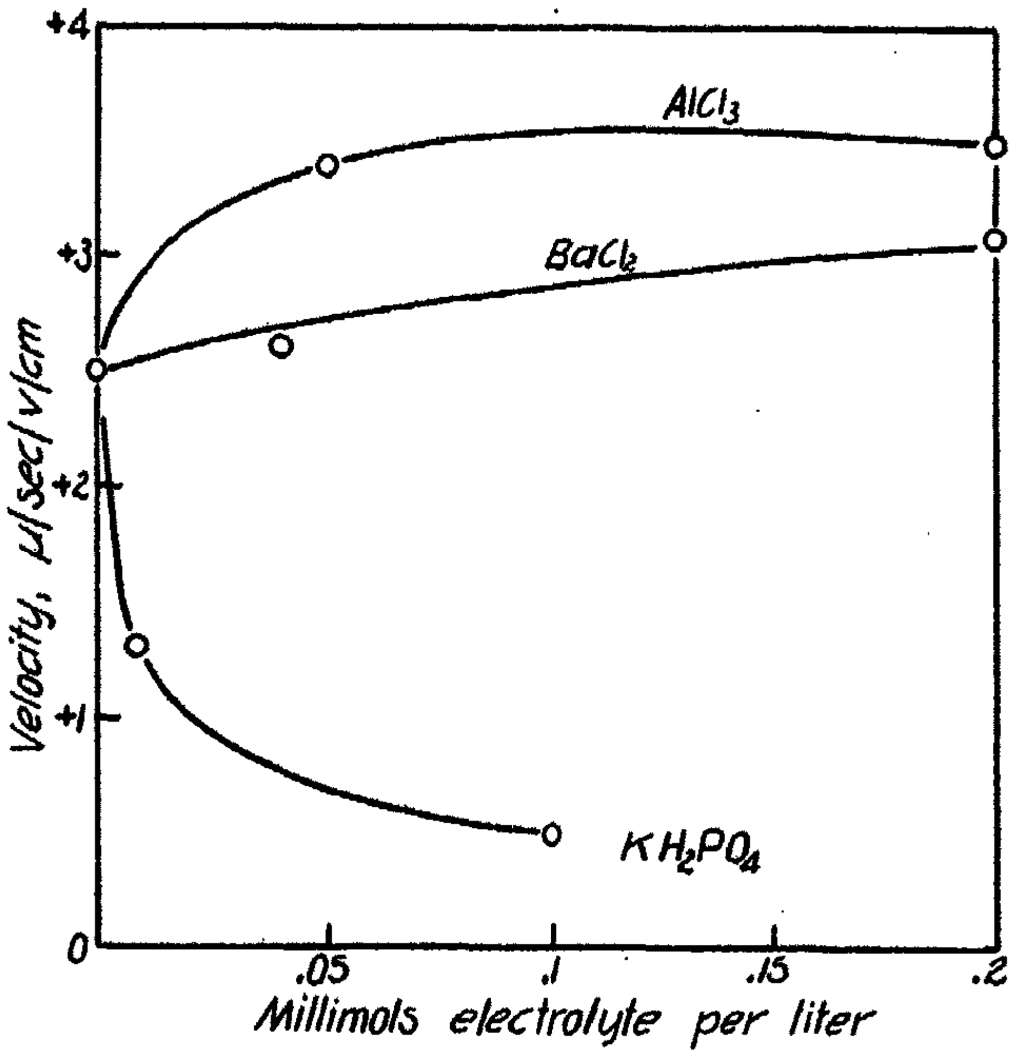


FIG. 1. ALUMINUM OXIDE-MANGANESE DIOXIDE MIXTURE
25 cc. Al_2O_3; 10 cc. MnO_2; 15 cc. H_2O

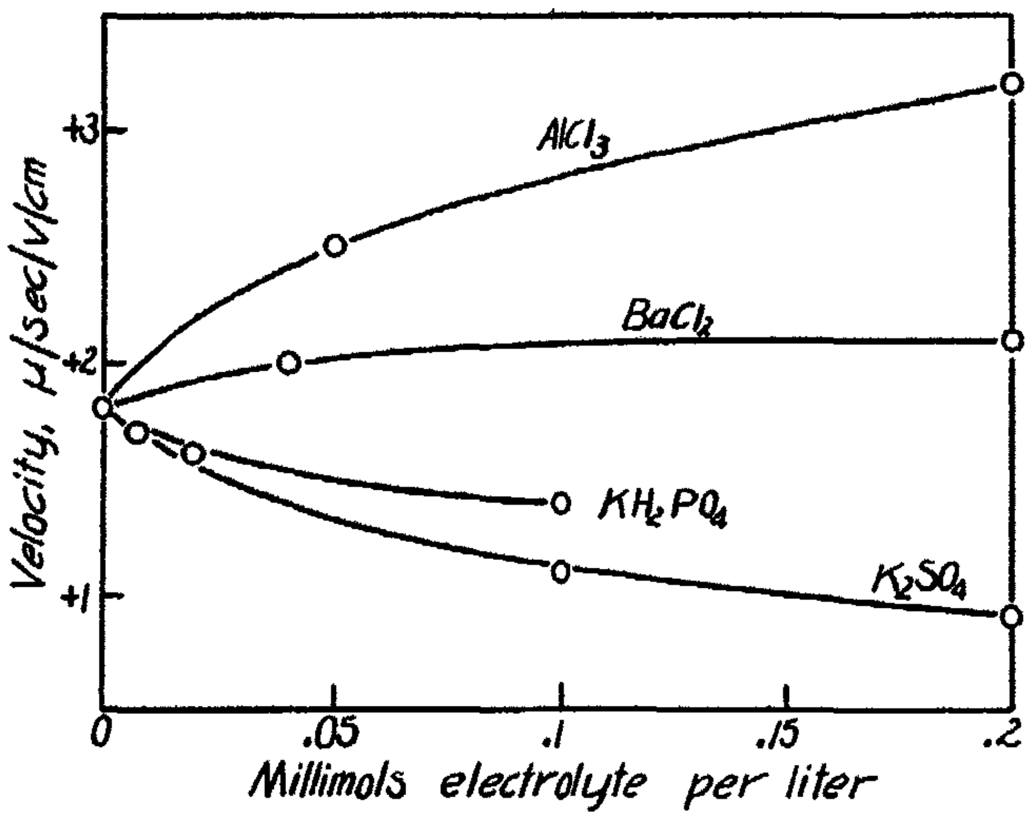


FIG. 2. ALUMINUM OXIDE-ARSENIC TRISULFIDE MIXTURE
20 cc. Al_2O_3; 5 cc. As_2S_3; 15 cc. H_2O

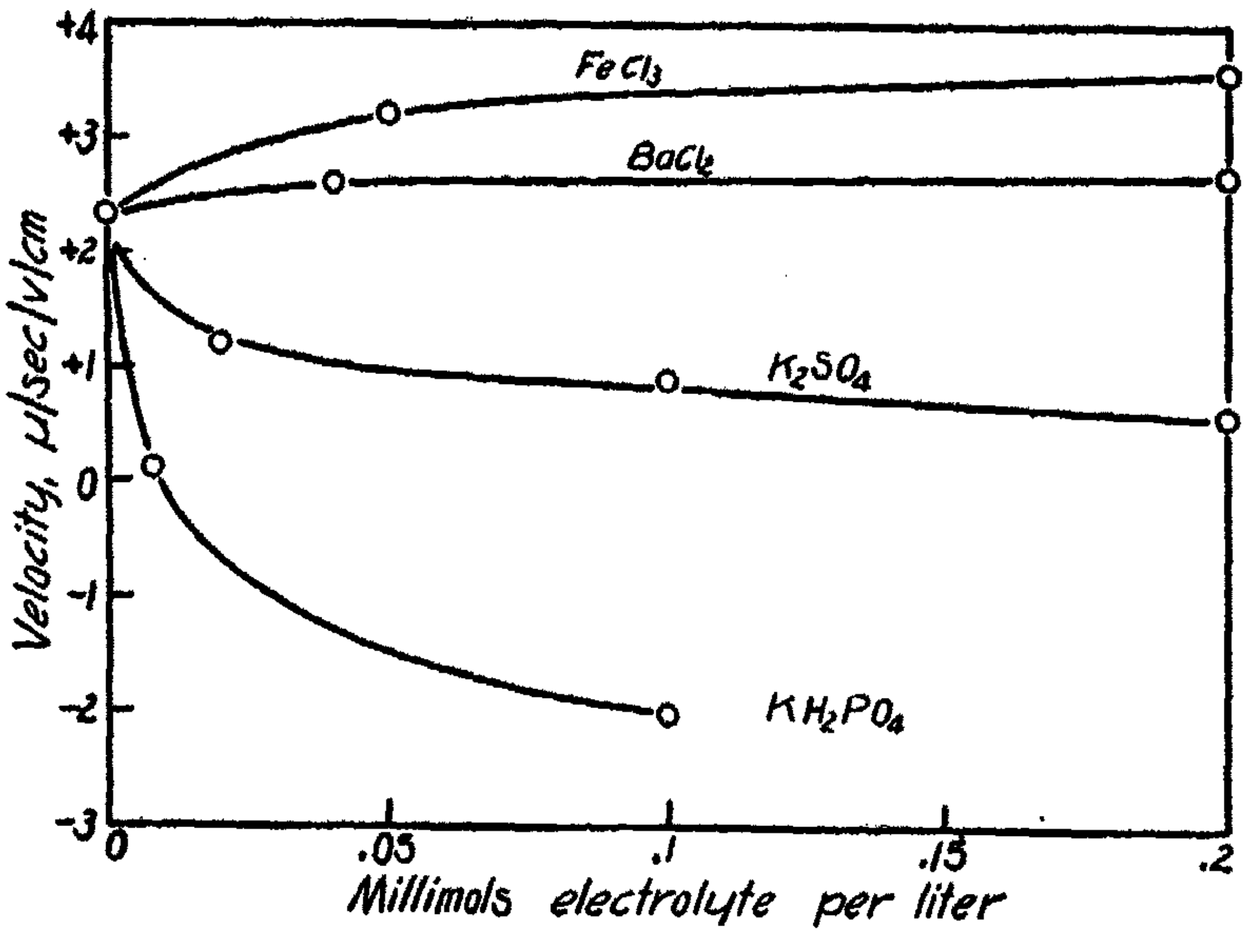


FIG. 3. IRON OXIDE-MANGANESE DIOXIDE MIXTURE
50 cc. Fe_2O_3; 1 cc. MnO_2; 49 cc. H_2O

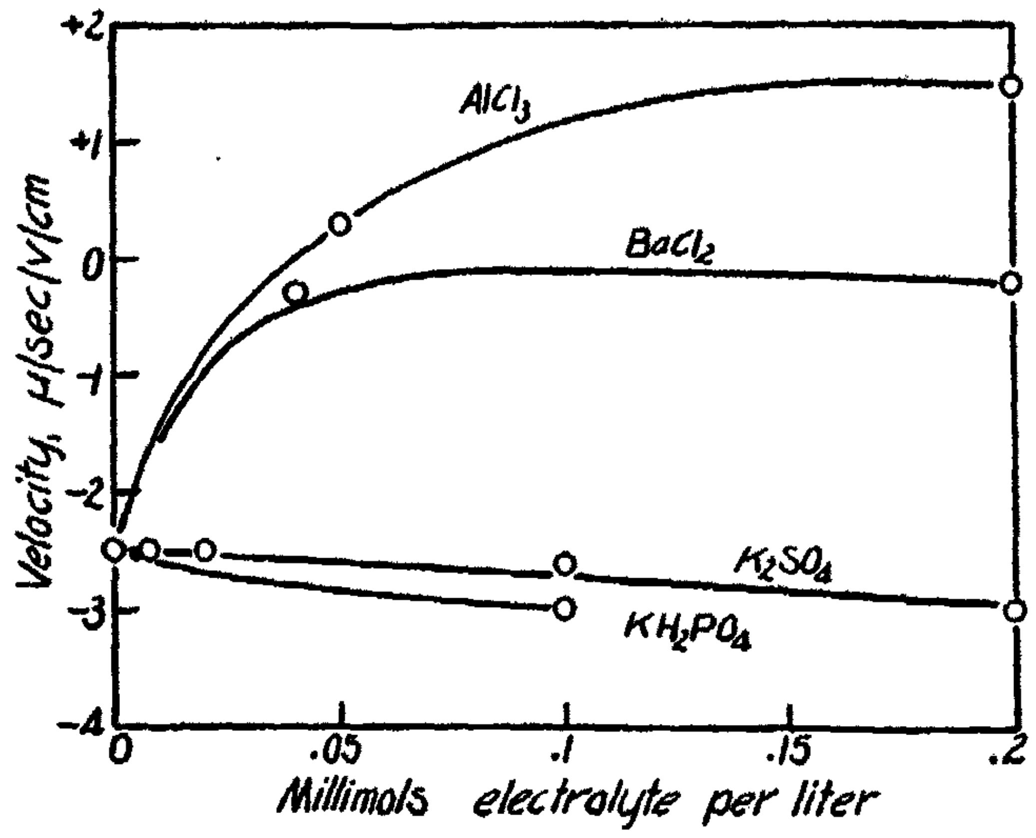


FIG. 4. MANGANESE DIOXIDE-ALUMINUM OXIDE MIXTURE
100 cc. MnO_2; 2 cc. Al_2O_3; 98 cc. H_2O

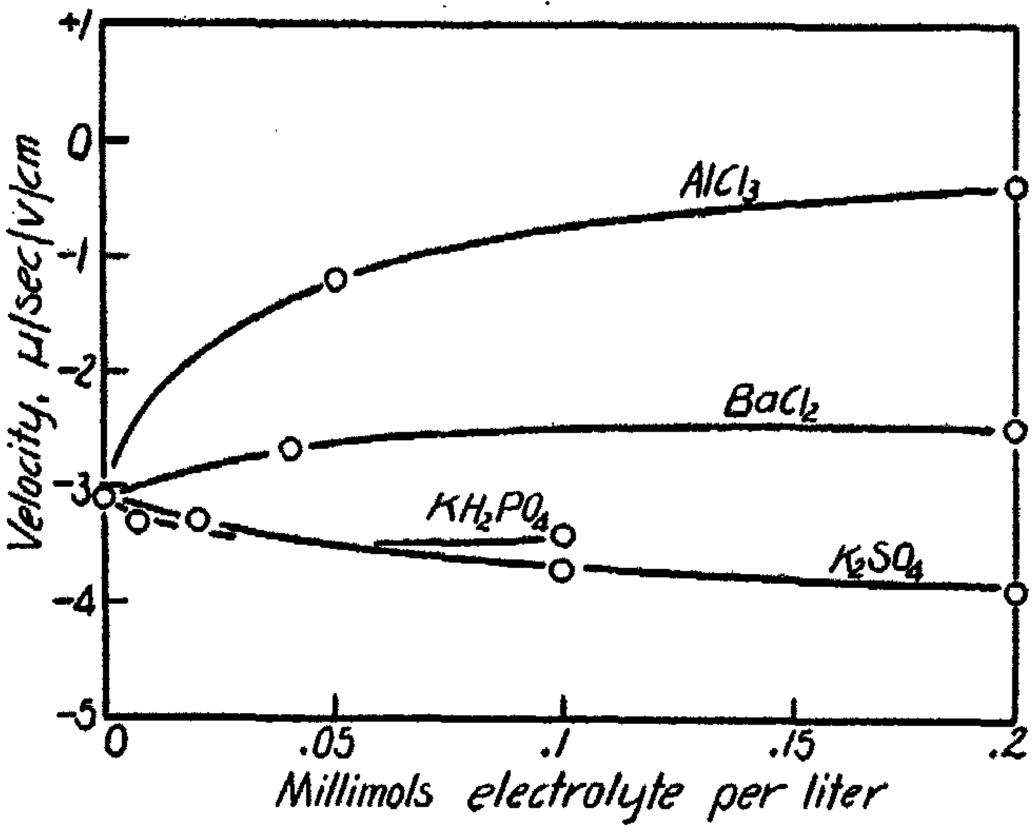


FIG. 5. ARSENIC TRISULFIDE-ALUMINUM OXIDE MIXTURE
50 cc. As_2S_3; 1 cc. Al_2O_3; 49 cc. H_2O

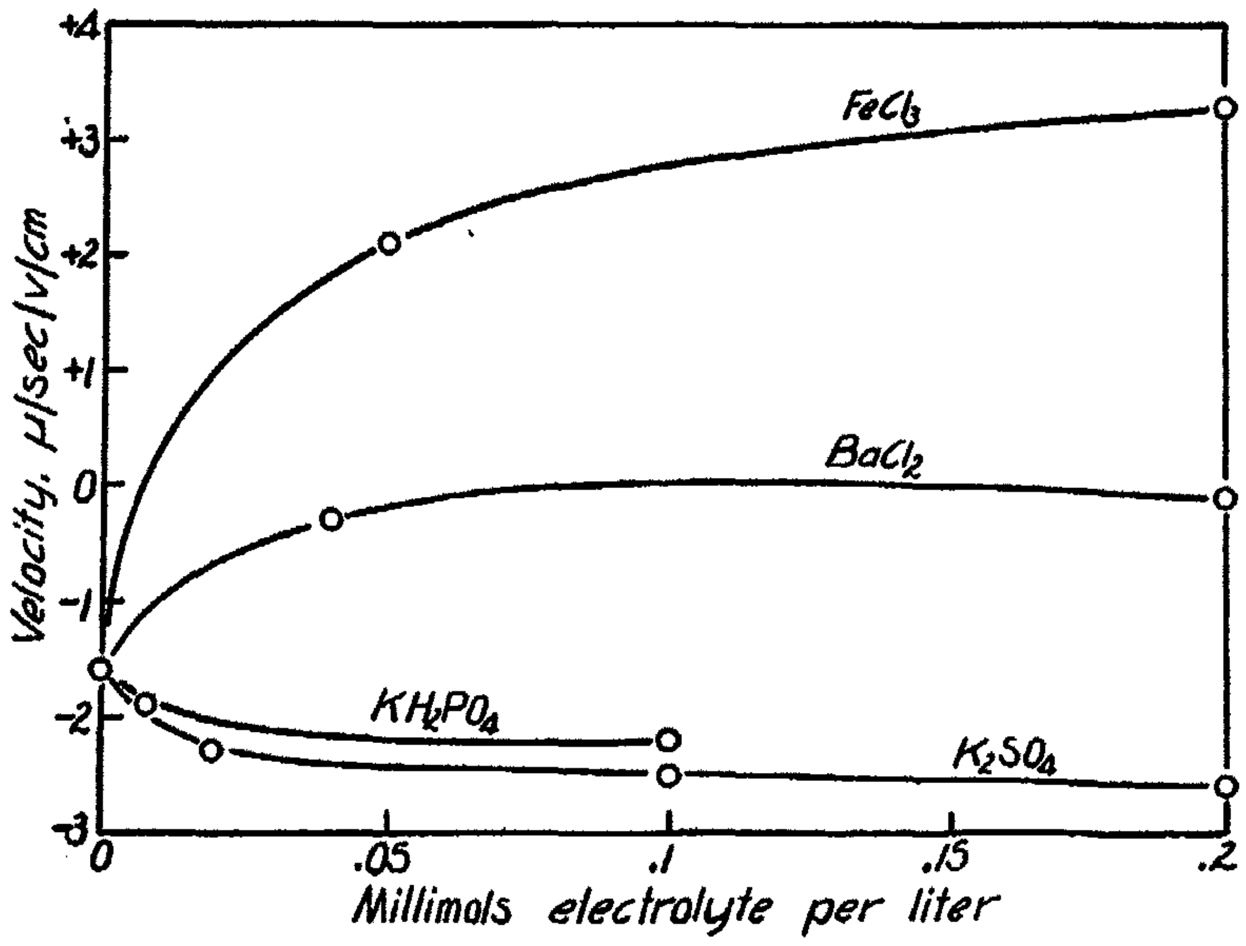


FIG. 6. MANGANESE DIOXIDE-IRON OXIDE MIXTURE
100 cc. MnO_2; 1.5 cc. Fe_2O_3; 98.5 cc. H_2O

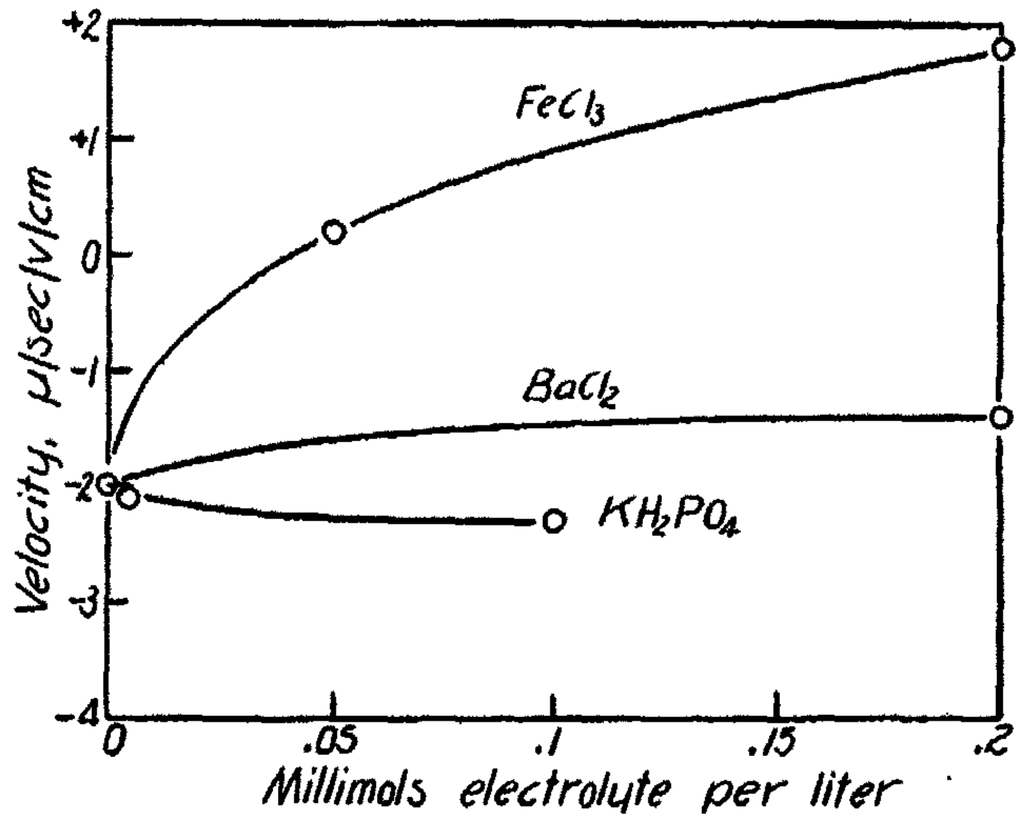


Fig. 7. Arsenic Trisulfide-Iron Oxide Mixture I
25 cc. Fe_2O_3; 10 cc. As_2S_3; 15 cc. H_2O

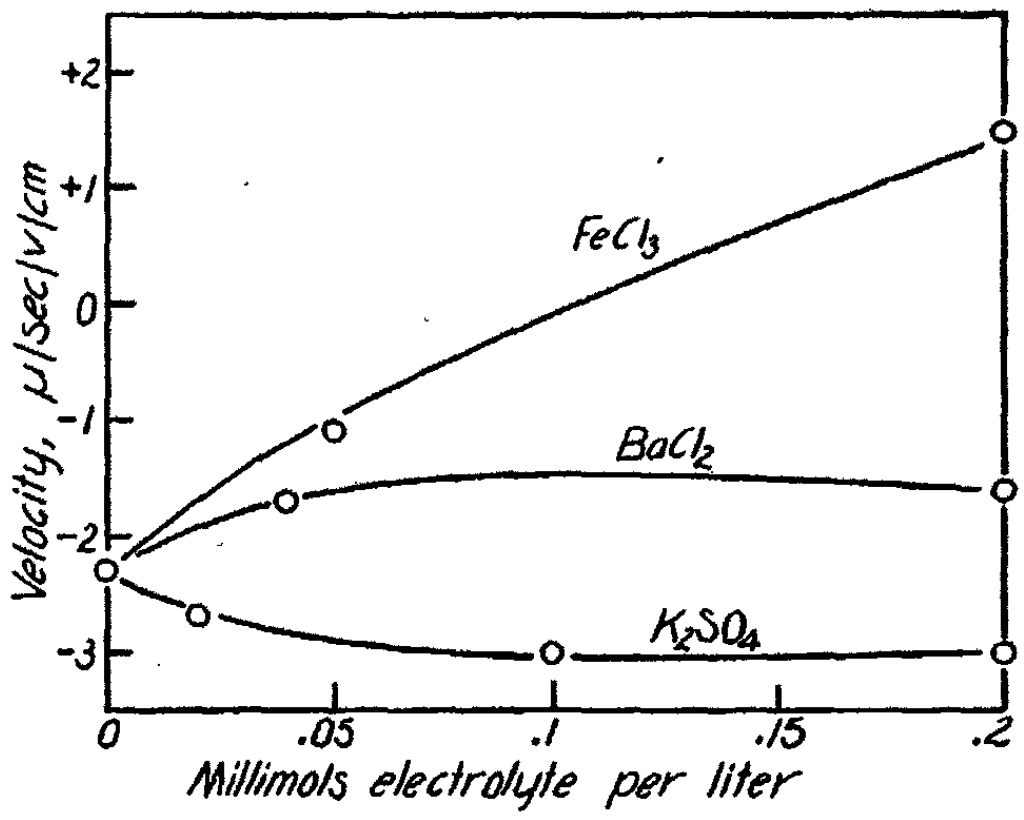


Fig. 8. Arsenic Trisulfide-Iron Oxide Mixture II
25 cc. Fe_2O_3; 12.5 cc. As_2S_3; 12.5 cc. H_2O

TABLE 1

MILLIMOLS $BaCl_2$ PER LITER	TIME IN SECONDS		VELOCITY μ/SEC./V./CM.	
	Al_2O_3	Mixture*	Al_2O_3	Mixture*
0	6.7	10.0	+3.6	+2.5
0.2	6.5	7.9	+3.9	+3.1
1.0	7.2	6.8	+3.5	+3.7

* The mixture is the same as that referred to in figure 1, i.e., 25 cc. Al_2O_3, 10 cc. MnO_2, 15 cc. H_2O.

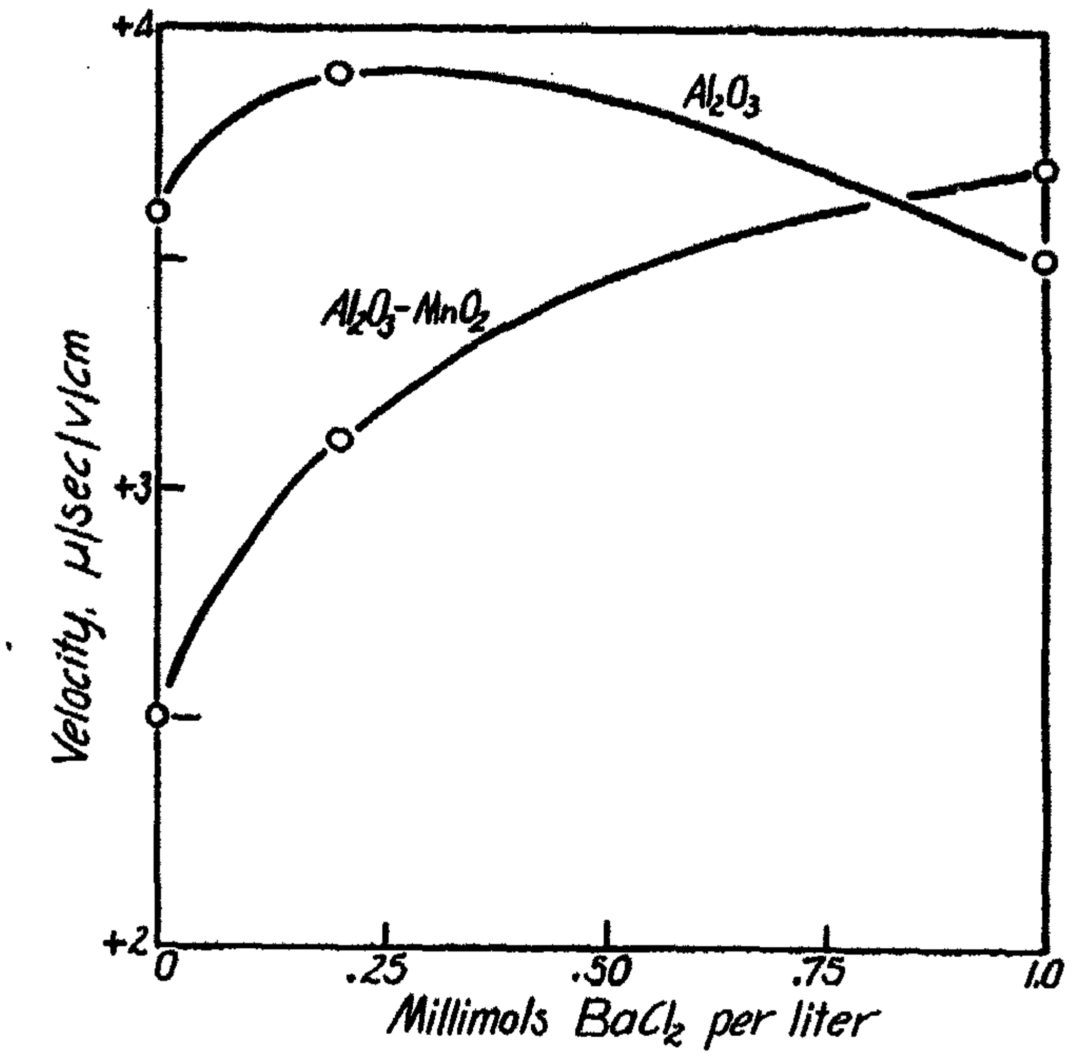


FIG. 9

DISCUSSION

In approaching the subject of mutual coagulation with the purpose of formulating a general theory for its mechanism, we are faced with the fact that in at least two ways a mixture of oppositely-charged colloids behaves like a simple system and in at least one way it is different. The flocculation of a mixed system occurs in the same manner and apparently for the same reasons as that of a "pure" sol. Also, the particles in a mixed system under the influence of an electric field migrate in the same direction and with the same velocity.[1] The deviation from the behavior of a simple, unmixed system is apparent from a consideration of table 1 and figure 9. That is, the charging effect observed when the added ion is of high adsorbability and the same sign does not fall off at moderately high concentrations.

When two oppositely-charged sols are mixed the stability of the system as a whole is lessened in some manner and an agglomeration of particles may or may not take place. Leaving aside for a moment the manner in which the stability is lowered, let us consider the probable nature of the particles in the mixture. If an aggregation does not take place and there are present only single particles of two different chemical substances, one would expect to find two different sets of velocity values in any given system, for the simple reason that in a competition for the excess ions which give the mixture a net positive or negative charge, the adsorbing powers of the substances are not the same.

The environment in which mutual coagulation takes place has been found to be well adapted to a mutual adsorption of the two colloids (14). If adsorption of the oppositely-charged particles does take place, then some clue to the arrangement of the charges around the aggregates might be afforded by the behavior of the mixed system toward electrolytes. An aggregation to compound particles with the excess charges remaining after neutralization distributed uniformly around the aggregates would account for the fact that the particles in a mixed system migrate as single particles, i.e., in the same direction with uniform velocity. Moreover, the effect of electrolytes on the mobility of particles in a mixed system resembles the behavior of systems containing single particles under the same conditions, i.e., the mobility of particles in mixed systems is decreased by addition of ions of opposite sign to the mixture and enhanced by addition of ions of the same sign. However, a simple aggregation with uniform distribution of charges would not account for the fact that the charging effect does not fall off when the antagonistic ion is present in higher concentrations.

From the shape of the curves in figures 1 to 8 it appears as if the increased stabilities of the mixtures were due to a discharge of the colloid of opposite sign present in the system. This may be a consequence of an unequal distribution of charges on the aggregate so that, for example, the arsenic trisulfide particles in a positive aluminum oxide–arsenic trisulfide mixture are still able to adsorb strongly a given cation. The phenomenon appears analogous to the ionic antagonism observed by several investigators (15), but a simple antagonistic effect presumably due to a regular preferential adsorption of an ion by the whole particle would not account for the continued increase in stability at higher electrolyte concentrations. If the

---

[1] Although this statement is true for all of the mixed systems reported and also in an overwhelming number of other cases, the authors have encountered systems possessing two different mean velocity values.

adsorption is unequal for the two parts of the double particle, then one would expect the mixtures containing a small amount of one sol to show the charging effect only to a limited degree. That this is borne out is apparent from figures 3 to 6. The concept of an unequal charge distribution making the double particle, in some instances, effectively a distorted dipole with possibly a strong electrostatic attraction holding the component parts together seems to afford the best explanation of the data presented in this paper. An experimental verification or disproof might be furnished by a measurement of the dipole moment of a particle of this type. Under a very high potential gradient it might also be possible, in some cases, to split apart the double particles.

The manner in which the stability of the system as a whole is lowered will now be considered. Thomas (16) considers that mutual coagulation is a result of chemical interaction between the ions stabilizing the oppositely-charged sols. As the amount of added sol is increased the stabilizing ion of the added colloid presumably reacts with an equivalent amount of the ion stabilizing the oppositely-charged sol, forming a definite amount of a slightly-ionized compound. Presumably also, there then occurs a redistribution of the excess charges so that the stability of the system is lowered uniformly. At the isoelectric point the two stabilizing ions are in exact chemical equivalence and there are no excess charges. Thus it follows that if one adds the stabilizing ion of a given positive colloid through the medium of an electrolyte, he should reach the isoelectric point of a given negative colloid at the same ionic concentration as in mutual coagulation. The above deduction assumes that all the added ions are effective in causing coagulation. If this is not true, then the ion concentration should be greater in the latter case than in the mutual coagulation process. This premise has been experimentally tested in mixtures of positive and negative ferric oxide sols.

From the migration velocities of positive iron oxide–potassium ferrocyanide mixtures (17) the amount of electrolyte present at the isoelectric point of a given positive sol may be calculated. Then, if a negative ferric oxide sol containing a known amount of potassium ferrocyanide per liter is added to the same positive sol, the electrolyte concentration in the isoelectric mixture may again be determined. A comparison of the two amounts, according to Thomas' theory, should reveal the former to be at least as large as the latter.

The results of the above procedure are given in table 2 for three different positive sols. In this case a mechanism solely dependent on a chemical reaction between the peptizing ions seems improbable. Also, in accounting for the variations in stability of certain mixtures, e.g., arsenic trisulfide–antimony trisulfide (18) and arsenic trisulfide–gamboge (19) on the basis of chemical reactions between the stabilizing ions, one is led to rather implausible speculations.

Various investigators (20) have demonstrated the fact that there exist inversions in orders of effectiveness for a given group of sols with several oppositely-charged sols. On the face of it one would be tempted to conclude that such being the case a unique explanation of mutual coagulation on the basis of electrical neutralization is impossible. That this does not necessarily follow even in the improbable case where no aggregation of particles is assumed, may be readily seen from the following considerations.

If a positive sol composed of n_1 particles, each carrying a charge of q_1 units, be mixed with a negative sol composed of n_2 particles each carrying a charge of q_2 units, the mixed system will contain n_3 particles each bearing a charge of q_3 units and the sign of the mixed colloid will be determined by the relation $n_3q_3 = n_1q_1 + n_2q_2$ (assuming a mere ionic neutralization). In the simplest case $n_3 = n_1 + n_2$. Since the product, n_3q_3, is not measured but is only some function of the charge, q_3, it is necessary to divide through by $n_1 + n_2$. This fact, of itself, may produce inversions in a series for suitable values of n_1q_1 and n_2q_2. When adsorption of the colloid particles takes place, $n_3 \neq n_1 + n_2$ and the inversions will be further complicated.

TABLE 2

Comparison of potassium ferrocyanide concentrations at the isoelectric point

POSITIVE SOL	MILLIMOLS $K_4Fe(CN)_6$ PER LITER	
	Electrolyte	Negative sol
1	0.0008	0.0025
2	0.0022	0.0075
3	0.0033	0.0048

The variations in order of effectiveness of positive sols in decreasing the stability of negative sols observed in the first paper of this series should be scrutinized rigidly with a view of ascertaining whether they are the same as the variations in effectiveness of the stabilizing ions. The stabilizing ions of the positive sols, iron oxide, aluminum oxide, chromium oxide, arsenic trisulfide, may be considered to be H^+ in each case, together with Fe^{+++}, Al^{+++}, and Cr^{+++} for the respective hydrous oxides, and Th^{++++} for arsenic trisulfide. The orders of the above positive sols with negative stannic oxide, manganese dioxide, arsenic trisulfide, and iron oxide have been found (13) to be:

Negative sol	*Order of positive sols*
SnO_2	$Al_2O_3 > As_2S_3 > Cr_2O_3 > Fe_2O_3$
MnO_2	$Cr_2O_3 > Al_2O_3 > As_2S_3 > Fe_2O_3$
As_2S_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$
Fe_2O_3	$As_2S_3 > Cr_2O_3 > Al_2O_3 > Fe_2O_3$

whereas the order of the stabilizing ions with the negative sols has been found to be:

Negative sol	*Order of stabilizing ions*
SnO_2	Al, Th > Cr > Fe
MnO_2	Th > Cr, Fe > Al
As_2S_3	Th > Cr > Fe > Al
Fe_2O_3	Th > Cr > Al > Fe

From a comparison of these lyotropic effects it will be seen that there is no direct parallel between the relative effectiveness of the various positive sols and that of their stabilizing ions with the negative sols. Thus, a simple preferential adsorption of the stabilizing ions does not appear to be the effective mechanism in the systems reported in this study.

Boutaric and Perreau (21) in the system positive iron oxide–negative iron oxide have obtained results supporting a simple selective adsorption of the phosphate ion which was stabilizing the negative sol. They found that the amount of phosphate ion per milligram of iron oxide necessary to flocculate the positive sol was the same whether the ion was furnished by an electrolyte or by the negative sol, when the dilution of the system was taken into account. It was believed of interest to perform a similar experiment keeping the amount of ferric oxide the same in each mixture of positive and negative sol and using the ferrocyanide ion (to which iron oxide is more sensitive than to the phosphate ion) as the stabilizing ion of the negative sol. When this was done it was found that the positive sol was isoelectric at a concentration of 0.0022 millimol per liter of potassium ferrocyanide. When the ion was furnished by the negative ferric oxide sol the same amount of ferric oxide was isoelectric at a concentration of 0.0040 millimol per liter. A simple selective adsorption does not explain these results.

The case when a stabilizing ion is in excess need not be considered here since the sols were relatively pure. However, the presence of free electrolyte would obviously render a sol more effective as a precipitating agent and further complicate the mechanism of adsorption.

SUMMARY

1. Data have been presented to show the influence of electrolytes upon the migration velocities of mixtures of positive and negative colloids.

2. The mechanism of the mutual coagulation process has been deduced to be a lowering in stability of the system caused by mutual adsorption of the two colloids with a consequent unequal redistribution of the total charges around the aggregate.

3. A mechanism solely dependent upon chemical reactions between the stabilizing ions or a simple preferential adsorption of one of these ions has been shown to be improbable in the general case.

REFERENCES

(1) Graham: J. Chem. Soc. **15**, 246 (1862).
(2) Linder and Picton: J. Chem. Soc. **71**, 568 (1897).
(3) Lottermoser: Anorganische Kolloide, page 76. Stuttgart (1901).
Neisser and Friedmann: Münch. med. Wochenschr. **51**, 465, 827 (1903-4).
Henri and others: Compt. rend. soc. biol. **55**, 1666 (1903).
Bechhold: Z. physik. Chem. **48**, 385 (1904).
(4) Biltz: Ber. **37**, 1095 (1904).
(5) Lottermoser: Kolloid-Z. **6**, 78 (1910).
(6) Freundlich and Natansohn: Kolloid-Z. **28**, 258 (1920).
(7) Thomas and Johnston: J. Am. Chem. Soc. **45**, 2532 (1923).
(8) Wintgen and Löwenthal: Z. physik. Chem. **109**, 391 (1924).
(9) Freundlich: Kapillarchemie, Vol. II, p. 208. Akademische Verlagsgesellschaft, M. B. H. Leipzig (1932).
(10) Thomas: in Bogue's Colloidal Behavior, Vol. I, pp. 325–6. McGraw-Hill Book Company, New York (1924).
(11) Bancroft: J. Phys. Chem. **19**, 363 (1915).
(12) Weiser and Chapman: J. Phys. Chem. **35**, 543 (1931).
(13) Hazel and McQueen: J. Phys. Chem. **37**, 553 (1933).
(14) Raehlmann: Pflüger's Archiv. ges. Physiol. **112**, 128 (1906).
Bechhold: Z. physik. Chem. **60**, 299 (1907).
Bancroft: Applied Colloid Chemistry, p. 306 et seq. McGraw-Hill Book Company, New York (1926).
(15) Freundlich and Scholz: Kolloidchem. Beihefte **16**, 267 (1922).
(16) Bogue: Colloidal Behavior, Vol. I, p. 329 et seq. McGraw-Hill Book Company, New York (1924).
(17) Hazel and Ayres: J. Phys. Chem. **35**, 2930 (1931).
(18) Jablczynski and Lorentz-Zienkowska: Bull. soc. chim. **37**, 612 (1925).
(19) Boutaric and Dupin: Bull. soc. chim. **43**, 1059 (1928).
(20) Bancroft: J. Phys. Chem. **19**, 363 (1915).
Weiser and Chapman: J. Phys. Chem. **35**, 543 (1931).
Hazel and McQueen: J. Phys. Chem. **37**, 553 (1933).
(21) Boutaric and Perreau: J. chim. phys. **27**, 250 (1930).

REFRACTIVITIES OF LIQUID COMPOUNDS OF PHOSPHORUS

WILLIAM J. JONES, WALTER CULE DAVIES, AND W. J. CECIL DYKE
Tatem Laboratories, University College, Cathays Park, Cardiff, Great Britain

Received September 16, 1932

The number of compounds of phosphorus hitherto examined refractometrically is small, the only investigator of an homologous series of such substances being Kowalewski (1). The present work has been undertaken with a view to extension of our knowledge in this field, particularly with respect to types of compounds and their number.

The first to determine the atomic refractivity of phosphorus was Haagen (2), who from measurements on phosphorus trichloride with C light, deduced the value 14.93, in terms of the Gladstone-Dale (3) formula. For the Fraunhofer lines A and H, Gladstone (4) gave the values 18.3 and 21.3, respectively, for the atomic refractivity of fused phosphorus. Zecchini (5) calculated the atomic refractivity of phosphorus in terms both of the Gladstone-Dale and of the Lorenz-Lorentz (6) formulas in eight of its liquid compounds. He found that the value of the Lorenz-Lorentz atomic refractivity of phosphorus for D light was 4.17 in triethyl phosphate and 4.97 in phosphorus oxychloride, whilst for trivalent phosphorus the value varied from 9.47 for triethylphosphine to 9.72 for phosphorus tribromide, including the value 8.10 for ethoxydichlorophosphine. Zecchini's results with solutions of phosphorus compounds are here left out of consideration, and so also his data for triethyl phosphite, on which doubt has been cast by Arbusow and Ivanow (7). Kowalewski, from his measurements on the alkoxydichlorophosphine series, obtained values varying from 7.60 to 8.22. The values derived from the measurements of Arbusow and Ivanow and of Arbusow and Arbusow (8) on the esters of the oxy-acids of phosphorus are given and discussed in the sequel. Johnson (9) has recently measured the refractive indices of three derivatives of methylphenylphosphinic acid for D light; in his paper, without acknowledgment, he uses results experimentally obtained and refractivities calculated by workers in this field, including those due to Kowalewski, Emmett and Jones (10), Grüttner and Wiernik (11), Grüttner and Krause (12), and Jackson, Davies, and Jones (13).

In the present work the refractive indices were measured with Pulfrich refractometers made by Wolz of Bonn and by Zeiss of Jena, with an Abbé refractometer by Hilger of London and a hollow-prism refractometer (14)

TABLE 1

Molecular refractivities of compounds of phosphorus

NO.	SUBSTANCE	TEMPERATURE $t°$	DENSITY $d_{4°}^{t°}$	REFRACTIVE INDEX			MOLECULAR REFRACTIVITIES						REFERENCES
				$n_F^{t°}$	$n_D^{t°}$	$n_C^{t°}$	$[R_G]_F$	$[R_G]_D$	$[R_G]_C$	$[R_L]_F$	$[R_L]_D$	$[R_L]_C$	
1	P	44	1.7528	2.1131	—	2.0501	19.70	—	18.58	9.49	—	9.14	D (20)
2		55.3	1.7133	2.0994	—	2.0375	19.90	—	18.78	9.63	—	9.28	D (20)
3	P_2O_3	27.4	1.9317	1.5518	1.5403	1.5358	31.43	30.78	30.52	18.20	17.88	17.76	T. T. (21)
4	PCl_3	14	1.598	1.525	1.516	—	45.13	44.36	—	26.35	25.97	—	M (22)
5		15.4	1.598	1.533	—	1.520	45.82	—	44.70	26.68	—	26.14	N. C. (23)
6		20	1.5774	1.5231	—	1.5083	45.57	—	44.28	26.61	—	25.98	H (2)
7		21	1.5696	1.5235	1.5122	1.5087	45.83	44.84	44.53	26.77	26.28	26.13	J. D. D. (24)
8	$POCl_3$	17	1.68	1.497	1.488	—	45.37	44.55	—	26.72	26.30	—	G. D. (3)
9		25.1	1.666	—	1.460	—	—	42.35	—	—	25.22	—	Z (5)
10		22	1.6619	1.4636	1.4572	1.4544	42.79	42.20	41.94	25.45	25.15	25.02	J. D. D. (24)
11	$PSCl_3$	11.1	1.654	1.575	—	1.563	58.91	—	57.68	33.85	—	33.27	N. C. (23)
12	PBr_3	25	2.88	1.708	1.687	—	66.57	64.59	—	36.66	35.81	—	G. D. (3)
13		26.6	2.859	—	1.697	—	—	66.01	—	—	36.48	—	Z (5)
14		20	2.8761	1.7176	1.6935	1.6864	67.56	65.29	64.62	37.09	36.13	35.84	J. D. D. (24)
15	$P(C_2H_5)_3$	18.6	0.8001	—	1.4580	—	—	67.63	—	—	40.29	—	Z (5)
16	$P(n\text{-}C_3H_7)_3$	25	0.8073	1.4635	1.4560	1.4529	91.97	90.49	89.88	54.70	53.94	53.62	J. D. D. (24)
17	$P(n\text{-}C_4H_9)_3$	25	0.8120	1.4638	1.4570	1.4542	115.52	113.82	113.12	68.70	67.83	67.47	J. D. D. (24)
18	$P(n\text{-}C_5H_{11})_3$	25	0.8206	1.4673	1.4606	1.4578	139.18	137.18	136.35	82.69	81.67	81.24	J. D. D. (24)
19	$P(C_6H_5)(n\text{-}C_3H_7)_2$	25	0.9251	1.5401	1.5283	1.5234	113.36	110.89	109.86	65.86	64.66	64.16	J. D. D. (24)
20	$P(C_6H_5)(n\text{-}C_4H_9)_2$	25	0.9116	1.5326	1.5212	1.5165	129.82	127.04	125.90	75.60	74.24	73.68	J. D. D. (24)
21	$P(C_6H_5)[CH_2 \cdot CH(CH_3) \cdot CH_2]_2$	25	0.9096	1.5289	1.5180	1.5135	129.13	126.47	125.37	75.29	73.98	73.44	J. D. D. (24)
22	$P(C_6H_5)(n\text{-}C_5H_{11})_2$	25	0.9021	1.5251	1.5148	1.5105	145.66	143.81	141.61	85.02	83.62	83.03	J. D. D. (24)
23	$P(C_6H_5)[CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2]_2$	25	0.9061	1.5259	1.5153	1.5109	145.24	142.32	141.10	84.76	83.32	82.72	J. D. D. (24)
24	$P(C_6H_5)[CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2]_2$	25	0.8996	1.5235	1.5129	1.5085	145.54	142.59	141.37	85.00	83.55	82.98	J. D. D. (24)
25	$P(C_6H_5)(n\text{-}C_6H_{13})_2$	20	0.9006	1.5207	1.5110	1.5067	160.89	157.89	156.56	94.04	92.56	91.90	J. D. D. (24)

26	$P(C_6H_5)(n\text{-}C_7H_{15})_2$	20	0.8946	1.5168	1.5073	1.5033	176.95	173.69	172.32	103.55	101.94	101.26	J. D. D. (24)
27	$P(C_6H_5)(n\text{-}C_8H_{17})_2$	20	0.8899	1.5129	1.5036	1.5000	192.71	189.22	187.86	112.91	111.18	110.51	J. D. D. (24)
28	$P(p\text{-}CH_3\cdot C_6H_4)(n\text{-}C_3H_7)_2$	25	0.9210	1.5390	1.5272	1.5224	121.84	119.17	118.08	70.81	69.52	68.99	J. D. D. (24)
29	$P(p\text{-}CH_3\cdot C_6H_4)(n\text{-}C_4H_9)_2$	25	0.9077	1.5325	1.5214	1.5168	138.58	135.69	134.49	80.70	79.29	78.70	J. D. D. (24)
30	$P(p\text{-}CH_3\cdot C_6H_4)(n\text{-}C_5H_{11})_2$	25	0.8981	1.5249	1.5144	1.5101	154.44	151.35	150.09	90.16	88.64	88.01	J. D. D. (24)
31	$P(p\text{-}CH_3\cdot C_6H_4)[CH_3\cdot CH_2\cdot CH(CH_3)\cdot CH_2]_2$	25	0.9022	1.5249	1.5145	1.5102	153.76	150.71	149.45	89.75	88.26	87.64	J. D. D. (24)
32	$P(p\text{-}CH_3\cdot C_6H_4)[CH_3\cdot CH(CH_3)\cdot CH_2\cdot CH_2]_2$	25	0.8941	1.5232	1.5127	1.5084	154.63	151.53	150.26	90.31	88.79	88.16	J. D. D. (24)
33	$P(p\text{-}CH_3\cdot C_6H_4)[CH_3\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CH_2]_2$	25	0.8882	1.5137	1.5041	1.5001	169.06	165.90	164.59	99.03	97.46	96.81	J. D. D. (24)
34	$P(p\text{-}CH_3\cdot CH_2C_6H_4)(n\text{-}C_3H_7)_2$	25	0.9147	1.5370	1.5255	1.5208	130.45	127.65	126.51	75.87	74.51	73.95	J. D. D. (24)
35	$P(p\text{-}CH_3\cdot CH_2C_6H_4)(n\text{-}C_4H_9)_2$	25	0.9042	1.5319	1.5208	1.5162	147.20	144.13	142.86	85.75	84.24	83.62	J. D. D. (24)
36	$[2,5\text{-}(CH_3)_2C_6H_3]\cdot P(C_2H_5)_2$	25	0.9393	1.5533	1.5405	1.5355	114.42	111.77	110.74	66.21	64.94	64.43	J. D. D. (24)
37	$[2,5\text{-}(CH_3)_2C_6H_3]\cdot P(n\text{-}C_3H_7)_2$	25	0.9282	1.5430	1.5313	1.5266	130.04	127.24	126.11	75.49	74.13	73.58	J. D. D. (24)
38	$[2,5\text{-}(CH_3)_2C_6H_3]\cdot P(n\text{-}C_4H_9)_2$	25	0.9125	1.5335	1.5229	1.5182	146.36	143.45	142.16	85.21	83.79	83.16	J. D. D. (24)
39	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_3H_7)_2$	25	0.9738	1.5477	1.5352	1.5301	126.09	123.21	122.04	73.09	71.70	71.13	J. D. D. (24)
40	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_4H_9)_2$	25	0.9600	1.5389	1.5274	1.5226	141.58	138.56	137.30	82.29	80.82	80.21	J. D. D. (24)
41	$(p\text{-}CH_3O\cdot C_6H_4)\cdot P(n\text{-}C_5H_{11})_2$	25	0.9382	1.5289	1.5178	1.5132	157.99	154.67	153.30	92.11	90.49	89.81	J. D. D. (24)
42	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(CH_3)_2$	20	1.1037	1.6243	1.6074	1.6005	130.18	126.65	125.21	73.65	72.05	71.38	J. D. D. (24)
43	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(C_2H_5)_2$	20	1.0711	1.6079	1.5918	—	146.52	142.64	—	83.34	81.54	—	J. D. D. (24)
44	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(n\text{-}C_3H_7)_2$	20	1.0562	1.5993	1.5838	1.5774	162.40	158.19	156.46	92.61	90.66	89.85	J. D. D. (24)
45	$(p\text{-}C_6H_5O\cdot C_6H_4)\cdot P(n\text{-}C_4H_9)_2$	20	1.0310	1.5847	1.5705	1.5647	178.21	173.88	172.11	102.10	100.07	99.23	J. D. D. (24)
46	$(CH_2)_4{>}P\cdot C_6H_5$	22.5	1.0335	—	1.5894	—	—	93.60	—	—	53.55	—	G. K. (12)
47	$(CH_2)_5{>}P\cdot C_6H_5$	20	1.0317	—	1.5886	—	—	101.63	—	—	58.16	—	G. W. (11)
48	$(CH_2)_5{>}P\cdot C_6H_4\cdot CH_3\text{-}p$	22.2	0.9991	—	1.5729	—	—	110.14	—	—	63.37	—	G. W. (11)
49	$C_6H_5PCl_2$	5.8	1.3369	—	1.6050	1.5984	—	80.99	80.11	—	46.61	45.70	Z (5)
50		7	1.3351	—	1.6053	1.5987	—	81.15	80.26	—	46.19	45.78	Z (5)
51	$(p\text{-}CH_3\cdot CH_2\cdot C_6H_4)PCl_2$	25	1.2250	1.5930	1.5775	1.5711	100.21	97.59	96.51	57.26	56.04	55.53	J. D. D. (24)
52	$[2,5\text{-}(CH_3)_2C_6H_3]PCl_2$	25	1.2371	1.6016	1.5857	1.5791	100.66	98.00	96.90	57.37	56.14	55.62	J. D. D. (24)
53	$(p\text{-}CH_3O\cdot C_6H_4)PCl_2$	25	1.3303	1.6184	1.6000	1.5924	97.15	94.26	93.07	55.07	53.75	53.19	J. D. D. (24)
54	CH_3OPCl_2	20	1.3980	—	1.4773	—	—	45.39	—	—	26.89	—	K (1)
55	$C_2H_5OPCl_2$	20	1.2857	—	1.4718	—	—	53.93	—	—	32.00	—	K (1)
56		24.5	1.2718	—	1.4641	1.4609	—	53.63	53.26	—	31.90	31.70	Z (5)
57	$n\text{-}C_3H_7OPCl_2$	20	1.2278	—	1.4660	—	—	61.11	—	—	36.3[illegible]	—	K (1)

TABLE 1—*Concluded*

NO.	SUBSTANCE	TEMPERATURE $t°$	DENSITY $d_{4°}^{t°}$	REFRACTIVE INDEX $n_F^{t°}$	$n_D^{t°}$	$n_C^{t°}$	MOLECULAR REFRACTIVITIES $[R_G]_F$	$[R_G]_D$	$[R_G]_C$	$[R_L]_F$	$[R_L]_D$	$[R_L]_C$	REFERENCES
58	n-$C_4H_9OPCl_2$	20	1.1657	—	1.4608	—	—	69.19	—	—	41.18	—	K (1)
59	$(C_2H_5 \cdot O)_2PCl$	20	1.0746	—	1.4350	—	—	63.38	—	—	38.02	—	A. A. (8)
60	$OPH(OC_2H_5)_2$	20	1.0757	1.4130	1.4082	1.4062	53.03	52.41	52.16	32.02	31.69	31.55	A. I. (7)
61		20	1.0734	—	1.4082	—	—	52.52	—	—	31.76	—	A. A. (8)
62		20	1.0720	1.4151	1.4101	1.4081	53.48	52.83	52.58	32.27	31.93	31.79	J. D. D. (24)
63	$P(OC_2H_5)_3$	20	0.9687	1.4192	1.4131	1.4107	71.89	70.85	70.45	43.33	42.78	42.56	A. I. (7)
64		20	0.9574	—	1.4132	—	—	71.70	—	—	43.29	—	A. A. (8)
65		20	0.9629	1.4186	1.4127	1.4098	72.23	71.21	70.71	43.54	43.00	42.73	J. D. D. (24)
66	$[CH_3 \cdot CH(CH_3) \cdot CH_2O]_3P$	25	0.8969	1.4283	1.4225	1.4201	119.49	117.88	117.21	71.80	70.97	70.62	J. D. D. (24)
67	$(n$-$C_5H_{11} \cdot O)_3P$	25	0.9023	1.4412	1.4353	1.4329	142.92	141.01	140.23	85.57	84.57	84.17	J. D. D. (24)
68	$OP(C_2H_5)(OC_2H_5)_2$	20	1.0259	1.4211	1.4163	1.4143	68.20	67.42	67.11	41.07	40.66	40.50	A. I. (7)
69	$(C_2H_5 \cdot O)_4P_2O_2$	20	1.1268	—	1.4284	—	—	104.25	—	—	62.66	—	A. A. (8)
70	$(C_2H_5 \cdot O)_4P_2O_3$	20	1.1846	—	1.4222	—	—	103.43	—	—	62.28	—	A. A. (8)
71	$(C_2H_5 \cdot O)_4P_2O_2S$	20	1.1885	—	1.4508	—	—	116.16	—	—	69.35	—	A. A. (8)
72	$(C_2H_5 \cdot O)_2PO \cdot O \cdot PO(O \cdot C_2H_5)(C_2H_5)$	20	1.1526	—	1.4280	—	—	101.82	—	—	61.21	—	A. A. (8)
73	$(CH_3 \cdot O)_3PO$	25	1.2052	1.3990	1.3950	1.3934	46.38	45.91	45.73	28.12	27.87	27.77	J. D. D. (24)
74	$(C_2H_5 \cdot O)_3PO$	5.7	1.0822	—	1.4107	—	—	69.11	—	—	41.76	—	Z (5)
75		17.1	1.0701	—	1.4067	—	—	69.23	—	—	41.89	—	Z (5)
76		20	1.0682	1.4107	1.4062	1.4044	70.04	69.26	68.95	42.31	41.90	41.73	A. I. (7)
77		28.1	1.0618	—	1.4027	—	—	69.07	—	—	41.83	—	Z (5)
78		25	1.0637	1.4082	1.4039	1.4021	69.90	69.16	68.85	42.26	41.87	41.70	J. D. D. (24)
79	$(n$-$C_3H_7 \cdot O)_3PO$	25	1.0023	1.4182	1.4136	1.4118	93.54	92.51	92.11	56.39	55.85	55.63	J. D. D. (24)
80	$(n$-$C_4H_9 \cdot O)_3PO$	25	0.9727	1.4274	1.4224	1.4203	116.99	115.62	115.05	70.33	69.61	69.31	J. D. D. (24)
81	$[CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot O]_3PO$	25	0.9617	1.4222	1.4173	1.4152	116.89	115.53	114.95	70.38	69.66	69.36	J. D. D. (24)
82	$(n$-$C_5H_{11} \cdot O)_3PO$	25	0.9497	1.4332	1.4283	1.4262	140.62	139.03	138.35	84.40	83.56	83.21	J. D. D. (24)
83	$SP(OCH_3)_3$	10.5	1.2112	—	1.4583	1.4552	—	59.08	58.69	—	35.20	34.99	E. J. (10)
84	$CH_3SPO(OCH_3)_2$	10	1.2565	—	1.4683	1.4660	—	58.24	57.91	—	34.59	34.42	E. J. (10)

by Bellingham and Stanley of London. The last named instrument was used for acid halides. These refractometers were frequently standardized by the use of water and of benzene. Where refractive indices were measured at temperatures other than the standard temperature of the instrument, the necessary corrections were applied. To ensure constancy of temperature a stream of water, electrically warmed by means of a Bowden (15) pre-heater, was passed through the Pulfrich and Abbé refractometers during the measurements.

The compounds of phosphorus used in this investigation were prepared by methods (16) already described and were redistilled under low pressure immediately before the measurements of density and of refractive index were made. In every case the constant-boiling, middle fraction was chosen. Temperatures were corrected for thermometric errors and densities for air-buoyancy. In view of the ease of oxidation of many of these compounds, due precautions were observed to prevent protracted contact with air.

In table 1 are given densities, d; refractive indices, n, for the F, D, and C lines; molecular refractivities, $[R_G]$, calculated by means of the Gladstone-Dale expression, $(n-1)M/d$; molecular refractivities, $[R_L]$, calculated with the Lorenz-Lorentz formula, $(n^2-1)M/(n^2 + 2)d$; and references. The molecular weights, M, have been calculated on the basis of the international atomic weights (17) for 1932. From this table are excluded all refractive indices for the G′ hydrogen line, for the green lithium line, and for the red cadmium line, the refractive index of phosphine determined by Bleekrode (18), which has been criticized by Brühl (19), that of triethyl phosphite by Zecchini (5), whose preparation had suffered oxidation, and that of isoamyloxydichlorophosphine measured by Kowalewski (1).

Table 2 contains the values of the atomic refractivity of phosphorus and of the group refractivities of certain of its radicals in terms of both the Gladstone-Dale and the Lorenz-Lorentz expressions.

The refractivities given in table 2 have been found by deducting Eisenlohr's (24) values of the refractivities of carbon, hydrogen, ether oxygen, chlorine, and bromine from the Lorenz-Lorentz molecular refractivities given in table 1. That for ether oxygen has been used only when oxygen is present in the group $\equiv C—O—C\equiv$. The Gladstone-Dale values employed are given in table 3.

Analysis of tables 1 and 2 reveals the following facts.

(a) In the case of the trialkylphosphines, deduction of Eisenlohr's refractivities of carbon and hydrogen for D light from the molecular refractivities leaves a constant remainder of mean value, 9.14; this would seem to indicate that Eisenlohr's values for carbon and hydrogen hold in the case of these phosphines, and that in them the atomic refractivity of phosphorus for D light is 9.14. The corresponding Gladstone-Dale constant is 14.23.

TABLE 2

Atomic and group refractivities

NO.	SUBSTANCE	ATOM OR GROUP	GLADSTONE-DALE F	GLADSTONE-DALE D	GLADSTONE-DALE C	LORENZ-LORENTZ F	LORENZ-LORENTZ D	LORENZ-LORENTZ C
1	P	P	19.70	—	18.58	9.49	—	9.14
2		P	19.90	—	18.78	9.63	—	9.28
3	P_2O_3	P_2O_3	31.43	30.78	30.52	18.20	17.88	17.76
4	PCl_3	P	13.84	13.46	—	8.22	8.07	—
5		P	14.53	—	13.98	8.55	—	8.34
6		P	14.28	—	13.56	8.48	—	8.18
7		P	14.54	13.94	13.81	8.64	8.38	8.33
8	$POCl_3$	PO	14.08	13.65	—	8.59	8.40	—
9		PO	—	11.45	—	—	7.32	—
10		PO	11.50	11.30	11.22	7.32	7.25	7.22
11	$PSCl_3$	PS	27.62	—	26.96	15.72	—	15.47
12	PBr_3	P	17.85	16.59	—	9.66	9.21	—
13		P	—	18.01	—	—	9.88	—
14		P	18.84	17.29	16.95	10.09	9.53	9.43
15	$P(C_2H_5)_3$	P	—	14.91	—	—	9.28	—
16	$P(n\text{-}C_3H_7)_3$	P	14.87	14.22	13.96	9.34	9.08	8.97
17	$P(n\text{-}C_4H_9)_3$	P	14.61	14.00	13.76	9.34	9.11	9.03
18	$P(n\text{-}C_5H_{11})_3$	P	14.47	13.80	13.54	9.32	9.10	9.01
19	$P(C_6H_5)(n\text{-}C_3H_7)_2$	P	18.24	17.11	16.69	9.95	9.54	9.40
20	$P(C_6H_5)(n\text{-}C_4H_9)_2$	P	18.83	17.56	17.10	10.35	9.89	9.72
21	$P(C_6H_5)[CH_2\cdot CH(CH_3)\cdot CH_3]_2$	P	18.14	16.99	16.57	10.04	9.63	9.48
22	$P(C_6H_5)(n\text{-}C_5H_{11})_2$	P	18.80	18.63	17.18	10.43	10.03	9.88
23	$P(C_6H_5)[CH_3\cdot CH_2\cdot CH(CH_3)\cdot CH_2]_2$	P	18.38	17.14	16.67	10.17	9.73	9.57
24	$P(C_6H_5)[CH_3\cdot CH(CH_3)\cdot CH_2\cdot CH_2]_2$	P	18.68	17.41	16.94	10.41	9.96	9.83
25	$P(C_6H_5)(n\text{-}C_6H_{13})_2$	P	18.16	17.01	16.49	10.12	9.74	9.56
26	$P(C_6H_5)(n\text{-}C_7H_{15})_2$	P	18.35	17.11	16.62	10.29	9.88	9.72

27	$P(C_6H_5)(n\text{-}C_8H_{17})_2$	P	18.24	16.93	16.53	10.32	9.88	9.78
28	$P(p\text{-}CH_3 \cdot C_6H_4)(n\text{-}C_3H_7)_2$	P	18.78	17.54	17.09	10.23	9.79	9.63
29	$P(p\text{-}CH_3 \cdot C_6H_4)(n\text{-}C_4H_9)_2$	P	19.65	18.36	17.87	10.78	10.32	10.15
30	$P(p\text{-}CH_3 \cdot C_6H_4)(n\text{-}C_5H_{11})_2$	P	19.65	18.33	17.84	10.91	10.43	10.26
31	$P(p\text{-}CH_3 \cdot C_6H_4)[CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_3]_2$	P	18.96	17.68	17.20	10.50	10.05	9.89
32	$P(p\text{-}CH_3 \cdot C_6H_4)[CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_3]_2$	P	19.84	18.50	18.01	11.06	10.58	10.41
33	$P(p\text{-}CH_3 \cdot C_6H_4)[CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH_3]_2$	P	18.39	17.17	16.70	10.44	10.02	9.87
34	$P(p\text{-}CH_3 \cdot CH_2C_6H_4)(n\text{-}C_3H_7)_2$	P	19.46	18.17	17.70	10.62	10.16	9.99
35	$P(p\text{-}CH_3 \cdot CH_2C_6H_4)(n\text{-}C_4H_9)_2$	P	20.34	18.95	18.42	11.16	10.65	10.47
36	$[2,5\text{-}(CH_3)_2C_6H_3] \cdot P(C_2H_5)_2$	P	19.30	18.00	17.56	10.30	9.82	9.67
37	$[2,5\text{-}(CH_3)_2C_6H_3] \cdot P(n\text{-}C_3H_7)_2$	P	19.05	17.76	17.30	10.24	9.78	9.62
38	$[2,5\text{-}(CH_3)_2C_6H_3] \cdot P(n\text{-}C_4H_9)_2$	P	19.50	18.27	17.72	10.62	10.20	10.01
39	$(p\text{-}CH_3O \cdot C_6H_4) \cdot P(n\text{-}C_3H_7)_2$	P	20.18	18.74	18.21	10.86	10.32	10.13
40	$(p\text{-}CH_3O \cdot C_6H_4) \cdot P(n\text{-}C_4H_9)_2$	P	19.80	18.39	17.84	10.72	10.21	10.02
41	$(p\text{-}CH_3O \cdot C_6H_4) \cdot P(n\text{-}C_5H_{11})_2$	P	20.34	18.80	18.21	11.21	10.64	10.42
42	$(p\text{-}C_6H_5O \cdot C_6H_4) \cdot P(CH_3)_2$	P	22.11	20.38	19.75	10.20	9.66	9.46
43	$(p\text{-}C_6H_5O \cdot C_6H_4) \cdot P(C_2H_5)_2$	P	22.58	20.67	—	10.55	9.91	—
44	$(p\text{-}C_6H_5O \cdot C_6H_4) \cdot P(n\text{-}C_3H_7)_2$	P	22.59	20.51	19.74	10.49	9.79	9.54
45	$(p\text{-}C_6H_5O \cdot C_6H_4) \cdot P(n\text{-}C_4H_9)_2$	P	22.53	20.50	19.76	10.64	9.97	9.73
46	$(CH_2)_4 > P \cdot C_6H_5$	P	—	19.27	—	—	9.87	—
47	$(CH_2)_5 > P \cdot C_6H_5$	P	—	19.45	—	—	9.86	—
48	$(CH_2)_5 > P \cdot C_6H_4 \cdot CH_3\text{-}p$	P	—	20.11	—	—	10.45	—
49	$C_6H_5PCl_2$	P	—	17.46	17.07	—	9.47	8.84
50		P	—	17.62	17.22	—	9.05	8.92
51	$(p\text{-}CH_3 \cdot CH_2 \cdot C_6H_4)PCl_2$	P	19.76	18.36	17.83	10.16	9.66	9.47
52	$[2,5\text{-}(CH_3)_2C_6H_3]PCl_2$	P	20.21	18.77	18.22	10.27	9.76	9.56
53	$(p\text{-}CH_3O \cdot C_6H_4)PCl_2$	P	21.78	20.04	19.37	10.99	10.35	10.09
54	CH_3OPCl_2	PO	—	15.07	—	—	9.24	—
55	$C_2H_5OPCl_2$	PO	—	15.76	—	—	9.73	—
56		PO	—	15.46	15.29	—	9.63	9.55
57	$n\text{-}C_3H_7OPCl_2$	PO	—	15.09	—	—	9.43	—

TABLE 2—*Concluded*

NO.	SUBSTANCE	ATOM OR GROUP	GLADSTONE-DALE			LORENZ-LORENTZ		
			F	D	C	F	D	C
58	n-$C_4H_9OPCl_2$	PO	—	15.32	—	—	9.67	—
59	$(C_2H_5\cdot O)_2PCl$	PO_2	—	28.24	—	—	11.38	—
60	$OPH(OC_2H_5)_2$	PO_3	15.60	15.40	15.32	10.00	9.92	9.89
61		PO_3	—	15.51	—	—	9.99	—
62		PO_3	16.05	15.82	15.74	10.25	10.16	10.13
63	$P(OC_2H_5)_3$	PO_3	18.59	18.13	17.98	11.98	11.77	11.70
64		PO_3	—	18.98	—	—	12.28	—
65		PO_3	18.93	18.49	18.24	12.19	11.99	11.87
66	$[CH_3\cdot CH(CH_3)\cdot CH_2\cdot O]_3P$	PO_3	18.58	18.06	17.85	12.44	12.25	12.18
67	$(n\text{-}C_5H_{11}\cdot O)_3P$	PO_3	17.81	17.63	17.42	12.20	12.00	11.94
68	$OP(C_2H_5)(OC_2H_5)_2$	PO_3	14.90	14.70	14.64	9.72	9.65	9.64
69	$(C_2H_5\cdot O)_4P_2O_2$	P_2O_6	—	33.96	—	—	21.32	—
70	$(C_2H_5\cdot O)_4P_2O_3$	P_2O_7	—	33.14	—	—	20.94	—
71	$(C_2H_5\cdot O)_4P_2O_2S$	P_2O_6S	—	45.87	—	—	28.01	—
72	$(C_2H_5\cdot O)_2PO\cdot O\cdot PO(O\cdot C_2H_5)(C_2H_5)$	P_2O_6	—	31.53	—	—	19.87	—
73	$(CH_3\cdot O)_3PO$	PO_4	16.89	16.75	16.71	10.77	10.72	10.70
74	$(C_2H_5\cdot O)_3PO$	PO_4	—	16.39	—	—	10.75	—
75		PO_4	—	16.51	—	—	10.88	—
76		PO_4	16.74	16.54	16.48	10.96	10.89	10.87
77		PO_4	—	16.35	—	—	10.82	—
78		PO_4	16.60	16.36	16.38	10.91	10.86	10.84
79	$(n\text{-}C_3H_7\cdot O)_3PO$	PO_4	16.44	16.24	16.19	11.03	10.99	10.98
80	$(n\text{-}C_4H_9\cdot O)_3PO$	PO_4	16.08	15.80	15.69	10.97	10.89	10.87
81	$[CH_3\cdot CH(CH_3)\cdot CH_2\cdot O]_3PO$	PO_4	15.98	15.71	15.59	11.02	10.94	10 92
82	$(n\text{-}C_5H_{11}\cdot O)_3PO$	PO_4	15.91	15.65	15.54	11.04	10.99	10.98
83	$SP(OCH_3)_3$	PO_3S	—	29.92	29.67	—	18.05	17.92
84	$CH_3SPO(OCH_3)_2$	PO_3S	—	29.08	28.89	—	17.44	17.35

(b) It will also be seen that the former value also holds good for liquid phosphorus itself. The discrepancy between the Gladstone-Dale values is to be attributed to the exceptionally high refractive index of fused phosphorus.

(c) The *atomic* refractivity of phosphorus in phosphorus trichloride is distinctly different from that in phosphorus tribromide or from that in trialkylphosphines. *This shows that when the linkage of phosphorus to carbon is taken as standard, the linkages of phosphorus to halogens possess specific effects.* Alternatively, it might be considered that when linked to phosphorus, chlorine and bromine do not possess the same atomic refractivities as when they are linked to carbon, and, consequently, that Eisenlohr's values for the halogens are inapplicable here.

(d) The attachment of an aryl group to a phosphorus atom is a cause of optical exaltation, an indication of the presence of loosely held electrons of low frequency of oscillation, and, consequently, of the appearance of absorption bands at abnormally long wave-lengths. The similar exaltative effect of aromatic groups attached to nitrogen has been attributed to the establishment of a virtual conjugation involving the nitrogen atom and the endocyclic double bonds (28).

TABLE 3

Gladstone-Dale atomic and bond refractivities

ATOM OR BOND	REFRACTIVITY		
	F	D	C
Carbon	4.145	4.111	4.102
Hydrogen	1.895	1.870	1.857
Ether oxygen	2.856	2.845	2.839
Chlorine	10.43	10.30	10.24
Bromine	16.24	16.00	15.89
Ethylene bond	3.126	2.970	2.889

(e) The interposition of an oxygen atom between an atom of carbon and one of phosphorus raises the molecular refractivity by an amount different from that due to ether oxygen. In fact, the atomic refractivity of oxygen in the $\equiv C—O—P=$ group may be evaluated in the following ways:

(1) Subtraction of the molecular refractivity of

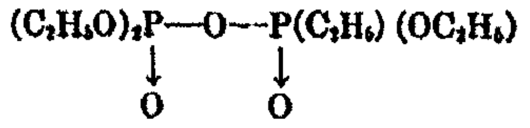
$$O \leftarrow P(C_2H_5)(OC_2H_5)_2 \text{ (No. 68, table 1)}$$

from that of

$$O \leftarrow P(OC_2H_5)_3 \text{ (No. 74)}$$

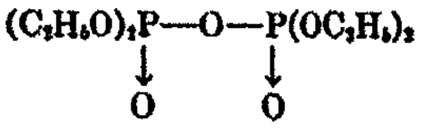
which gives 1.10 for D light.

(2) Subtraction of the molecular refractivity of



$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}—O—\underset{\overset{\downarrow}{O}}{P}(C_2H_5)(OC_2H_5)$ (No. 72)

from that of



$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}—O—\underset{\overset{\downarrow}{O}}{P}(OC_2H_5)_2$ (No. 70)

which gives 1.07.

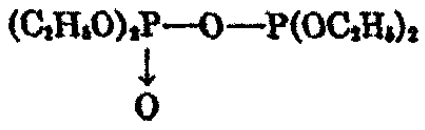
(3) Subtraction of the atomic refractivity of phosphorus, 9.14, from the mean value of the group refractivity for PO_3 in the trialkyl phosphites (Nos. 63, 64, 65, 66, 67, table 2), 12.02, and division of the remainder by 3, gives 0.96 for sodium light. The mean value of the atomic refractivity of oxygen in the ≡C—O—P≡group is given in table 4, viz., 0.98 for D light on the Lorenz-Lorentz notation, and 1.38 for that of Gladstone-Dale.

(f) The value of the atomic refractivity of oxygen linked by a semipolar bond to phosphorus, ≡P→O, may be obtained by the following considerations:

(1) Subtraction of the molecular refractivity of phosphorus trichloride (No. 7, table 1) from that of phosphoryl chloride (No. 10) gives −1.13 for D light.

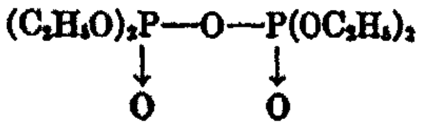
(2) Subtraction of the mean group refractivity for PO_3 in trialkyl phosphites (Nos. 63, 64, 65, 66, 67, table 2) from that for PO_4 in trialkyl phosphates (Nos. 73, 74, 75, 76, 77, 78, 79, 80, 81, 82) gives −1.15.

(3) Subtraction of the molecular refractivity of



$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}—O—P(OC_2H_5)_2$ (No. 69, table 1)

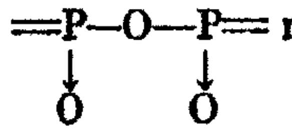
from that of



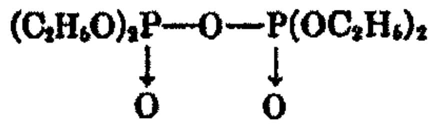
$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}—O—\underset{\overset{\downarrow}{O}}{P}(OC_2H_5)_2$ (No. 70)

gives −0.38, not in good agreement with the values obtained above.

The mean of (1) and (2) gives −1.15 as the atomic refractivity of oxygen in the ≡P→O group for D light. The corresponding Gladstone-Dale refractivity is −2.13.

(g) The value of the atomic refractivity of the covalent oxygen in the group  $=\underset{\overset{\downarrow}{O}}{P}-O-\underset{\overset{\downarrow}{O}}{P}=$ may be obtained in the following manner:

(1) Subtraction of the increments due to carbon, hydrogen, phosphorus [(a)] and the oxygen [(e) and (f)] from the molecular refractivity of

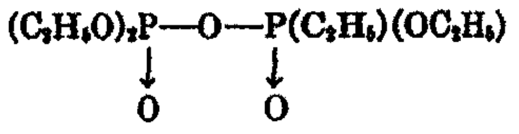


$$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}-O-\underset{\overset{\downarrow}{O}}{P}(OC_2H_5)_2$$

(No. 70, table 1)

which gives the value 1.04 for sodium light.

(2) Similar consideration of the compound



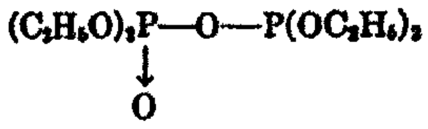
$$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}-O-\underset{\overset{\downarrow}{O}}{P}(C_2H_5)(OC_2H_5)$$

(No. 72)

gives 0.95.

(h) The optical effect of sulfur joined by a coördinate link to phosphorus may be calculated as follows:

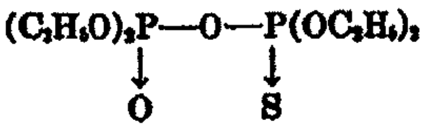
(1) Deduction of the molecular refractivity of



$$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}-O-P(OC_2H_5)_2$$

(No. 69, table 1)

from that of



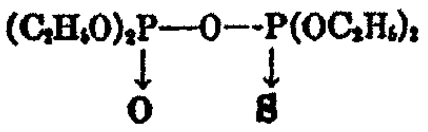
$$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}-O-\underset{\overset{\downarrow}{S}}{P}(OC_2H_5)_2$$

(No. 71)

leaves the value 6.69 for D light.

(2) The value obtained by subtracting the mean value of the group refractivity for PO_3 from that for PO_3S (No. 83, table 2) is 6.03.

(3) Subtraction of Eisenlohr's values for carbon and hydrogen, that for phosphorus given in (a), and that for oxygen in (e), in (f) and in (g), from the molecular refractivity of



$$(C_2H_5O)_2\underset{\overset{\downarrow}{O}}{P}-O-\underset{\overset{\downarrow}{S}}{P}(OC_2H_5)_2$$

(No. 71)

leaves the value 5.96.

The mean value of the Lorenz-Lorentz atomic refractivity of sulfur in the $\equiv P\rightarrow S$ group for D light is 6.23; the Gladstone-Dale, 11.43.

(j) Deduction of Eisenlohr's values for carbon and hydrogen, the present values for phosphorus given in (a), and for oxygen given in (e) and (f), from the molecular refractivity of

$(CH_3S)(CH_3O)_2P{\rightarrow}O$ (No. 84, table 1)

gives 7.49 as the value of the atomic refractivity of covalent sulfur in the group $\equiv C{-}S{-}P{=}$; that for the Gladstone-Dale formulation is 14.22, for sodium light.

TABLE 4

Mean values of atomic refractivities in phosphorus compounds on the assumption that the atomic refractivity of phosphorus is constant

ATOM	GLADSTONE-DALE			LORENZ-LORENTZ		
	F	D	C	F	D	C
P	14.65	14.23	13.75	9.33	9.14	9.00
O in $\equiv C{-}O{-}P{=}$	1.24	1.38	1.37	0.96	0.98	0.97
O in $\equiv P{\rightarrow}O$	−2.26	−2.13	−1.92	−1.25	−1.15	−1.05
O in $=\underset{\overset{\downarrow}{O}}{P}{-}O{-}\underset{\overset{\downarrow}{O}}{P}{=}$	—	3.31	—	—	1.00	—
S in $\equiv P{\rightarrow}S$	—	11.43	11.81	—	6.23	6.01
S in $\equiv C{-}S{-}P{=}$	—	14.22	14.32	—	7.49	7.46
Cl	—	10.21	10.13	—	5.71	5.69

TABLE 5

Mean values of the atomic refractivity of phosphorus in various classes of compounds

CLASS	GLADSTONE-DALE			LORENZ-LORENTZ		
	F	D	C	F	D	C
Trialkylphosphines	14.65	14.23	13.75	9.33	9.14	9.00
Phenyldialkylphosphines	18.42	17.32	16.75	10.23	9.81	9.66
p-Tolyldialkylphosphines	19.21	17.93	17.45	10.65	10.20	10.03
p-Ethylphenyldialkylphosphines	19.90	18.56	18.06	10.89	10.40	10.23
p-Xylyldialkylphosphines	19.28	18.01	17.53	10.39	9.93	9.77
p-Methoxyphenyldialkylphosphines	20.11	18.64	18.08	10.93	10.39	10.19
p-Phenoxyphenyldialkylphosphines	22.45	20.51	19.75	10.47	9.83	9.58
Trialkyl orthophosphites	9.91	9.72	9.35	7.25	7.09	7.00
Trialkyl orthophosphates	4.96	4.85	4.72	4.36	4.39	4.32

(k) Adding to the molecular refractivity of phosphorus trichloride (No. 7, table 1) the Eisenlohr values for alkyl groups and that for oxygen in the group $\equiv C{-}O{-}P{=}$, and subtracting from the sum the molecular refractivity of the corresponding alkoxydichlorophosphine (Nos. 55, 56, 57, 58, table 1), we obtain values for the atomic refractivity of chlorine attached to phosphorus; excluding the result for the methyl member (No.

54), the mean value is 5.71 for D light. For chlorine attached to carbon Eisenlohr gives 5.967. The mean Gladstone-Dale values are given in table 4.

Mean values are given in table 4, in the derivation of which the atomic refractivities of carbon and hydrogen given by Eisenlohr and those in table 3 have been employed, and, where necessary, suitable weighting has been applied for the sake of probable greater accuracy.

Up to this stage it has been assumed in this discussion that phosphorus possesses, independently of its state of combination, a constant atomic refractivity. The alternative view, however, must also be borne in mind, viz., that the atomic refractivity may have various values, dependent on the manner of the attachment of phosphorus to the other elements and on their character. For instance, assuming Eisenlohr's values for carbon, hydrogen, and ether oxygen, and that oxygen in phosphites and phosphates possesses the ether oxygen value, we can draw up a table (table 5) giving the various atomic refractivities of phosphorus.

The consideration of molecular refractivity as an additive property of bonds and of octets, rather than of atoms, has been brought forward by von Steiger, Fajans and Knorr, and Smyth (26). From this standpoint the value here obtained for the Lorenz-Lorentz atomic refractivity of phosphorus in tertiary phosphines, p, enables us to calculate the refractivity, $[R_0]$, of the octet

$$\begin{array}{c} \mathrm{C:\ddot{P}:C} \\ \mathrm{\ddot{C}} \end{array}$$

Thus for D light,

$$[R_0]_D = \tfrac{3}{4}c + p = 10.954$$

wherein c denotes the atomic refractivity of carbon, given by Eisenlohr.

From what has been here stated it will be gathered that the refractive constants given in tables 4 and 5 and in the preceding paragraph must be looked upon not so much as possessing intrinsic theoretical significance, but as being of the nature of empirical constants whereby the molecular refractivity, and, therefore, also the refractive index, of a phosphorus compound may be determined when once its constitutional formula has been established. The converse use of these refractive constants to detect, for example, the presence of semipolar or of covalent bonds from refractometric measurements is obvious.

In conclusion it must be stated that, even in its modern form, the theory of the Mosotti-Clausius (27) equation, from which that of Lorenz-Lorentz and its limiting case, that of Gladstone-Dale, are theoretically derived, makes certain postulates regarding the mobility of the positive and negative charges in the molecule, and regarding the value of the constant of the inner field in the case of liquids (29), which are not strictly fulfilled. Moreover, the Maxwellian relation between dielectric constant and refractive index, assumed in the derivation of the Lorenz-Lorentz equation, holds only for electromagnetic oscillations of low frequency, that is, in regions far removed from absorption bands.

REFERENCES

(1) Kowalewski: J. Russ. Phys. Chem. Soc. **29**, 217 (1897).
(2) Haagen: Pogg. Ann. **131**, 119 (1867).
(3) Gladstone and Dale: Phil. Trans. **153**, 320 (1863).
(4) Gladstone: Proc. Roy. Soc. London **42**, 407 (1887).
(5) Zecchini: Gazz. chim. ital. **23**, 97 (1893); **24**, 34 (1894).
(6) Lorenz: Kgl. Danske Videnskab. Selskabs Skrifter **8**, 230 (1870); Wied. Ann. **11**, 70 (1880).
Lorentz: Wied. Ann. **9**, 641 (1880).
(7) Arbusow and Ivanow: J. Russ. Phys. Chem. Soc. **47**, 2015 (1915).
(8) Arbusow and Arbusow: J. prakt. Chem. **130**, 103 (1931); Ber. **65**, 197 (1932).
(9) Johnson: Ber. **65**, 302 (1932).
(10) Emmett and Jones: J. Chem. Soc. **99**, 714 (1911).
(11) Grüttner and Wiernik: Ber. **48**, 1473 (1915).
(12) Grüttner and Krause: Ber. **49**, 437 (1916).
(13) Jackson, Davies, and Jones: J. Chem. Soc. **1930**, 2300.
(14) Davies and Jones: J. Phys. Chem. **35**, 1490 (1931).
(15) Bowden: J. Soc. Chem. Ind. **49**, 257T (1930).
(16) Davies and Jones: J. Chem. Soc. **1929**, 33.
Davies, Pearse, and Jones: J. Chem. Soc. **1929**, 1262.
Evans, Davies, and Jones: J. Chem. Soc. **1930**, 1310.
Jackson, Davies, and Jones: J. Chem. Soc. **1930**, 2298.
Jackson and Jones: J. Chem. Soc. **1931**, 575.
Jackson, Davies, and Jones: J. Chem. Soc. **1931**, 2109.
(17) See J. Am. Chem. Soc. **54**, 1277 (1932).
(18) Bleekrode: Proc. Roy. Soc. London **37**, 339 (1884).
(19) Brühl: Z. physik. Chem. **7**, 19 (1894).
(20) Damien: Ann. École Norm. sup. **10** (1881).
(21) Thorpe and Tutton: J. Chem. Soc. **57**, 565 (1890).
(22) Martens: Verhandl. deut physik. Ges. **4**, 138 (1902).
(23) Nasini and Costa: Pubbl. dell 'Inst. chim. Roma, p. 111 (1891).
(24) Present work.
(25) Eisenlohr: Z. physik. Chem. **75**, 585 (1910).
(26) von Steiger: Ber. **54**, 1388 (1921).
Fajans and Knorr: Ber. **59**, 256 (1926).
Smyth: Phil. Mag. **50**, 361 (1925).
(27) Clausius: Mechanische Wärmetheorie, Vol. 2, p. 94 (1876).
(28) Brühl: Ber. **40**, 900, 1155 (1907).
Eisenlohr: Ber. **44**, 3188 (1911); Z. physik. Chem. **79**, 129 (1912).
(29) Loeb: Kinetic Theory of Gases, p. 397. McGraw-Hill Book Company, New York (1927).
Hückel: Theoretische Grundlagen der organischen Chemie, Bd. 2, p. 30. Akademische Verlagsgesellschaft, Leipzig (1931).

RECOVERY BY FLOTATION OF MINERAL PARTICLES OF COLLOIDAL SIZE

A. M. GAUDIN AND PLATO MALOZEMOFF

Ore Dressing Laboratories of the Montana School of Mines, Butte, Montana

Received September 19, 1932

In the early stages of the development of the flotation process for concentrating ores, the belief arose that at last a process of ore concentration was available for the successful treatment of the finest particles (1), which in water suspension are collectively known as "slime." It was thought that all mineral particles that are too fine to be recovered by gravity concentration and yet comprise a wide range of sizes float equally well. And, indeed, it is true that flotation is applicable to a wider size range than any of the three principal methods of gravity concentration—jigging, tabling, and vanning. Nevertheless the introduction of ball-mill grinding made it increasingly obvious that particles of all sizes do not float equally well or rapidly. The presence of an upper size limit beyond which flotation is impossible was recognized even before the advent of *selective* flotation (as contrasted with *collective* flotation). The existence of a lower size limit beyond which flotation is difficult was suspected, but the limitations of laboratory sizing technique made it difficult to more than surmise that particles of colloidal size are refractory to modern selective flotation operation (2).

Definite reduction in floatability with reduction in particle size beyond a critical size of maximum floatability was recently demonstrated (3). The size limits within which recovery by flotation is good were found to be more or less peculiar to each mineral. In general, however, the optimum size of mineral particles for concentration by flotation is between 50 and 10 microns, and the recovery is markedly lower for particles finer than 5 microns.

This dependence of flotation upon the size of particles was found to hold true in practical mill operations as well as in the flotation of synthetic mineral mixtures. About 10 per cent by weight of the ore treated in a modern mill is ground too fine to be recovered efficiently by flotation. The economic loss thus involved is appreciable.

It is therefore of considerable economic importance as well as of scientific interest to look into the possible causes for this behavior of fine particles and to devise, if possible, a more effective means of recovering them by flotation.

This paper deals with the study of the flotation behavior of exceedingly fine particles—those which in modern practice can be recovered only with difficulty.

The size range of these particles embraces the entire scale from 5 microns to the truly colloidal particles which have as their limiting size the unit crystal of the mineral (4).

In the size range considered the particles of near-colloidal size (5 to 0.5 microns) obey in kind, if not in degree, the same general laws of flocculation and dispersion (5) as the truly colloidal particles. Thus it is proper to examine and interpret the behavior of these fine particles in the light of colloid chemistry.

CAUSES FOR NON-FLOTATION OF COLLOIDAL PARTICLES

In the study of the effect of particle size on flotation a number of hypotheses were considered (3) to account for the non-flotation of particles of colloidal size. Of these hypotheses the most likely is that very fine particles do not float because it is difficult for them to come in contact with gas bubbles.

In recent years the emphasis laid upon the physicochemical properties of the mineral surfaces as determinants of flotation behavior have subordinated the equally important mechanical problem of bringing gas and solid together. The importance of gas-solid attachment is self-evident from a careful definition of flotation.[1]

Attachment of mineral particles to bubbles usually results from contact becoming established by direct encounter of particles with bubbles. It can be shown (6) that the probability of encounter between a mineral particle and a bubble varies directly as the size of the particle, provided the particle is small compared to the bubble. In other words, the finer the particle the poorer its chance of being recovered. Also, it appears likely that mineral recovery can be enhanced by flocculating the mineral.[2]

A further consideration, more directly deriving from customary colloid phenomena, also points to the desirability of flocculating the mineral which is to be floated. It is known that fine mineral particles suspended in an electrolyte are electrically charged (7); it is logically certain, furthermore, that the charge on particles of the same kind is of the same sign.

---

[1] Flotation is a process of separation of mixed dissimilar solid particles, applied to the concentration of finely ground ores in aqueous pulp. The separation is caused by the selective adhesion of some species of solids to gas bubbles and the simultaneous adhesion of other species of solids to the aqueous solution; segregation of the resulting froth from the remaining pulp yields the desired separation.

[2] In this article the term "floccule" is used to describe an aggregation of solid particles suspended in a liquid in the absence of gas bubbles. In flotation literature the term "flocculation" has been used by some to refer to the formation of highly mineralized gas-solid aggregates. This confusing terminology is regrettable.

Accordingly, if it is proposed to cause electrically charged (dispersed) particles to adhere to a somewhat mineralized gas bubble, it should be expected that the mineral particles already attached to the bubble will prevent the adherence of more particles (8) and, hence, will prevent the formation of highly mineralized bubbles. Since flocculation in conducting media usually involves neutralization or great reduction of the charges responsible for dispersion, flocculation of the mineral may help flotation by eliminating or decreasing the electric charge at the surface of the particles.

From these considerations of the mechanics of gas-solid attachment, it seems likely that if fine particles can be made to lose their identity as such by coalescing into floccules, they may be expected to behave as coarse, uncharged particles, that is, to be more readily recovered by flotation.

MINERAL FLOCCULATION

The obvious means of flocculating a dispersed solid suspended in an electrolyte is to add to the electrolyte suitable soluble salts capable of discharging the dispersed phase.

Another means of flocculating the mineral is to form an insoluble heteropolar coating on the surface of the mineral, oriented in such a way as to make the transition from one phase to another abrupt (9). This is suggested by the following considerations. Dispersion can result either if the two phases are of like polarity or if there is established between them an intermediate zone or atmosphere of molecules or ions which is of a polarity intermediate between that of the two phases, so that a gradual transition is set up. Conversely, if the phases are very dissimilar, or if a film can be caused to develop on the solid, of a vastly different polarity than the liquid, the transition between the film-coated solid and the liquid will be abrupt and flocculation will tend to occur. Some of the experimental vindication for this argument is as follows:

H. E. Kamprath (10) studied the behavior of polar and non-polar minerals in polar and non-polar liquids. He found, for example, that silicate minerals, which are polar, flocculate in a non-polar liquid, but that in a heteropolar, nonconducting liquid they remain dispersed. One of the heteropolar liquids used was butyl alcohol, in which dispersion can hardly be attributed to electric charges. It would appear as though butyl alcohol molecules adhere to the solid in definite orientation so as to cause the surface of the coated silicate particles to have the same polarity as the liquid. That dispersion can be obtained under certain conditions without the presence of substantial electric charges was recently confirmed by Basil C. Soyenkoff (11), who concluded that "... the majority of colloid dispersions in hydrocarbons either are uncharged or carry only a small fraction (less than 10^{-4}) of the charge possessed by the particles in water."

Kamprath also found that graphite, which is non-polar, flocculates in polar liquids, but remains dispersed in non-polar liquids. The same behavior was noticed in the case of galena, provided it is kept from oxidizing. Thus, when galena is ground in water in a nitrogen atmosphere, it flocculates invariably, which may be considered to derive from its low polarity as compared with water.

EFFECT OF FLOCCULATION BY USE OF ELECTROLYTES ON FLOTATION OF GALENA

In order to ascertain the effect of flocculation by electrolytes on flotation it was thought wise to study extensively a simple system whose normal behavior is otherwise well known. Accordingly, mixtures of pure galena with granite (Butte quartz monzonite) were ground wet, long enough (twenty-four hours) to reduce all particles to 5 microns and finer. Various electrolytes were added to the pulp, after grinding, in the hope of improving flotation under standard conditions (12) (2.0 lb. of potassium amyl xanthate and 0.16 lb. of terpineol per ton). None of the substances investigated (lime, sodium hydroxide, aluminum sulfate, sodium carbonate) improved the recovery, although flocculation was obtained in many instances.

To study the problem further, galena and granite were ground separately for the time required to insure sufficient reduction in size, flocculating agents were added, the pulps were mixed, and flotation operations were conducted. Potassium *n*-amyl xanthate (2 to 4 lb. per ton) was used as collector, and terpineol (0.04 to 0.16 lb. per ton) as frother. The experiments showed that suitable flocculation of the mineral actually permits flotation of extremely fine mineral particles. Thus, if fine galena be first completely flocculated and then mixed with gangue minerals, an effective separation by flotation may be obtained. On the contrary, if the mineral be first completely dispersed and then mixed with gangue, recovery of the mineral is decidedly poor.

These experiments, however, do not simulate practice, as the sulfide and gangue minerals were ground separately, and flocculated (or dispersed) separately, so that the minerals exercised minimum influence on each other's behavior and that the system perhaps had not time to come to equilibrium. However, the experiments yield the valuable information that fine mineral particles are capable of ready attachment to bubbles if flocculated.

To apply this important experimental result to practice, care would have to be exercised to flocculate *selectively* the mineral to be floated, or else compound floccules of mineral and gangue would result. Such compound floccules would of course be a hindrance rather than a help to the separation of the minerals from each other. Thus, of the four possible states of aggregation of the minerals, that of flocculation of the mineral, together with dispersion of the gangue, is the most desirable. The other three, of course, are dispersion of mineral with dispersion of gangue, dispersion of mineral with flocculation of gangue, and flocculation of mineral with flocculation of gangue.

However, if the mineral and the gangue are ground together it is difficult to obtain simultaneously satisfactory flocculation of the sulfide and dispersion of the gangue. Dissimilar mineral particles tend to precipitate on the surface of one another (13), possibly because of the occurrence of unlike charges at their surfaces. Thus, some fine galena adheres to the surface of relatively coarse quartz, and, conversely, quartz adheres to galena. This phenomenon appears to take place in the grinding mill as soon as particles are formed fine enough to be affected by the charges that obtain at their surface. Hence, in order to prevent this action, it appears necessary to have present at the time when the fine particles are produced the agency that will cause the desired selective flocculation; that is, the selectively flocculating agent should be present in the grinding mill during the grinding.

TABLE 1

Comparison between amyl xanthate and amyl dixanthogen as collectors for colloidal galena

	XANTHATE	DIXANTHOGEN
Time of grind (hours)	24	30
Place of addition of reagent	Flotation machine	Pebble mill
Quantity of reagent (pounds per ton)	4.0	3.0
Time required for rougher flotation (minutes)	60	5
Rougher concentrate (lead, per cent)	43.1	39.3
Tailing (lead, per cent)	4.4	0.30
Lead recovery (per cent)	80.5	98.7
Rougher selectivity index* Lead:Granite	4.0	15.5
Cleaner concentrate (lead, per cent)	—	69.4
Cleaner tailing (lead, per cent)	—	1.10

* For method of calculation see A. M. Gaudin: Flotation, p. 526 (see reference 5).

The search for a means to cause simultaneously the selective flocculation of the sulfide mineral and the dispersion of the gangue by the use of electrolytes was abandoned after much experimentation because the action of electrolytes did not appear to be selective enough.

FLOCCULATION AND FLOTATION OF COLLOIDAL SULFIDE MINERALS, USING CERTAIN SULFUR-BEARING HETEROPOLAR COMPOUNDS

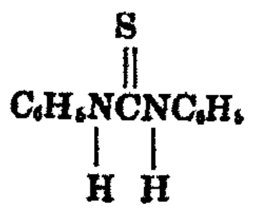
Remarkably successful flotation of colloidal sulfide minerals may be obtained by the use of certain heteropolar organic compounds. These compounds have a structure such as to make possible the formation of oriented coatings of molecular dimensions on the sulfide minerals, and thereby produce selective flocculation of the sulfide minerals. This is true provided the flocculating-floating compounds are added to the mineral mixture before grinding.

In this connection it should be stated that in the experiments discussed in the preceding section a sulfur-bearing heteropolar compound was used in each test as a flotation collector. The reagent used was potassium *n*-amyl xanthate, a reagent known to be exceptionally effective in the flotation of coarse sulfide minerals. Nevertheless, under normal conditions this compound is not capable of floating slimed galena. On the contrary, *n*-amyl dixanthogen, a non-ionized oxidation product of *n*-amyl xanthate, under certain conditions is capable of recovering colloidal galena. This discovery led to a broadening of the investigation to include non-ionized as well as ionized organic compounds containing single- or double-bonded sulfur atoms and an amyl, a phenyl, or a cresyl hydrocarbon group.

Some of the reagents investigated and their formulas are as follows:

Potassium *n*-amyl thiocarbonate	 $KS\overset{O}{\overset{\|}{C}}OC_5H_{11}$
Potassium *n*-amyl dithiocarbonate (xanthate)	 $KS\overset{S}{\overset{\|}{C}}OC_5H_{11}$
Potassium isoamyl trithiocarbonate	 $KS\overset{S}{\overset{\|}{C}}SC_5H_{11}$
n-Amyl formate disulfide	 $C_5H_{11}O\overset{O}{\overset{\|}{C}}SS\overset{O}{\overset{\|}{C}}OC_5H_{11}$
n-Amyl thioformate disulfide (dixanthogen)	 $C_5H_{11}O\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}OC_5H_{11}$
Isoamyl dithioformate disulfide	 $C_5H_{11}S\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}SC_5H_{11}$
Isoamyl disulfide	$C_5H_{11}SSC_5H_{11}$
Isoamyl sulfide	$C_5H_{11}SC_5H_{11}$
Isoamyl mercaptan	$C_5H_{11}SH$
p-Thiocresol	$HSC_6H_4CH_3$
Phenyl thiourethane	 $C_2H_5O\overset{S}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}C_6H_5$

Thiocarbanilide..



$$C_6H_5\underset{H}{N}\overset{\overset{\displaystyle S}{\|}}{C}\underset{H}{N}C_6H_5$$

Tri-*o*-cresyl thiophosphate................................ $(C_6H_4CH_3O)_3PS$

Of the above, the first six belong to a group of which xanthate and dixanthogen are representative. The compounds in this group other than the xanthate and dixanthogen were especially prepared in order to clarify the mechanism of attachment of the compound to the mineral. For this reason the double-bonded, or thione, sulfur atoms in xanthates and dixanthogen, which are commonly regarded by flotation engineers as being at least partly responsible for the attachment of minerals to bubbles, were replaced by oxygen atoms to form formate disulfide and potassium thiocarbonate; also, the oxygen atoms were entirely eliminated by replacing them with sulfur atoms in the case of dithioformate disulfide and potassium trithiocarbonate.

With the exception of the potassium salts, the compounds enumerated are but sparingly soluble in water, but since the organic solvents necessary to dissolve the agents may interfere in an undetermined manner with flotation, the undiluted agents were added directly to the grinding mill so as to be in intimate contact with the mineral throughout the grinding operation.

Flotation was conducted in a 500-g. Fahrenwald flotation machine. The products were analyzed for the valuable metal content. A flotation operation was arbitrarily termed successful when the tailing assayed less than 0.5 per cent (in valuable metal), and if the recovery exceeded 96 per cent. (Ordinarily, flotation under standard conditions, with the reagents added after grinding, yields a tailing having a metal content exceeding 3 per cent). It was found unnecessary to use any frother in most of the flotation operations.

The mineral mixtures were ground in porcelain jars ("assay" pebble mills) long enough to be reduced to the near-colloidal size. Investigation was confined to five of the commonest mineral sulfides (galena, chalcocite, chalcopyrite, pyrite, and sphalerite) and to the gangue minerals occurring in quartz monzonite (quartz, andesine, magnetite, biotite, hornblende). The grinding was conducted in contact with air in the case of every reagent and of every mineral mixture. Identical tests, except for grinding in contact with nitrogen, were also conducted. The tests in which the minerals were ground in nitrogen were undertaken to supply some information concerning the very peculiar behavior of some mineral–reagent combinations. It is well known that sulfide minerals are readily oxidized. It has been currently assumed (14) that surface oxidation of sulfide minerals is prerequisite for modern flotation. Obviously, even in the case of particles ground in the presence of a restricted amount of oxygen —as in the tests under consideration—much oxidation may take place during a period of grinding of many hours. Also, change in the reagent may take place when the reagent is added so as to be in contact with a mineral and air for many hours during grinding. Clearly, when the mineral is ground in the presence of nitrogen, such reactions are largely inhibited and the reagent then acts on relatively unchanged sulfide surfaces.

Table 2 summarizes the floatability of the different minerals with some of the more effective agents.

Flotation of colloidal sphalerite can be accomplished by none of the reagents listed, unless, of course, the mineral is first activated.[3]

Of the compounds which are similar in structure to amyl xanthate and dixanthogen (thioformate disulfide), namely, the thiocarbonate, trithiocarbonate, formate disulfide, and dithioformate disulfide, none showed any great promise to collect colloidal galena. The formate disulfide showed some tendency to collect galena, but it was too weak to be considered satisfactory. The action of these substances on other minerals was not investigated.

TABLE 2

Flotation of slimed sulfide minerals ground in contact with air when using some heteropolar sulfur-bearing compounds

	GALENA	CHALCOCITE	CHALCOPYRITE	PYRITE
Potassium amyl xanthate	Fair	Good	Good	Good
Amyl dixanthogen	Good	Good	Good	Good
Isoamyl disulfide	None	Good	Fair	None
Isoamyl sulfide	None	None	Good	None
Isoamyl mercaptan	None	Good	Good	—
Thiocresol	None	Good	—	—
Phenyl thiourethane	Good	None	—	—

Isoamyl disulfide was effective for chalcocite only.

Isoamyl sulfide promoted the flotation of chalcocite and pyrite only when these minerals were ground in nitrogen. Its effect was nil when the minerals were ground in air. It was effective for flotation of chalcopyrite irrespective of the atmosphere in which the mineral was ground.

Isoamyl mercaptan was effective only for chalcocite and chalcopyrite. Its action on the flotation of galena and sphalerite was nil. Its action on pyrite was not investigated.

---

[3] By activation is meant the formation on the surface of the mineral of a layer which will react with the collector to which the unactivated mineral surface fails to respond.

Thiocresol exhibited good collecting properties in the case of chalcocite, but none at all in the case of galena and sphalerite. Its action on other minerals was not studied.

The experimental results related above give little grounds from which sweeping generalizations can be drawn for predicting the action of the same compound on different minerals, or for designating a definite compound as one likely to be effective in promoting selective slime flocculation and the collection of floccules in flotation. In the present state of our knowledge, all that can be said is that the action of a given compound seems, to a large extent, to be specific to each mineral. It is hoped, however, that significant broad conclusions will be possible following the experimentation now in course.

DRY VERSUS WET FROTHS

During the investigation with the organic compounds as selective flocculators a curious phenomenon was observed: in the case of some of the reagents a peculiar "dry" froth was obtained in the flotation operation. This unusual type of froth occurred if an amount of agent greater than a certain critical amount was used; when the amount of the agent used was less than this critical amount, the froth had the normal or "wet" appearance. The "dry" froth contains very little interbubble water and is in the form of a thick, dry mass which is made up of extremely fine bubbles, difficultly distinguishable by eye. Whenever a dry froth was obtained, most of the mineral floated in the dry mass in one minute, whereas flotation of colloidal material with the usual wet froth requires twenty minutes or longer. What mineral did not float in the dry froth came up in the form of a dull dry film, which formed persistently at the surface of the pulp for some time and which had to be raked off painstakingly. This remainder could not be induced to float in the form of a froth even with the addition of large amounts of frother. By the use of reagents giving the usual type of froth, a good recovery of colloidal mineral in the cleaning operation is always difficult, but whenever a dry froth is obtained the cleaner tailing is but slightly higher in metal content than the rougher tailing. Moreover, owing to the dry character of the dry froth, the concentrate obtained is very clean, devoid of the usual adulterating interbubble gangue suspension. Most of the froth remained indefinitely in the dry condition, resembling stiff whipped cream in plasticity. The small part that did disintegrate settled to the bottom of the water layer in very large floccules. Instead of cleaning the rougher concentrate by flotation, therefore, simply draining or filtering off the water (containing dispersed gangue suspension) could be used as a substitute.

Wet froths obtained by the use of heteropolar reagents were examined to determine whether the mineral floats in the form of floccules or whether it floats as dispersed mineral particles attached to gas bubbles. Samples of froth were dried, then pieces were broken off and the thickness of the bubble wall was measured. This thickness was found to vary between 4 and 7 microns. The dried bubble was then broken up, and the individual particles in it were likewise measured after dispersion in pure terpineol. Most of the particles were smaller than half a micron. From a microscope examination of slides of the pulp, the diameter of the average floccular unit of the mineral was determined to be in the neighborhood of 4 to 7 microns. Hence, it appears that the bubbles in the froth are made up of the same floccules that occur in the pulp. Similar determinations could not be obtained with dry froths because of the minuteness of the bubbles. From the partial disintegration of dry froths to form very coarse floccules, and from their dull luster it appears likely that they consist of floccules even larger than those occurring in wet froths.

It was observed that coarse floccules float before finer fleules, a sequence analogous to that observed for the flotation of dispersed particles (3).

SUMMARY

1. Hypotheses were considered to account for the non-flotation of colloidal particles. It is believed that non-flotation of colloidal sulfide mineral particles is due to their being unable to come in contact with gas bubbles because of fine size and state of dispersion.

2. Selective flocculation of colloidal mineral makes its flotation more complete and easier.

3. Owing to the possibility of mutual flocculation of fine gangue and sulfide minerals in a flotation pulp, it appears necessary, in order to effect selective flocculation, to act on the mineral particles at the time they are produced in the grinding operation.

4. Flotation of colloidal sulfide mineral particles may be successfully accomplished by using as reagents certain heteropolar sulfur-bearing organic substances. These agents effect selective flocculation of the sulfide mineral particles.

REFERENCES

(1) Megraw, H. A.: The Flotation Process, p. 157. McGraw-Hill Book Co., New York (1916).

(2) Megraw, H. A.: The Flotation Process, pp. 28, 143.

Hoover, T. J.: Concentrating Ores by Flotation, p. 158. Mining Mag., London (1912).

Taggart, A. F.: Handbook of Ore-Dressing, p. 859. Wiley and Sons, New York (1927).

(3) Gaudin, A. M., Groh, J. O., and Henderson, H. B.: Am. Inst. Mining Met. Engrs., Tech. Pub. 414 (1931). Effect of Particle Size on Flotation.

Brunner, J. J.: Effect of Particle Size on Flotation; Part II Master of Science Thesis, Montana School of Mines.

(4) Gross, J., and Zimmerley, S. R.: Am. Inst. Mining Met. Engrs., Milling Methods, p. 30 (1930). Crushing and Grinding, II.—Relation of Measured Surface of Crushed Quartz to Sieve Sizes.

(5) Gaudin, A. M.: Flotation, pp. 44-9. McGraw-Hill Book Co., New York (1932).

(6) Gaudin, A. M.: Flotation, pp. 88-90.

(7) Ince, C. R.: Am. Inst. Mining Met. Engrs., Milling Methods, p. 261 (1930). A Study of Differential Flotation.

Callow, J. M.: Mining Sci. Press **111**, 854 (1915). Notes on Flotation. Kolloidchem. Beihefte **2**, 84 (1914); Z. physik. Chem. **89**, 91 (1914).

(8) Taylor, N. W.: Trans. Electrochem. Soc. **60**, 305 (1931). Discussion of "An Outline of Some Physicochemical Problems of Flotation" by A. M. Gaudin.

(9) McBain, J. W.: Colloid Symposium Monograph IV, 7 (1926). A Survey of the Main Principles of Colloid Science.

Fahrenwald, A. W.: Trans. Electrochem. Soc. **60**, 311 (1931). Solubility, Peptization, Wetting and Flotation.

(10) Kamprath, H. E.: A Study of the Dispersion and Flocculation of Pure Mineral Suspensions in Liquids. Master of Science Thesis, Montana School of Mines, 1931.

(11) Sotenkoff, Basil C.: J. Phys. Chem. **34**, 2519 (1930). Benzene Dispersions of Basic Soaps of Nickel and Iron. J. Phys. Chem. **35**, 2993 (1931). Hydrocarbons as Dispersion Media: A Review.

(12) Groh, J. O., and Henderson, H. B.: Effect of Particle Size on Flotation. Master of Science Thesis, Montana School of Mines.

(13) Taggart, A. F., Taylor, T. C., and Ince, C. R.: Am. Inst. Mining Met. Engrs., Milling Methods, p. 285 (1930). Experiments with Flotation Reagents.

(14) Taggart, A. F., Taylor, T. C., and Knoll, A. F.: Am. Inst. Mining Met. Engrs., Milling Methods, p. 217 (1930). Chemical Reactions in Flotation.

THE PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS. II

THE FREEZING POINTS OF SOME OF THE THERMOMETER CALIBRATION STANDARDS FOR LOW TEMPERATURES OF THE BUREAU INTERNATIONAL DES ETALONS PHYSICO-CHIMIQUES[1]

EVALD L. SKAU[2]

Department of Chemistry, Trinity College, Hartford, Connecticut

Received January 4, 1933

In the course of another investigation requiring a careful thermocouple calibration at low temperatures, accurate freezing point determinations were made on a number of samples of organic compounds supplied "for thermometer calibration" by the Bureau International des Etalons Physico-Chimiques, University of Brussels, in order to add to the certainty of our temperature scale and also to prove that our method of determining freezing points by means of heating curves is satisfactory and has advantages over the usual methods. The freezing point values attributed to these samples were based upon measurements made by Professor Timmermans against the helium thermometer of the Laboratoire Cryogénique de l'Université de Leiden in 1922 (1) and repeated in 1928 (2), when slightly different values were assigned to chlorobenzene, carbon disulfide, and methylcyclohexane.

Our freezing point measurements were made by means of a method particularly adapted to the accurate determination of this physical constant at low temperatures. We believe, therefore, that the results may help to establish definitely the true freezing points of these samples. The "accepted values" of Timmermans are identical with ours within the claimed limits of accuracy except in two cases, and in both of these cases we have been able to show that his values published in 1922 are more nearly

---

[1] Contribution No. 258 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts. A part of the experimental work for this paper was completed at Trinity College, Hartford, Connecticut, thanks to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences and to Curtis H. Veeder of Hartford, for grants to defray the expenses, and also to the Yale University Physics Department for supplying the necessary liquid air at cost.

[2] National Research Fellow, 1926–28, at the Massachusetts Institute of Technology; Guggenheim Fellow, 1930–31, at the Universities of Munich, Frankfurt a. Main, and Brussels.

correct than those he assigned to them on the basis of his 1928 determinations.[3]

METHOD

The observations here reported were made by means of a cooling-curve and heating-curve apparatus which is being described in detail elsewhere (3). This apparatus involves a cryostat whose temperature can be very carefully regulated and in which a 0.5 – 1.0 g. sample is suspended in an hermetically sealed "freezing point tube." The latter is made of extremely thin-walled 6-mm. glass tubing (about 0.08-mm. wall thickness) in order that its heat capacity may be negligibly small with respect to that of the sample, and is so constructed that the temperature of the sample may be followed by means of a single-junction thermocouple, one element of which fits snugly into a thin-walled capillary tube extending down through the center of the tube to within 5 mm. of the bottom. The cold junction is kept at 0°C. The readings are made to the nearest microvolt by means of a Leeds and Northrup Type K potentiometer.

The freezing point is determined by running heating curves and cooling curves on the sample, always controlling the temperature of the surroundings to rise or fall, as the case may be, at a definite recorded rate. The reproducibility of the curves so obtained, their interpretation, and the advantages of heating curves over cooling curves for the determination of freezing point and also as a criterion of purity have already been pointed out (3).

Since the thermocouple calibration was only to the nearest microvolt (±0.02°C., at 0°C., to ±0.05°C. at liquid air temperature), and since our freezing point values are also read only to the nearest microvolt, our freezing points cannot be said to have an accuracy greater than ±0.04°C. at 0°C., to ±0.10°C. at -183°C.

THERMOCOUPLE CALIBRATION

Five different thermocouples, made of No. 30 constantan and No. 36 copper wire, were used. Two of these were calibrated simultaneously at

---

[3] In order to clear up a misunderstanding in regard to the samples prepared by R. S. Taylor, and studied by Keyes, Townshend, and Young (J. Math. Phys. Mass. Inst. Tech. 1, 302 (1922)), which have been criticised by Timmermans, it should be pointed out that the sole claim made by these authors was as follows: "The freezing point found for an organic liquid depends somewhat upon the method employed and the thoroughness of the purification. The results here given will be found reproducible provided the general method of procedure is followed." In a letter to the author Professor Keyes states: "The use to which these samples were put was in connection with the production of helium in Texas. Whether the samples were of the highest purity or not made little difference in this connection, since they served to transfer temperature indications obtained from my hydrogen thermometer and platinum resistance thermometers to the operators at the Texas helium plant."

the ice point, at the freezing point of mercury (−38.87°C.) (4), at the sublimation point of carbon dioxide (−78.51°C.) (4), and at the boiling point of oxygen (−183.00°C.) (4). The last two points were established by measuring the vapor pressure of the carefully purified substances in a constant temperature cryostat in which the thermocouple was immersed (5). In each case the purity of the sample was tested by evaporating to one-half volume and then redetermining the vapor pressure. The calibration at the mercury point was carried out in the same apparatus as the freezing points and under identical conditions.

The other three thermocouples were calibrated against these two, all being inserted simultaneously in a constant temperature bath of pentane, the cryostat described by Taylor and Smith (6), and all five being read several times in rotation while the temperature of the cryostat was kept constant at various temperatures at intervals of about ten degrees along the scale, until at least three consecutive series of readings at each temperature gave identical values.

MATERIALS

Samples of the following compounds were obtained from Professor Timmermans, Director of the Bureau International des Etalons Physico-Chimiques: carbon tetrachloride, chlorobenzene, chloroform, ethyl acetate, carbon disulfide, ethyl ether, and methylcyclohexane, each in a tube sealed *in vacuo*. Each sample was introduced without further treatment into a freezing point tube with the minimum possible exposure to the atmosphere and was sealed off by the usual procedure without evacuating. Though the samples may not have been identical with those used by him in his freezing point determinations, they were similarly purified, and had the same densities within ±.0001 in all cases (7).

RESULTS

A number of heating and cooling curves were run on each substance at various intervals in the course of eighteen months, employing more than one thermocouple for each sample. The samples were always kept in a dark cupboard between measurements.

With the exception of ethyl acetate and methylcyclohexane, the values accepted for the freezing points are based on both heating and cooling curves. In all these cases all except the highest, cooling curve values were rejected, since obviously the effect of an unsatisfactory degree of supercooling, or of a failure to reach true equilibrium between the solid and liquid phases, is to give a freezing point which is too low. This was an important factor only in the case of the ethyl ether sample, where the highest cooling curve values agreed satisfactorily with the heating curve values, but where many cooling curves gave values from two to four microvolts lower. It was not found possible to measure the freezing points of the ethyl acetate and methylcyclohexane by our cooling curve method; all the values so obtained were not only low but inconsistent. This was particularly true for the methylcyclohexane. The best value obtained for the ethyl acetate, for example, was −83.84°C. Thus, the advantage of the heating curve method was particularly evident in these cases.

The stable form of ethyl ether was the one most often obtained by cooling curves, though a preliminary halt of five to twenty seconds at the freezing point of the unstable form was usually noted. It seems possible that crystals of the unstable form always appear first in accordance with Ostwald's step-by-step theory (8). It should also be mentioned that our experiments showed definitely that transition from the unstable to the stable form of ether can take place completely in the solid phase. This was proved by the fact that heating curves for the stable form were obtained on samples which had solidified completely as the unstable form as shown by the complete cooling curves.[4]

TABLE 1

Freezing points of Timmermans' thermometer standards

SUBSTANCE	TIMMERMANS' VALUES				FREEZING POINT (SKAU)	DIFFERENCE FROM ACCEPTED VALUE
	On label	(1922)	(1928)	Accepted value (1928)		
	degrees C.	*degrees C.*	*degrees C.*	*degrees C.*	*degrees C.*	*degrees C.*
Carbon tetrachloride*....	−22.9	−22.894	−22.82	−22.85	-22.8^{6}	+0.01
Chlorobenzene...........	−45.2	−45.175 −45.382	−45.35	−45.35	-45.2^{3}	−0.13
Chloroform..............	−63.5	−63.495	—	−63.5	-63.4^{1}	−0.09
Ethyl acetate............	−83.6	−83.6	—	−83.6	-83.6^{3}	+0.03
Carbon disulfide.........	−111.6	−111.613	−111.84	−111.8	-111.8^{8}	+0.08 (0.04)
Ethyl ether (stable)......	−116.3	−116.322	−116.35 −116.37	(−116.3)†	-116.2^{9}	−0.01
Ethyl ether (unstable)...	−123.3	−123.301	−123.47 −123.50	−123.3	-123.2^{6}	−0.05
Methylcyclohexane.......	−126.3	−126.35	−126.85	−126.85	-126.3^{4}	−0.51

* The transition point of carbon tetrachloride was also determined on this same sample. Transition point = −47.55 ±0.12°C.; see Skau and Meier: J. Am. Chem. Soc. **51**, 3517 (1929).

† Private communication.

---

[4] The behavior of ether here described has a bearing on a statement made by Smits (Z. physik. Chem. **153A**, 287 (1931)): "Der Umwandlungspunkt der flüssigen Phase liegt bei −105.4° und weiterhin kennt man zwei Schmelzpunkte bei −116° und bei −123.4°. Die Modifikation mit dem niedrigsten Schmelzpunkt, die am leichtesten erhältlich ist, hat man bisher als die metastabile Modifikation betrachtet. Da man

In no case was there found to be an appreciable change in freezing point with time, though the determinations were carried out over the course of about eighteen months using the original samples throughout. This brings out another advantage of our freezing point method for, as has been pointed out by Timmermans (9), pure chloroform, for example, is very sensitive on exposure to the air.[5]

The results have been summarized in table 1. Column 2 shows the freezing point values given on the labels of the sample tubes as received; columns 3 and 4 give Timmermans' Leiden values of 1922 and 1928 respectively; column 7 shows the differences between our values, column 6, and the final accepted values of Timmermans, column 5.

Since the accuracy claimed by Timmermans for his freezing points is only 0.1°C., all of our values can be said to check his final "accepted values," with the exception of that for methylcyclohexane and probably that for chlorobenzene. In both of these cases, however, our values agree very closely with those determined by him[6] in 1922. On the other hand, our value for carbon disulfide agrees with his more recent value, which was 0.23°C. lower than the value he reported in 1922.

It is suggested that the following be accepted as the freezing points of these substances[7] on the basis of the data now available:

Carbon tetrachloride	-22.8^{5}°C.
Chlorobenzene	-45.2^{0}
Chloroform	-63.4^{5}
Ethyl acetate	-83.6^{0}

---

aber nunmehr weiss, dass die Flüssigkeit allotrop ist, kann auch . . . die Modifikation mit dem höheren Schmelzpunkt die metastabile Modifikation sein. Wir sind damit beschäftigt diese Frage experimentell zu klären". Our results show that for ether the form with the lower melting point is the unstable form, which is, in fact, in agreement with more recent experiments by Smits (private communication).

[5] Professor Keyes suggests the desirability of designing a freezing point tube similar in construction to the one here described but with a larger capacity so that it could be used with a platinum resistance thermometer with a correspondingly modified technique. This could probably be used solely for the cooling-curve method, but would be decidedly advantageous in that (1) it would make available for temperature comparison a number of substances which crystallize well but which become impure on exposure to air, and (2) it would obviate the necessity of handling the sample before freezing point determinations, with the resulting possibility of the introduction of impurities.

[6] The reason suggested by Professor Timmermans for the lowness of his value for the freezing point of methylcyclohexane in 1928 is that considerable air may have dissolved in the sample, for by his method the sample is stirred vigorously without excluding air (private communication).

[7] Professor Timmermans has expressed his willingness to endorse this revision of his "accepted values" in the light of the evidence now at hand (private communication).

Carbon disulfide	−111.8°C.
Ethyl ether (stable)	−116.3°
Ethyl ether (unstable)	−123.3°
Methylcyclohexane	−126.3°

The values for toluene and isopentane, which also belong to this series but which, unfortunately, were not included here, will be determined at the earliest opportunity.

This investigation bears out the fact that accurate freezing points can be measured by heating curves. It should be pointed out that our method has the decided advantage of being applicable to all substances which can be caused to crystallize within the temperature range from 250°C. down to very low temperatures, irrespective of their viscosities or other properties, such as a slow rate of crystallization, which interfere with obtaining good values by the usual cooling-curve or Beckmann method (3). It requires only a small sample, an important factor where rare substances are being dealt with, and any number of determinations can be made on the same sample. Most important, the sample can be introduced into the freezing point tube and sealed off entirely out of contact with air, and the determination made *in vacuo*. This is particularly important not only in the case of compounds which are hygroscopic (like ethyl alcohol), or which absorb carbon dioxide in contact with air (like polyphenols), but also in the case of any liquid freezing below 0°C., for at low temperatures the condensation of moisture and of carbon dioxide, as well as the dissolving of the other constituents of the atmosphere, are a very grave source of contamination.

REFERENCES

(1) Timmermans, Van der Horst, and Onnes: Arch. néerland. sci. IIIA, **6**, 180 (1922). See also: Communications Phys. Lab. Univ. Leiden, Suppl. 51b, p. 35 (1924).
(2) Timmermans: Communications Phys. Lab. Univ. Leiden, Suppl. 84, p. 3 (1928).
(3) Skau: Proc. Am. Acad. Arts Sci. **67**, 551 (1933).
(4) International Critical Tables, Vol. I, p. 53.
(5) Keyes, Townshend, and Young: J. Math. Phys. Mass. Inst. Tech. **1**, 302 (1922), for a full description of the details of this method. See also, Loomis and Walters: J. Am. Chem. Soc. **48**, 3101 (1926), and Henning: Ann. Physik **43**, 282 (1914).
(6) Taylor and Smith: J. Am. Chem. Soc. **44**, 2450 (1922).
Keyes, Taylor, and Smith: J. Math. Phys. Mass. Inst. Tech. **1**, 211 (1922).
See also, Cardoso: J. chim. phys. **15**, 317 (1915).
(7) Private communication.
(8) Ostwald: Z. physik. Chem. **22**, 306 (1897).
(9) Timmermans: Helv. Chim. Acta **14**, 445 (1931).

A NEW METHOD FOR THE PREPARATION OF OXIDE CATALYSTS FOR THE CARBON MONOXIDE OXIDATION[1]

C. M. LOANE

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

Received December 2, 1932

INTRODUCTION

The study of the catalytic oxidation of carbon monoxide was begun in 1917 as a result of the war gas investigations. At first, in view of the practical nature of the problem, attention was focused upon the preparation of some cheap and durable catalyst, efficient at temperatures as low as 0°C. As a result of these studies there were prepared commercial catalysts consisting of mixtures of oxides. The preparation of a single pure oxide in sufficiently active state to be 100 per cent efficient at low temperatures was first accomplished in the case of manganese dioxide (1). Later an equally active cobalt sesquioxide (2) was prepared. In 1930, Bennett and Frazer (3) made a thorough study of seventeen pure metallic oxides, of which oxides eleven were partially efficient below 200°C. and three were 100 per cent efficient at freezing temperatures. These three active catalysts were the oxides of manganese, cobalt, and nickel.

A survey of the above work emphasizes several requisites for an efficient catalyst: (1) It must be finely divided. Any heat treatment reduces the active surface by sintering and is thus detrimental to the efficiency of the catalyst. This was recognized at the beginning of the investigation, and precipitation methods have been used throughout. (2) An oxide of a single metal, in order to be an efficient catalyst, must be extremely pure. Traces of impurities may inhibit or even entirely destroy the activity of the oxide. The success of Bennett's oxide catalysts was largely dependent on his method of purification of the hydroxides by electrolytic filtration. In previous experiments, the finely divided state of the oxide has been invariably secured by precipitation methods, and purity of the oxide by washing. Precipitation did secure a finely divided oxide, but it invariably resulted in contamination of the catalyst by the precipitant, usually sodium hydroxide. Lengthy and tedious washing was depended upon to remove the impurity.

The low temperature oxidation of pyrophoric metals provides a means

---

[1] From the dissertation submitted by C. M. Loane to the Faculty of Philosophy, The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

for the preparation of oxide catalysts whereby no impurity is introduced in large concentration and what foreign matter is present is easily removed. It is the purpose of this paper to develop in detail this new method for obtaining the oxides of nickel, cobalt, iron, manganese, and copper.

Two procedures were used for the preparation of the finely divided, pyrophoric metals: (1) Preparation of the metallic amalgams and subsequent removal of the mercury by distillation (4); (2) Reduction of the metallic salt by sodium in ammonia solution (5).

PREPARATION OF OXIDES OF METALS FROM AMALGAMS

The metallic amalgams were prepared by electrolysis of a slightly acid solution of the sulfates over a mercury cathode. The amalgams were vacuum distilled and the metal obtained in a pyrophoric condition. After oxygen had gradually come in contact with the metal so that at no time was a larger amount of heat generated, the product was tested for its catalytic efficiency.

Since the oxides prepared by the above method were not washed before testing, care was taken to purify the mercury and the sulfates used in the electrolysis.

The mercury was passed through a 6-foot nitric acid column four times and distilled three times.

Chemically pure sulfates were twice recrystallized. The electrolysis was carried out in a 400-cc. beaker. The concentration of the salt was chosen so that, by complete electrolysis of 300 cc. of solution, an approximately 2 per cent amalgam would be obtained. A few drops of sulfuric acid were added to the solution so prepared. Thirty cubic centimeters of mercury formed the cathode in the bottom of the beaker. The anode was of platinum gauze, except in the case of the manganese and iron salts. A current of approximately one ampere was used, so that the electrolysis was generally completed in twenty-four hours. Excess electrolyte was removed by washing the amalgam with distilled water.

In the case of the electrolytic preparation of the iron amalgam, an iron wire anode was used instead of the platinum gauze.

If the usual platinum anode was used when preparing the manganese amalgam, the amalgam was contaminated by scales of manganese dioxide forming at the anode and falling down on the amalgam. This difficulty was overcome by enclosing the anode in a glass tube, the bottom of which was formed by a porous clay disc. The inside of the tube was filled with concentrated ammonium nitrate solution. With these precautions observed, the electrolysis proceeded smoothly, without the formation of any dioxide. However, owing to the porous disc between the electrodes, only a small current could pass, and a week was necessary before a sufficiently concentrated amalgam was obtained.

In table 1 are listed the results of the above procedures.

Another method of obtaining the oxide catalysts was also used. The concentrated amalgam was exposed to the air until sufficient metal had separated as the oxide, and the powder was mechanically separated. Oxides of cobalt and of iron were readily obtained in this way. Nickel and manganese oxides were obtained in sufficient quantity only after several months. Copper amalgam was stable, no apparent oxidation taking place.

TABLE 1

Metallic oxides prepared from amalgams

METAL	NATURE OF AMALGAM	DISTILLATION TEMPERATURE *degrees C.*	NATURE OF METAL	CONDITIONS OF OXIDATION	NATURE OF OXIDE
Nickel..........	Thick, smooth	190	Dull grey, fluffy mass	O_2 stream 2 hours at 200°C.	Grey
Cobalt..........	Lumpy	250	Hard, grey, metallic lump	O_2 stream 3 hours at 200°C.	Grey, metallic
Iron............	Thick, lumpy	250	Hard, black lump	240°C. 3 hours	Dark red
Manganese......	Smooth, dilute	200	Grey, porous lump	200°C. 18 hours	Dark brown
Copper.........	Thick, lustrous	200	Red, spongy	200°C. 10 hours	Surface—dark blue

PREPARATION OF OXIDES OF METALS OBTAINED BY REDUCTION IN AMMONIA

Selected anhydrous salts of the metals were dissolved in ammonia and sodium added. The metals precipitated by the sodium were filtered, washed by ammonia, and allowed to oxidize slowly.

Anhydrous nitrates were used wherever possible. The nitrates cannot be dehydrated by heat treatment alone, for they decompose at a lower temperature than is necessary to drive off the water. A special method was necessary. That of Guntz and Martin (6) for the preparation of anhydrous cobalt and nickel nitrates seemed the most convenient. The nitrate was dissolved in its own water of crystallization at as low a temperature as possible and the solution poured into a large excess of fuming nitric acid. In several minutes the anhydrous salt precipitated. The excess nitric acid was decanted, and the precipitate washed several times with fuming nitric acid. Most of the acid was decanted and the rest removed by vacuum distillation over quicklime and phosphorus pentoxide. This procedure was successfully applied to the nitrates of nickel, cobalt, and copper.

Ferric nitrate (nonahydrate) was partially dehydrated by a modification of the above method and was used in this imperfect state of dehydration.

Guntz also prepared anhydrous manganous nitrate by treating the hydrate with nitric anhydride. As this method is too involved to be practical, it was decided to prepare the iodide, even though the halides are generally undesirable in that they are poisons for the carbon monoxide oxidation. Manganous iodide, $MnI_2 \cdot 4H_2O$, was prepared by bubbling hydrogen iodide through a mixture of manganous carbonate and water. A concentrated solution of manganous iodide was thus prepared and, when dried in vacuum, it readily yielded the anhydrous iodide (7) as a pale brownish-pink solid.

TABLE 2

Oxides prepared by slow oxidation of metals obtained by reduction in ammonia

METAL	NATURE OF PRECIPITATE IN AMMONIA	TIME OXIDE WAS WASHED *hours*	FINAL PRODUCT
Nickel	Brownish-black	24	Black
Cobalt	Very fine black	48	Black
Iron	Black	48	Red-brown
Manganese	Grey-brown	60	Grey-brown
Copper	Bronze	60	Brownish-black

An unsilvered 300-cc. Dewar flask was used as the reaction chamber. The use of such a vessel prevented the ammonia from evaporating rapidly and allowed the outer surface of the vessel to remain unfrosted so that the reaction could be observed.

The usual procedure for the reduction was as follows: the anhydrous salt was dissolved in ammonia, and sodium, freshly cut under petroleum ether, was added piece by piece as long as any reaction took place. This method was satisfactory for nickel, cobalt, manganese, and copper.

If the above routine was followed, the reduction of the incompletely dehydrated ferric nitrate was complicated by the formation of a complex and by the tendency of the added sodium to explode. In view of these difficulties, the roughly calculated amount of sodium was added first and the ferric nitrate later. The reduction then proceeded smoothly.

The precipitated metals were in all cases separated from the ammonia by suction filtering. The suction flask had to be immersed in an ether–dry ice mush to prevent the ammonia from boiling during the filtration. The precipitate was washed on the filter by approximately one half liter of liquid ammonia. At no time was the precipitate sucked dry from ammonia; and, while the metal was still moist, it was removed from the filter and placed in a vessel such as an Erlenmeyer flask, into which air could enter only by diffusion. Although the metals all became hot enough to glow when the ammonia was removed rapidly (as was the case when the suction filtering was continued too long), the method of gradually admitting air as the ammonia slowly evaporated served as an efficient means of slow oxidation. Several hours usually suffice for the oxidation.

Manganese was so active that it became warm in the Erlenmeyer while still moist with ammonia. A cork placed loosely in the mouth of the flask cut down the supply of air sufficiently so that rapid oxidation ceased.

The metal oxides, along with sodium oxide, hydroxide, and amide as impurities, were then placed on the suction filter and washed with water. The purification was continued until the water in the suction flask failed to give any test for sodium. The oxides (see table 2) were then dried and tested for catalytic effect.

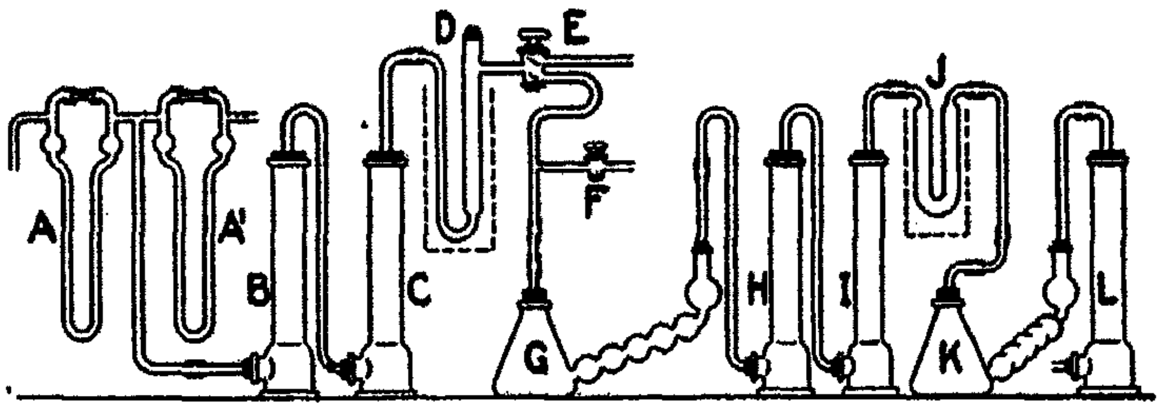


FIG. 1. CARBON MONOXIDE OXIDATION TRAIN

The results of the above procedures are given in table 2.

METHOD OF TESTING CATALYTIC EFFICIENCIES

The apparatus for testing the efficiency of the catalyst is shown in figure 1. Two flowmeters, A and A′, controlled the rate of the flow of carbon monoxide and oxygen. The valves of the carbon monoxide and oxygen storage tanks were adjusted to give a 1 per cent mixture of carbon monoxide in oxygen at a rate of 100 cc. per minute. The gases passed through a soda-lime tower, B, and a phosphorus pentoxide tower, C. The gaseous mixture then passed through the U-tube, D, which contained a 1 sq. cm. x 10 cm. bed of the catalyst. The carbon dioxide, formed during the passage over the catalyst, was absorbed in a solution of barium hydroxide contained in G. The residual gases were then swept through the soda-lime tower, H, and the phosphorus pentoxide tower, I. The dry mixture then passed through the U-tube, J, containing hopcalite maintained at 150°C. Any carbon monoxide which remained in the gas was completely oxidized by the hopcalite and was absorbed by the barium hydroxide in K. The remaining gas passed out through the soda-lime tower, L.

Stopcocks E and F were convenient for sweeping out the system and for regulating pressure when introducing barium hydroxide into the bubble tubes.

The catalysts obtained as hard lumps were broken up into smaller granules and sealed into the U-tube. Others of the oxides, in the form of fine powder, were packed in the tube with pieces of broken glass so as to decrease the resistance to the gas stream. The tube containing the catalyst was placed in the train and heated to 150–200°C. while a current of oxygen passed through the system. This treatment, continued for several hours, served at once to dry the catalyst, to further the oxidation of any of the metal that had not been oxidized at room temperatures, and to remove any carbon dioxide from the train. Fifty cubic centimeters of a standard solution of barium hydroxide was introduced into each bubble tube, and the flow of the gases through the system started. After running

TABLE 3

Efficiencies of the catalysts expressed in per cent

TEMPERATURES	−78°C.	−40°C.	0°C.	30°C.	100°C.	150°C.
Oxides prepared by distillation of mercury and activation in oxygen						
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Nickel				6	49	90
Cobalt	80	100				
Iron				7	50	100
Manganese*				5	38	62
Copper				2	24	
Oxides of metals prepared by reduction in ammonia						
Nickel				24	72	100
Cobalt†	100					
Iron					40	100
Manganese		0	100			
Copper				52	100	100

* Manganese and cobalt oxides, prepared by direct oxidation of the amalgam, were even more active, the latter being 100 per cent efficient at −78°C.

† The cobalt oxide was also tested before washing, when it contained at least 10 per cent impurity. Even with this large amount of sodium present, the oxide was 100 per cent efficient at 0°C. All the carbon dioxide formed by the oxidation was taken up by the sodium oxide, no carbon dioxide showing up in either bubble tube.

the test for the desired length of time, usually twenty minutes, the efficiency of the catalyst (see table 3) could be obtained by a determination of the amounts of barium hydroxide used up in the two bubble tubes. The percentage efficiency is the amount of barium hydroxide used up in the first bubble tube divided by the amount used in both bubble tubes. This was determined by titrating the unchanged barium hydroxide with standard acid.

COMPOSITION OF THE CATALYSTS

The catalysts from the amalgams were examined for mercury by precipitating with hydrogen sulfide. The cobalt and nickel catalysts showed the presence of a trace of mercury, but in the case of the other metals no mercury was found. It is unlikely that the small amount of mercury present would have any effect on the reaction.

In the case of the catalysts prepared by oxidation of metals precipitated in ammonia, sodium must have been present in small amounts. However, alkalies have been shown to be poisons for this reaction (8) and could certainly have exerted no promoter action.

TABLE 4

Comparison of activities of oxides

METALS	PRECIPITATED OXIDES (BENNETT)		OXIDES FROM AMALGAMS		OXIDES OF METALS FROM AMMONIA	
	At 30°C.	At 100°C.	At 30°C.	At 100°C.	At 30°C.	At 100°C.
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Nickel	100	100	6	49	24	72
Cobalt	100	100	100	100	100	100
Iron	0	1	7	50		40
Manganese	100	100	5	38	100	100
Copper	Reduction	100	2	24	52	100

The amount of oxygen in the catalyst had no meaning. For example, analysis of one of the cobalt catalysts showed slightly less oxygen than corresponded to 2 oxygen:3 cobalt. In all cases the amount of oxygen varied according to the conditions of activation.

As is evident, it was not attempted to obtain a catalyst of definite composition, but it *was* shown here that the active metallic surface may be changed into an active oxide surface by a process of low temperature oxidation.

RELATIVE EFFICIENCIES OF OXIDIZED METALS AS CATALYSTS

Some idea of the activities of these oxides relative to those of precipitated oxides may be obtained from table 4.

As is evident from table 4, the method developed in this paper does not give oxides any more active than those precipitated and carefully purified. It does, however, offer another general method of preparing oxides whose activity is certainly comparable to that of those prepared by precipitation.

The percentage efficiencies given for the oxidized metals may be made to parallel those for the precipitated oxides even more closely if the following facts are taken into account.

The low results for nickel and manganese oxides from the amalgams are due to the insufficient oxidation of the metal. The oxides can be made more efficient by longer heating in oxygen.

Higher efficiencies may be expected in the case of nickel and manganese oxides (prepared by reduction in ammonia) if the washing is continued longer. The results given in table 4 are for the oxide washed for only one or two days. Longer purification slowly increased the efficiency.

The efficiencies of oxidized iron and copper are listed higher than those of the precipitated oxides. The results given in this work, however, are for a twenty minute run. At least part of the carbon monoxide oxidation below 100°C. involves chemical reduction of the oxides, for subsequent runs show decreasing efficiency of the catalyst.

The results obtained in this present work bring out an interesting point. It is the general belief that manganese dioxide is more active catalytically than the other oxides and that its presence as the essential oxide in commercial catalysts is uniquely responsible for the efficiency of those catalysts. The data presented here seemed to show that the oxide of cobalt is more active, or, at least, that it is less sensitive to impurities and generally easier to prepare in an active form.

SUMMARY

1. Methods have been developed for the low temperature oxidation of pyrophoric metals.

2. The oxidized metals have been tested as catalysts for the carbon monoxide oxidation. They have been found to be comparable in activity to the most carefully purified precipitated oxides.

REFERENCES

(1) WHITESELL AND FRAZER: J. Am. Chem. Soc. **45**, 2481 (1923).
(2) WILLIAMS: Dissertation, The Johns Hopkins University, 1928.
(3) BENNETT: Dissertation, The Johns Hopkins University, 1930.
(4) FEREE: Compt. rend. **121**, 822 (1895).
(5) BURGESS: Chem. Rev. **8**, 271 (1931).
(6) GUNTZ AND MARTIN: Bull. soc. chim. **5**, 1004 (1909).
(7) PETERS, W.: Ber. **42**, 4826 (1909).
(8) BENNETT: Dissertation, The Johns Hopkins University, 1930.

THE PHYSICAL CHEMISTRY OF FLOTATION. I

The Significance of Contact Angle in Flotation

IAN WILLIAM WARK

Department of Chemistry, University of Melbourne, Melbourne, Australia

Received September 17, 1932

CONTENTS

INTRODUCTION

Adhesion between a bubble of air and a solid surface is the basis of the flotation process. In order that a small particle of mineral may become incorporated in the froth at the top of the machine, it is necessary first for it to become attached to (i.e., to adhere to) an air bubble of sufficient buoyancy to carry it upwards. It is the purpose of this communication to investigate some of the physical and chemical principles underlying the adhesion between a bubble of air and a single solid particle and to draw attention to some of the problems awaiting solution before an explanation of the physical nature and behavior of froth systems can be obtained. The froth differs from the simple case in which a single particle is considered, in that each bubble is coated by numerous small particles of mineral instead of merely being attached to one particle. Nevertheless a discussion of the principles involved for a single particle may be of some value in considering the general case.

It has been shown (1) in the course of an investigation being carried out in the University of Melbourne for and at the expense of a group of mining companies[1] that an air bubble in water will not adhere to a clean surface of any of the common sulfide or gangue minerals or to metals. When, however, a unimolecular film of a xanthate is adsorbed by the mineral, the air of the bubble spreads to a limited extent over the mineral surface, partly replacing the aqueous phase in so doing. Spreading continues until a definite angle between the air–water interface and the water–mineral interface, θ, is attained which is determined by the well-known relationship:-

$$\cos \theta = \frac{T_{as} - T_{sw}}{T_{wa}}$$

where T_{as}, T_{sw}, and T_{wa} are the surface tensions at the air–solid, solid–water, and water–air interfaces, respectively. Different conditions of the mineral surface and different reagents lead to variations in the contact angle. One of the major objects of this paper is to investigate the significance of changing contact angle on the tenacity of contact between air and mineral and, through it, on floatability. Incidentally, it should be noted that the molecular mechanism through which adhesion is achieved is unimportant in thermodynamical and mechanical discussions.

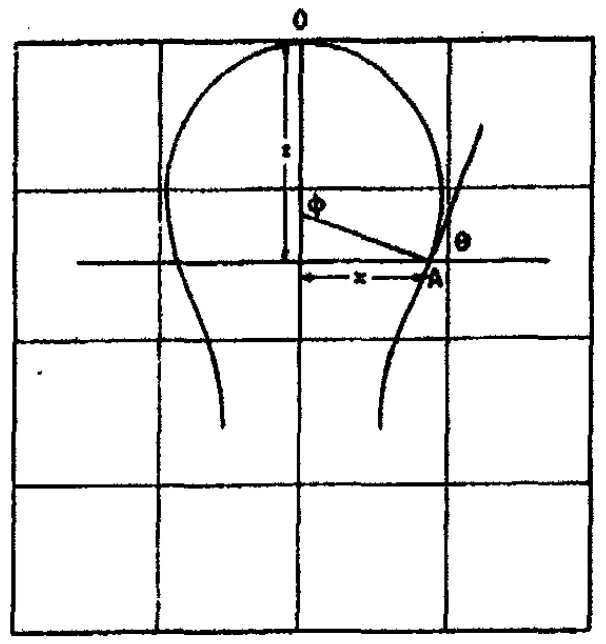


FIG. 1

I. EQUATION TO THE SURFACE OF A STATIONARY BUBBLE OF AIR IN WATER

All theories of capillarity are in agreement concerning the difference in pressure on the two sides of a curved interface between two fluids, namely, that this pressure difference at any point is equal to

$$T_{wa}\left(\frac{1}{R} + \frac{1}{R'}\right)$$

---

[1] Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Co. of A/asia Ltd., Mt. Lyell Mining and Railway Co., Burma Corporation Ltd.

where T_{wa} is the surface tension and R and R' are the two principal radii of curvature at that point. Assuming this difference in pressure, Bashforth and Adams (2) show how the equation to the surface may be derived. Since this work is not generally available, a modified development is presented here. Let P_O and P_O' be the pressures on the inner and outer sides, respectively, of the surface at O and P_A and P_A' be the corresponding pressures at any point A. Let ϕ be the angle which the normal to the surface at A makes with the axis of revolution, and let θ be its supplement. The two principal radii of curvature are equal at O; let each be denoted by b. One of the two principal radii of curvature at A is $x/\sin\phi$; let the other be denoted by ρ. It is obvious that

$$P_A - P_O = \sigma_1 g z \tag{1}$$

and

$$P_A' - P_O' = \sigma_2 g z \tag{2}$$

where σ_1 and σ_2 are the densities of air and water respectively. Then

$$P_O - P_O' = T_{wa} \cdot 2/b \tag{3}$$

$$P_A - P_A' = T_{wa}\left(\frac{\sin\phi}{x} + \frac{1}{\rho}\right) \tag{4}$$

Whence, subtracting equations 3 and 4 and substituting from equations 1 and 2,

$$gz\,(\sigma_1 - \sigma_2) = T_{wa}\left(\frac{\sin\phi}{x} + \frac{1}{\rho} - \frac{2}{b}\right) \tag{5}$$

or

$$\frac{2}{b} + \frac{gz\,(\sigma_1 - \sigma_2)}{T_{wa}} = \frac{\sin\phi}{x} + \frac{1}{\rho} \tag{6}$$

In the case of a bubble of air in a liquid, $\sigma_1 - \sigma_2$ is negative.

Following Bashforth and Adams let

$$\frac{gb^2\,(\sigma_1 - \sigma_2)}{T_{wa}} = \beta$$

Equation 6 then becomes

$$\frac{1}{\rho} + \frac{\sin\phi}{x} = \frac{2}{b} + \frac{\beta z}{b^2} \tag{7}$$

in which β is negative.

If ρ and ϕ are expressed[2] in terms of x and z it becomes apparent that the differential equation cannot be exactly solved. Using equation 6, Bashforth and Adams have constructed tables by which corresponding values

---

[2] Expression of ρ and ϕ in terms of x and z:

$$\frac{1}{\rho} = \frac{d^2z}{dx^2} \div \left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{3/2}$$

$$\sin\phi = \frac{dz}{dx} \div \left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{1/2}$$

of x, ϕ, and z may be approximately obtained for any given values of b and β. β determines the form of the bubble and b its magnitude, but since β depends partly on b, the magnitude of the bubble partly determines its form. These tables are extensive enough for the calculation of the shape of the interface between two fluids for which $\sigma_2 > \sigma_1$, i.e., where β is positive. Where β is negative, however, they are not nearly as comprehensive, and for bubbles of air in water it is only over a limited range that the calculations are possible.

It will be apparent that the nature of any solid surface to which the bubble of air may be attached has no influence on the shape of the bubble, for the nature of the solid cannot affect any of the pressure terms used in deriving the equation to the surface. The bubble fits on to the surface of the solid with a definite angle of contact, and above the plane of contact the shape is the same as that of a bubble of greater depth. Fortunately Bashforth and Adams tabulate the angle ϕ, which is he supplement of the angle of contact, θ, measured across the water, at the line of triple contact. This angle was directly measured in the paper already cited (1).

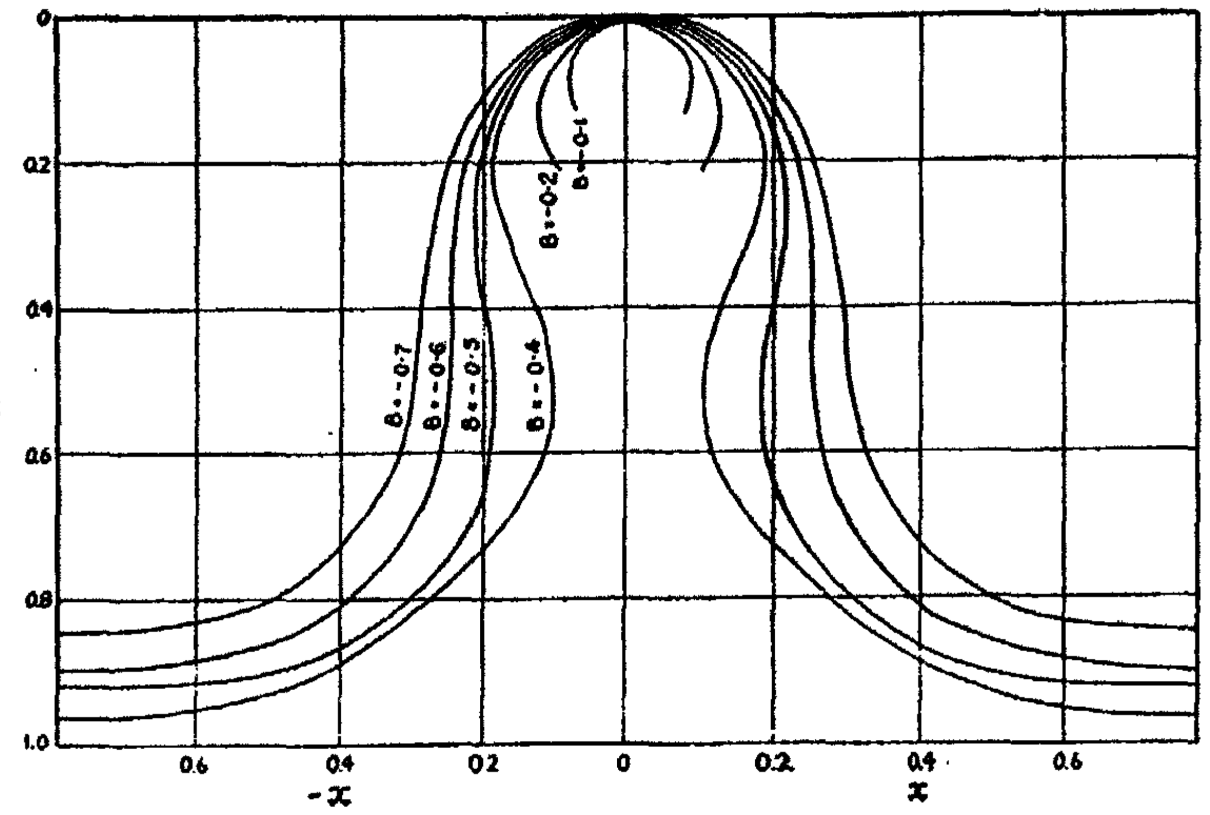


FIG. 2. SHAPES AND SIZES OF STATIONARY AIR BUBBLES IN WATER (IN CM.)

II. ARITHMETICAL SOLUTION OF THE EQUATION FOR BUBBLES OF DIFFERENT SIZES

Since

$$\beta = g \frac{(\sigma_1 - \sigma_2)}{T_{wa}} \cdot b^2$$

and, from Kaye and Laby's Physical and Chemical Constants, $g = 980$ cm. per sec.^{2} for Melbourne, $(\sigma_1 - \sigma_2) = 0.997$ at 20°C., allowing for the saturation of the air by water vapor, and $T_{wa} = 72.8$ dynes per centimeter (Bohr's value), the value of β reduces to $-\ 13.43\ b^2$.

Figure 2 shows not only the shapes but the actual sizes in centimeters of a series of bubbles of air in water corresponding to different values of β. These have been calculated from Bashforth and Adams' values of x/b and z/b, and the value of b corresponding to each value of β. There is good agreement between the shapes of calculated curves and photographs of actual bubbles.

Worthington (3) states that pendant drops of liquids are unstable with regard to surface oscillations at points where they are reëntrant. The writer has not been able to obtain any reasonably stable reëntrant surfaces, though if the buoyancy of the bubble is balanced by an upper supporting tube, reëntrant surface may persist for some time in the absence of vibrations.

III. EQUATION CONNECTING VOLUME OF BUBBLE, ANGLE OF CONTACT, AND AREA OF AIR-SOLID CONTACT

Bashforth and Adams develop by two methods a formula for the volume contained by a bubble above any given plane in the bubble. The following analysis is based upon their second derivation. Assume that a mass of water of the same size and shape as that portion of the bubble being considered replaces it in the water. The vertical forces acting on this mass of water, which obviously is in equilibrium, are:

(1) Its weight $V \cdot \sigma_2 \cdot g$ acting downwards.
(2) The force due to the hydrostatic pressure P_A' at the base of the volume, $P_A' \cdot \pi \cdot x^2$ upwards.
(3) The resultant, F, (acting downwards) of the hydrostatic pressure over the curved part of the surface.

Whence

$$F + V\sigma_2 g = \pi x^2 P_A' \qquad (8)$$

For the bubble of air, the vertical forces acting on the portion under consideration are:

(1) The same force, F, acting downwards.
(2) Its weight $V\sigma_1 g$ acting downwards.
(3) The surface tension force, $2\pi x T_{wa} \cdot \sin\phi$, acting downwards.
(4) The pressure of the air lying under the plane considered, $\pi x^2 P_A$. (If the bubble is cut off, not by an imaginary plane but by a solid surface, this pressure term is placed by an equal reaction acting upwards.)

Whence

$$F + V\sigma_1 g + 2\pi x T_{wa} \sin\phi = \pi x^2 P_A \qquad (9)$$

Equations 8, 9, and 4 reduce to the equation of Bashforth and Adams, viz.,

$$V = \frac{\pi x^3 T_{wa}}{g(\sigma_1 - \sigma_2)} \cdot \left(\frac{1}{\rho} - \frac{\sin \phi}{x}\right) \tag{10}$$

or, introducing β,

$$V = \frac{\pi b^2 x^3}{\beta} \cdot \left(\frac{1}{\rho} - \frac{\sin \phi}{x}\right) \tag{11}$$

where, as before, β is negative. Since V is always positive, $\sin \phi / x$ must always be greater than $1/\rho$. Bashforth and Adams have constructed numerical tables for different values of β and b which enable a numerical solution for V—correct, if necessary, to 1 part in 100,000—to be made over a limited range.

It would be possible to construct a three-dimensional model to show corresponding values of the three variables, V, θ, and x for any two fluids, assuming T_{wa}, $\sigma_1 - \sigma_2$, and g to be known, i.e., b^2/β to be fixed. It is, however, easier in the first place to construct sectional diagrams which represent the relationship between any two of the three variables when the third is constant. These sectional diagrams are now considered.

IV. ARITHMETICAL SOLUTION OF THE EQUATION OF III

(*a*) *θ constant.* Figure 3 shows the relationship between V and x for a series of different (constant) values of θ. The irregular choice of angles in constructing this figure was necessitated by the incompleteness of the tables upon which the calculations were based.

The meaning of the graph is best illustrated by considering for one of the curves (for example that for 90°) the shapes of the bubbles corresponding to a number of points on the curve. The numbers 3, 4, etc., correspond to those portions of the bubbles of figure 2 above $\theta = 90°$ for values of β of $-$ 0.3, 0.4 etc., respectively. The points marked 4a and 4b correspond to bubbles, one of which (4b) is merely a continuation of the other to a position where, for the second time, an angle of 90° develops. As explained above, this involves a reëntrant surface and thus for flotation the portion of the curve beyond 6a is probably unimportant.

Two important curves follow from figure 3. These show respectively (1) maximum volume of bubble for a given value of θ (figure 4) and (2) maximum value of x for given values of θ (figure 5).

The figures of figure 5 are immediately applicable in flotation, but the maximum values of V given in figure 4 all correspond to bubbles with reëntrant surfaces. The maximum values for non-reëntrant bubbles are also plotted in the dotted curve; these would be of more interest with regard to flotation.

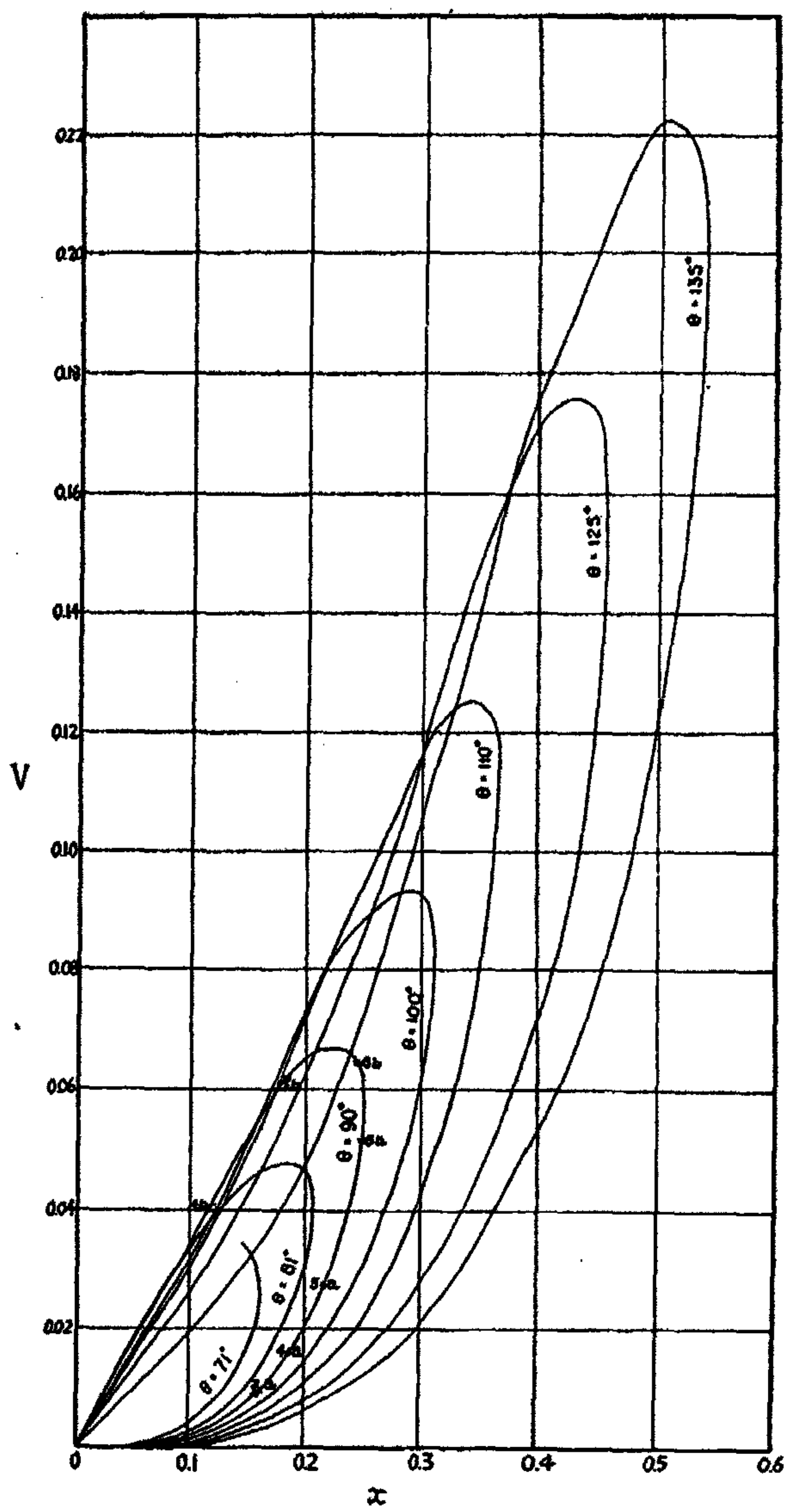


FIG. 3. RELATIONSHIP BETWEEN VOLUME OF BUBBLE AND RADIUS OF CIRCLE OF CONTACT FOR VARIOUS ANGLES OF CONTACT

Experimental verification. Figure 5 has been verified experimentally, the points marked by a circle being experimental values. This verification

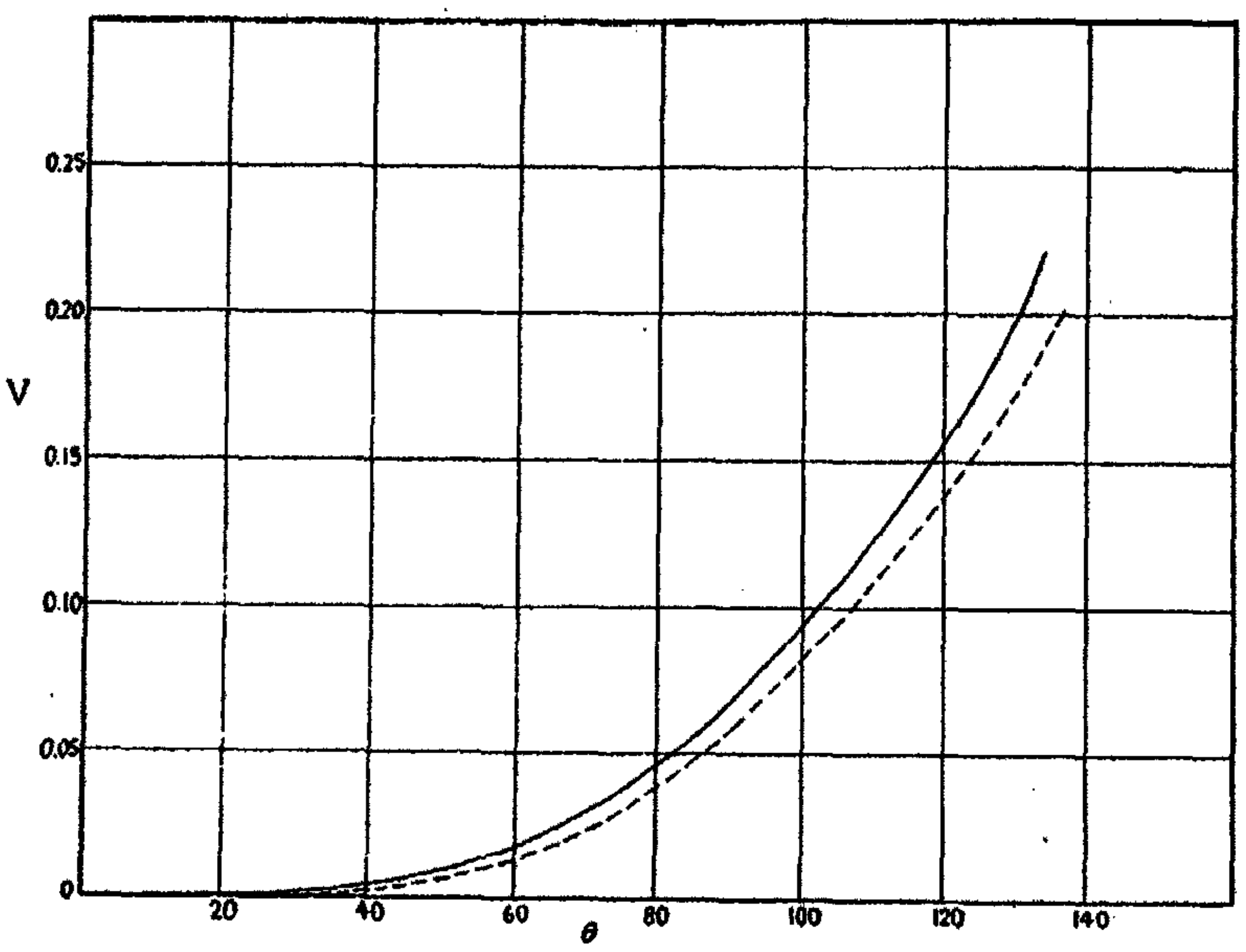


FIG. 4. MAXIMUM BUBBLE VOLUMES FOR GIVEN CONTACT ANGLES

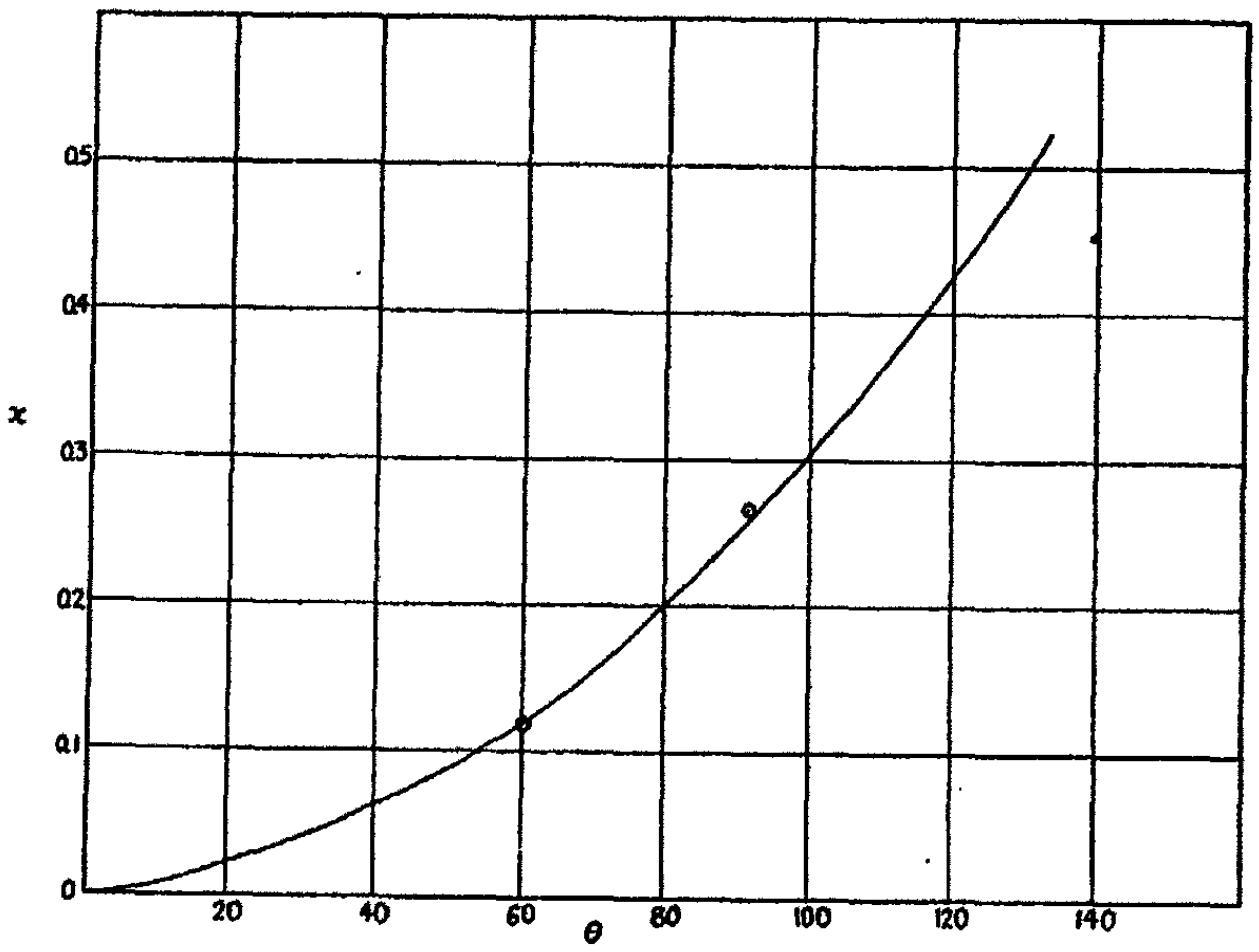


FIG. 5. MAXIMUM VALUES OF RADIUS OF CIRCLE OF CONTACT FOR GIVEN CONTACT ANGLES

⊙ Experimental points

is tedious, a large number of bubbles which will just hang to the surface being measured for a series of different xanthates, which give characteristic contact angles. The experimental points were determined by Mr. A. B. Cox without preknowledge of the position of the theoretical curve.

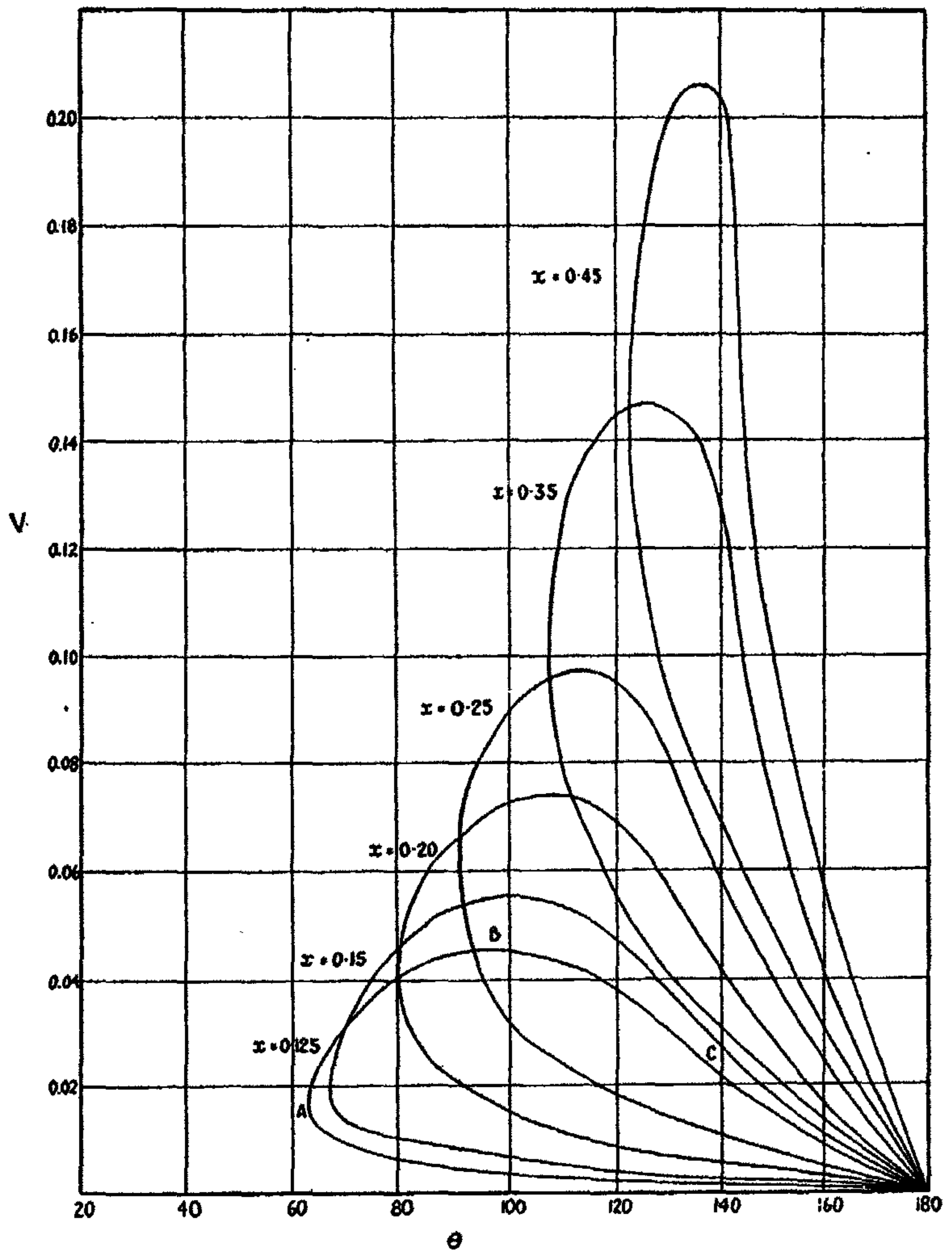


FIG. 6. RELATIONSHIP BETWEEN VOLUME OF BUBBLE AND ANGLE OF CONTACT FOR VARIOUS VALUES OF RADIUS OF CIRCLE OF CONTACT

(b) *x constant.* Figure 6 shows the relationship between V and θ for a series of different (constant) values of x. The meaning of the curves is

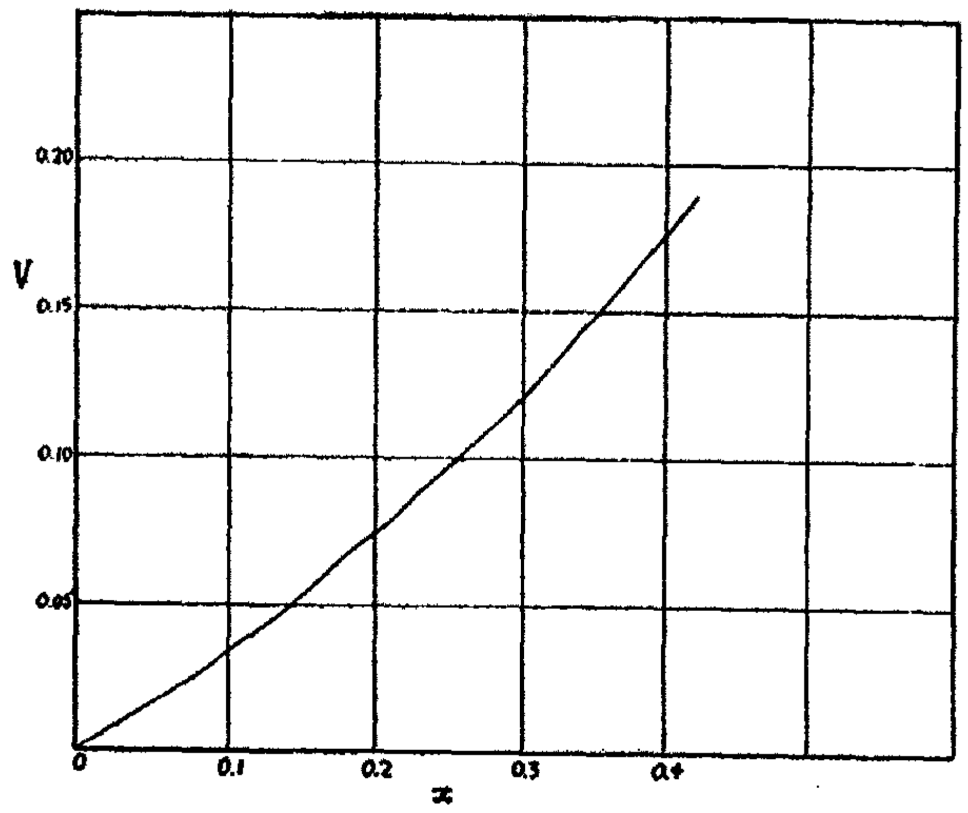


Fig. 7. Maximum Bubble Volumes for Given Values of Radius of Circle of Contact

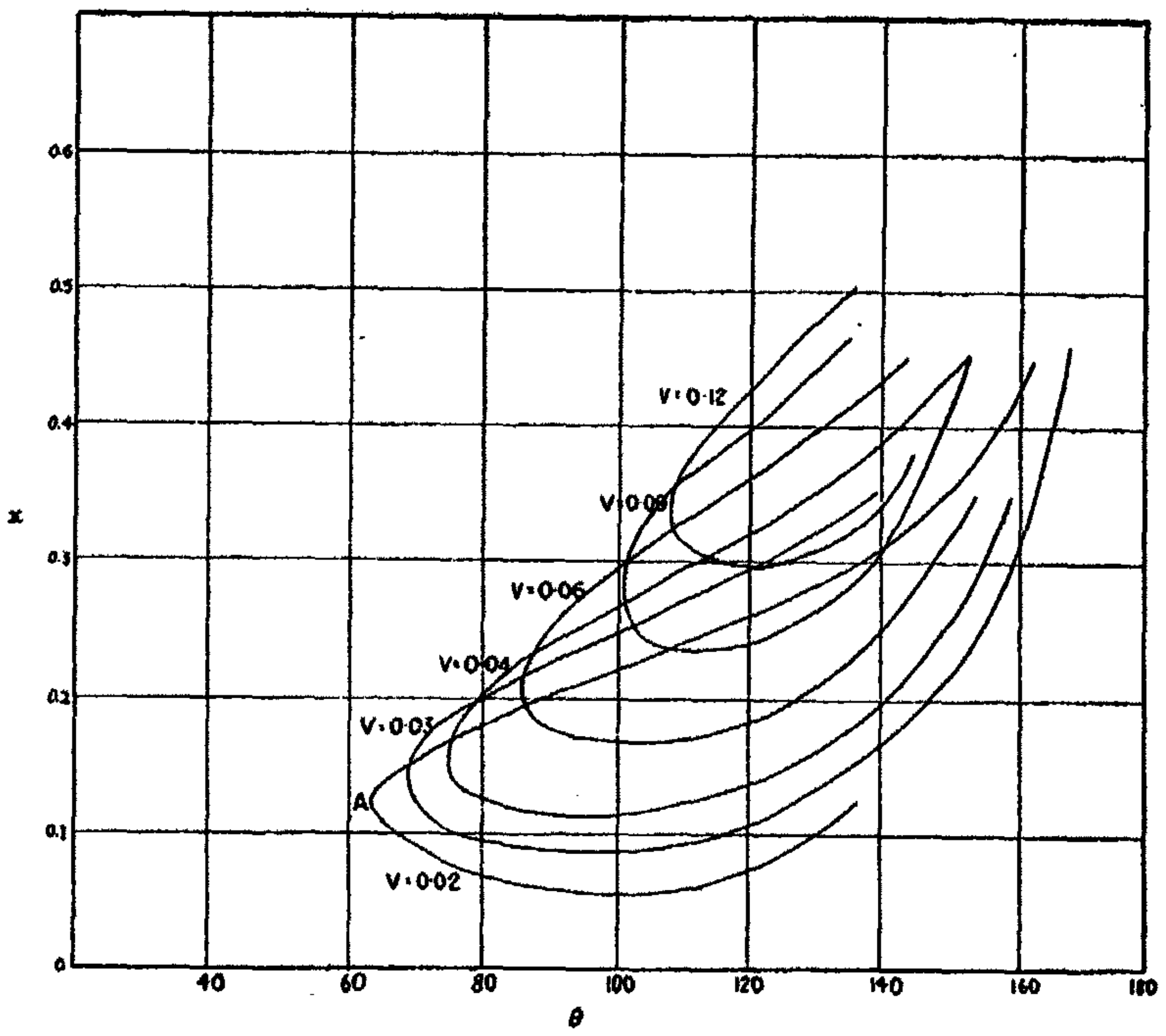


Fig. 8. Relationship Between Radius of Circle of Contact and Angle of Contact for Various Values of Bubble Volume

again best understood by tracing, for one of the curves—e.g., that for x = 0.125 cm.—the shapes of the bubbles corresponding to various points on the curve. Along the portion OA the angle of contact is steadily decreasing to the minimum value, but along AB it increases again as reëntrant surfaces appear. From B to C, though the angle is still increasing, the volume is diminishing, owing to increasing flatness of the bubble.

Two important curves follow immediately from figure 6. These show, respectively, (1) the minimum value of θ for given values of x, and (2) the maximum value of V for given values of x (figure 7). It is obvious that the curve showing the minimum values of θ plotted against x is identical with that of figure 5, which shows the maximum value of x plotted against θ.

(c) V *constant.* Figure 8 shows the relationship between θ and x for a series of different (constant) values of V. It will be seen that both arms of any of these curves approach the x-axis asymptotically. The points on the lower arm all represent bubbles with reëntrant surfaces; at A, however, reëntrant surfaces disappear and from A back to the x-axis the bubbles have the simplest form.

V. REPLACEMENT OF SOLID–WATER CONTACT BY SOLID–AIR CONTACT

Tenacity of adhesion

The conditions which determine whether air will displace water at the surface of a solid follow immediately from thermodynamics. This has been realized by several writers, but others have given incorrect analyses. Restatement may be helpful. For any rearrangement of the surfaces to occur when an air bubble is brought into contact with a submerged mineral surface, it is necessary that the potential energy should decrease. Since, under the conditions of flotation practice, the air–mineral interface cannot be created without the simultaneous destruction of mineral–water and water–air interfaces, the condition for replacement of water by air is evidently[3]

$$T_{as} < T_{wa} + T_{sw}$$

and

$$W = T_{wa} + T_{sw} - T_{as} \tag{12}$$

is the measure in ergs of the work done per unit area by the system during this rearrangement.

No satisfactory method is available for the determination of the surface tensions at the solid–liquid and solid–air interfaces, but the value of T_{wa}

---

[3] It is shown in textbooks of physics that free surface energy in ergs per unit area and surface tension in dynes per unit length are numerically equal. Surface tensions may therefore be used in place of surface energies in these equations.

may be measured by a variety of methods. Both T_{as} and T_{sw} may be eliminated, however, by introduction of the contact angle.

When equilibrium is reached,

$$\cos \theta = \frac{T_{as} - T_{sw}}{T_{wa}}$$

and substituting for $T_{as} - T_{sw}$ in equation 12

$$W = T_{wa} (1 - \cos \theta) \tag{13}$$

which is the work done per unit area in forming the contact between air and solid (free energy of formation) at the expense of the solid–water and water–air contacts, or alternatively is the work[4] which must be expended in destroying the air–solid contact. It may thus be regarded as a measure of the tenacity of adhesion. When $\theta = 0$, the expression reduces to zero and there is no tendency for sticking; when $\theta = 180°$, the expression reaches a maximum of $2T_{wa}$. The adhesive tendency may conceivably be greater than corresponds to complete wetting by air, if $T_{as} - T_{sw} > T_{wa}$ (4), but no such cases are known.

VI. TRUE AND APPARENT AREA OF CONTACT

When a submerged bubble of air is pressed against a solid surface it sometimes fails to spread uniformly. Portions of the surface are in true contact with the air, but others may be fouled or for some other reason the air makes no true contact with them. The area of true contact will not then be identical with the apparent area of contact, and in estimating the tenacity of contact from the equation, $W = T_{wa} (1 - \cos \theta)$ ergs per unit area, the true rather than the apparent area of contact must be employed.

It is important that the relationship between these two areas should be known. Some experiments at a cerussite surface using a bubble of carbon tetrachloride throw light on this question. If the surface be freshly prepared in the manner described in the third paper of this series, the carbon tetrachloride does not spread immediately over the whole surface. Contact first occurs at a series of small isolated areas whose extent gradually increases. The water is gradually forced out between them and ultimately, save for a few irregular patches, there is a complete disc of contact between the carbon tetrachloride and the mineral. A few patches of the surface remain wetted by thin layers of water. These observations,

---

[4] Since the surface of the bubble is curved at the point of contact, and since, further, there is a rearrangement of the air–water interface after disruption, small corrections are necessary. The curvature introduces a "pressure" correction; that it is neligible for fairly large bubbles is proved by the absence of variation in contact angle with size of air bubble, and also follows from Lyons' work on floating lenses (J. Chem. Soc. **1930**, 623).

which extend over only a fraction of a minute, are possible because of the high refractive index of the carbon tetrachloride. The line of vision should be at right angles to an illuminating beam of light and inclined at 20° to the horizontal.

If, however, the surface of the mineral is oiled, or is coated by what is called in flotation an organic collecting agent, the carbon tetrachloride spreads outwards very quickly, and no surface inclusions of the aqueous phase remain. It may be concluded that where the surface is in a receptive condition for air-contact, the true and apparent areas of contact are identical. This conclusion is supported by the uniform manner in which a bubble of air leaves the surface if it is pulled away.

Ostwald (5) has formulated an ingenious theory in which he claims that only a unimolecular ring of the organic collecting agent is necessary to ensure attachment of the bubble to the particle. His main evidence in favor of this theory is the very doubtful statement that sufficient collector is not present to form a unimolecular film over the whole surface. The above expression for the tenacity of sticking proves, however, that such a ring contact would be so unstable as to collapse with the slightest displacement unless the moving air–water–mineral boundary carried with it the ring of collector, i.e., that the attraction between mineral and collector was so small as to permit free movement of collector molecules over the surface. This it is not, for if a mineral which has had contact with a xanthate solution for a minute be removed and washed in several changes of water, it still retains over its whole surface the power of attachment to an air bubble. Recent measurements of surface tension (6) indicate moreover that there is little adsorption of xanthate in the air–water interface.

A contaminated patch in the center of the air–mineral contact will not, of course, influence the stability of the contact for small displacements, but it will cause a rapid unopposed contraction of the area of contact the moment the displacement of the bubble wall reaches it.

In the experiments described in the paper of Wark and Cox (1) and in those of the following papers, there has been little or no fouling of the surface. When one is approaching a region of non-sticking, however, as for example when alkali is added to a xanthate solution in contact with galena, the surface does change in such a way that the true area of contact is apparently greatly diminished. Even on a partly fouled surface, at points where sticking is possible, the full angle of contact may be developed.

VII. DIFFICULTIES IN THE EXPERIMENTAL DETERMINATION OF ANGLE OF CONTACT—HYSTERESIS

Sulman (7), Ablett (8), and Langmuir (9) have shown that the angle of contact varies according to whether the line of contact between air, water, and solid is advancing or receding. The angle θ'' is greater when the water–solid contact is being replaced by an air–solid contact than the angle θ' when the reverse is occurring. The difference $\theta''-\theta'$ is termed the "hysteresis."

Sulman has shown that the variation lies within certain well-defined limits, which he claimed were dependent on the mineral. Ablett also showed that the limits were clearly defined on a paraffin surface and, furthermore, that the mean of θ'' and θ' was very close to the equilibrium value, θ; also that the difference between θ'' and θ' was a function of the rate of motion, and was constant over a range from 0.4 to 4 mm. per second.

The angle of contact of a bubble in equilibrium on a solid surface is (subject to certain minor corrections) given by the expression

$$\cos \theta = \frac{T_{as} - T_{sw}}{T_{wa}}$$

Edser (10) concludes that if, owing to hysteresis, θ alters, T_{as} must have altered. (It is not stated why T_{as} and not T_{sw} has been assumed to alter.) This would be true if the bubble were still in equilibrium, but under such conditions it is not. If the vessel in which the mineral rests is shaken lightly, e.g., by tapping the table upon which it stands, the angle of contact reverts to the equilibrium value θ. Hundreds of tests have supported this contention. Apart from any experimental verification, however, it is obvious that the stress applied at a point of the bubble can have no effect on the surface energies of the distant interfaces mineral–water and mineral–air.

Some secondary force must assist in the maintenance of apparent equilibrium, if variations in T_{as}, T_{sw}, etc., are inadmissable. A frictional force alone could be responsible. To make the argument specific, let it be assumed that the stress at the base has been caused by an upward extension of the bubble which has the effect of narrowing it along its length.

When the top of the bubble is raised, an attempt is made to increase the volume of the bubble. This reduces the pressure of the bubble, and thereby creates an excess external pressure which tends to push in the bubble wall. Yet some force, resulting in the hysteresis, prevents the base of the bubble from contracting, though in equalizing the pressure the bubble wall alters in shape and a new angle of contact develops. Only a horizontal opposing force could be effective in preventing motion along the mineral surface under the stress of this pressure. This horizontal force is thus responsible for the new value of the angle. Furthermore this force must disappear when true equilibrium is reëstablished, for the original angle is again obtained. Such a force, which acts parallel to the direction of possible motion and disappears when stable equilibrium is reached, is customarily styled a frictional force. Hysteresis of contact angle is thus a manifestation of friction.[5]

Adam and Jessop (11) have already suggested that hysteresis is due to friction, but their paper has not received the attention it deserves. This is perhaps due to the fact that, beyond the statement that the degree of hysteresis is less at smooth than at rough surfaces, they give no reason for this interpretation.

Our experience confirms this statement. It is by no means certain that the laws of friction at solid surfaces may be applied when considering solid–fluid contacts, but, assuming that they may, it follows that the frictional force opposing motion of the bubble over the surface is proportional to our L of equation 16.

Assuming that hysteresis is due to friction, Adams and Jessop develop a formula for θ, namely,

$$\cos \theta = 1/2 \, (\cos \theta'' + \cos \theta') \tag{14}$$

In deriving this expression the authors equate terms of unequal dimensions, but their final expression is correct. If H dynes per centimeter of air–water–mineral boundary be the frictional force it may be shown that

$$H = 1/2 \, T_{wa} \, (\cos \theta' - \cos \theta'') \tag{15}$$

Since $\theta'' - \theta'$ may be as high as 60°, the frictional force may be of an order of magnitude as high as one-quarter that of the surface tension.

Ablett's results for paraffin wax are accurate enough for testing equation 14. He found that

$$\theta'' = 113°9'$$

and

$$\theta' = 96°20'$$

Whence

$$1/2 \, (\cos \theta'' + \cos \theta') = 0.2517$$

and

$$\theta_{\text{calc.}} = 104°35'$$

Ablett's θ, as measured, was 104°34′. Ablett wrongly expected $1/2 \, (\theta'' + \theta')$ to equal θ. The mean value is 104°44′ which differs from the deter-

---

[5] The difference between interfacial energy (or tension) and friction is as follows: Interfacial energy changes become manifest with destruction and creation of interfaces; the frictional force and energy consumed thereby are associated with displacements of surfaces, not primarily with changes in their extent.

mined value of θ by more than the experimental error. A better check of the theory could be obtained when using smaller values of θ, for which the difference between mean and cosine mean is greater.

VIII. THE STABILITY OF AIR–MINERAL ATTACHMENTS

There has been some misconception with regard to the influence of hysteresis on the stability of air–mineral aggregates. Though there may be some justification for Sulman's claim that hysteresis imparts a greater range of stability to a floated particle, there can be none for Edser's statement that, "No particle could float stably but for the possibility of variation of the contact angle, for if this were constant, a slight tilt would inevitably cause the particle to sink." Sulman later (b) states, "But for hysteresis a mineralized bubble could only have a brief existence." Were these statements correct the measurement of contact angle would lose some of the significance which we have given to it. It would need to be supported by an estimation of the hysteresis. It devolves upon us, therefore, to explain why it is considered that these statements are incorrect.

It has been proved above that when the air–mineral contact is formed there is a decrease in free energy of the system amounting to $T\ (1 - \cos\theta)$ ergs per cm.^{2} of contact. Since $(1 - \cos\theta)$ is always positive, there is invariably a *decrease* of free energy on the sticking of the bubble. This amounts to saying that the process occurs spontaneously. To liberate the air bubble from the surface would require the expenditure of an equal amount of work. This implies that the equilibrium is a stable one with regard to attempts at disruption.

While contact between mineral and air is being established, and the air is spreading over the surface of the mineral from a small nuclear point of attachment, frictional forces would tend to retard the spreading. There would thus be a tendency to prevent the true equilibrium angle and area of contact being reached, so that the maximum tenacity of sticking between air and mineral would develop rather slowly. Nevertheless, because of the violent agitation in the flotation boxes, it is probable that the true contact angle would develop within a reasonable time. The initial effect of hysteresis is therefore to prevent maximum attachment between air and mineral, which is the primary step in flotation.

The effects of hysteresis on the stability of an attachment already established must also be considered. It is obvious that, as the contact angle can be raised slightly by hysteresis, the stability of contact under a transient stress can be increased—momentarily at least. Sulman's claim that hysteresis imparts a greater range of stability is thus justified in this case.

An analysis of the effects of all possible types of stress which may be applied to a bubble in contact with a mineral surface leaves one in doubt whether hysteresis ever imparts much greater stability to the attachment.

The bubble and mineral must part company by relative motion in a direction at right angles to the surface and the force of friction, being parallel to the surface, cannot be effective in preventing such motion. On the other hand, friction does oppose easy motion of a bubble over the surface of a solid or of a solid over the surface of a bubble, but this is probably disadvantageous.

Some experiments with diphenyl ether $C_6H_5OC_6H_5$ confirm these views. The density of this substance is 1.07 and it melts at 28°C. If the melt be allowed to cool on a glass plate, very large smooth crystals form. On the smooth surface there is practically no hysteresis effect, yet nothing known to us floats so readily. It is true that the floatability of large plates of the compound by very small bubbles is due to the very small difference between its density and that of water, but the ability of the aggregate to withstand large stresses is, we suspect, due to the absence of hysteresis and the consequent flexibility which enables adjustment of the partners of the aggregate to meet any external stress.

Extension to moving systems

Even when air-mineral attachment is possible, there are certain other conditions to be fulfilled in order that a particle may float.

The capillary force of attraction between air and mineral must obviously be greater than their tendency to part. The capillary force of attraction, L, corrected for the hydrostatic pressure difference has been shown to be given by the expression,

$$L = 2\pi x T_{wa} \sin \theta - \pi x^2 T_{wa} \left(\frac{\sin \phi}{x} + \frac{1}{\rho} \right)$$

or, since θ is the supplement of ϕ,

$$L = \pi x T_{wa} \left(\sin \theta - \frac{x}{\rho} \right)$$

The tendency to part may be evaluated from considerations of the dynamics of the motion of the air–mineral aggregate. Let the tension between mineral and air be E. Let σ_1, σ_2, and σ_3 be the densities of air, flotation liquor, and solid respectively, and let V_1 and V_2 be the volumes of air and mineral in the small aggregate under consideration. Let the acceleration of the system be f upwards.

Considering the motions of the bubble and particle separately;

$$v_1 g(\sigma_2 - \sigma_1) - E = v_1 \sigma_1 f$$

and

$$E - v_2 g(\sigma_3 - \sigma_2) = v_2 \sigma_3 f$$

Whence

$$E = g\sigma_2 v_1 v_2 \left(\frac{\sigma_3 - \sigma_1}{v_1\sigma_1 + v_2\sigma_3}\right) \tag{17}$$

and

$$f = g\left\{\frac{(v_1 + v_2)\sigma_2 - (v_1\sigma_1 + v_2\sigma_3)}{v_1\sigma_1 + v_2\sigma_3}\right\}. \tag{18}$$

If σ_1 may be neglected, $E = v_1 g\sigma_2$, which is equal to the upward thrust due to the buoyancy of the air.

Three cases arise:

(1) The bubble and mineral both sink if f is negative, that is, if

$$v_1\sigma_1 + v_2\sigma_3 > (v_1 + v_2)\sigma_2 \quad \text{and} \quad L > E$$

(2) The bubble and mineral both rise if f is positive, i.e., if

$$v_1\sigma_1 + v_2\sigma_3 < (v_1 + v_2)\sigma_2 \quad \text{and} \quad L > E$$

(3) The bubble and mineral part company if

$$L < E$$

Yet another contingency may arise. It is possible that disruption of the bubble itself may occur in preference to separation of the air–mineral contact. Let S be the area of this contact. If S_1 be the area of the bubble at the level where disruption occurs, the work done against the cohesive forces is $2S_1T_{wa}$. If

$$2S_1T_{wa} < S \cdot T_{wa}(1 - \cos\theta)$$

the bubble will therefore break in preference to separation of air and mineral. Practically, this means that the bubble should have a reëntrant surface and in general is obtained only with bubbles whose contact angle exceeds 90°. This explains why only bubbles whose contact angle is is above 90° leave a residual small bubble if they are forced by increasing size to leave the surface.

IX. FROTHS AND AIR–MINERAL AGGREGATES

Regarding the size of the air bubble as infinite, the principles of the preceding sections are directly applicable to film flotation, but film flotation is unimportant nowadays. A frothing agent is invariably added to promote the formation of a relatively stable froth. A large surface for collecting the minerals is thereby provided.

The physical principles underlying the formation of a froth have been clearly defined by Edser (10), but there is much confusion in the subsequent literature of flotation. They will be summarized here in so far as this is necessary for the development of certain deductions. For froth formation it is necessary that the soluble frother should be used in such a concentration that there is a finite (positive or negative) rate of change of surface tension with respect to concentration. Only when this condition is satisfied is there adsorption of the frother in the air-liquid interface, but the amount of adsorption is dependent on $-C \cdot \frac{dT_{wa}}{dC}$ where C is the concentration, and T_{wa} is the static surface tension. The dynamic surface tension differs less from that of pure water than does the static. Edser demonstrates that any sudden strain applied to the surface will displace the adsorption equilibrium in such a manner that the surface tension is raised; in extreme cases the dynamic value may be reached. The value of the restorative force is therefore dependent upon the difference between the static and dynamic values of the surface tension.

Certain observations which do not seem to have been recorded elsewhere, though they must surely be familiar to the operators of flotation plants, may be explained along similar lines. There is a correlation between the size of bubble in and stability of the froth and the concentration of the frother. Starting with very dilute solutions the stablest bubbles are large; as the concentration of the frother is increased, the average size of the relatively stable bubbles becomes smaller, until ultimately (12), no stable froth can be obtained when the solution becomes saturated. In the most dilute solutions there is probably insufficient adsorption of the frother at the surface to prevent coalescence between the bubbles or to exert much stabilizing influence on those that are formed; the bubbles are large and ephemeral. With more of the frother present coalescence is inhibited, for with each coalescence there is a decrease in total area of film surface and a consequent additional increase in the concentration of the frother in the new bubble. Relatively stable bubbles form and the size of these does not vary over very wide limits. Some coalescence still occurs, resulting in larger bubbles which collapse on rising to the surface. The reason for the empirical rule of Gaudin, Haynes, and Haas is not clear, but it must be connected with the appearance of a film of oil as a discrete phase.

Air-mineral aggregates

Bartsch (13) has investigated the influence of insoluble oils, of colloidal particles, of gangue and sulfide minerals and of soluble salts on the solubility of the froth produced by a soluble frother. This paper is of outstanding importance with respect to stability of froth systems. It is of an empirical nature, however, and some consideration of the theoretical basis is desirable.

Some of the conclusions of the preceding sections may be applied in the study of air-mineral aggregates. It follows, for instance, from the fundamental equation for contact angle, that the contact angles at each of the mineral particles armoring a bubble are uninfluenced by the presence of the other particles.[6] The shape of the bubble, however, would be determined by the particles.

The particles collected by a bubble on its way to the surface slide downwards until they receive lateral support from the more or less continuous film of particles at the bottom. As the bubble becomes mineralized, each particle becomes more and more nearly surrounded by others, but each particle makes contact with both air and water. When the bubble reaches the froth proper, it meets a shower of particles from collapsed bubbles sliding downwards between the bubbles, and many of these are captured. Those bubbles which become most completely covered are the most stable. If they are not collected when they reach the surface, they, too, collapse. The rate of collapse may, however, be exceedingly slow. The slow rate of collapse is probably due to prevention of rapid draining by the solid particles. At the top of the froth, much of the mineral liberated as the bubbles collapse is supported by those particles which are still securely bound to the froth. Lower down, the bubbles are separated by columns of liquid, some of which are thin, and it is at the surfaces between the water columns and the air bubbles that the particles ride. Some particles may effect contact with two neighboring bubbles of air, but whether this would increase or decrease the stability of the mineralized froth systems, it is difficult to decide.

X. MAXIMUM SIZE OF PARTICLE WHICH WILL FLOAT

Edser (10) shows that a very large particle can be floated by "skin flotation" at an air-water interface. A disc of large radius is supported almost entirely by the hydrostatic pressure of the water, "the surface tension serving merely to prevent the liquid from flowing over the disc." Such a disc must be thin, however, and Edser shows how its thickness may be calculated.

Gaudin, Groh, and Henderson (14) have attempted to calculate the maximum size of a galena particle floatable by skin flotation. They have, however, neglected the term due to hydrostatic pressure differences. They show that the surface tension forces are large enough to float a cube of galena with an edge length of 2 mm., but they do not demonstrate that sufficient water is displaced to provide sufficient buoyancy, which is of course an essential for flotation. Figure 9 of Edser's paper suggests that the buoyancy would be insufficient.

---

[6] If water drains away the particle may ultimately be supported by other particles and not by capillary forces; there would be no angle of contact in such a case.

If applied to flotation by a single bubble, their method is therefore equivalent to using the expression

$$V_1(\sigma_2 - \sigma_1)g = 2\pi x T_{wa} \sin \theta$$

in place of our equation 10.[7]
When $f = 0$,

$$V_1(\sigma_2 - \sigma_1) = V_2(\sigma_3 - \sigma_2)$$

and from these equations V_2 can be calculated. However, using the principles of the preceding sections, allowance can be made for the differences in hydrostatic pressure, and thus a closer approximation to maximum floatable size of particle by a submerged bubble may be obtained. It should be remembered, however, that the calculation is valid only for a particle possessing a large flat surface. This surface must be of sufficient extent for the bubble of maximum volume for a given contact angle to fit on the surface without touching the edges of the particle. The maximum volume of air for a given contact angle may then be determined from figure 3, and also the corresponding area of contact. The values apply strictly only for stationary systems, but they would also be applicable to the limiting case of a particle just so big that the bubble could carry it to the surface with an infinitesimally small acceleration. Then if σ_1 may be neglected it follows, since $f = 0$, that

$$V_1\sigma_2 = V_2(\sigma_3 - \sigma_2) \tag{19}$$

To take a specific case, let us calculate the size of the largest particle of galena which could be floated for an angle of contact of 90°. From figure 3 the maximum value of x is 0.25 cm., i.e., the diameter of the circle of contact with the bubble must be 0.5 cm. and its volume, read from figure 3, is 0.06 cm.^{3} (The bigger volumes of figure 3 correspond to bubbles with reëntrant surfaces, which are of no interest in flotation.) A bubble of this size could, by equation 19, float a particle of galena (density 7.5) of volume 0.06/(7.5 − 1) cm.^{3} i.e., 0.0092 cm.^{3} The thickness of this particle would be not greater than 0.005 cm.

For an angle of contact of 125°, the maximum value of x is 0.46 and the corresponding volume of air is 0.15 cm.^{3} This would float a particle of galena 0.023 cm.^{3} If, however, still keeping θ at 125° we again make x = 0.25, V becomes 0.015 cm.^{3} and the biggest particle which can be floated is but one-quarter the thickness that can be floated for the smaller angle of 90°. This is because the bubble corresponding to the higher angle is the flatter. It is apparent, therefore, in the special case of the flotation of

---

[7] This approximation is similar to that formerly in use for the estimation of surface tension by the drop weight method, but now rendered unnecessary by the use of certain tables based upon the equation of Bashforth and Adams.

a single particle by a single bubble that the higher of two possible contact angles may not lead to the best flotation. It might be wondered whether the observed low collecting power of the higher xanthates may be due, in part, to the high angles of contact produced by them, but it must be borne in mind that amyl xanthate, which is a good collector, leads to an angle of contact not far short of the maximum value for xanthates.

In practical flotation there are several other factors which influence the maximum floatable size of particle. Firstly, the air–water interface may touch the edges of the particle. The contact angle might then differ slightly from that at a plane surface and in any case it no longer determines the slope of the air–water interface with the vertical. Larger bubbles may therefore be attached for a given contact angle, and very small cubes of galena may be floated because of this factor alone. Secondly, contact with more than one face of the particle may be possible. Thirdly, when the bubble is armored by a large number of small particles, it may, for a given base of contact and a given contact angle with one particle, have a much larger volume than is possible if that particle alone were attached to it. It is impossible to evaluate mathematically the significance of these factors and therefore the maximum floatable size of particle in a flotation machine cannot be exactly evaluated. Gaudin, Groh, and Henderson state that the coarsest galena particles on which reliable flotation was obtained in machines is about 0.4 mm. diameter.

The writer wishes to express his thanks to Mr. A. B. Cox and Professor T. M. Cherry for their help in the preparation of this paper.

REFERENCES

(1) Wark and Cox: Am. Inst. Mining Met. Engrs., Tech. Pub. 461.
(2) Bashforth and Adams: Capillary Action. Cambridge (1883).
(3) Worthington: Proc. Roy. Soc. London **32**, 362 (1881).
(4) Bartell and Osterhof: Colloid Symposium Monograph V, 113 (1928).
(5) Ostwald: Kolloid-Z. **58**, 179 (1932).
(6) de Will et al.: J. Am. Chem. Soc. **54**, 444, 455 (1932).
(7) Sulman: Trans. Inst. Mining Met. **29**, 44 (1919), and Third Empire Min. and Met. Congress, South Africa, 1930.
(8) Ablett: Phil. Mag. **46**, 244 (1932).
(9) Langmuir: Trans. Faraday Soc. (Pt. III) **15**, 62–74 (1920).
(10) Edser: Brit. Assocn. Repts. on Colloid Chemistry 4, 263 (1922).
(11) Adam and Jessop: J. Chem. Soc. **1925**, 1865.
(12) Gaudin, Haynes, and Haas: Flotation Fundamentals, Part 4, p. 19. University of Utah.
(13) Bartsch: Kolloidchem. Beihefte 20, 1 (1924).
(14) Gaudin, Groh, and Henderson: Am. Inst. Mining Met. Engrs., Tech. Pub. 414 (1931).

THE APPLICATION OF THE LAW OF MATHEMATICAL PROBABILITY TO THE BEHAVIOR OF GASES IN THEIR PRESSURE-VOLUME-TEMPERATURE RELATIONS[1]

GEORGE A. LINHART

Department of Mathematics, Riverside Junior College, Riverside, California

Received October 18, 1932

The equation,

$$y = y_\infty kx^K/(1 + kx^K)$$

has been shown to hold for the course of a large variety of natural processes (1), and it is of interest to find that it also applies to the behavior of a gas in its pressure–volume–temperature relations. In the present case the equation assumes the form,

$$1/V_P = kP^K/(1 + kP^K)V_\infty \tag{1}$$

where V_P denotes the volume at any pressure, P; V_∞, the ultimate molal volume of the gas; and k and K are constants, characteristic of the gas considered.

V is expressed in standard units, i.e., the volume of a mole of gas at standard conditions is taken as unity. P is expressed in atmospheres. Equation 1 may also be written in the form,

$$V_\infty/(V_P - V_\infty) = kP^K \tag{2}$$

and, at 1 atmosphere pressure may be written,

$$V_\infty/(V_1 - V_\infty) = k \tag{3}$$

Dividing equation 2 by equation 3, we obtain,

$$(V_1 - V_\infty)/(V_P - V_\infty) = P^K \tag{4}$$

In testing the constancy of K in equation 4, it was assumed for convenience of calculation that at 1 atmosphere pressure Charles' Law is obeyed, i.e., $V_1 = V_0T/T_0$, where $V_0 = 1$ and $T_0 = 273°\text{A}$. V_∞ is given by the point of inflection on the curve obtained by plotting on a rather

---

[1] Read before the Mathematical Association of America, Southern California Section, San Diego Teachers College, March, 1932.

TABLE 1

Hydrogen gas

P	T = 0°C.		T = 15.5°C.		T = 99.3°C.		T = 200.3°C.	
	1/V	K	1/V	K	1/V	K	1/V	K
atm.								
1	1		0.9463		0.7334		0.5768	
100	93.5	0.999	88.6	0.998	101.6	0.998	81.2	0.999
150	136.0	0.999	129.0	0.998	132.2	0.997	106.2	0.998
200	175.7	0.999	166.9	0.998	161.3	0.997	130.2	0.998
250	213.2	0.999	202.4	0.997	189.2	0.997	153.4	0.998
300	248.1	0.998	236.5	0.997	215.7	0.997	175.6	0.997
350	280.9	0.998	268.2	0.997	241.1	0.997	197.0	0.997
400	311.8	0.997	298.3	0.997	265.5	0.997	217.8	0.997
450	340.9	0.997	326.6	0.996	288.8	0.996	237.5	0.997
500	368.6	0.996	353.4	0.996	311.1	0.996	257.0	0.996
550	394.8	0.996	378.8	0.995	332.7	0.996	275.7	0.996
600	318.9	0.995	402.9	0.995	353.2	0.995	293.9	0.996
650	442.7	0.995	426.1	0.994	373.1	0.995	311.4	0.996
700	465.1	0.994	447.9	0.994	392.0	0.995	328.4	0.996
750	487.1	0.994	469.3	0.994	410.5	0.994	344.8	0.995
800	507.6	0.994	489.0	0.993	428.1	0.994	360.8	0.995
850	532.2	0.995	509.2	0.993	445.6	0.994	376.4	0.995
900	544.9	0.992	527.5	0.993	460.0	0.993		—
950	563.8	0.993	545.8	0.993	477.8	0.993		
1000	579.7	0.992	562.8	0.993		—		
1100	610.9	0.991	593.5	0.992				
1200	642.0	0.991	623.4	0.991				
1300	670.7	0.990	652.3	0.991				
1400	698.3	0.990	679.3	0.991				
1500	724.6	0.991	705.2	0.991				
1600	749.3	0.991	729.9	0.991				
1700	772.5	0.991	754.1	0.992				
1800	794.9	0.992	776.4	0.992				
1900	816.3	0.992	797.1	0.993				
2000	837.2	0.993	818.0	0.993				
2100	857.3	0.993	837.5	0.994				
2200	876.4	0.995	855.8	0.994				
2300	894.5	0.995	873.7	0.994				
2400	911.1	0.995	887.4	0.994				
2500	927.6	0.996	908.3	0.996				
2600	948.2	0.998	923.7	0.997				
2700	959.7	0.998	940.7	0.998				
2800	975.8	0.999	956.9	1.000				
2900		—	972.8	1.001				
3000			987.6	1.002				
				—				
		Av. =		Av. =		Av. =		Av. =
∞	1500.0	0.994	1500.0	0.995	1500.0	0.996	1500.0	0.997

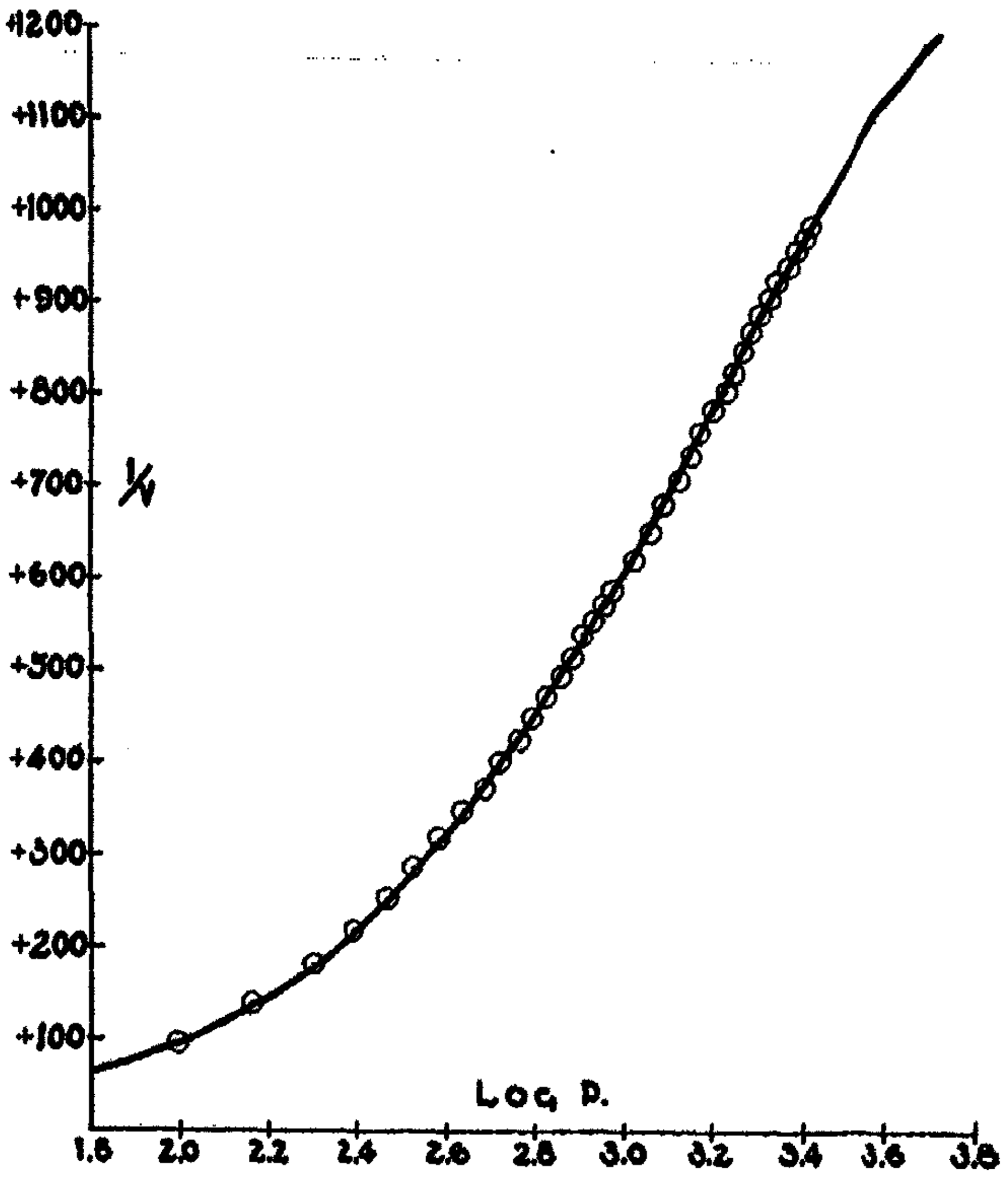


Fig. 1. Hydrogen Gas at 0°C.

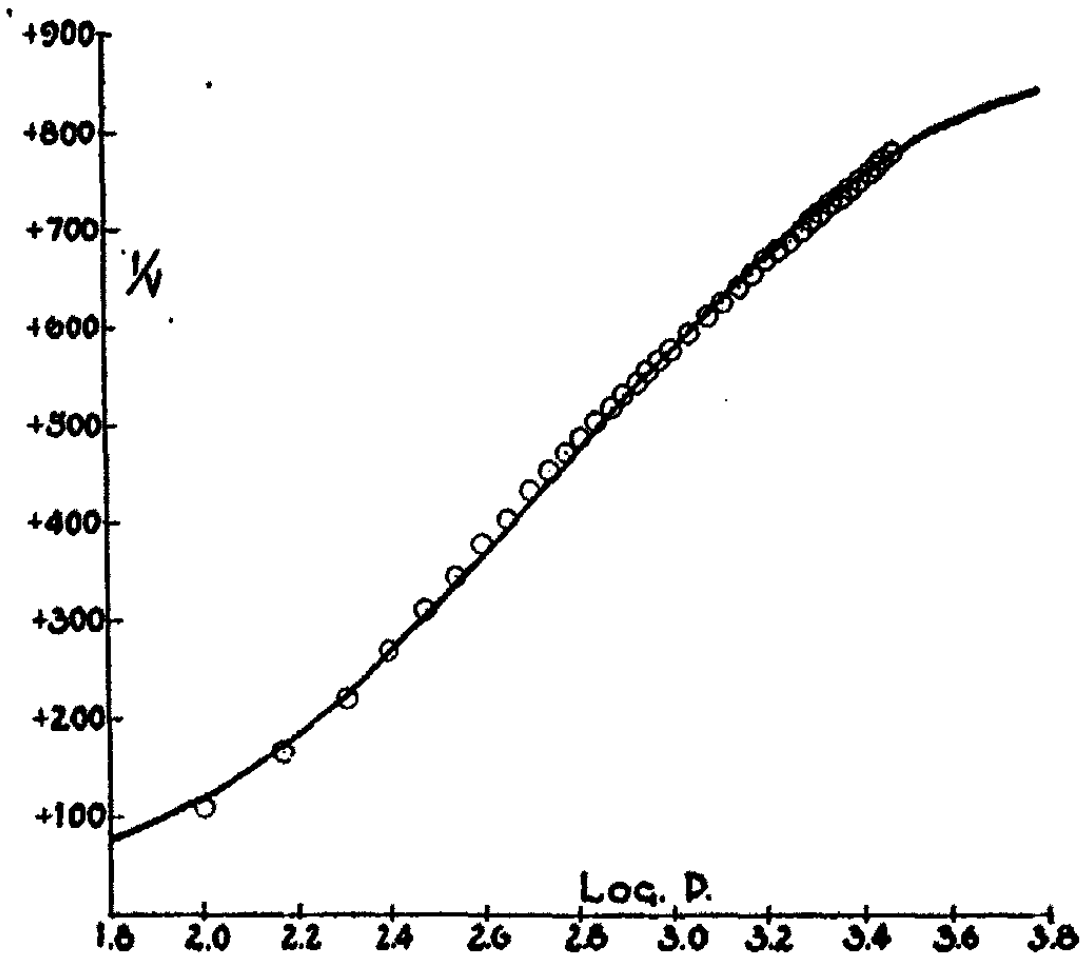


Fig. 2. Oxygen Gas at 0°C.

TABLE 2

Oxygen gas

P	*T* = 0°C.		*T* = 15.6°C.		*T* = 99.5°C.		*T* = 199.5°C.	
	1/*V*	*K*	1/*V*	*K*	1/*V*	*K*	1/*V*	*K*
atm. 1	1		0.9459		0.7329		0.5778	
100	107.9	1.043	99.6	1.036	72.7	1.016	83.3	1.011
150	164.2	1.058	151.2	1.049	108.5	1.022	110.0	1.015
200	218.8	1.068	201.1	1.058	142.9	1.027	135.1	1.017
250	268.4	1.075	246.7	1.064	175.6	1.031	159.2	1.019
300	311.7	1.079	287.9	1.068	206.5	1.033	182.1	1.020
350	348.6	1.080	324.0	1.070	234.9	1.035	204.0	1.021
400	380.4	1.080	355.6	1.071	261.1	1.036	224.6	1.022
450	408.2	1.080	383.0	1.071	285.5	1.037	243.9	1.022
500	432.5	1.079	407.5	1.070	308.3	1.038	262.5	1.023
550	453.7	1.077	429.2	1.069	329.5	1.038	280.1	1.023
600	472.5	1.075	448.8	1.068	348.8	1.038	296.6	1.023
650	489.7	1.073	466.4	1.066	366.7	1.038	312.3	1.024
700	505.3	1.072	481.9	1.065	383.1	1.038	327.2	1.024
750	519.5	1.070	497.3	1.064	398.7	1.037	341.4	1.024
800	532.2	1.068	510.5	1.062	413.7	1.037	355.6	1.024
850	543.2	1.066	523.3	1.061	427.7	1.037	367.9	1.024
900	555.6	1.065	534.5	1.060	440.9	1.037	380.4	1.024
950	566.3	1.064	546.1	1.059	453.3	1.036		——
1000	576.4	1.062	555.6	1.057	464.9	1.036		
1100	594.5	1.060	574.7	1.055	——	——		
1200	611.6	1.059	592.1	1.053				
1300	627.4	1.058	607.9	1.052				
1400	642.3	1.058	623.0	1.052				
1500	655.3	1.057	636.5	1.051				
1600	667.8	1.057	649.4	1.051				
1700	679.3	1.057	660.7	1.051				
1800	690.3	1.057	671.8	1.051				
1900	700.8	1.058	682.6	1.051				
2000	710.2	1.058	692.5	1.051				
2100	719.4	1.059	702.2	1.052				
2200	728.0	1.060	711.2	1.053				
2300	736.4	1.061	719.4	1.054				
2400	744.3	1.062	727.8	1.055				
2500	752.2	1.064	735.3	1.056				
2600	759.6	1.065	742.9	1.057				
2700	766.9	1.068	750.8	1.059				
2800	774.0	1.070	757.9	1.061				
2900	791.3	1.073	765.1	1.063				
3000		——	771.6	1.065 ——				
∞	920.0	Av. = 1.066	920.0	Av. = 1.058	920.0	Av. = 1.034	920.0	Av. = 1.021

TABLE 3

Nitrogen gas

P	T = 0°C.		T = 16.0°C.		T = 99.5°C.		T = 199.5°C.	
	1/V	K	1/V	K	1/V	K	1/V	K
atm. 1	1		0.9446		0.7329		0.5780	
100	100.9	1.031	94.2	1.026	103.5	1.015	80.6	1.006
150	148.5	1.040	138.7	1.033	134.3	1.018	104.9	1.008
200	192.5	1.044	179.5	1.038	162.6	1.015	127.6	1.009
250	230.9	1.047	216.0	1.041	188.6	1.020	148.9	1.009
300	264.1	1.048	247.8	1.041	212.6	1.021	168.9	1.010
350	292.9	1.047	276.2	1.041	234.5	1.020	187.6	1.010
400	318.3	1.046	301.0	1.041	254.9	1.020	205.1	1.009
450	340.1	1.045	322.8	1.039	273.6	1.020	221.5	1.009
500	359.7	1.043	342.7	1.038	291.0	1.020	237.1	1.009
550	377.1	1.041	360.4	1.037	306.9	1.019	251.7	1.009
600	393.2	1.039	376.4	1.035	321.7	1.019	265.5	1.009
650	407.8	1.038	391.2	1.034	335.6	1.018	278.6	1.008
700	421.2	1.036	404.9	1.032	348.3	1.017	291.1	1.008
750	433.5	1.035	417.2	1.031	360.4	1.017	303.0	1.008
800	445.0	1.034	428.8	1.030	371.8	1.016	314.1	1.007
850	455.6	1.032	439.8	1.029	382.3	1.015	324.8	1.007
900	465.3	1.031	449.6	1.028	392.9	1.014	334.8	1.007
950	474.6	1.030	459.1	1.027				
1000	483.3	1.029	468.2	1.026				
1100	499.1	1.027	485.0	1.024				
1200	513.9	1.025	500.0	1.023				
1300	527.3	1.024	514.1	1.022				
1400	539.7	1.023	527.1	1.021				
1500	551.4	1.023	539.4	1.021				
1600	562.3	1.023	550.1	1.021				
1700	573.1	1.023	560.5	1.021				
1800	583.3	1.024	570.8	1.021				
1900	592.3	1.024	579.9	1.021				
2000	601.1	1.025	588.6	1.022				
2100	609.4	1.026	597.0	1.022				
2200	617.3	1.027	605.0	1.023				
2300	624.6	1.028	612.7	1.024				
2400	631.5	1.029	619.8	1.025				
2500	637.7	1.029	626.6	1.026				
2600	643.9	1.030	633.3	1.027				
2700	649.8	1.031	639.4	1.028				
2800	655.7	1.033	645.4	1.029				
2900	665.8	1.039	651.0	1.030				
3000	667.1	1.036	656.8	1.032				
∞	800.0	Av. = 1.032	800.0	Av. = 1.029	800.0	Av. = 1.018	800.0	Av. = 1.007

TABLE 4

Air

P	T = 0°C.		T = 15.7°C.		T = 99.4°C.		T = 200.4°C.	
	1/V	K	1/V	K	1/V	K	1/V	K
atm. 1	1		0.9453		0.7329		0.5766	
100	102.8	1.035	95.6	1.029	71.3	1.014	81.4	1.009
150	152.4	1.044	141.8	1.038	104.8	1.018	106.0	1.010
200	198.0	1.050	184.3	1.043	130.8	1.020	129.3	1.011
250	238.3	1.053	222.0	1.045	165.5	1.022	151.0	1.012
300	273.4	1.054	255.6	1.047	192.5	1.023	171.5	1.012
350	303.3	1.054	285.7	1.048	219.6	1.024	190.8	1.012
400	329.4	1.053	311.6	1.047	240.6	1.025	209.0	1.012
450	352.5	1.052	334.3	1.046	261.6	1.025	226.1	1.012
500	373.1	1.050	354.4	1.044	280.7	1.024	242.3	1.013
550	391.7	1.049	373.1	1.043	298.2	1.023	257.5	1.012
600	408.2	1.047	390.2	1.042	314.8	1.023	272.0	1.012
650	423.2	1.045	405.8	1.041	330.5	1.023	285.5	1.012
700	437.1	1.044	420.0	1.040	344.8	1.022	298.4	1.012
750	449.4	1.042	432.5	1.038	358.4	1.022	310.7	1.012
800	461.3	1.041	444.5	1.037	371.2	1.021	322.4	1.012
850	472.6	1.040	455.8	1.035	383.3	1.021	333.3	1.011
900	482.9	1.039	466.4	1.035	394.2	1.020	344.5	1.011
950	492.6	1.038	476.0	1.033	404.4	1.020	353.6	1.010
1000	502.0	1.037	485.4	1.033	414.2	1.019		
1100	515.7	1.033	502.0	1.031				
1200	531.1	1.031	517.3	1.029				
1300	545.3	1.031	531.9	1.028				
1400	558.2	1.030	545.3	1.028				
1500	570.1	1.029	557.6	1.028				
1600	581.2	1.028	569.2	1.027				
1700	591.5	1.029	579.7	1.027				
1800	601.7	1.029	590.0	1.027				
1900	610.9	1.030	599.5	1.028				
2000	620.0	1.030	608.6	1.028				
2100	628.7	1.031	613.9	1.026				
2200	636.9	1.033	625.8	1.030				
2300	645.0	1.034	633.7	1.031				
2400	652.1	1.035	641.2	1.032				
2500	659.4	1.037	648.5	1.033				
2600	666.7	1.039	655.7	1.035				
2700	673.6	1.041	662.3	1.036				
2800	680.5	1.043	668.9	1.038				
2900	687.3	1.046	675.4	1.040				
3000	694.0	1.049	682.1	1.043				
		Av. =		Av. =		Av. =		Av. =
∞	822.0	1.040	822.0	1.035	822.0	1.022	822.0	1.012

large scale $1/V_P$ against log P, for at this point, $kP^K = 1$. This may be verified by taking the second derivative of $1/V$ with respect to log P, and

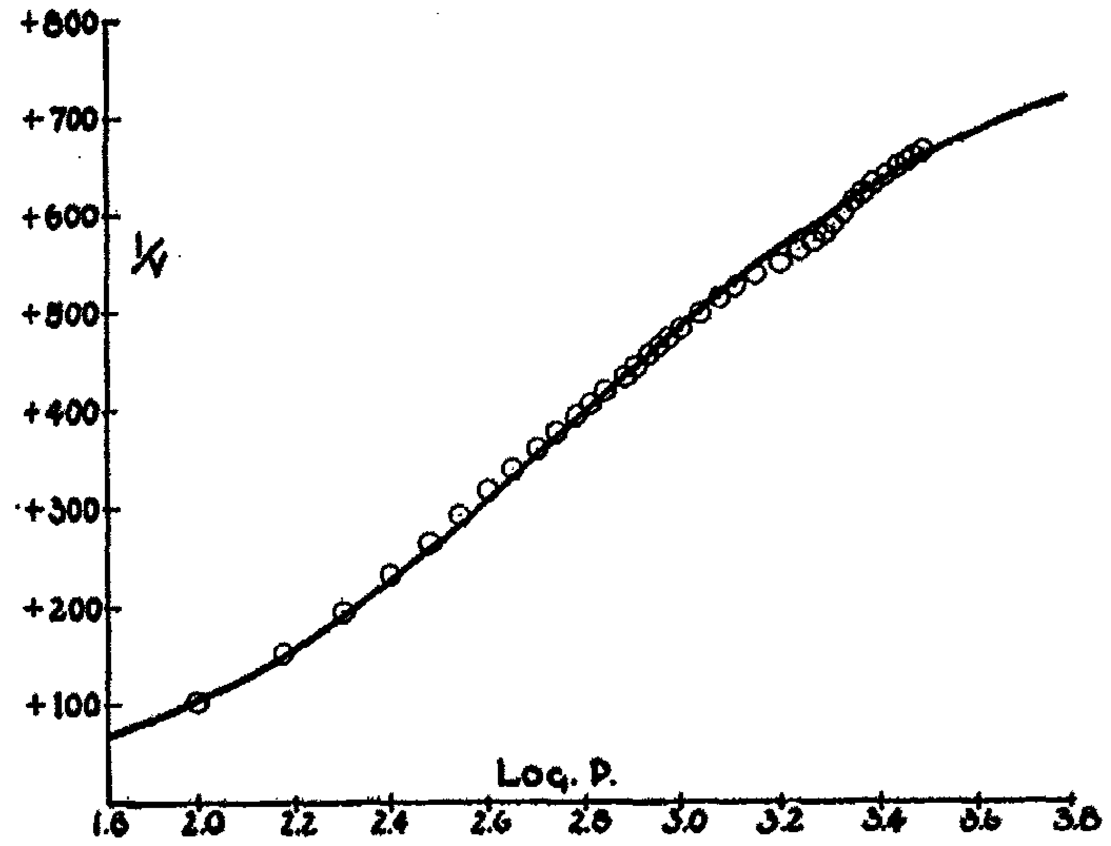


Fig. 3. Nitrogen Gas at 0°C.

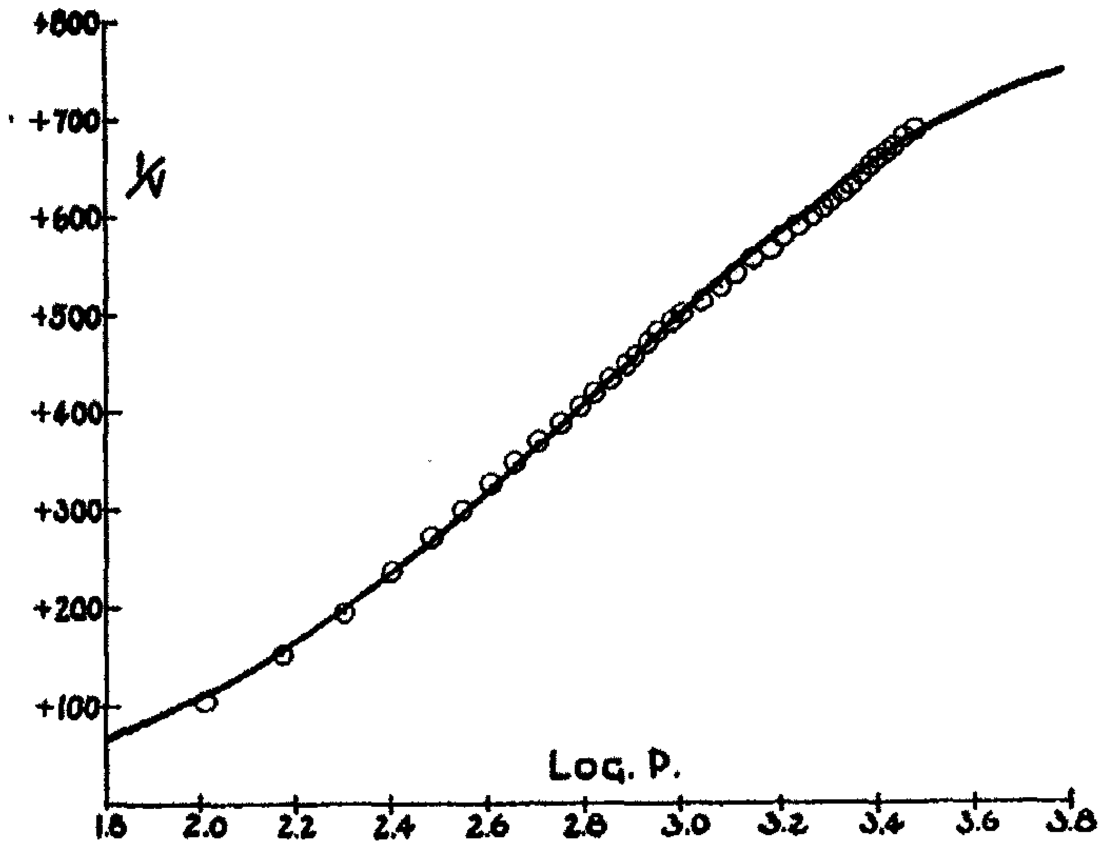


Fig. 4. Air at 0°C.

placing the resulting expression equal to zero. Hence, by equation 1, $1/2V_\infty = 1/V$ at inflection, which can be easily located from the perfect symmetry of the curve. Only one curve for each gas is given, since they are all of the same general trend and of nearly equal accuracy. V_∞ may also be obtained approximately from density measurements of the given substance in its solid state near the absolute zero of temperature, since V_∞ is practically independent of temperature and pressure. However, the inflection point method is preferable, for density measurements at extremely low temperatures are not likely to be generally reliable.

The gases chosen for this study are hydrogen, oxygen, nitrogen and air. As the most complete P–V–T data (2) available are those of Amagat, ranging from 0°C. to 200°C. and from 1 atmosphere pressure to 3000 atmospheres pressure, these data were used in the calculation of K.

RESULTS OF CALCULATIONS

The data for hydrogen gas are those of tables 4 and 8 of the original article cited above; for oxygen gas, of tables 4 and 7; for nitrogen gas, of tables 5 and 9; and for air, of tables 5 and 10.

TABLE 5

Variation of K with the absolute temperature: a summary

T	HYDROGEN	OXYGEN	NITROGEN	AIR
273	0.994	1.066	1.032	1.040
290	0.995	1.058	1.029	1.035
373	0.996	1.034	1.018	1.022
473	0.997	1.021	1.007	1.012
∞	1.000	1.000	1.000	1.000

DISCUSSION OF THE CONSTANTS

The concordance of the constants in each of the sixteen sets of results is quite remarkable and justifies the assumption that at 1 atmosphere pressure Charles' Law is valid. It is also of considerable interest to note that with rise in temperature of the gas the constant, K, in every case approaches unity (see figure 5). This phenomenon is in accord with the kinetic theory of gases, leading to the simple expression, PV = a constant. The conditions postulated by the kinetic theory can be fulfilled only at high temperature and at moderately low pressure, in which case equation 4,

$$(V_1 - V_\infty)/(V_P - V_\infty) = P^K$$

reduces to PV = a constant, since at high temperatures and low pressures K approaches, in all cases, unity, and V_∞ becomes negligibly small as compared with either V_1 or V_P.

It may be noted that K for hydrogen approaches unity from below, while in the other cases K approaches unity from above. This phenomenon is shown on figure 5, where K is plotted to four significant figures against the absolute temperature.

In conclusion, it may be pointed out that equation 4 is an empirical one, in that y of the general equation is replaced by $1/V$ without any theoretical reason for doing so. The general equation, however, does possess a theoretical foundation, since, as will be shown in a subsequent paper, it is based upon the law of mathematical probability. Furthermore, equation 4 is not intended either for extrapolation or interpolation purposes, for, as stated in the first paragraph of this article, the writer is merely endeavoring to show that the equation,

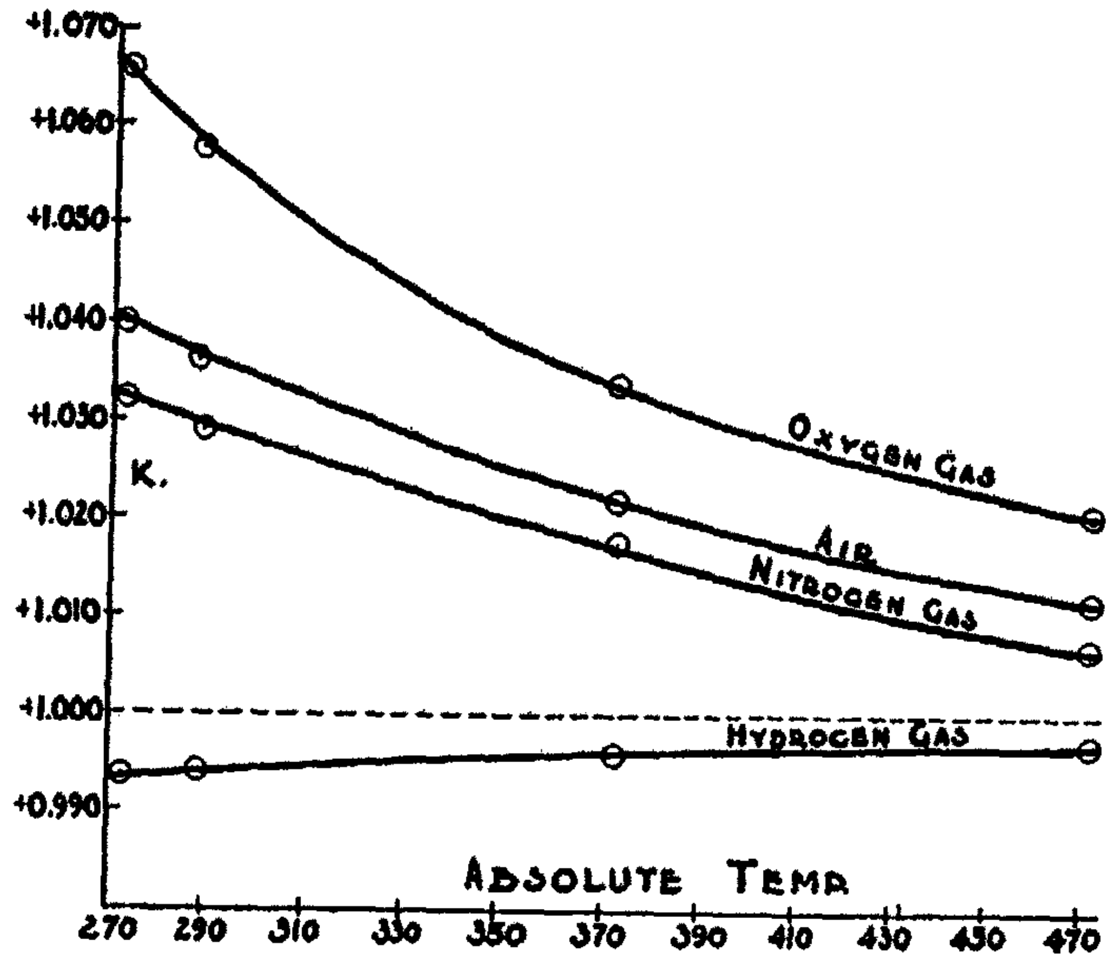


FIG. 5. RELATION OF K TO T

$$y = y_{\infty}kx^{K}/(1 + kx^{K})$$

describes the general trend of a vast variety of natural processes in the fields of chemistry, physics, botany, biology, bacteriology and sociology, and even in practical engineering; for example, the depreciation and the life expectancy of physical property.

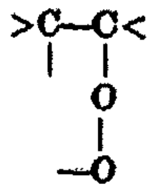
REFERENCES

(1) LINHART: J. Phys. Chem. 36, 1908 (1932).
(2) AMAGAT: Ann. chim. phys. 29, 68 (1893). Extensive work in this field is contemplated by Mitchells: Proc. Roy. Soc. London A1930, 127-258.

COMMUNICATIONS TO THE EDITOR

THE INITIAL ACT IN AUTO-OXIDATION

In a recent paper in This Journal (J. Phys. Chem. **37**, 209 (1933)), it might have been pointed out that the viewpoint of Staudinger and Lautenschläger (Ann. **488**, 1 (1931)) is not regarded as conflicting with the general theory advanced by the writer. When oxygen adds to a C═C bond through pairing of the odd electrons of the oxygen molecule with two of the electrons from the double bond, it seems reasonable to suppose that, at the instant of formation, the excess energy of the peroxide molecule would reside in these newly established electron pairs. The above authors attempt to represent this energy-rich molecule by an ordinary structural formula, showing one of the bonds actually open.



In the opinion of the writer, such a structure should be regarded merely as an attempt to express in terms of time-honored artifices, a fact which does not lend itself to accurate description in these terms. If, for some purposes, however, a conventional structure must be assigned, probably the one of Staudinger and Lautenschläger is more satisfactory than any other.

H. N. Stephens.

School of Chemistry
University of Minnesota
Minneapolis, Minnesota

INDUCED REACTIONS AND THE HIGHER OXIDES OF IRON

Remarks Upon a Paper by D. R. Hale

Hale (J. Phys. Chem. **33**, 1633 (1929)) published in 1929 a study under the above title which contains a careful and objective analysis of numerous works in this field. Among these Hale has occupied himself with my work in this field and has found himself in agreement with my experiments with regard to the autoxidation of ferrous iron (Manchot: Z. anorg. Chem. **27**, 420 (1901); Ber. **65**, 98 (1932)). On the other hand, he is of a different opinion with regard to the oxidation of ferrous iron by means of hydrogen peroxide in presence of potassium iodide as acceptor, in so far as he finds that here not two but three equivalents of free iodine occur per atom of iron.

In his discussion of this difference we find on p. 1651 the following sentence: "Unfortunately, he (Manchot) omitted to state how much ferrous iron, or what proportion of ferrous iron to acceptor, was used."

This remark is the result of a misunderstanding which was discovered in the course of a personal conversation with Mr. Hale, who was so good as to visit me in Munich in the summer of 1930 on the occasion of an European journey made by him. The work in question (Manchot and Lehmann: Ann. **460**, 179 (1928)) contains a definite statement with regard to the quantity of iron employed, but only in a very short form, owing to the limited space at my disposal in the journal, as it was merely a question of confirming and repeating former results. I wrote on p. 185: "Gef. z.B. 2,4 bezw. 4,5 ccm, ber. 2,4 bezw. 4,4 1/10 Jod," where, as is obvious from the context, "ber. 2,4 bezw. 4,4 ccm. 1/10 Jod" is the quantity which equals 2 equivalents of iodine to 1 of Fe, so that the quantity of iron used in the first experiment was 1.2 cc., and in the second 2.2 cc. of 1/10 ferrous sulfate.

While in this case there was only question of a misunderstanding, I must nevertheless state emphatically that I am not in agreement with Hale's results. In this connection a full account of detailed experimental investigations will appear in the Zeitschrift für anorganische und allgemeine Chemie.

WILHELM MANCHOT.

Anorganisches Laboratorium
Technische Hochschule
München

NEW BOOKS

Catalytic Oxidation of Organic Compounds in the Vapor Phase. By L. F. MAREK AND DOROTHY A. HAHN. American Chemical Society Monograph Series, No. 61. 428 pp New York: The Chemical Catalog Co., Inc., 1932. Price, $9.00.

The appearance of this volume seems especially timely in view of the increasing application of catalysis to the problems of organic chemistry. The broad scope of the work is indicated by the chapter headings: Introduction; catalysis; catalytic decomposition of alcohols; oxidation of alcohols to aldehydes and acids; reactions involved in the synthesis of hydrocarbons and alcohols from water gas; oxidation of methanol to formaldehyde; oxidation of gaseous paraffin hydrocarbons; oxidation and hydration of olefins and acetylene; oxidation of petroleum oils; production of hydrogen from methane; surface combustion; the cause and suppression of knocking in internal combustion engines; oxidation of benzene and its derivatives; oxidation of naphthalene; oxidation of anthracene and miscellaneous polynuclear compounds; apparatus. In the preface the authors state that they believe it best "to consider the facts regarding both the developed and undeveloped processes and to review these critically in so far as possible. The subject could have been approached from several angles, but it was believed that a consideration of the reactions involved and products formed constituted the most satisfactory method of treatment for the present purpose." The reviewer believes that the authors have admirably fulfilled their purpose and that this volume will be an important addition to the library of those interested in catalytic oxidation.

In the introductory chapter on catalysis a fairly complete picture is given of the current ideas and theories on the subject; however, a more complete discussion of the rôle that catalysts play in initiating and breaking chain reactions would have strengthened this discussion. The authors have wisely discussed such reactions as catalytic decomposition, which are so intimately related to the problem of oxidation. The chapter devoted to the cause and suppression of knocking in internal combustion engines is one of the best reviews to be found on this important and controversial subject. Very complete references are given to the literature as footnotes, including numerous references to patents. The usefulness of the book might be improved by the addition of an author index. The section on apparatus will be found very useful to those entering this important field of industry. It is the opinion of the reviewer that this volume is an important and valuable addition to the Monograph Series of the American Chemical Society.

L. H. REYERSON.

Introduction to Organic Chemistry. By ROGER J. WILLIAMS. Second edition. New York: D. Van Nostrand Co., 1931.

The revision of this text since the first edition (1927) includes more recent information on commercial processes and on certain rapidly developing fields such as carbohydrate chemistry. The author is successful in introducing many modern concepts at the earliest possible moment, building up a viewpoint which will not need to be greatly modified after advanced study. The detail is well chosen, the presentation direct, and the scheme always apparent. Although popular as a premedical text, the book is not limited in usefulness to short or special courses.

P. D. BARTLETT.

Kristallchemie der anorganischen Verbindungen. (Sammlung chemischer und chemisch-technischer Vorträge, Heft 17). By M. C. Neuburger. 25.5 x 16.5 cm.; 115 pp. Stuttgart: Ferdinand Enke, 1933. Price, RM. 9.70.

From the very large amount of information which has been made available by the methods of x-ray crystal analysis, it has been found possible in recent years to deduce a number of laws governing the crystalline structure of inorganic compounds. Chiefly owing to the work of V. M. Goldschmidt and L. Pauling, these rules are sufficiently well established to enable the crystalline structure and physical properties of a not too complex substance to be predicted with some degree of certainty; there is at least one case on record where the experimental verification of such a prediction has given results of considerable technical importance.

Much of Prof. Goldschmidt's work has not been easily accessible, and Dr. Neuburger's book should commend itself both to the specialist as a useful summary of the present state of the subject, and to the more general reader as a very lucid introduction. Crystal chemistry is defined as that branch of chemistry dealing with those mutual interactions of atoms and molecules which lead to the formation of numerically unlimited ordered aggregates: its aims are taken to be the prediction of the types of crystals which can be formed from given elements, and the determination of the relations between the properties of a crystal and the properties of its constituent atoms.

The problem of atomic and ionic radii is first considered; to a first approximation the atoms and ions can be regarded as rigid spheres, so that the structure types can be classified according to the ratios of the radii of the ions involved. In the succeeding chapters it is shown how this simple consideration is modified by the influence of the charges carried by the ions, by their polarization properties, and other factors. Isomorphism, polymorphism, and morphotropism are then discussed; these terms have been endued with a new precision since the advent of crystal chemistry as an exact science. The following section on chemical binding in crystals will perhaps be disappointing to the chemist who is accustomed to differentiate fairly sharply between electrovalencies, covalencies, and coördinate links; it is apparent throughout the book, however, that valency is a subordinate factor in the construction of crystals, and it is very difficult to distinguish between the various linkages merely by measurements of interatomic distances. It is here that various physical properties can very usefully be employed, and in particular the relation between hardness and the strength of interatomic bonds is discussed

As the book is intended as an introduction, many fascinating topics, such as the configuration of complex ions and the structure of the silicates, are not considered in any detail, but within the limits which the author has set himself the subject is treated in a very clear and logical manner. It should be said that actual structures are not described; these are adequately dealt with in such publications as the "Strukturbericht" and Wyckoff's "Structure of Crystals." The book is practically free from misprints; an index would be a useful addition. Dr. Neuburger is to be congratulated on an attractive presentation of this important subject.

E. G. Cox.

Die Valenz der Metalle Fe, Co, Ni, Cu und ihre Verbindungen mit Dioximen. (The Valency of the Metals Fe, Co, Ni, Cu and their compounds with Dioximes.) By Erich Thilo. 25.5 x 16.5 cm.; 71 pp. Stuttgart: Ferdinand Enke, 1932. Price, M. 6.4.

This monograph, as its title implies, deals with the metallic complexes of oximes, mainly dimethyldioxime (DH_2), with some four metals of the first transition series.

The author first discusses the valency of the metals iron, cobalt, nickel, copper, and then, using the Born-Häber cycle (*Kreisprozess*), obtains values for the heat of formation for univalent, divalent, and tervalent halides of the foregoing metals.

After this discussion the dioxime compounds are considered separately.

Iron. Dimethylglyoxime and ferrous salts give [Fe 2DH] which combines with ammonia or pyridine giving [Fe 2DH, $2NH_3$] and [Fe 2DH, 2py] respectively. A definite compound with ferric iron has not yet been obtained.

Cobalt. (a) In dry acetone cobaltous chloride and the glyoxime give a blue solution from which red [Co $2DH_2Cl_2$] is obtained and this passes into a more stable green isomeride. The red and green derivatives are said to be related as *cis-* and *trans-*forms and evidence is adduced in support of this conclusion. The green chloride hydrolyzes to [Co $2DH_2ClOH$], while the bromide [Co $2DH_2Br_2$] with ethylenediamine gives

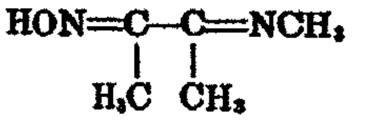
$$[H_2O\ 2DH_2\ Co\ en\ Co\ 2DH_2H_2O]^{Br_2}_{OH}$$

and with ammonia

$$[Co\ 2DH_2\ H_2O\ NH_3]^{Br}_{OH}$$

Cobalt. (b) Three types of cobaltic salts are recognized: (1) Cobalt in the cation [Co 2DH 2A] X, where A = NH_3, py, ½en, and X = Cl, OH, NO_3, ½SO_4, *etc.* (2) [Co 2DH AX] where A = NH_3, py, acridine, and X = Cl, Br, I, N_3, NO_2, SCN, OCN. (3) [Co 2DH 2X] A with cobalt in the anion, where A = H, Na, K, and X = Cl, I, NO_2, and SCN. These compounds are obtained by replacement of NH_3 in a suitable cobaltammine, e.g., [Co 2DH NH_3 Cl] from [Co $5NH_3$ Cl]Cl_2.

Nickel. In addition to the well-known [Ni 2DH], nickel forms the compound [Ni $2DH_2$]Cl_2 which has been prepared in two ways. A number of salts of the type [Ni $2DH_2$]X_2 where X is a univalent radical are described. The foregoing chloride easily forms a green hydrate [Ni DH_2 H_2O]Cl_2 which can be dehydrated; moreover, this hydrate decomposes with acetic acid, water, and alcohol in the sense 2[DH_2 Ni H_2O]Cl_2 → [Ni 2DH] + $NiCl_2$ + 2HCl + $2H_2O$. The author then passes to a consideration of the structure of [Ni 2DH] and various possibilities are discussed. In the course of this work the nickel compound of the oxime



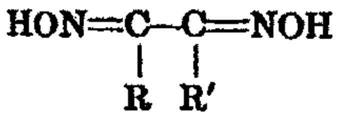
$$\begin{array}{c} HON{=}C{-}C{=}NCH_3 \\ \quad\ \ |\qquad | \\ \quad H_3C\ \ CH_3 \end{array}$$

was made.

Copper. Apart from the brown [Cu 2DH], copper chloride furnishes the bluish green [Cu DH_2 Cl_2]. The sulfate [DH_2 Cu SO_4] and phosphate [Cu DH_2 $(H_2PO_4)_2$] ½H_2O were also prepared. Water causes hydrolysis of these copper compounds.

$$2\ [DH_2\ Cu\ X_2] \rightleftharpoons [Cu\ 2DH] + CuX_2 + 2HX$$

Some metallic compounds of substituted dioximes are discussed,



$$\begin{array}{c} HON{=}C{-}C{=}NOH \\ \quad |\quad\ | \\ \quad R\quad R' \end{array}$$

where R and R′ may be OH, C_6H_5, H, $CH_3C_6H_4$, C_6H_5CO, Cl. The replacement of the hydrogen atoms in the oxime group was also considered. The concluding chapter deals with physical data such as heat of formation of the metallic halides, coördination capacity, heat of dissociation, heat of sublimation, etc.

The author has compiled an interesting little book in a rather limited field. It should, however, appeal to those interested in the coördination theory.

G. T. M. AND F. H. B.

Thermionic Vacuum Tubes. By E. V. APPLETON. 113 pp. New York: E. P. Dutton and Co., Inc., 1932. Price, $1.25.

This little book, which may be read with pleasure in an evening, might well have been called "The Physics of Vacuum Tubes." Its nine chapters are divided about equally between *internal action* of tubes and *applications;* but the applications are examples of fundamental principles rather than popular use, and include many non-radio applications. The book is strictly scientific and yet very readable, with only a moderate use of mathematics and few wasted words.

A. W. HULL.

Les Problèmes de la Biochimie Moderne. Par G. FLORENCE, Professor à la Faculté de Médecine de l'Université de Lyon, et J. ENSELME, Chief des Travaux de Chimie à la Faculté de Médecine de Lyon. 16 x 24.5 cm.; 312 pp., 8 fig. Paris: G. Doin and Co., 1932. Price, 45 fr.

The title of this book is somewhat of a misnomer. In place of calling attention to some of the major "problems" or "fields of activity" of modern biochemistry, the reviewer feels that the authors have instead presented a rather disjointed collection of more or less isolated and too brief chapters.

The book is divided into three major sections which are called "Static Biochemistry—The Biochemical Molecules," "Kinetic Biochemistry—The Agents of Chemical Activity," and "Physiological Chemistry." Static biochemistry includes chapters on the atom, colloids, surface tension, absorption spectrum in the ultra-violet, the amino acids, peptides, the constitution of the proteins, the modern view of the problem of the constitution of the hexoses, the disaccharides, the polysaccharides, the sterols, and the nucleic acids.

The section on kinetic biochemistry includes chapters on homogeneous reactions, heterogeneous reactions, pH, the membrane as a chemical agent, glutathione, constitution and mode of action of enzymes, reversability of enzyme action, the chlorophyll molecule in syntheses.

The third section on physiological chemistry includes chapters on fermentation, muscle utilization of carbohydrates, the origin of the bile salts and acids, problems of immunity, and a concluding philosophical chapter on the place of biochemistry as a special science. Two appendices follow: one having to do with biochemical nomenclature, following the recommendations of G. Bertrand as presented by him to various meetings of the "Conference Internationale de la Chimie" and the other a condensed (10 pages) statement of the three laws of thermodynamics. Author and subject indices close the volume.

The authors rightly point out that modern biochemistry requires a knowledge of organic chemistry, of physical chemistry, of physics, and of mathematics. Nevertheless, the reviewer does not feel that the brief, sketchy treatment which is accorded most of the topics discussed in these chapters is of much value either to the beginner or to the expert in biochemistry. The literature is not up to date. Only one reference to the literature of 1930 (none later) was found in the entire volume. Loeb's views of the colloidal behavior of proteins are accepted in their entirety, as is evidenced by the statement (p. 38): "The same laws which regulate the combinations of crystalloids also direct both qualitatively and quantitatively the chemical reactions of the proteins;" and later, in discussing colloids in general (p. 41), "It seems as though the specific colloidal property resides, for both hydrophobic and hydrophilic colloids, in the Donnan equilibrium." (The reviewer only wishes that colloid chemistry were as simple as that!)

The chapters on absorption spectra, the amino acids, proteins, and carbohydrates present fairly good statements of certain phases of the knowledge in these fields up to 1927 or 1928. The sterols are allowed six pages of text. The last citation is to 1929 literature. The last citation to work by Windaus is to a paper which appeared in 1913! No mention is made of ergosterol and vitamin D which is formed from ergosterol by ultra-violet radiation! But the experiments of d'Hugounenq, whereby sterols, following exposure to the air and light or to ultra-violet radiation, acquired the property of affecting the photographic plate, are given at length in spite of the fact that the weight of later evidence seems to be against such acquired photoactivity.

Glutathione is given an entire chapter. The last reference is to literature of 1927. It is discussed as a dipeptide, although it was shown to be a tripeptide in 1929. (A footnote on p. 209 states, "The recent notes tend to show that it is a tripeptide.")

The bile pigments and hemin again occupy a separate chapter. The last reference is to 1928 literature. Only a single paper by Windaus (1919) is referred to and only one by Hans Fischer (1914!), in spite of the fact that Nobel prizes were awarded both Fischer and Windaus for work in this and related fields.

In the chapter on muscle biochemistry the glucose ⇄ lactic acid theory of muscle energy is elaborated upon. The last reference is to 1928 literature. Since that time this theory has been completely overthrown and replaced by the phosphagen concept, regarding which no mention is made in the present volume. Rather interestingly, A. V. Hill is not even mentioned in connection with muscle biochemistry! Of what avail is a Nobel prize?

The authors state that problems of immunity involve *only proteins* in some particular colloidal state. They state that mineral colloids, fats, or carbohydrates do not form precipitins or give rise to specific antibodies; nevertheless it was demonstrated as early as 1926 that certain polysaccharides of bacterial origin are immunologically specific and that the specificity is of high order.

The authors do not appear to be well acquainted with English or American literature. The names of English and American scientists are frequently misspelled, *e.g.*, Dunès for Dennis, Clarck for Clark, Chieck for Chick, Mendell for *Mendel*, etc. No mention is made of vitamins, hormones, uronic acids, and many other groups of compounds which involve problems of modern biochemistry. There seems to be little justification for the publication in late 1932 of material obviously collected at a considerably earlier date (presumably used as a basis for a course of lectures in 1929–30) and covering a field which is changing as rapidly as is modern biochemistry.

Ross Aiken Gortner.